COMPARATIVE STUDIES ON REFINING OF PALM OIL USING NIGERIAN CLAYS

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M.ENG/SEET/2001/725

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AUGUST, 2005

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A PROJECT SUBMITTED TO THE POSTGRADUATE SCHOOL, FEDERAL UNIVERSITY OF TECHNOLOGY, MINNA IN PARTIAL FULFILLMENT OF THE AWARD OF MASTER OF ENGINEERING (M.ENG.) IN CHEMICAL ENGINEERING

AUGUST, 2005

DECLARATION

I, Salawudeen Taofeek Olalekan (**M.ENG/SEET/2001/725**) declare that this thesis: Comparative Studies on Refining of Palm Oil Using Nigerian Clays presented for the award of Masters of Engineering has not been presented for any other degree elsewhere.

T.O. ……………………………………
Signature

05/09/05
……………………
Date

CERTIFICATION

This thesis titled "***Comparative Studies on Refining of Palm Oil Using Nigerian Clays***" Salawudeen Taofeeq Olalekan meet the regulations governing the degree of (M.Eng) of Federal University of Technology, Minna and is approved for its contribution to scientific knowledge and literal presentation.

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DEDICATION

This project is dedicated to the memory of my late mother Alhaja Alimotu Salawudeen (Ajiboye). May her gentle soul rest in perfect peace.

ACKNOWLEDGEMENT

My sincere appreciation goes to Almighty God for the successful completion of this programme. I wish to express my profound gratitude to my supervisor, HOD, Dr. F. Aberaugba, for his invaluable suggestions and corrections that facilitated a lot of improvement on this project. I wish to express my appreciation to my lecturers: Dr. K.R. Onifade, Dr. J.O. Odigure, Dr. D. Aloko, Dr. M.O. Edoga, Engr. A.S. Abdulkareem, Engr. O.D. Adeniyi, Engr. M.A. Olutoye, Engr. U.G. Akpan, Engr. (Mrs) E.J. Eterigho and all other members of the department.

I would like to thank my beloved brother Engr. F.B. Akande and Mal. K.A. Akande for their substantial care during the course of the programme.

My appreciations go to my friends and neighbors most especially Engr. E.O. Dada and Afolabi Eyitayo (SIR TEE) for going through the manuscript. My sincere gratitude goes to Mrs. Oyeronke Ola Ajiboye for her understanding during the programme.

Finally my appreciation goes to the members of the family for their moral and financial support. They are Dr & Mrs F.O. Ajiboye, Mr. & Mrs O.O. Ajiboye. Miss Abiola Idowu, Mr. & Mrs Idowu and my beloved father Pa Salawudeen Oyemomilara Ajiboye and the rest of the family.

ABSTRACT

This project work evaluated the bleaching power of some selected clays found in Nigeria with the aim of developing substitute bleaching agents for the palm oil refining industries. Five clay samples were collected from different localities in Oyo and Osun States. The physiochemical properties of the clays were determined by both physical and chemical analysis, and their performances in bleaching palm oil were assessed before and after activation with varying concentration of H_2SO_4 and HCl. A percentage colour reduction of 74% was achieved with HCl activated clay and 67% with H_2SO_4 activated clay at 100°C with 5% dose of the adsorbent in 10 minutes. The result compared favorably with imported bleaching earth (Bentonite). When the bleached oil was deodorized, the percentage colour reduction of the best activated clay increased to 87% and this compared favorably with commercial refined palm oil with all the properties falling within the recommended standards. When these results were statistically analyzed, variation existed and the analysis of the variance showed that at 95 % confidence limit, clay sample 5 (CaO- 0.02±0.00%, MgO- 0.30±0.00%, Fe_2O_3- 2.52±0.01%, Al_2O_3- 5.18±0.03%, SiO_2- 91.29±0.01%) ranked the most effective followed by sample 1 (MgO- 0.03±0.01, Fe_2O_3- 3.30±0.00%, Al_2O_3- 5.22±0.00%, SiO_2- 90.36±0.01%) and sample 2 (MgO- 0.02±0.00%, Fe_2O_3- 3.13±0.01%, Al_2O_3-6.22±0.01% , SiO_2- 90.09±0.01%) while clay samples 3 (MgO- 0.06±0.01%, Fe_2O_3-3.12±0.01%, Al_2O_3- 8.04±0.03%, SiO_2- 88.22±0.03%) and 4 (MgO-0.01±0.00%, Fe_2O_3-10.80±0.01%, Al_2O_3-6.51±0.01%, SiO_2- 81.89±0.01%) were less effective. These results agreed with those obtained when the experimental results were subjected to Freudlich Adsorption Isotherm.

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NOTATIONS, SYMBOLS AND ABBREVIATIONS

ξp-Porosity

ρ_s – Solid Density (gcm^{-1})

ρ_p – Porous particle Density (gcm^{-1})

Vg- pore volume (cm^3)

% CR- Percentage Colour Reduction (%)

Ab- Absorbance

AV – Acid value (gmol^{-1})

CPO- Crude Palm Oil

EIA- Environmental Impact Assessment

EV- Ester Value

FFB- Fresh Fruit Bunches

FFA- Free Fatty Acid (%)

IV- Iodine Value (gramme of iodine/100 gramme of sample)

PV- Peroxide Value (milligramme equivalent/ gramme of sample)

RPO- Refined Palm Oil

RBD- Refined Bleached and deodourized

SE- Saponification Equivalent

SV- Saponification Value

T- Student T-test

CHAPTER ONE

INTRODUCTION

1.1 Background

Palm oil is widely used for cooking and for making soap throughout the world. Other non-edible uses include manufacture of grease, lubricants, candles and paints etc. It is produced from palm trees that historically originated from West Africa (Sierra Leone, Nigeria and Ghana, e.t.c). Palm oil has been in use for more than 5000 years. After the fifteenth century, it was introduced to other parts of Africa, South East Asia and Latin America along the equatorial belt. It was introduced to Malaysia in 1870 as an ornamental plant. The first commercial planting was undertaken in 1917 for some of its products. Today, Nigeria is one of the largest producers of palm oil in Africa, while Malaysia leads in the world.

On a per hectare basis, yield of palm oil tree is more than any other tree. A unique feature of palm oil tree is that it produces two types of oil, Crude Palm Oil (CPO) from the outer layer of the fruit, and Palm Kernel Oil (PKO) from the seed or kernel (Godwin and Spensely, 1971). Palm oil is used in numerous food and non-food applications, but it is used primarily as edible oil, and to make soap. After the oil is extracted from the outer layer of the fruit, and refined, much of it is used as cooking oil and to make shortenings. It is also used to make margarine and other products.

Numerous researches have been carried out on clay activation and bleaching of vegetable oil using activated and non-activated clays. For instance, clays in the old Bendel State, now Edo and Delta States, were used both in crude state and activated state to bleach palm oil with a percentage colour reduction above 90% Hymore and Iyaayi (1989). Ukpor clay was used by Okeke [1990] for the adsorption bleaching of sheanut oil at 140°C bleaching temperature with over 80% colour reduction achieved.

From all indications of the previous research work, much has not been done on the clays found in the northern and western parts of the country, hence this research work focuses attention on the clays found around Oyo and Osun States of Nigeria with a view of comparing their adsorptive power to that of imported bleaching earth and clays found in other parts of the country. This will initiate a new research area in the field of science, engineering and technology, hence, our local clays will be better utilized as a solid mineral, once the process methodology is established.

1.2 Aim and Objectives

1.2.1 Aim of study

Since the discovery of commercial quantity of clay in Nigeria, a lot of work has been carried out to determine the effectiveness of those clays in refining of vegetable oil. However, the aim of this project is to produce local activated clay for use as an adsorbent in refining of palm oil.

1.2.2 Objectives

The set objectives are to:

(i) Use five different clay samples for oil refining

(ii) Determine the physiochemical characteristics of the clay samples.

(iii) Activate the clay samples using various concentrations of hydrochloric and sulphuric acids.

(iv) Use the activated clay samples to bleach palm oil and thus determine the adsorbent that has the highest adsorption capacity.

(v) Determine the physiochemical properties of the crude and refined palm oil.

(vi) Compare the properties of the refined palm oil with imported refined palm oil and thus establish the efficiency or otherwise of the adsorbent.

(vii) Determine the adsorption isotherm for the activated clays.

1.3 Scope of the Project Work

Different types of clay exist in nature depending on the geographical location and soil chemistry of a place, but the scope of this project work is limited to the clay commonly found around Oyo and Osun states of Nigeria. Hence, five different clay samples where characterized, activated and used as media for decolourization of palm oil. The bleaching was carried out and the effectiveness of the clay samples were monitored by the following parameters: - percentage colour reduction, percentage free fatty acid, acid value, iodine value, saponification value, ester value, peroxide value, and finally the yield of the oil after neutralization and bleaching.

1.4 Significance of the Project Work

(1) This project will initiate a new research area in the field of Science, Engineering and Technology with a view of enhancing better utilization of an abundant solid mineral (clay).

(2) Once the process methodology and operating conditions are established, our local activated clays could be used to replace the expensive imported fullers or bleaching earth.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 History of Palm Oil

Palm oil tree is commonly found around Benin Republic, Cameroon, Ghana, Ivory Coast, Sierra Leone, Nigeria and Congo Republic, hence, it is considered to be of West Africa origin. Nigeria is the leading country in West Africa in palm oil production as can be seen in Table 2.1

The oil palm was introduced to Malaysia in about 1870 as an ornamental plant. By 1917, it was being cultivated on a commercial scale for some of its products. Currently, Malaysia is the world leading producer of palm oil as the tree production occurs in about three million hectares (Mha), with well over one third of Malaysia's total cultivated area. The perennial crop is harvested throughout the year and the trees usually remain productive for 20 to 25 years.

2.2 The Oil – Palm Fruit and Crude Palm - Oil

The oil palm is a monoecius plant (having unisexual male and female flower in one plant). The female flower gives fruit commonly referred to as Fresh Fruit Bunches (FFB). Each plant is capable of bearing about 10 to 12 bunches per year. The number of fruits per bunch varies from 1000 to 3000 in mature palm and the average weights of each bunch can vary between 20 to 30 kg (Purseglove, 1982).

Crude palm oil (CPO) is obtained from the mesocarp (the fleshy portion of the fruit wall) and depending on the variety and age of the palm, oil to bunch ratio is within the range of 25 to 28% (Waise, 1983).

On a per hectare basis, the palm oil tree yields more oil than any other oil producing plant, producing five and nine times as much oil as groundnuts and soy beans respectively. A unique feature of the palm oil tree is that it produces two types of oil: -

palm oil from the outer layer (or fleshy) of the fruit and palm kernel oil (PKO) from the seed of kernel. For every ten units of palm oil produced about one unit of palm kernel oil is produced.

2.3 World Palm – Oil Producers

Palm oil has been very competitive in the edible oil market because of relatively low land prices, limited pest pressures, and cheap labour in countries such as Indonesia and Thailand. All these and other palm oil comparative advantage has encouraged many countries like Latin America, South America and Papua/New Guinea into cultivation of oil palm.

The second largest producer of palm oil in the world is Indonesia. Since 1995 to 1996, production has increased by about 60% to record of 7.3 million tonnes (Mt) in 2000 to 2001, which is attributed mostly to large investments from outside sources looking to capture the economic advantage of Indonesian cheap labour. Africa is also a major producer of palm oil. From 2000 to 2001, Nigeria, Ivory Coast, Cameroon and Ghana are expected to produce a total of 1.3Mt of palm oil, of which about 10% will likely be exported. The major exporting country is Ivory Coast, which exports about one third of its annual production. Table 2.1 shows the world palm oil producers.

TABLE -2.1 WORLD'S PALM OIL PRODUCERS

		1998 – 1999 (Thousand Tonnes)	1999 – 2000 (Thousand Tonnes)	2000 – 2001 (Thousand Tonnes)
Malaysia		9759.1	10491.9	12114.0
Indonesia		5920.0	6784.0	7330.0
	Angola	49.5	49.0	49.0
	Benin	33.6	35.4	37.4
	Cameroon	146.0	156.6	161.3
	Ghana	110.0	108.5	111.0
	Ivory Coast	280.6	277.0	73.4
	Nigeria	712.6	135.1	747.5
	Sierra Leone	38.0	40.7	46.0
	Congo	98.5	97.3	96.2
Africa		**1468.8**	**1499.6**	**1521.8**
	Brazil	90.6	105.1	109.4
	Colombia	466.0	512.6	514.0
	Ecuador	236.1	248.0	254.0
	Peru	34.8	37.3	38.8
South America	Venezuela	64.7	77.1	83.0
		892.2	**980.1**	**1029.2**
Thailand				
Papua/New		468.0	561.0	530.0
Guinea		256.6	300	301.0
	Cotta Rica	118.6	123.0	122.6
	Dominican Rep			
	Guatemala	23.8	25.5	26.0
	Honduras	50.5	61.3	69.9
	Mexico	90.6	91.4	93.4
	Nicaragua	17.5	24.6	33.2
	Panama	8.0	8.2	8.0
Latin America		11.2	11.6	11.8
Other		**320.2**	**345.6**	**364.9**
Total		273.1	296.0	324.0
		19358.0	**21258.2**	**23516.0**

Source: Michael, 2001.

2.4 Component of Palm Oil

Palm oil contains mainly an equal proportion of unsaturated acids, consisting about 40% oleic acid (monounsaturated), 44% palmitic acids, with oleic acids as the major fatty acids produced by the body. Palm oil also contains 10% polyunsaturated and 50% saturated acid (Michael, 2001).

Other components include vitamin E, the tocopherols and tocotirenols. These components are dietary essentials, whose main function is to act as antioxidant substance that prevent oxidation and scavenging of the free radicals in the body and hence hypothesized to play protective role against cellular organ, atherosclerosis and cancer. Unprocessed palm oil is used in a number of countries for cooking and is also a very rich source of β-carotene, an important source of vitamin A. Table 2.2 compares the components of palm oil with those of other vegetable oils.

Table-2.2 Components of vegetable oils

Oil Type	Mono	Poly	Saturates
Palm Oil	40%	10%	50%
Peanut Oil	39%	42%	19%
Butter Fat	30%	44%	26%
Corn Oil	30%	54%	16%
Soyabean Oil	25%	60%	15%
Safflower Oil	13%	77%	10%
Coconut Oil	5%	1%	94%

Source: Michael, 2001.

2.5 Palm Oil Refining and Down Stream Processing

Palm oil mills form an essential part of the oil palm industry. They are usually located in close proximity of plantations because Fresh Fruit Bunches (FFB) must be processed soon after harvesting if high quality oil is to be obtained. The numbers of mills and refineries have increased in consonance with the rapid growth of oil planting and production.

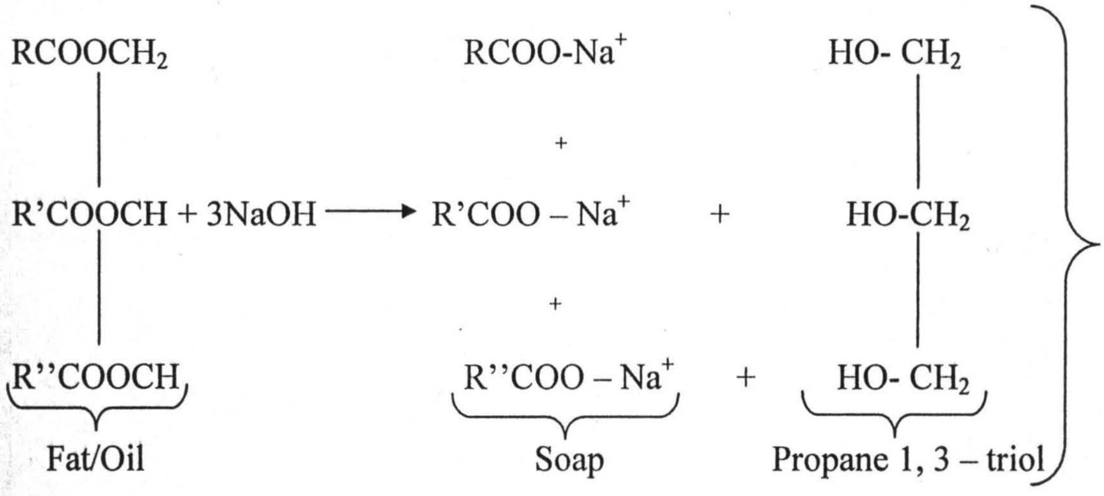
Palm oil is physically refined without the use of chemical solvents, thereby reducing the risk of residue contamination. Essentially, refining of palm oil undergo four major processes.

(i) Degumming Process

Degumming is the treatment of the oil with hot water, salt solution or acids such as phosphoric acid to remove phosphatides, waxes and other impurities. These impurities are present only in the range of 0.03 to 3% and their importance lies in their emulsifying properties, which increase losses during caustic refining by the entrainment of large quantities of neutral oil in the soap stock. However, palm oil has a relatively low content of phosphatides because of the steam treatment during the extraction process, hence, degumming is considered unimportant during refining.

(ii) Neutralization or Caustic Refining

Neutralization process is the process of removal of the Free Fatty Acids (FFA) from the crude palm oil by caustic treatment (Tewari and Vishnols, 1980). When a measured quantity of caustic soda (NaOH) is allowed to react with the free fatty acids, which normally exist in the crude oil, a soap is formed which is easily removed by salting out. The reaction is as shown in Equation 2.1.



$$\underbrace{\begin{array}{l}\mathrm{RCOOCH_2}\\ |\\ \mathrm{R'COOCH}\\ |\\ \mathrm{R''COOCH}\end{array}}_{\text{Fat/Oil}} + 3\mathrm{NaOH} \longrightarrow \underbrace{\begin{array}{c}\mathrm{RCOO\text{-}Na^+}\\ +\\ \mathrm{R'COO - Na^+}\\ +\\ \mathrm{R''COO - Na^+}\end{array}}_{\text{Soap}} + \underbrace{\begin{array}{c}\mathrm{HO\text{-}\ CH_2}\\ |\\ \mathrm{HO\text{-}CH_2}\\ |\\ \mathrm{HO\text{-}\ CH_2}\end{array}}_{\text{Propane 1, 3 – triol}} \qquad 2.1$$

Equation – 2.1 Neutralization of FFA with NaOH

(iii) Bleaching

The process termed bleaching for oils and fats is more correctly a process that removes the colour bodies, which include carotenes, chlorophyll and other pigments as impurities. The process renders the oil or the product from the oil more appealing and convenient for use.

Bleaching could be performed in various ways by heat, chemical/or adsorptive means. Heat bleaching is the removal of colouring matters at high temperatures, while chemical bleaching is simply the removal of colours by process of neutralization.

On the other hand, colouring matter is removed by the use of adsorbents like activated carbon or activated clay. This process is otherwise called Adsorption Bleaching.

Much progress has been made in downstream processing so much that very little palm oil is exported in crude form. Palm oil is very versatile and has many uses, other than for cooking, the production of vitamin E and vitamin A on a commercial scale are being pursued along with the possible use of oil palm trunks for furniture. In the non-edible sector, a very exciting area of development is the new but fast growing Oleo Chemical Industry to utilize about 750,000 tonnes of bleached palm oil and palm kernel as basic raw materials.

(iv) Deodorization

Deodorization relies on the large difference in the volatility (Partial Vapour Pressure) between the oil (triglyceride) and the mostly unwanted substances that affect its flavour, odour, colour, and stability (Brace, 1973). It is essentially a mass transfer process whereby these substances are evaporated from the oil at a temperature below what is damaging to the oil. This is accomplished by subjecting the oil to reduced pressure (vacuum) at an elevated temperature in the presence of an agitating and stripping gas, normally stream. The vacuum serves to enhance the pressure differential and minimize the amount of gas needed, and also protects the hot oil from atmospheric oxidation and reduces hydrolysis of the oil when stream is used (Hui, 1996).

In practice, in order to create a sufficient difference in vapour pressure between a triglyceride (oil) and its undesired flavour and odourous compounds, the temperature of the oil must be increased to 200 – 275°C and the system pressure reduced to under 1 kPa. The amount of stripping stream at, say 0.4 kPa and 260^0C, varies from under 0.5% for true thin-film systems to as much as 5% for some batch applications.

2.6 Uses of Palm Oil

Palm oil is available in a variety of forms: Crude palm oil, palm oleic, palm stearin, Refined, Bleached and Deodourized (RBD) palm oil, RBD oleic, double fractionated palm oleic and palm mid fraction. (Oil World 2002) while Nigeria and other West African Countries export is in form of Crude Palm Oil (CPO), Malaysia's export is RBD palm oil and RBD oleic. The range of products is available to suit a variety of manufacturing needs and in forms that are "ready to use" and require no further processing.

Palm oil is very versatile oil with a range of distinctive properties, which enable it to meet most of the technological requirements for formulating fat-based products. On the nutritional side, studies have concluded that palm oil is a highly nutritious edible oil with a balanced fatty acid composition comprising 50% unsaturated, 50% saturated fatty acid (Table 2.2). It provides adequate amount of essential fatty acids and is a rich source of vitamin E. Like other edible fats and oil, palm oil is easily digestible, absorbed, and utilized (Hamilton and Bhatti, 1980). Numerous recent experiments conducted in man and animals showed that palm oil reduces blood cholesterol and the harmful Low-Density Lipoprotein (LDC) cholesterol levels when compared to several other sources of dietary fats and oils. Palm also has the unusual effect of raising the level of wood cholesterol, which is the High – Density Lipoprotein (HDL) in man and animals.

Some of the edible and non-edible uses of palm oil and its products are as follows:

Margarine

Malaysian palm oil is most suitable for the manufacture of margarine. It has the correct consistency and does not turn rancid easily.

Frying Fats for Snacks Food/Fast Foods

The production of a number of conveniences of snacks foods such as French fries, instant nodules and doughnuts involves a frying operation. In this regard, palm oil and palm oleic with its good physical properties and oxidative stability, is more stable and cheaper material to use.

Other edible products that depend directly or indirectly on palm oil are: non-diary creamers, ice cream that is vegetable oil based ice cream and coal butter substitute.

Non-edible Uses

The single target non-edible uses of palm oil are in the manufacture of soaps and detergent, greases, lubricants and candles, paint, ink and additives, etc. It is currently possible to use vegetable oil fuel to run cars, which have been fitted with new or suitable materials on the Crude Palm Oil (CPO) fuel would be carried out. It is the cost of using CPO fuel that will be the determining factors for its wide scale adoption as an alternative fuel for the future.

2.7 Preservation of Palm Oil (Hydrogenation)

Like all other vegetable oils, palm oil has the advantage of being preserved to increase shelf life by the process of hydrogenation. Fats in foods that contain unsaturated fatty acids tend to spoil easily. Those acids can be made less susceptible to oxidation and to spoilage by hydrogenation. The process is carried out by adding hydrogen at the place of the double bond in the unsaturated fatty acid to produce a more solid fatty acid. As a result of the hydrogenation process, trans fatty acid is formed which may have an adverse effect on health. Palm oil on the other hand is usually used without hydrogenation to minimize the production cost.

$$\begin{array}{l} CH_2O.\ CO.\ C_{17}H_{35} \\ CHO.\ CO.\ C_{17}H_{35} \\ CH_2O.\ CO.\ C_{17}H_{35} \end{array} \xrightarrow{3H_2} \left.\begin{array}{l} CH_2O.\ CO.\ C_{17}H_{37} \\ \quad\quad\quad\ | \\ CHO.\ CO.\ C_{17}H_{37} \\ \quad\quad\quad\ | \\ CH_2O.\ CO.\ C_{17}H_{37} \end{array}\right\} \quad 2.2$$

Eqn. 2.2: Conversion of Oleic (Mp 17°C) to stearin (Mp 71°C) by Hydrogenation.

2.8 Factors used in Determining the Quality of Vegetable Oils.

The following parameters are used to determine the quality of good oil.

(i) Fat Acidity (Acid Value and Free Fatty Acid)

Deterioration of grains and milled products is accompanied by increased acidity. The acid formed include FFA, and amino acids deterioration, fat acidity increases at a much greater rate than either of the other two types of all types of acidity combined (Gunstone, 1996).

The organic acidity of fats and oil can be expressed in several ways. The "**Acid Value**" is the number of milligrams of alkali required to neutralise 2-gram of fat or oil while the **Free Fatty Acid** (.FFA) content is expressed as percentage of weight of a specified fatty acid (either oleic with a molecular weight of 282 or an average and specified molecular weight appropriate to the nature of the analysed fat or oil) (Yashajau, 1996). Acid Value (AV) can be converted to FFA (expressed as oleic acid) by the following expressions.

$$AV = 1.99 \times \%\,FFA \qquad (2.3)$$

$$\%FFA = 0.503 \times AV \qquad (2.4)$$

(ii) Peroxide Value (PV)

Peroxide value is the most commonly used assay of oxidation in fats and oil (Chan 1987). Many materials have been devised for its measurement (Barnard and Hargove 1951) reviewed the value of the various methods and found the iodometric procedures were most commonly used. Hence, the peroxide value is an indicator of the procedure of primary oxidation. It measures rancidity of degree of oxidation.

(iii) Saponification Value (S.V)

Saponification value was originated by Koettdorfer and is sometimes known by this name. Saponification value is defined as a measure of the amount of alkali required to saponify a definite weight of fat. It is expressed as milligrams of alkali required to saponify 1 gram of fat, that is, to neutralize the FFA and the fatty acid present in the form of glycerides. The saponification equivalent (S.E), which is the amount of oil or fat saponified by 1 gram equivalent of an alkali is related to SV by the equation:

$$SE = \frac{56,108}{SV} \qquad (2.5)$$

The saponification value is an indication of the average molecular weight of fat. For pure fatty acids S.V. = AV.

(iv) Ester Value (EV)

The ester value is the difference between the Saponification Value (S.V) and the Acid Value (A.V).

$$\mathrm{EV} = \mathrm{S.V} - \mathrm{A.V} \qquad (2.6)$$

(v) Fat Stability and Rancidity

The term rancidity is used to describe development of objectionable flavours and odours. Rancidity may be caused by either hydrolytic or oxidative changes in the fat.

Hydrolytic rancidity involves chemical or enzymatic hydrolysis of fats into FFA and glycerol, while oxidative rancidity involves the addition of atmospheric oxygen in the presence of enzymes or certain chemicals. Hydrolytic activity is important in diary products and coconut items, which contain glycerides of low molecular – weight fatty acids such as butyric, caproic, caprylic, or capric. Cereal lipids, on the other hand contain high – molecular – weight fatty acid, which when hydrolyzed do not produce the same type of off-flavours and odours as are produced by the hydrolysis of low – molecular – weight glycerides.

The resistance of oil to the development of rancidity is therefore called Stability.

2.9 Environmental Implication of Vegetable Oil base Industries.

An environmental assessment shows that vegetable oil-based oleochemicals are biodegradable and environmental friendly compared to raw materials from petrochemicals. Also, by-product utilization and recycling of waste and effluent from palm oil mill for use as fertilizer help to improve the efficiency and economic viability of the palm oil industry.

2.10 Clays and Clay Minerals

Clays and clay minerals have been mined since the Stone Age. Today, they are among the most important minerals used by manufacturing and environmental industries. The studies of the properties of clays, the mechanism of clay formation and the behaviour of clays during weathering can tell us how and where these minerals form and provide industry and land-planning agencies with the information necessary to decide how and where clay and clay mineral deposits can be developed safely with minimal effect on the environment. The studies also enhance better understanding of clay. Therefore, useful information on how it can be used by processing industries is known. An example is the use of clay in catalyst production and production of adsorbent.

2.11 Definition of Clay

The term "Clay" by itself means different things to different users of the word. Hence, we have the following definitions:-

(i) **As a size term:** - Clay is applied both to materials having a particle size of less than 2 – micrometers. (25400 microns = l inch) in dimension.

(ii) **As a mineral term:** - Clay is defined as any sediment particle that contains the clay minerals like silica and alumina. Other minerals like quartz, carbonate and metal oxides may also be present.

(iii) **As a ceramic or building material:**- Clay refers to any sediment that is plastic when wet and indurate when dry.

2.12 How and Where Clays and Clay Deposit Form

Clays and clay minerals occur under a fairly limited range of geological conditions. The environment of formation includes soil horizon, continental and marine sediments, geothermal fields, volcanic deposits and weathering rock formations (Brain, 1973). Most clay minerals are formed where rocks are in contact with water, air or steam. Examples of these situations include weathering boulders on the hillside, sediments on sea or lake bottoms, deeply buried sediments containing pore water and rocks in contact with water heated by magma (mother rock). All of these environments may cause the formation of clay minerals from pre-existing minerals. Extensive alteration of rocks to clay minerals can produce relatively pure clay deposits that are of economic interest (for example, bentonite – primarily montmorillonite – used for drilling muds, adsorbent and clays used in ceramics).

Clearly, clays and clay minerals are critical components of both ancient and modern sedimentary environment (Blatt _et_ _al_., 1980). There are some physical/chemical processes that lead to formation of clays. These include: -

Weathering, digenesis and at times erosion.

2.12.1 Weathering

Weathering of rocks and soil is the primary way that clays and clay minerals form at the earth surface today. The weathering process involves physical disintegration and chemical decomposition that change original mineral to clay minerals. Weathering is uneven, and many stages of breakdown may be found in the same clay sample (Velde, 1995). Factors governing rock weathering and soil formation include the initial type of rock, the temperature, presence of organism, organic materials and the amount of time. The types of clay minerals found in weathering rocks strongly control how the weathered rock behaves under various climatic conditions (such as humid – tropical, dry-tropical and temperate conditions).

Kaolinite is formed in most weathering zones and soil profiles. Monntmorillonites, which are chemically more complex than kaolinite are common in the lower part of weathering profiles, nearer the rock, where chemistry exerts a strong control on mineralogy. Complex mixed layered clay minerals (such as illitesmectites) are abundant in clay assemblages that develop from mica – bearing precursor rocks, such as granite, plutons that occur in temperate regions.

2.12.2 Digenesis

It is the in-place alteration of mineral to more stable form excluding surficial alteration (which is weathering). Digenesis occurs, for example when minerals stable in one depositional environment are exposed to another by burial and compaction. The formation of bentonite bed containing smectite – group clay minerals including montmorrilonite or fuller's earth (a type of clay mineral deposit that has high capacity to absorb water) may occur primarily by digenesis, although some deposits may also form by hydrothermal process.

2.12.3 Erosion

Erosion is the transport and deposition of clays and clay minerals produced by eroding older continental and marine rocks and soils. They also form important parts of the cycle.

2.13 Uses and Type of Clay

2.13.1 Uses of clays and clay minerals

The economic use of a clay mineral is determined largely by its clay mineral composition, which determines the physical and chemical properties of each clay type. In the ceramic industries, only certain clays of a particular clay mineral composition will withstand high temperature and can be used for making refractory. The oil industry requires certain types of bentonite clay for the preparation of drilling mud. Other types of bentonite clay are used for the preparation of catalyst in refining of petroleum products and in the manufacture of activated Bleaching Earth. The paper industry utilizes certain types of kaolinite clays for the coating and filling of papers. A certain property of clay (affinity for water) is used by the paint industry to disperse pigments (colour) evenly throughout paint. Without clay to act as a carrier or extender, it would be difficult to evenly mix the paint base and colour pigment. Knowledge of clay material on or through which a structure is to be built is essential in construction engineering. Clay is used as source of Silical (SiO_2) and Aluminal (Al_2O_3).

2.13.2 Types of clay

The variation in clay types depends primarily on how the clay is formed (weathering, digenesis and erosion) and mineral composition of each clay. Thus we have:

(i) **Kaolinite Clay:** Clay containing a preponderance of the clay mineral. Examples are China clay, Kaolinite ball clays, fire clay and flint clay e.t.c.

(ii) **Betonite Clay:** These are clays that contain mainly the clay minerals montmorillonite, smectite and are formed by alteration of volcanic ash.

(iii) **Mullite Clay:** It is a high temperature conversion product of many allumino-silicate minerals, including kaolinite, pinite, topaz, pirophyllite and kyanite e.t.c.

(iv) **Attapulgite Clay:-** It is another type of clay, which contains the mineral diaspore and kaolinite.

(v) **Miscellaneous Clay:-** Most of these clays contain mixtures with differing proportions of illite, chlorite, kaolinite plus a variety of non-clay minerals. They are been used in the manufacture of bricks, drain tiles, and sewer pipes e.t.c.

2.14 Physical and chemical properties of clays

The characteristics common to all clay materials are controlled by at least five major factors:-

(i) Clay mineral composition (SiO_2 and Al_2O_3 composition)

(ii) Non-clay mineral composition (mica, metal oxide e.t.c.)

(iii) Organic material

(iv) Soluble salts and exchangeable ions.

(v) Texture

Generally, the clay mineral composition is the most important factor, and sometimes as little as five percent (5%) of a particular clay mineral may largely determine the properties of the whole clay. The following are the physical properties of the clays: -

2.14.1 Affinity for water

Clay minerals all have a great affinity for water. Some swell easily and may double the thickness when wet. Water molecules are strongly attracted to mineral surfaces hence, when a little clay is added to water, a slurry forms because the clay distributes itself evenly throughout the water. This property of clay is exploited in the paint industries to disperse pigments (colour) evenly throughout paint. But such clay is not a good material for construction.

2.14.2 Ion exchange

Most clays have the ability to soak up ions (electrically charged atoms and molecules) from a solution and release the ions later when condition change. This property of clays is utilized in ion exchange processes due to the presence of permanently bound "Co-ion" groups of opposite change in clay.

2.14.3 Plasticity

Most clays become plastic when mixed with water. A plastic mud formed can be shaped and dried to form a relatively rigid solid. This property is exploited by potters and ceramics industries to produce plates, cups, bowls, and pipes e.t.c.

2.14.4 Adsorptivity

This is the property of clay exploited in decolourization and clarification. Adsorbents are natural or synthetic materials of amorphous or microcrystalline structure. Those used on a large scale include activated carbon, activated alumina, silica gel, fuller's earth, and other clays (Timur et al, 2001).

Adsorption involves, in general, the accumulation of solute molecules at an interface. At ordinary temperatures, intermolecular forces usually cause adsorption rather than by formation of new chemical bonds, it is then called physical adsorption, or physic-sorption. At higher temperatures (above 200°C), the activation energy is available to make or break chemical bonds, and if such a mechanism prevails, the adsorption is called chemisorptions or actuated adsorption (Perry and Chilton, 1987).

2.14.5 Absorptive properties

The absorptive properties of bentonite and fuller's earth make them ideal for such divers uses as drilling mud, foundry – sand bond, binder for pelletizing iron ore and bleaching liquids, absorbents for oil, grease and animal waste, and carriers for pesticides and fertilizers.

2.15 Clay Mineralogy

Clay mineralogy is the study and science of mineral present in the clay. The study is very important because it enable us to characterize our natural clays into various types according to their chemical composition (Hiller, 1985). The investigation of clay minerals goes far back into antiquity because of their importance in industry, agriculture and geology. Most of the concept of clay mineral is concerned with the way in which the chemical components are put together in clays. With the advent of X-ray diffraction analysis, the crystalline nature of the extremely small clay minerals can be produced.

2.15.1 Clay minerals

The clay minerals are the major components of clay materials. They occur in extremely small particles, which are essentially crystalline and are limited in number. Clay minerals are essentially hydrous aluminium silicates. Alkalis or alkaline earth metals are present as principal constituents in some of them. Also, in some clay minerals, magnetism, iron or both substitute wholly or in parts for the aluminium (Richard and Brain, 1982). The ultimate chemical constituents of the clay minerals vary not only in amount, but also in the way in which they are combined or are present in various clay minerals.

2.15.2 Clay classification

No completely satisfactory classification of the clay minerals has yet been suggested. The following classification has proved to be workable one. A major subdivision into amorphous and crystalline group is made on the basis of physical properties and chemical composition. Only one type of amorphous clay is known and that is allophanes (Kirk, 1987). The crystalline group fall into four main classes on the basis of physical properties and chemical composition. These are:-

(a) Two – Layer Type

The sheet structure composed of units of one layer of silica tetrahedrone and one layer of alumina octahedron $(Al_4(Si_4O_{14})CO)_8$. There are two types:

(i) Elongates e.g. Halloysite group

(ii) Equi-dimensional e.g. Kaolinite group.

(b) Three – Layer types

The sheet structures composed of two layers of silica tetrahedrons and central di-octahedral or tri-octahedron layer. Example is montmorillonites group: $(\frac{1}{2}\ Ca, Na)_{0.7}$ (Al, Mg(Fe)$_4$ $((Si, Al)_4O_{10})_2\ (OH)_4.nH_2O$.

We have:-

(i) Expanding structure e.g. montmorillonite, Salconite and Vermiculite.

(ii) Non-Exapanding structure e.g. illite group:-

$KA_{l4}(AlSi_7O_{20})(OH)_4$

(c) Regular Mixed – Layer Types

The sheet structures composed of ordered stacking of alternate structural types, e.g. chlorite group:- $Mg_{10}\ Al_2\ (Si_6Al_2)\ O_{20}\ (OH)_{16}$

(d) The sheet structure is similar to hornblend-e-China of silica tetrohedrons linked together by octahedral groups of oxygen and hydroxyls containing alumium (Al) and magnesium (Mg) atoms. Like in vermiculite group $(Mg, Ca)_{0.7}\ (Mg, Fe, Al)_8$ $((Si, Al)_4O_{10})_2\ (OH)_4.8H_2O)$ e.g. attapugite, Sepilite, and Palygorskite e.t.c the structure resembles that of **b** above.

2.16 Clay Mining and Processing

Almost all the commercial clays are mined by open-pit method, with overburden – to – clay ratios ranging as high as 10:1(Nutting, 1933). The overburden is removed by motorized scrapers, bulldozers, shovels or draglines. The clay is won with draglines, shovels or bucket loaders and transported to the processing plants by truck, rail, aerial train ways, or belt conveyors, or as slurry in pipelines.

The clay is processed dry or in some cases wet. The dry processes usually consist of crushing, drying, and pulverizing. Thus, the clay is crushed to smaller size and dried in rotary driers. After drying, it is pulverized or sieved to a specified mesh-size.

Where more exerting products or clay of certain degree of purity is expected as in the case of kaolins, for the paper industries, bentonite for certain pharmaceutical uses, wet "processing" is used. The process is as follows:-

- The clay material (e.g. Kaolin) is slurried in water at the mine face at about 35 to 40% solids with the aid of dispersant.
- After dispersing, the slurry is pumped to a degritting station where the very coarse impurities are removed and then pumped to the processing plant through the pipe line.

The general processing steps are:-

(1) Particle size fractionation

(2) Leaching out iron impurities

(3) Dewatering by filtration

(4) Drying and Pulverization

If the clay is the raw material for bleaching earth, certain tests must be conducted for quality control. Such tests include:- test for oil bleaching and retention capacity, speed of filterability, residual acidity, moisture content, density, surface area and particle size as per international standard. The constant and stringent tests carried out during production ensure quality bleaching earth of the high standards.

2.17 Theory and Principle of Adsorption in Clay

Adsorption is a separation process in which a solute in a liquid is deposited at the surface of a solid termed the adsorbent. It could be physical or chemical depending mainly on the operating temperature and the interaction between the solute and the solid. At ordinary temperatures, physical adsorption predominates and result from intermolecular forces while at elevated temperatures, chemical bonds are either broken or created due to the increase in activation energy and forms the basis for chemical adsorption commonly referred to as chemisorptions.

The capacity of the adsorbent for the solute is directly proportional to the concentration of the dissolved material (Hui, 1996). This is expressed by the Freudlich adsorption equation given by:-

$$x/m = KC^{n} \qquad (2.7)$$

Where: -

x = amount of substance adsorbed (g)

m = amount of adsorbent (g/mass of oil)

K, n = constants.

Expressing (4) in logarithmic form gives

$$\log\left(x/m\right) == \log K + n\log C \qquad (2.8)$$

A log – log plot of x/m versus C gives a straight line graph called adsorption isotherm with a slope n and intercept k.

CHAPTER THREE

3.0 EXPERIMENTAL METHOD

3.1 Equipment/Instruments

The items of equipment used in this project work included vacuum drier, tray drier, water bath, and hot plate. They were manufactured by Golden Kemp.Ind. Ltd. USA. The instruments used included atomic absorption spectrophotometer (AAS), spectrophotometer, colorimeter, pH-meter, electronic Scale and mercury thermometer. These were manufactured by Cole-Parmer Instrument Company East Bunker Court USA. All the glasswares were products of pyrex and Technico Ltd England.

3.2 Materials

The chemicals used were: Sulphuric acid, Hydrochloric acid, caustic soda, caustic potash, ethanol, acetic acid, sodium thiosulphate and bromine. All were of analytical grade, manufactured by Fisons Plc, England. Clay samples 1 and 2 were obtained from Ogbomosho, Oyo State. Clay samples 3, 4 and 5 were obtained from Ejigbo, Oshogbo, (Osun State) and Ibadan, (Oyo State) respectively. The crude palm oil was obtained from Ogbomosho, Oyo State.

3.3 Methodology

3.3.1 Clay Characterization

Characterization of the clays involved the determination of the percentage composition of the clay minerals such as Al_2O_3, SiO_2, Fe_2O_3, MgO, and CaO, and determination of pore volume, solid density, particle density and the porosity of the clay samples.

3.3.1.1 Sio_2 determination (Gravimetary method)

The gravimetary method involved digestion of the clay sample in the appropriate solution and taking the difference in weight. Five grammes of the clay samples were weighed into a cleaned beaker of 250 ml capacity and labelled Wo. This was followed by the weighing of 15 – grams HNO_3/HCl acid (mixing ratio 2:1) into the clay sample in the beaker. The entire mixture was allowed to digest for 24 – hours after which the mixture was filtered to remove SiO_2 which did not go into solution. The filtered SiO_2 was washed with water, oven dried and weighed W_1. The percentage composition of SiO_2 was calculated from the relation:-

$$\%\,\text{composition} = \frac{\mathrm{W}_0 - W_1}{W_0} \times 100 \qquad 3.1$$

Where:-

W_0 represents mass of the sample before digestion.(g)

W_1 represents mass of the sample after digestion. (g)

3.3.1.2 Al_2O_3 Determination (Colorimetry method)

Two grammes of the digested sample from Section 3.3.1.1 was weighed in a beaker (75 ml capacity) and mixed with 0.2g Aluminium reagent. About 0.1g of the mixture was aspirated to Spectrophotometer and the intensity of the colour of the mixture was read. The intensity of the colour of the mixture was directly proportional to the concentration of the alumina (Al_2O_3) present in the sample. The percentage composition of the alumino was then calculated from the relation:-

$$\%\,\text{Composition}\,(\mathrm{Al_2O_3}) = \frac{\text{Mass of }\mathrm{Al_2O_3}}{\text{Mass of the clay sample}} \times 100 \qquad 3.2$$

3.3.1.3 CaO, MgO, and Fe_2O_3 Determination using Atomic Absorption Spectrophotometry (AAS)

Two hundred milligrams of the digest from Section 3.3.1.1 was weighed and aspirated into the Atomic Absorption Spectrophotometer. The concentration of each of the oxide (CaO, MgO, and Fe_2O_3) in the mixture was read. The percentage composition of each of the oxide was determined using the same expression as in Section 3.3.1.2 above.

3.3.2 Determination of Clay Porosity (ξ_p), Pore Volume (Vg), Solid Density (ρ_s) and Particle Density (ρ_p) Using Helium –Mercury Method.

Hundred millimetres of mercury was weighed in a measuring cylinder (250 ml capacity). This was followed by weighing of 10g of the clay sample into the same measuring cylinder that contained the mercury. The volume of the mercury displaced by the clay sample was read. The same procedure was carried out using helium in place of mercury and the volume of helium displaced was read on the measuring cylinder. The difference in volume of mercury displaced and that of helium gave the pore volume, while the volume of helium displaced gave the volume occupied by the clay. Hence, the void fraction or particle porosity was calculated from the expression

$$\xi_p = \frac{V_g \rho_s}{V_g \rho_s + 1}. \qquad 3.3$$

Where:-

Vg represent Void volume per gram of particle (cm^3/g)

$Vg = (V_{Hg} - V_{He})/m$

V_{Hg} represent volume of mercury displaced (cm^3)

V_{He} represents volume of Helium displaced (cm^3)

m represents mass of clay sample used.(g)

ρ_s represent Solid density (g/cm^3) = mass of clay sample/vol of clay sample.

3.4 Clay Preparation

3.4.1 Raw Clay Preparation

Each clay sample was ground and mixed with water in a 2-litre beaker. Impurities like sand and stones first settled at the bottom of the beaker. The purified clay was then removed from the top and the sand and stones were discarded. The clay was after this oven dried, ground in a mortar and sieved with 750 micron sieve. This was the clay used in bleaching without acid treatment or activation.

3.4.2 Activated Clay Preparation

Slurry of the purified clay (from 3.4.1) was made with distilled water in a 500 ml beaker. Sulphuric acid and hydrochloric acid each of concentration of 15%, 25%, 35% and 45% were used for activation.

Activation was carried out by adding the acid of chosen strength to the clay slurry and the mixture boiled for 2-hours at 100°C. The mixture was then washed with distilled water to remove excess acid. Point of neutrality was determined by litmus paper. After this, the clay slurry was oven dried, ground and sieved. This was the activated clay used in the experiment.

3.5 Crude Palm Oil Refining

3.5.1 Determination of the Optimum Concentration of NaOH for Neutralization of the Crude Palm Oil

This experimental procedure was carried out to know the actual concentration of the alkali required for neutralization of the crude palm oil.

Given oil sample was slightly warmed to reduce the viscosity and to make the saponification reaction visible to the naked eyes. 25 ml (22g) of the oil sample was measured with a pipette into a conical flask. A selected concentration (say 0.5M) of NaOH was prepared and put in a burette mounted on a retort stand. This was then titrated against the oil sample in the conical flask. The titration was stopped immediately cloud occupied the entire solution in the conical flask. The soap formed was allowed to settle and the excess oil (i.e. the neutral oil) decanted and weighed. The volume of NaOH that neutralized the FFA in the oil was read. The same procedure was used when the concentration of NaOH was 1.0 M, 1.5M, 2.0M, 2.5M and 3.0M.

The yield was calculated thus:-

Yield = mass of neutral oil/ Total oil used x 100%

The concentration of NaOH that gave the highest yield was considered the optimum concentration to neutralise the crude palm oil for the subsequent experiment.

3.5.2 Degumming

Six hundred and fifty grammes of crude palm oil were weighed in a beaker of 2000 ml capacity. 1-litre distilled water at 100°C was added to the crude palm oil in the beaker. The mixture was stirred continuously for 10-minutes in a water bath maintained at 90°C. The mixture was then allowed to settle and gums were separated from the oil using separating funnel. This procedure was repeated three times to ensure complete removal of the gums. This degummed oil was used for the subsequent experiments.

3.5.3 Neutralization

Neutralization of the FFA was carried out by adding 30 gram of 2M NaOH at 90°C to the degummed oil from 3.5.2 above. The mixture was stirred continuously for 5 minutes. This was followed by the addition of 60g NaCl for salting out of the soap stock. After 30 minutes, the neutral oil was separated from the stock by decanting, and washed with hot distilled water to remove the excess soap. The neutral oil was finally dried by heating at 60°C in a water bath until no more bubbling of gas was observed.

3.5.4 Adsorption Bleaching

30 grams of the degummed, neutralized and dried oil was weighed into a 250 ml beaker and heated at constant temperature of 100°C for 5 minutes in a water bath. This was followed by the addition of 1.5g of clay sample into the oil and was stirred for 10 minutes to allow interaction between the oil and the clay. The bleached oil was then filtered and the properties such as colour, AV, FFA, SV, EV, IV and P V were determined.

3.5.5 Adsorption Isotherms

The concept of Freudlich adsorption isotherms was employed because the Freudlich equation is valid for any method of colour measurements, as long as the units of measurement are additive and proportional to the actual concentration of colouring materials in the oil. The mathematical expression relating adsorption to the residual solute concentration at a given temperature was given as:

$$\log {}^{x}\!/_{m} = \log k + n \log C \qquad 3.4$$

Where x represents the amount of substance adsorbed, m, the amount of adsorbent and C the concentration of the residual oil after bleaching.

The adsorption bleaching was carried out using the same procedure as in 3.5.4 above. The mass of the adsorbent (clay) was varied between 3% and 10% mass of the oil. Selected mass of clay sample was used to bleach 30g of oil at a temperature of 100^{o}C for 10-minutes. Then, x, m, and c were determined and the result used in the log plot of x/m versus c for the evaluation of n, which is the slope of the graph and k, which represents the intercept. The same procedure was carried out for all the five clay samples to know their effectiveness based on the values of n and k.

3.5.6 Deodorization

Fifty (50) grams of the bleached palm oil was charged to the vapourizer flask with the vacuum pump set in motion. The vapourizer temperature was set at 260^{0}C and pressure of 0.4kpa. This condition was maintained for 15 minutes before opening the valve of superheated steam to pass through the oil continuously, for 15 minutes. At the end of this period, the heater was turned off and the steam discontinued. The oil was allowed to cool down before putting off the vacuum pump. The oil sample was then removed and the properties like AV, FFA, SV, EV,PV and %CR were measured.

3.6 Crude and Refined Palm Oil Analysis

Certain physiochemical properties of the crude palm oil (CPO) and refined palm oil (RPO) were determined. These include colour, Acid Value (AV), free fatty acid (FFA), Saponification Value (SV), Iodine Value (I.V) Ester Value (EV) and Peroxides Value (P.V). Comparisons were made between that of CPO and RPO and between RPO using imported bleaching earth.

The procedures for the analysis were as follows:-

3.6.1 Colour and Percentage Colour Reduction

A sample of the crude palm oil was placed on a Griffin colorimeter and the colour was determined in terms of absorbance at selected wavelengths. The highest value of colour was obtained when the wavelength was 470 mm and this was considered the suitable wavelength for determining the absorbance of the subsequent bleached palm oil and the absorbance at this wavelength corresponds to the initial colour of the CPO.

Sample of the bleached palm oil was also placed in the colorimeter and the absorbance was read at 470 mm wavelength. Percentage colour reduction (%CR) for each of the bleached palm oil was calculated using the formula:

$$\%CR = \frac{Ab_0 - Ab_X}{Ab_0} \qquad 3.5$$

Where:-

Ab_0 = the absorbance of the CPO

Ab_X = the absorbance of each of the bleached oil.

3.6.2 Determination of Acid Value (Indicator Method)

Acid Value (AV) was determined by measuring 5g of the oil sample into a 250 ml conical flask. 75 ml of equal volume mixture of ethanol and diethyl ether was added to the sample. A few drops of phenolphthalein indicator were added and the contents were titrated against 0.5 M solution of ethanolic potassium hydroxide until the indicator turn pink. The same procedure was used for other samples. The acid value was then calculated using the expression below:-

$$A..V = \frac{56.1 \times N \times V}{m} \qquad 3.6$$

Where-

V = Volume of the mixture used i.e. titre value (cm^3)

N = Molarity of KOH used (M)

m = mass of palm oil used (g)

56.1 = molar mass of KOH in grams/mole.

3.6.3 Determination of Percentage Free Fatty Acid (FFA)

The free fatty acid content was expressed as percentage of weight of a specified fatty acid. Therefore, AV was converted to FFA using the formula:-

$$\% \text{ FFA} = 0.503 \times \text{AV} \qquad 3.7$$

3.6.4 Determination of Saponification Value (S.V).

Saponification value or number was expressed as the number of milligrams of KOH required to saponify completely 1g of fat (Eterigho 2001). Using the indicator method, a dry and clean pipette was used to transfer 2.0g of the oil sample into a round bottom flask. 25 ml of 0.5 M ethanolic KOH solution was added into the flask and fixed to the reflux condenser. The content was gently brought to boiling using a heating mantle for 1-hour. A few drops of phenolphthalein were added to the hot solution and the content was titrated with 0.5mol/litre HCl until the pink colour disappeared. The same procedure was used for the whole samples and the blank which contained no sample.

The Saponification Value (S.V) was calculated using the expression:-

$$S.V = \left(\frac{56.1 \times C \times (V_0 - V_1)}{m} \right) \qquad 3.8$$

Where:-

m = Mass of oil sample (g)

C = Concentration of HCl (M)

V_o = Volume of HCl solution used for blank. (cm^3)

V_1 = Volume of HCl used for the sample (cm^3)

3.6.5 Determination of Ester Value (E.V)

In oils or fats, the ester value is a measure of the amount of glycerides present and it is the difference between the saponification (S.V) and acid value A.V.

$$E.V. = S.V - A.V. \qquad 3.9$$

3.6.6 Determination of Iodine Value (I.V.)

Iodine value or number is the accepted parameters for expressing the degree of carbon to carbon unsaturation of a fat, oil, or their derivatives (Yeshajau and Clifton 1996). 2g of the oil sample was weighed into a conical flask. 2.0 ml of carbon tetrachloride and 25 ml of Dam's reagent was added to the flask. The flask was then stoppered and vigorously swirled. The whole content was then placed in the dark for 1 hour 30 minutes. This was followed by the addition of 20 ml potassium iodine solution and 150 ml of water. The content of the flask was titrated with 0.1 mol/litre of sodium thiosulphate solution until the yellow colour due to iodine completely disappeared. Few drops of starch solution were then added and the titration continued until the blue colour disappeared after vigorous shaking.

The iodine value was then calculated using the expression below:-

$$I.V = \frac{[12.69C(V_1 - V_2)]}{m} \qquad 3.10$$

Where:- C = Concentration of sodium thiosulphate (M)

V_1 = Volume of sodium thiosulphate for blank test (cm^3)

V_2 = Volume of sodium thiosulphate used for determination ($cm^{3)}$

m = mass of the test sample (g).

3.6.7 Determination of Peroxide Value (P.V.)

The peroxide value is the quantity of those substances, in the sample expressed in terms of milliequivalent of active oxygen per kilogram, which oxidizes potassium iodide under the described operating condition. The experiment was carried out in diffused day light. 2g of oil sample was weighed into a 500 ml conical flask, 10 ml of chloroform was added to dissolve the sample quickly by stirring. This was then followed by the addition of 15 ml acetic acid and 1 ml of freshly prepared saturated potassium iodide solution. The flask was then closed immediately, stirred for 1 minute and kept for exactly 5 minutes away from light at room temperature. After 5 minutes, 75 ml of water was added to the flask and shaken vigorously. Few drops of starch solution were then added as indicator. The librated iodine was then titrated against 0.01N sodium thiosulphate solution. The blank test was carried out and the same procedure was followed for all samples. The P.V was then calculated by using the formula:-

$$P.V = \frac{[(V_1 - V_0) \times T]}{m} \times 1000 \qquad 3.11$$

Where:-

V_o = volume of sodium thiosulphate solution used for blank test.(cm^3)

V_1 = volume of the sodium thiosulphate solution used for determination of sample oil (cm^3).

T = the normality of the sodium thiosulphate used (M).

m = mass of test sample (g).

CHAPTER FOUR

4.1 Results

Table 4.1 shows the average values for the mineralogical test results of 5 clay samples obtained from different locations in Oyo and Osun States of Nigeria. The clays in their neutral state, varied in chemical composition as shown in the table. However, they generally contained between 80 and 90% SiO_2, and between 5 and 10% Al_2O_3 with smaller quantities of MgO, Fe_2O_3. Only samples - 5 had very little quantity of CaO while samples 1 to 4 had none.

Table 4.1 The Average Value for Mineralogy Test

Clay Sample	*CaO%*	*MgO%*	*Fe_2O_3%*	*Al_2O_3%*	*SiO_2%*
1	0.00±0.00	0.03±0.01	3.30 ±0.00	5.22±0.00	90.36±0.01
2	0.00±0.00	0.02±0.00	3.13±0.01	6.22±0.01	90.09 ±0.01
3	0.00±0.00	0.06±0.01	3.12±0.01	8.04±0.03	88.22 ±0.03
4	0.00±0.00	0.01±0.00	10.80±0.01	6.51±0.01	81.89 ±0.01
5	0.02±0.00	0.30±0.00	2.52±0.01	5.18±0.03	91.29±0.01

Table 4.2 is the average values of the physical properties of the 5 clay samples in their natural state. The table shows the pore volume, solid density, particle density and the porosity for each of the clay samples. Clay samples 1, 3, and 5 have nearly equal porosity values (0.40 on the average). The highest value was recorded in clay sample 2 while sample 4 has the least.

Table 4.2 Average Values for the Physical Properties of the Clay Samples

Clay Sample	*Pore Vol. Cm^3*	*Solid Den. g/cm^3*	*Particle Dens. g/cm^3*	*Porosity*
1	0.40 ±0.01	2.00±0.04	0.90±0.14	0.444±0.14
2	0.60 ±0.01	1.67±0.14	0.833±0.14	0.500±0.14
3	0.45 ±0.01	1.54±0.01	1.00±0.14	0.410±0.14
4	0.30 ±0.01	2.00±0.14	1.25±0.14	0.375±0.04
5	0.40 ±0.01	2.00±0.14	1.11±0.14	0.444±0.14

Table 4.3 shows the average values for the physiochemical properties of the crude palm oil used in the investigation. The properties include the acid value (AV), the free fatty acid (FFA), Saponification value (SV), Iodine value (IV), Ester Value (E.V), Peroxide Value (PV) and the colour measured in terms of absorbance (Ab) at 470 nm wavelength.

Table 4.3: Average Values for the Physiochemical Properties of Crude Palm Oil Used.

Characteristics	*Experimental Value*
AV	15.71±0.01
FFA	7.90±0.01
S.V	144.18±0.01
EV	128.47±0.01
IV	50.87±0.01
PV	0.95±0.00
Ab	2.57±0.00

Table 4.4 shows the estimated yield of the crude palm oil after neutralization of the free fatty acid with NaOH at different concentrations. At a fixed mass of palm oil (22.00g), the highest yield was recorded when the concentration of NaOH was 2-M. Hence, 2-M was considered the best concentration of NaOH required for the neutralization of the crude palm oil used.

Table 4.4: Estimated Yield of Palm oil after Neutralization with various Concentration of NaOH

Conc. of NaOH (m)	*Mass of Oil After Neutralization (g)*	*Yield (%)*	*FFA (%)*
0.50	10.00 ±0.14	45.45±0.14	0.91±0.01
1.00	8.00±0.14	36.40±0.14	0.77±0.16
1.50	15.00±0.14	68.20±0.14	0.48±0.03
2.00	15.50±0.01	70.45±0.14	0.31±0.03
2.50	10.23±0.14	46.51±0.14	0.32±0.03
3.00	5.00±0.14	23.00±0.14	0.40±0.00
3.50	3.50±0.14	15.90±0.14	0.30±0.03

Table 4.5 shows the average values for the properties of the oil obtained when the 5-clay samples in their pure natural states were used as an adsorbent in the refining of palm oil.

Table 4.5: Average Values for the Properties of Oil obtained when Unactivated Clay Samples were used for Refining.

Clay Sample	*AV*	*FFA*	*S.V I/g)*	*I.V (gI/100g)*	*E.V*	*P.V g)*	*% CR*
1	12.51±0.00	6.29±0.01	160.42±0.01	58.26±0.03	147.91±0.0	0.98±0.01	45.02±0.00
2	12.56±0.00	6.32±0.00	142.53±0.04	58.23±0.01	129.97±0.0	1.04±0.00	45.53±0.00
3	13.23±0.01	6.65±0.00	162.42±0.03	58.31±0.01	149.20±0.0	0.96±0.00	41.63±0.01
4	12.34±0.00	6.21±0.02	160.27±0.03	57.98±0.01	147.93±0.0	0.96±0.00	43.20±0.00
5	12.67±0.01	6.37±0.01	144.17±0.04	58.12±0.03	131.50±0.0	1.26±0.03	45.14±0.01

Tables 4.6 - 4.10 show the average values for the properties of oil obtained when clay samples 1-5 activated with HCl at concentration ranges between 15% and 45% were used for refining palm oil. Samples A_{15} to A_{45} designate the bleached oil samples corresponding to the concentration of HCl used for activation for each of the clay samples. Similarly Tables 4.11-4.15 show the average values for the properties of oil obtained when clay sample 1-5 activated with H_2SO_4 at concentration ranges between 15 and 45% were used for refining of palm oil. The properties considered includes the acid value (AV), free fatty acid (FFA), Saponification Value (SV), Iodine Value (IV), Ester Value (EV), Peroxide Value (PV), Percentage colour reduction (%CR), and the yield after bleaching. Samples H_{15} to H_{45} designates the bleached oil samples corresponding to the concentration of H_2SO_4 used for activation of each of the clay.

Tables 4.16 – 4.18 show the average values of the results obtained for the adsorption isotherms when the mass of the adsorbent were varied in the bleaching process of palm oil.

Table 4.6: The Average Values for the Properties of Oil Obtained when HCl Activated Clay Sample 1 was Used for Oil Refining.

Oil Sample	*Acid Conc.*	*AV (g/mol)*	*FFA*	*S.V (mgKOH/g)*	*I.V (gI/100g)*	*E.V*	*P.V (milleq/g)*	*% CR (%)*	*Yield (%)*
$1A_{15}$	15%	14.70±0.14	7.39±0.07	144.16±0.14	51.14±0.14	129.46±0.00	0.96±0.00	60.31±0.01	97.12±0.16
$1A_{25}$	25%	14.74±0.14	7.41±0.07	143.80±0.14	51.11±0.14	129.06±0.00	0.96±0.00	60.31±0.01	88.33±0.00
$1A_{35}$	35%	14.81±0.14	7.45±0.06	143.62±0.15	50.98±0.00	128.81±0.00	1.12±0.03	65.00±0.00	80.33±0.01
$1A_{45}$	45%	15.68±0.14	7.88±0.06	143.60±0.14	50.98±0.00	127.92±0.00	1.16±0.00	64.80±0.03	80.00±0.00

Table 4.7: The Average Values for The Properties of Oil Obtained when Activated Clay Sample 2 was Used for Oil Refining.

Oil Sample	*Acid Conc.*	*AV (g/mol)*	*FFA*	*S.V (mgKOH/g)*	*I.V (gI/100g)*	*E.V*	*P.V (milleq/g)*	*% CR*	*Yield (%)*
$2A_{15}$	15%	14.79±0.03	7.41±0.01	144.16±0.03	51.132±0.04	129.42±0.05	1.02±0.03	3.49±0.01	97.20±0.14
$2A_{25}$	25%	14.80±0.14	7.44±0.05	143.80±0.01	51.13±0.14	129.00±0.14	1.04±0.14	62.10±0.14	87.12±0.14
$2A_{35}$	35%	14.81±0.14	7.45±0.05	143.64±0.14	51.10±0.14	128.83±0.01	1.04±0.14	64.82±0.14	78.17±0.14
$2A_{45}$	45%	14.83±0.09	7.45±0.04	143.64±0.14	51.10±0.14	128.83±0.01	1.01±0.14	64.61±0.14	78.20±0.14

Table 4.8: Properties of the Oil Obtained when HCl Activated Clay Sample – 3 was used for Oil Refining

Oil Sample	*Acid Conc.*	*AV (g/mol)*	*FFA*	*S.V (mgKOH/g)*	*I.V (gI/100g*	*E.V*	*P.V (molleg(g)*	*% CR*	*Yield (%)*
$3A_{15}$	15%	14.81±0.01	7.45±0.00	144.18±0.03	51.14±0.03	129.37±0.01	0.98±0.01	42.41±0.15	S 93.33±0.03
$3A_{25}$	25%	14.92±0.03	7.50±0.01	144.06±0.05	51.12±0.03	129.14±0.03	1.20±0.01	45.53±0.14	92.33±0.00
$3A_{35}$	35%	14.92±0.03	7.51±0.02	144.02±0.14	51.16±0.14	129.10±0.16	1.19±0.14	45.53±0.14	88.12±0.14
$3A_{45}$	45%	14.40±0.14	7.24±0.06	143.98±0.14	52.01±0.41	129.58±0.14	1.20±0.14	45.00±0.01	88.20±±0.14

Table 4.9: The Average Values for the Properties of Oil Obtained when HCl Activated Clay Sample 4 was Used for Oil Refining .

Oil Sample	*Acid Conc.*	*AV (g/mol)*	*FFA (g/mol)*	*S.V (mgKOH/g)*	*I.V (gI/100g)*	*E.V*	*P.V (molleg(g)*	*% CR*	*Yield (%)*
$4A_{15}$	15%	15.21±0.55	7.65±0.29	144.67±0.14	51.26±0.14	129.46±0.69	0.98±0.14	40.20±0.05	95.21±0.14
$4A_{25}$	25%	15.34±0.14	7.72±0.09	144.54±0.14	51.16±0.14	129.20±0.00	0.98±0.14	42.42±0.14	93.32±0.14
$4A_{35}$	35%	14.47±0.16	7.78±0.01	144.52±0.14	51.11±0.14	130.05±0.83	1.21±0.14	42.50±0.14	90.40±0.14
$4A_{45}$	45%	15.46±0.14	7.78±0.14	144.52±0.14	51.36±0.14	129.06±0.00	1.17±0.14	42.51±0.14	90.38±0.14

Table 4.10: The Average Values for the Properties of Oil Obtained when HCl Activated Clay Sample 5 was Used for Oil Refining .

Oil Sample	*Acid Conc.*	*AV (g/mol)*	*FFA*	*S.V (mgKOH/g)*	*I.V (gI/100g*	*E.V*	*P.V (millieq/g)*	*% CR*	*Yield (%)*
$5A_{15}$	15%	12.86±0.25	6.47±0.16	144.32±0.14	51.02±0.14	131.46±0.08	1.20±0.14	57.42±0.14	97.40±0.14
$5A_{25}$	25%	12.98±0.14	6.53±0.07	142.26±0.14	51.06±0.14	129.71±0.00	1.32±0.14	69.08±0.14	95.34±0.14
$5A_{35}$	35%	12.98±0.67	6.53±0.01	140.40±0.14	50.02±0.14	129.28±0.03	1.41±0.14	70.40±0.14	92.60±0.14
$5A_{45}$	45%	13.02±0.14	6.55±0.07	143.98±0.14	51.02±0.14	127.36±0.00	1.40±0.14	74.28±0.14	92.41±0.14

Table 4.11: The Average Values For The Properties Of Oil Obtained When Activated Clay Sample 1 was Used For Oil Refining .

Oil Sample	*Acid Conc.*	*AV (g/mol)*	*FFA*	*S.V (mgKOH/g)*	*I.V (gI/100g)*	*E.V*	*P.V (milleq/g)*	*CR (%)*	*Yield (%)*
$1H_{15}$	15%	15.15±0.14	7.62±0.07	144.56±0.14	51.32±0.14	129.41	0.96±0.14	43.20±0.14	94.88±0.14
$1H_{25}$	25%	15.50±0.14	7.80±0.07	144.31±0.14	51.24±0.14	128.81	0.98±0.14	45.53±0.14	90.00±0.14
$1H_{35}$	35%	14.25±0.14	7.20±0.07	144.12±0.14	51.23±0.14	129.87	0.96±0.14	45.46±0.14	84.33±0.15
$1H_{45}$	45%	14.30±0.14	7.19±0.07	144.11±0.14	51.23±0.14	129.81	0.96±0.14	44.36±0.14	83.53±0.14

Table 4.12: The Average Values for the Properties of Oil Obtained When H_2SO_4 Activated Clay Sample 2 was Used for Oil Refining Oil.

Oil Sample	*Acid Conc.*	*AV (g/mol)*	*FFA*	*S.V (mgKOH/g)*	*I.V (gI/100g*	*E.V*	*P.V (milleq/g)*	*% CR*	*Yield (%)*
$2H_{15}$	15%	15.23±0.14	7.66±0.07	144.61±0.14	51.34±0.14	129.38±0.00	1.03±0.14	42.41±0.14	94.92±0.14
$2H_{25}$	25%	15.22±0.14	7.65±0.07	144.56±0.14	51.27±0.14	129.35±0.00	1.12±0.14	43.26±0.14	93.12±0.14
$2H_{35}$	35%	15.21±0.14	7.65±0.01	144.31±0.14	51.23±0.14	129.10±0.00	1.12±0.14	43.74±0.14	93.10±0.14
$2H_{45}$	45%	16.42±0.12	8.30±0.41	144.31±0.14	51.23±0.14	127.89±0.00	1.30±0.14	43.42±0.14	92.86±0.14

Table 4.13: The Average Values for the Properties of Oil Obtained when H_2SO_4 Activated Clay Sample 3 was Used for Oil Refining.

Oil Sample	*Acid Conc.*	*AV (g/mol)*	*FFA*	*S.V (mgKOH/g)*	*I.V (gI/100g*	*E.V*	*P.V (millieq/g)*	*% CR*	*Yield (%)*
$5H_{15}$	15%	14.92±0.14	7.50±0.10	145.26±0.14	51.34±0.14	130.34±0.00	1.03±0.14	43.58±0.14	**92.00±0.14**
$5H_{25}$	25%	14.98±0.14	7.53±0.07	144.81±0.14	51.21±0.14	129.83±0.00	0.98±0.14	43.96±0.14	**91.33±0.14**
$5H_{35}$	35%	14.98±0.14	7.53±0.07	144.74±0.14	51.19±0.14	129.81±0.00	1.13±0.14	42.41±0.14	**88.13±0.14**
$5H_{45}$	45%	15.12±0.14	7.61±0.04	145.13±0.14	50.84±0.14	130.01±0.00	1.12±0.14	40.60±0.14	**89.34±0.14**

Table 4.14: The Average Values for the Properties of Oil Obtained when H_2SO_4 Activated Clay Sample 4 was Used for Oil Refining.

Oil Sample	*Acid Conc.*	*AV (g/mol)*	*FFA*	*S.V (mgKOH/g)*	*I.V (gI/100g*	*E.V*	*P.V (millieq/g)*	*% CR*	*Yield (%)*
$4H_{15}$	15%	15.43±0.06	7.76±0.01	144.48±0.14	51.36±0.14	129.05±0.78	0.97±0.14	40.16±0.14	97.12±0.14
$4H_{25}$	25%	15.46±0.04	7.78±0.13	144.54±0.14	51.24±0.14	129.08±0.14	0.95±0.14	40.18±0.13	96.80±0.14
$4H_{35}$	35%	15.52±0.47	7.81±0.01	144.62±0.14	51.23±0.14	129.10±1.27	0.98±0.14	40.21±0.14	96.50±0.14
$4H_{45}$	45%	15.51±0.01	7.80±0.27	144.67±0.14	51.24±0.14	129.16±0.15	1.01±0.14	41.72±0.14	95.48±0.07

Table 4.15: The Average Values for the Properties of Oil Obtained when H_2SO_4 Activated Clay Sample 5 was Used for Oilss Refining .

Oil Sample	*Acid Conc.*	*AV (g/mol)*	*FFA*	*S.V (mgKOH/g)*	*I.V (gI/100g*	*E.V*	*P.V (millieq/g)*	*% CR*	*Yield (%)*
$5H_{15}$	15%	12.92±0.14	6.49±0.01	144.46±0.14	51.08±0.14	131.54±0.01	0.98±0.14	52.86±0.14	97.42±0.00
$5H_{25}$	25%	12.96±0.16	6.52±0.01	144.32±0.14	52.14±0.14	131.36±0.01	1.14±0.14	56.42±0.14	96.13±0.14
$5H_{35}$	35%	13.17±0.14	6.62±0.01	144.42±0.14	51.83±0.14	132.25±0.01	1.21±0.14	69.46±0.14	93.14±0.14
$5H_{45}$	45%	13.34±0.14	6.71±0.01	144.26±0.14	51.08±0.14	129.92±0.01	1.26±0.14	58.13±0.14	93.18±0.14

Table 4.16 The Average Values for the Adsorption Isotherms Results for Clay Samples 1-5

Clay Sample -1					*Clay Sample -2*				
M	X	C	Log(x/m)	Log C	M	X	C	Log(x/m)	Log C
1.0	1.23±0.04	0.79±0.00	0.089±0.01	-0.089±0.01	1.0	0.94±0.03	1.20±0.31	-0.027±0.01	0.079±0.01
1.5	0.68±0.04	0.90±0.08	-0.343±0.02	-0.046±0.04	1.5	0.50±0.08	1.01±0.00	-0.477±0.07	0.004±0.00
2.0	0.60±0.03	0.82±0.01	-0.522±0.02	-0.086±0.01	2.0	0.46±0.03	0.82±0.01	-0.638±0.03	-0.086±0.01
2.5	0.42±0.03	0.70±0.03	-0.775±0.03	-0.155±0.01	2.5	0.37±0.00	0.76±0.01	-0.830±0.00	-0.119±0.01
3.0	0.20±0.00	0.41±0.01	-1.176±0.00	-0.387±0.26	3.0	0.20±0.00	0.61±0.01	-1.176±0.00	-0.215±0.00

Table 4.17 Adsorption Isotherms Results for Clay Samples 3 and 4

Clay Sample -3					*Clay Sample -4*				
M	X	C	Log (x/m)	Log C	M	X	C	Log (x/m)	Log C
1.0	0.98±0.05	1.32±0.03	-0.009±0.01	-0.121±0.01	1.0	1.20±0.03	0.887±0.01	-0.079±0.05	-0.052±0.03
1.5	0.54±0.03	1.02±0.00	-0.444±0.02	-0.009±0.00	1.5	1.00±0.00	0.68±0.00	-0.176±0.00	-0.168±0.00
2.0	0.52±0.03	0.98±0.03	-0.585±0.02	-0.009±0.01	2.0	0.88±0.05	0.62±0.05	-0.357±0.03	-0.208±0.04
2.5	0.48±0.00	0.82±0.03	-0.717±0.00	-0.086±0.01	2.5	0.67±0.00	0.56±0.00	-0.572±0.00	-0.252±0.00
3.0	0.40±0.00	0.64±0.00	-0.875±0.00	-0.194±0.00	3.0	0.58±0.03	0.48±0.08	-0.714±0.02	-0.319±0.07

Table 4.18: Adsorption Isotherms Result for Clay Sample- 5.

Clay Sample –5				
M	X	C	Log (x/m)	Log C
1.0	1.20±0.03	0.92±0.03	0.079±0.01	-0.036±0.01
1.5	0.70±0.03	0.90±0.00	-0.330±0.02	-0.045±0.00
2.0	0.58±0.03	0.89±0.03	-0.540±0.02	-0.051±0.01
2.5	0.40±0.03	0.68±0.01	-0.800±0.03	-0.167±0.01
3.0	0.30±0.00	0.60±0.00	-1.000±0.00	-0.222±0.00

Table 4.19 shows n and k-values of the five local clay samples used in the investigation. n designated the slope and k designated the intercept when Log (x/m) was plotted against Log C using Freudlich adsorption equation.

Table 4.19 Values of n and K from the Isotherms

Adsorbents	*n – Values*	*K – Values*
Clay – 1	3.86	0.28
Clay – 2	3.90	0.37
Clay – 3	4.70	0.55
Clay – 4	-	-
Clay – 5	3.60	0.14

Table 4.20 shows the average values for the property changes during various refining processes. The properties considered are: AV, SV, IV, FFA, EV, PV and colour.

Table 4.21, on the other hand, shows the results when comparing local activated clays with imported bleaching earth (bentonite). The percentage colour reduction (%CR), n and k – values from the adsorption isotherms plot were shown.

Table 4.20: The Average Values for the Property Changes During Various Refining Processes

Property Measurement	*Crude oil*	*Neutralized oil*	*Bleached oil*	*Deodorized oil*
AV	15.71±0.14	12.51±0.14	14.81±0.14	1.107±0.14
SV	144.18±0.14	128.12±0.14	143.62±0.14	101.87±0.14
IV	50.87±0.04	50.82±0.14	51.02±0.14	51.06±0.14
FFA	7.90±0.14	6.32±0.04	7.45±0.04	0.56±0.14
EV	128.47±0.14	115.61±0.14	128.81±0.14	90.79±0.14
PV	0.95±0.14	0.98±0.14	1.40±0.14	1.42±0.01

Table 4.21 show the percentage colour reduction (%Cr). Freudlich Adsorption isotherm constants (n and K) for clay samples 1, 5 and imported bleaching earth (Bentonite).

Table 4.21: %Cr, n and K Values for Local Activated Clay and Imported Bleaching Earth

Adsorbents	*%CR*	*N*	*K*
Bentonite	80%	3.30	0.14
Clay – 1	65%	3.86	0.28
Clay – 5	74.28%	3.60	0.14

Table 4.22 shows the physiochemical properties of the best locally refined and deodorized palm oil compared with imported refined palm oil [KINGS OIL produces by KUOK OILS and grain LIMITED, Singapore].

Table 4.22: Properties of Local and Imported Refined Palm Oil

Properties	*King's oil*	*Local refined oil*
AV	0.280	0.675
SV	186.50	150.40
IV	15.20	19.70
PV	1.45	1.40
EV	186.22	149.72
FFA	0.141	0.340

Fig 4.1 to 4.5 show the Adsorption Isotherm plots of the Clay Samples 1 to 5 when Freudlich Adsorption equation given in equation 2.8 was applied.

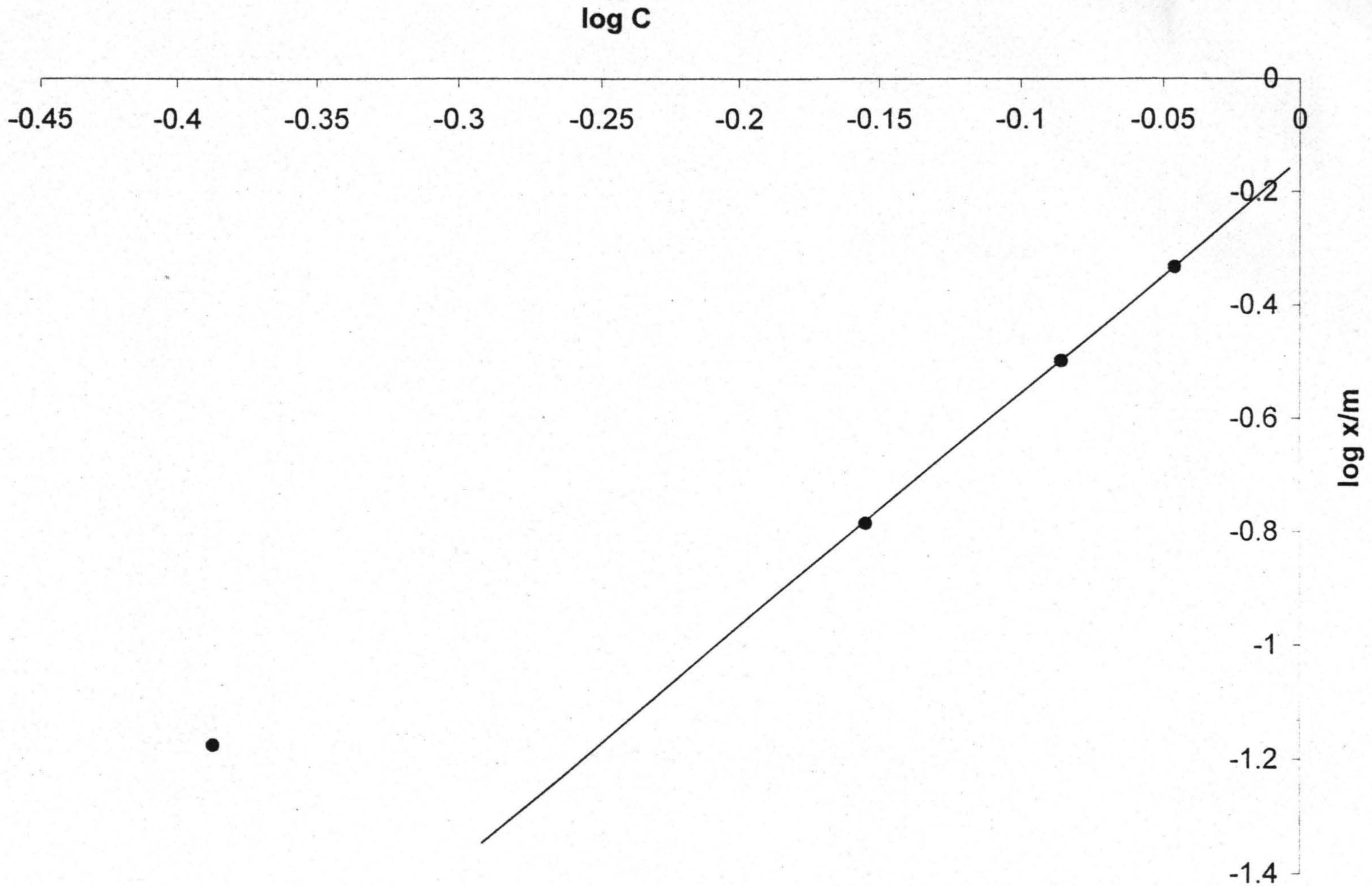


Fig 4.1: Adsorption Isotherm Plot for Clay Sample 1

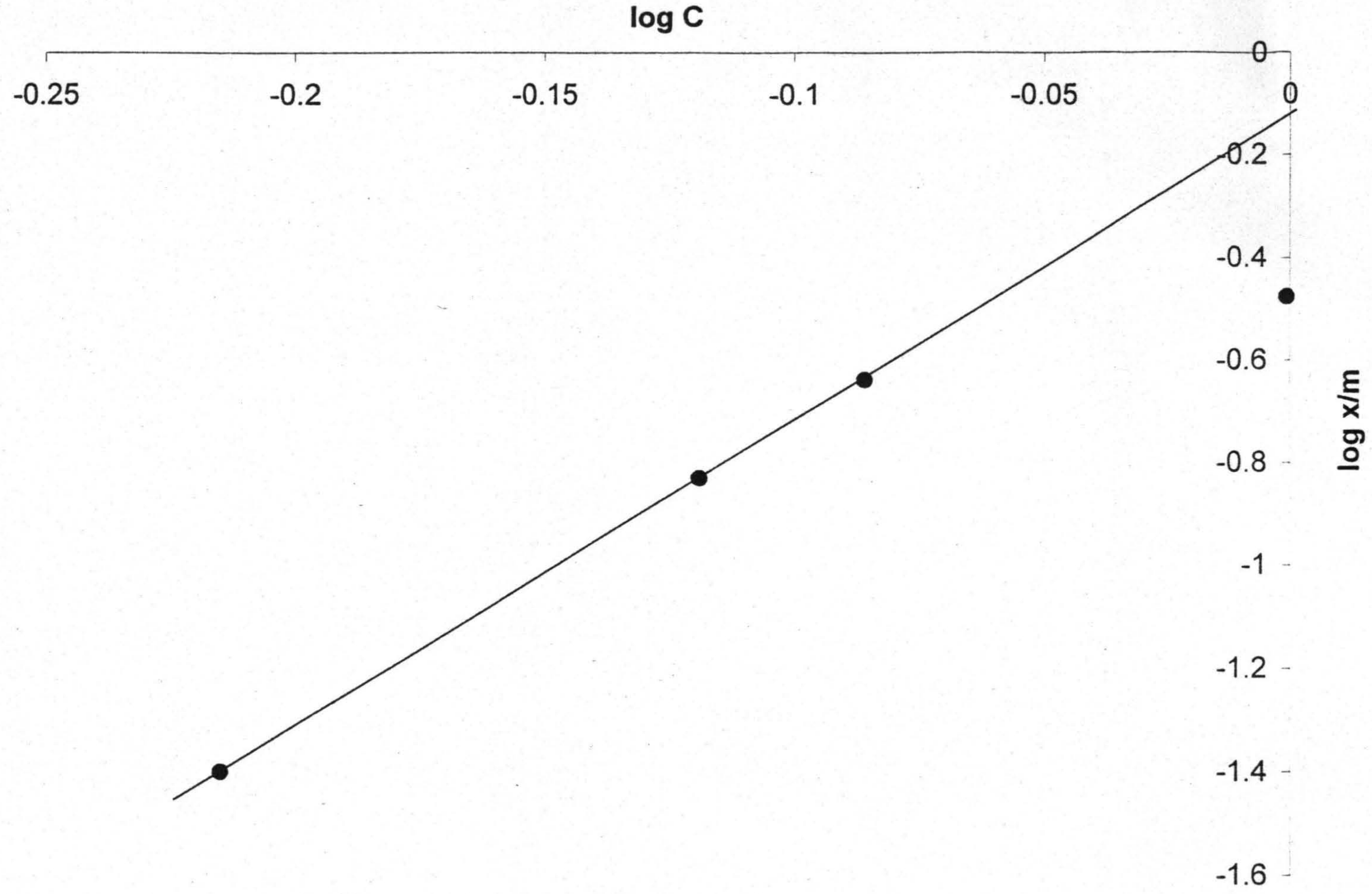


Fig 4.2: Adsorption Isotherm for Clay Sample - 2

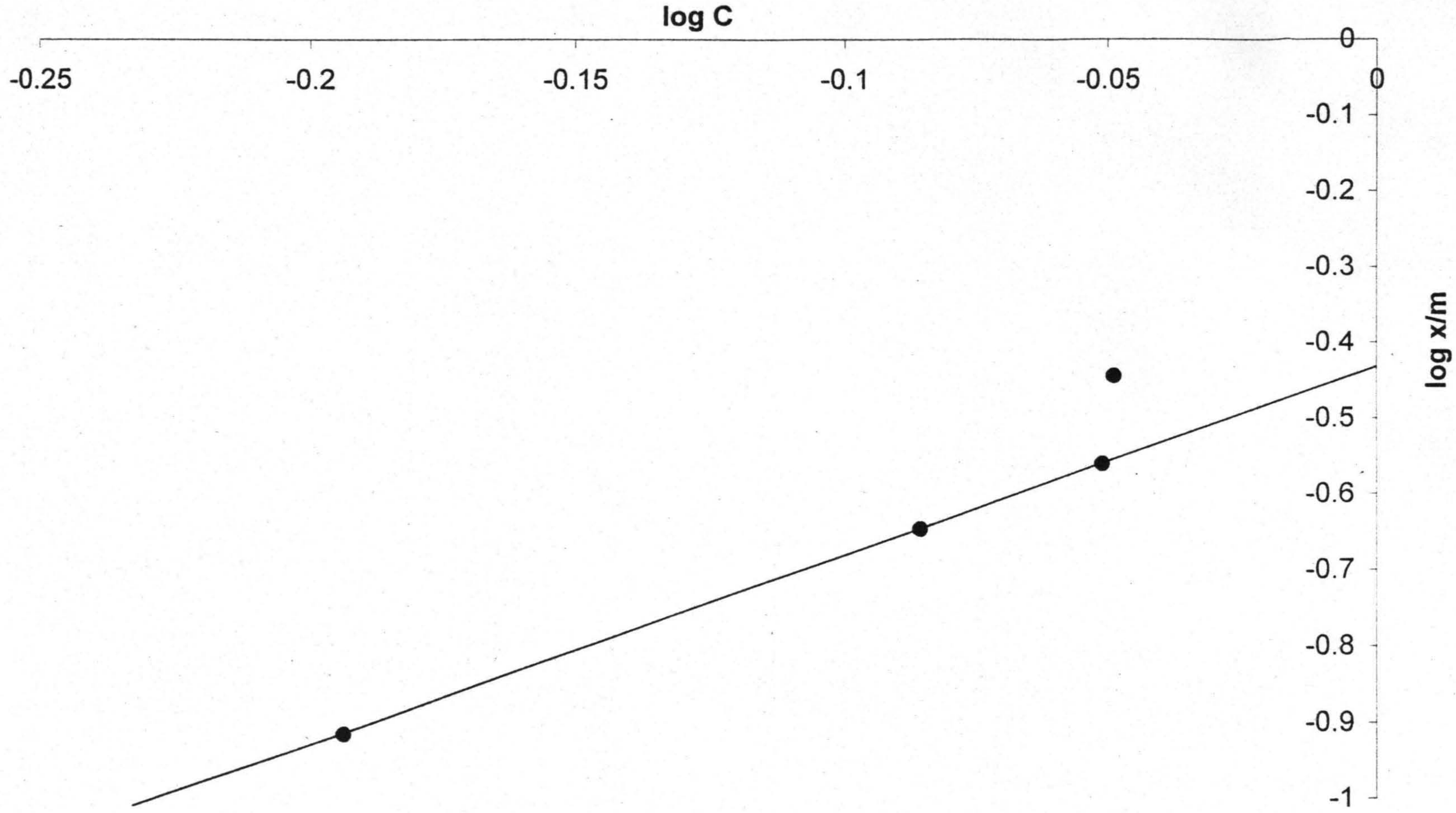


Fig 4.3: Adsorption Isotherm for Clay Sample 3

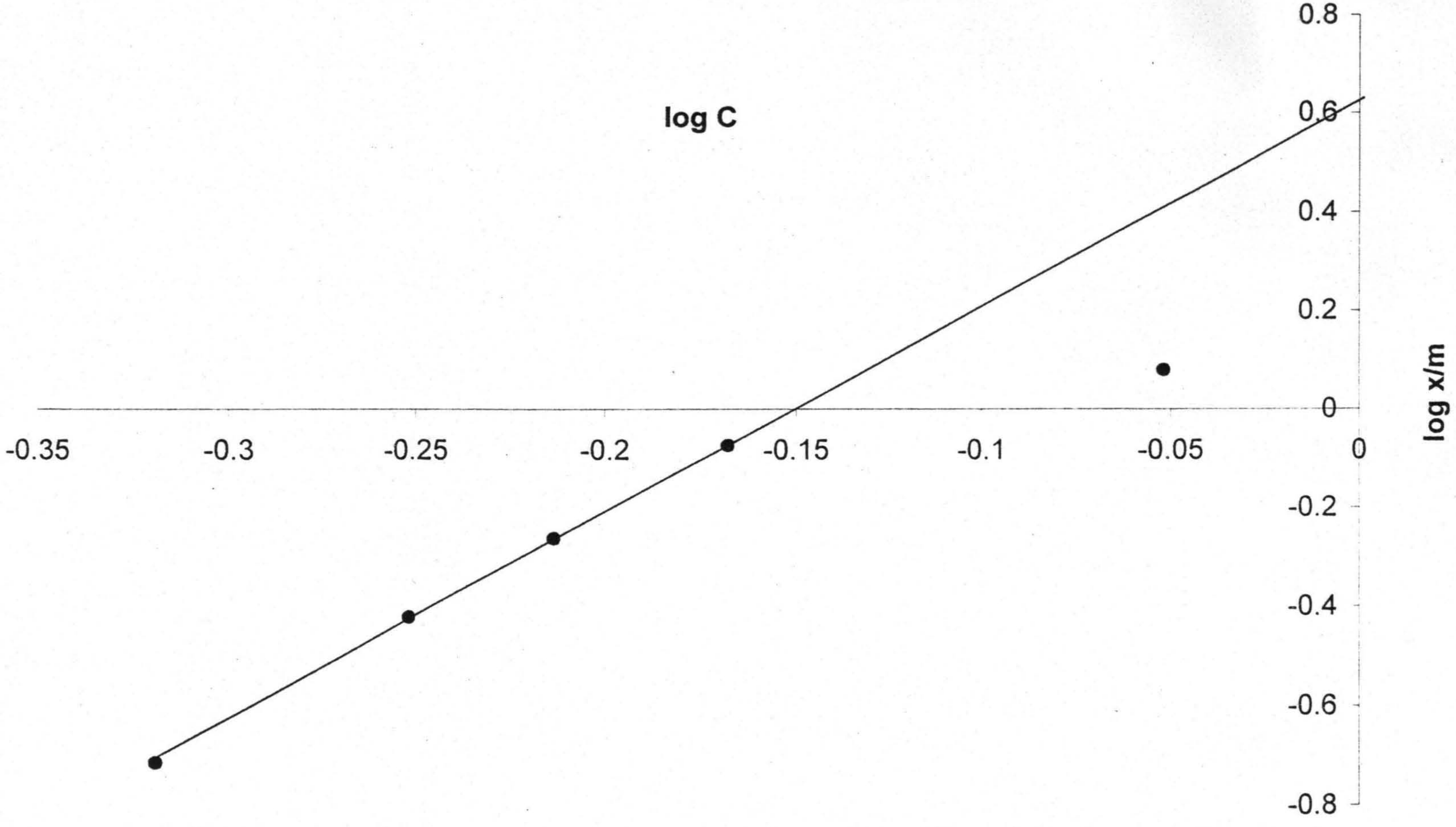


Fig 4.4: Adsorption Isotherm for Clay Sample 4

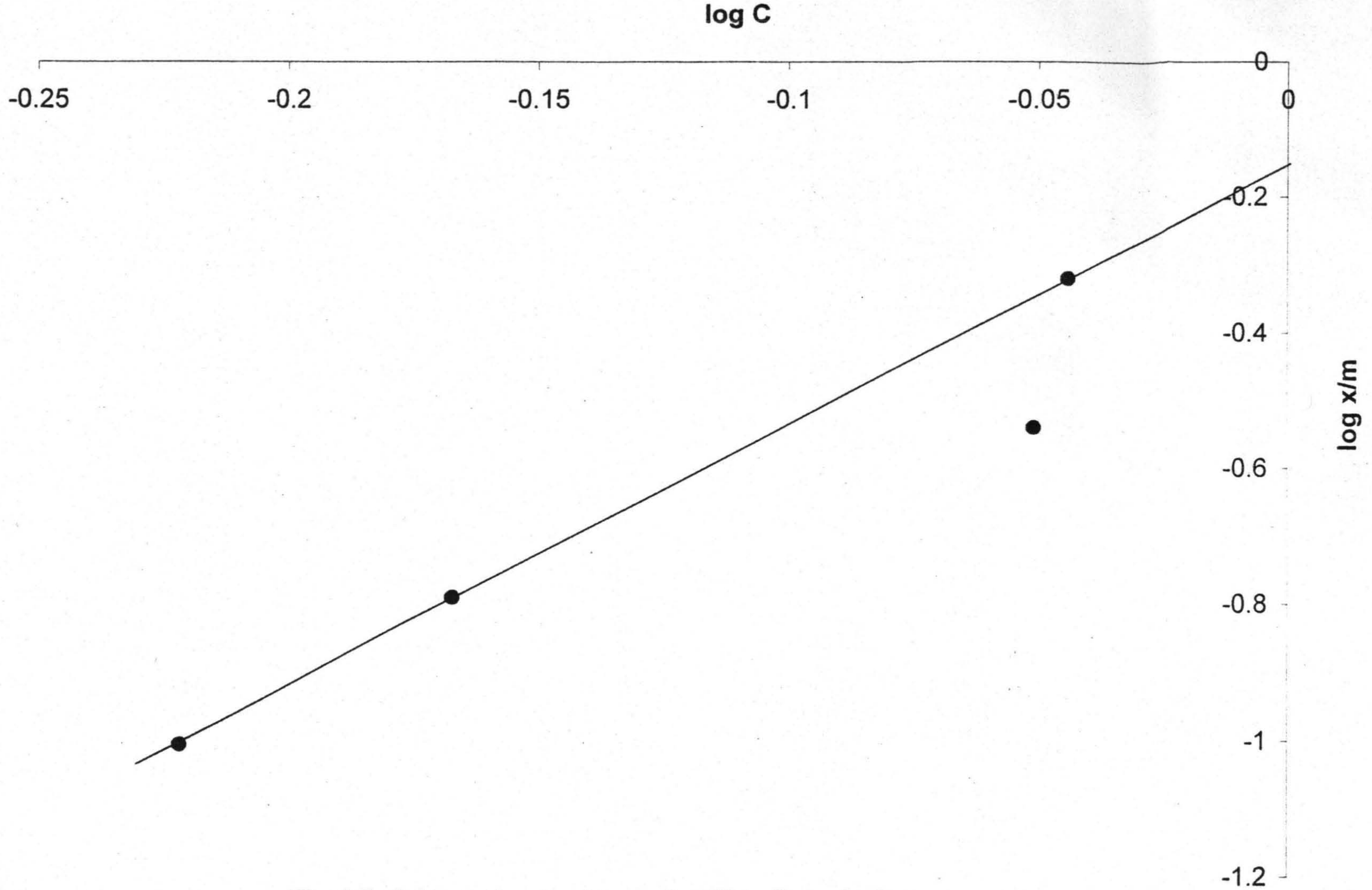


Fig 4.5: Adsorption Isotherm for Clay Sample 5

4.2 DISCUSSION OF RESULTS

4.2.1 Mineralogy and Porosity Results

Clays from different sources in their natural states varied in chemical composition as shown in Table 4.1. However, they generally contained SiO_2, Al_2O_3, with smaller quantities of MgO, Fe_2O_3, CaO and at times K_2O. Due to the variations in chemical composition, there were large variations in physical properties like pore volume, solid density, particle density and porosity of clays from different locations (Blatt *et al* 1980) as shown in Table 4.2. The results also showed that the clay samples 1, 2, and 5 contained predominantly montmorillonites, which is a very good bleaching earth, while clay samples 3, and 4 were mainly kaolinitic hence low bleaching power in their pure natural states. This was evident in the porosity values of the clays, where clay samples 1, 2, and 5 have higher porosity values of 0.444, 0.500 and 0.444 respectively when compared with clay samples 3 and 4 with corresponding values of 0.410, and 0.375 respectively. This indicated that the higher the porosity, the better the adsorptive power. This was further confirmed by the results obtained when the clay samples in their pure natural states were used for the refining of palm oil as shown in Table 4.5.The results showed that higher percentage colour reductions in clay samples 1, 2 and 5 with 45.02, 45.53 and 45.14% CR, compared with clay samples 3 and 4 with 41.63, and 43.20% CR respectively.

4.2.2 Effect of Adsorptive Bleaching on Physiochemical Properties of Palm Oil

In order to determine the effect of clay activation on the refining of palm oil, the results of the properties of unrefined palm oil as shown in Table 4.3 were compared with those of refined oil in Table 4.6. For clay sample – 1, when HCl was used as the acid of activation, the results shown in Table 4.6 showed that the percentage colour reduction (%CR) increased as concentration of acid increased with corresponding decrease in oil yield. This was because, as concentration of acid increased, porosity of the clays correspondingly increased and more colouring matter that formed the bulk oil were adsorbed. Hence, the percentage colour reduction ranged between 43.57% and 64.80% when the concentration of acid ranged between 15% and 45%. The same explanation holds for clay samples 2, 3, 4 and 5 with %CR ranged between 43.49% and 64.61, 42.41% and 45.00%, 40.20% and 42.50%, and 57.42% and 74.28% respectively. It is therefore obvious from these results that clay samples 1, 2, and 5 were more effective than clay samples 3, and 4.

When H_2SO_4 was used as acid of activation, the same trend was observed as when HCl was used except that maximum percentage colour reduction was recorded in clay samples – 5 with 69.46% when the concentration of H_2SO_4 was 35%. The results shown in Tables 4.11 – 4.15 showed that clay sample 5 proved more effective than the rest clays with 69.46% colour reduction. The better performance of clay sample 5 could be traced to the lesser percentage of Fe_2O_3 and presence of CaO (0.02%) in its composition. It could therefore be deduced from the results that activation with concentration of H_2SO_4 greater than 35% was not economical since most clay samples attained their maximum effectiveness between 25% and 35% H_2SO_4 concentration. It is also evident from the literature that the improvement in the bleaching power of activated clay was due to the removal of some oxides of Fe and Mg from the clay samples during activation, therefore increasing the clay porosity (Brace, 1973). Moreover, the better adsorptive power of HCl activated clays is traceable to the high solubility of the chlorides of Mg, Ca and Fe than the sulphates of the same metals.

In order to determine the effect of adsorption (using activated clays) on the bleached palm oil, the Peroxide Value (PV), which is the commonly used measure of oxidative rancidity (Chan, 1987) was used. The values obtained were compared with standards from literatures and international standard organization ISO 3960 [1977]. The PV obtained when unactivated clays were used for refining of palm oil ranged between 0.98 and 1.26 milliequvalent/kg. The results were in agreement with the standard stipulated by international standard organisation (ISO 3960, 1977), where the standards ranges between 0 – 12 millieq/kg when the mass of test portion ranges between 5.0 – 2.0g. When activated clays were used for refining of palm oil, the PV obtained ranged between 1.04 and 1.41 (as shown in Tables 4.6 to 4.10) for HCl activated clays and 0.98 and 1.30 (as shown in Tables 4.11 to 4.15) for H_2SO_4 activated clays. The results compared favourably with ISO 3960 1977 Standards shown in Table 4.23.

Iodine Value is the accepted parameter for expressing the degree of unsaturation of fat, oil or their derivatives (Yeshajau *et al.,* 1996). Non drying oils have an IV less than 100, drying oils between 130 – 200, and semi drying oils have intermediate values (Cocks and Van Rede, 1966). The results of the IV obtained (as shown in Table 4.5) ranges between 57.98 and 58.23gm iodine/100gm of oil sample when nonactivated clays were used for refining of palm oil. The results are in agreement with the values obtained in literatures as shown in Tables 4.24 (Cocks and Van Rede, 1966). When activated clays were used, the IV ranges between 50.98 and 52.01 for HCl activated clays and between

50.84 and 52.12 for H_2SO_4 activated clays. Therefore, it can be deduced from the results that the palm oil used is a non-drying type and contains mostly saturated fatty acids.

Saponification Value (SV) is an indication of the average molecular weight of fat or oil. It is used in combination with other physiochemical properties in identification and detection of adulteration in fats or oils. The results obtained as shown in Table 4.5 when nonactivated clays were used for refining of palm oil were in the range of 144.17 and 160.42. Similarly, when the best activated clays were used, the results obtained ranges between 143.98 & 144.32 (Table 4.10) and 144.26 & 144.46 (Table 4.15) for both HCl activated clays and H_2SO_4 activated clays. These results were slightly lower compared with the standard range (196 – 205) given by (Cocks and Van Rede, 1966). This may be due to adulteration or experimental error during the analysis of the oil.

The acid values [AV] obtained ranged from 12.23 to 12.67 when non-activated clays were used in the refining of palm oil. These results were in conformity with the values given by Cocks and Van Rede, (1966). Generally, non refined palm oil always has higher acid value, at times it may be up to 85g/mol, depending on the level of contamination during production. This implies that palm oil is prone to deterioration by hydrolysis of its triglyceride to yield free fatty acids and glycerol, if not properly refined. When activated clays were used, the acid values slightly increased to the range between 12.86 – 16.42 and this was due to the effect of residual acid on the activated clays. The residual acidity of the clay thus affected not only the performance of the clay but also the AV of the bleached oil. Therefore, the residual acidity after activation should not be too high so as not to impact other products to the oil and not to be too low so as not to reduce the performance of the clay (Hymore, 1989). The ester values (EV) depends on both the SV and AV, hence it is the difference between the SV and AV. In oils and fats, the EV is a measure of the amount of glycerides present. The EV obtained when non-activated clays were used for the refining of palm oil ranges between 131.50 – 149.20 and 127.36 – 131.46 when activated clays were used. These results agreed with the values given by Cocks and Van Rede (1966).

4.2.3 Effectiveness of Activated Local Clays Using Freudlich Adsorption Isotherms.

The effectiveness of the clay was further investigated by using the concept of Freudlich adsorption isotherms. Freudlich equation is valid for any method of colour measurement, as long as the units of measurement are additives and proportional to the actual concentration of colouring materials in the oil (Hui, 1996). The values of n and k (Freudlich adsorption constant) obtained from isotherm plots 4.1, 4.2, 4.3, 4.4, and 4.5 shows that clay samples 1, 2, 3 and 5 have n values equal to 3.86, 3.90, 4.70 and 3.60 respectively while their corresponding **k** values equal to 0.14, 0.37, 0.55 and 0.14. It can be deduced from these results that clay sample 5 was mostly effective followed by clay samples 1, 2 and finally 3. This could be attributed to the fact that the value of **n** determines the degree of decolourization within which the adsorbent exhibit its greatest relative effect. If **n** is high, the adsorbent is relatively inefficient as an agent for effecting a high degree of decolourization, if **n** is low the reverse is the case (Okeke, 1990). Furthermore, from the practical standpoint, **k** – value is a general measure of the activity of the adsorbent, whereas **n** is an indication of its characteristics manner of adsorption (Hui, 1996). **n** and **k** – values could not be determined for clay 4, and this could be traced to its low adsorptive power, hence, it is considered the least effective.

4.2.4 Comparison Between Activated Local Clays and Imported Bleaching Earth.

To draw a comparison between the imported bleaching earth and the local activated clays, the best two local clays (clay samples 1 and 5) and bentonite (imported clay) were used for refining of palm oil. It was observed from the results shown in Table 4.21 that at a bleaching temperature of 100°C using 10% weight dose of each adsorbent, the percentage colour reductions were 65.00%, 74.28% and 80% for clay samples 1, 5, and bentonite respectively. Their corresponding n and k-values equal to 3.86 & 0.28, 3.60 & 0.14 and 3.30 & 0.14 respectively. Those indicated that clay sample 5, can compete favourably with the imported bleaching earth.

To further investigate the effectiveness of locally produced activated clays, the bleached oil from clay sample 5 above was deodorized at 260°C and 0.4 kPa for 30 minutes. The results as shown in Table 4.22 show sharp improvement in the colour and odour of the oil with absorbance of 0.34 which corresponds to 87% CR. When the deodorized oil was compared with imported refined and deodorized palm oil, (KINGS OIL produced by Kuok Oils and Grain, Singapore) with absorbance of 0.57, all the properties fall within the standard as stipulated by International Standard Organization (ISO 3960), and that of Cocks and Van Rede (1966) as shown in Table 4.22.

4.2.5 Statistical Analysis

When the experimental results were statistically analysed using SPSS version 10, variation existed. When the variations were subjected to Duncan multiple range test (Douglas, 1991). The analysis of variance showed that at 95% confidence limit, clay sample 5 ranked the most effective followed by samples 1 and 2 while clay samples 3 and 4 were less effective.

CHAPTER FIVE

5.1 CONCLUSION

From the analysis of the results in this project work, the following conclusions were made: -

5.1 CONCLUSION

From the analysis of the results in this project work, the following conclusions were made: -

1. Nigerian clays contain enough clay minerals which when activated improve the adsorptive power of the clays. Therefore, the two best local activated clays are clay sample 1 which gave 64.80% colour reduction, acid value of 15.68g/mol, clay sample 5 which gave 74.28% colour reduction and acid value of 13.02g/mol. The final colour reduction of 87% after deodorization of oil obtained from clay sample 5 is an indication of better performance.
2. The dose of Nigerian clays required for palm oil bleaching ranged between 5 – 10% mass of the oil. Finally, HCl activated clays with 74.28% colour reduction were more effective than H_2SO_4 activated clays with 69.46% colour reduction.

5.2 RECOMMENDATIONS

i. Since local clays around Oyo and Osun States of Nigeria also proved effective when compared with the imported bleaching earth, after deodorization of the oil sample, the former is recommended for use in bleaching operation.

ii. Other mineral acids like nitric acid should be used for clay activation and the results compared to the acid used in this roject.

iii. Better performance could be achieved by better process of activation and particle size reduction. Therefore, the results of this work should be adopted as a basis for further studies and investigations of the clays found around Oyo and Osun State.

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APPENDIX 1
DETERMINATION OF CLAY POROSITY USING HELIUM-MERCURY METHOD

Clay Sample 1

Mass of clay= 10.00 g

Volume of helium displaced = 5.00 cm^3

Volume of mercury displaced = 9.00 cm^3

Since solid body when immersed in liquid displace volume of liquid equal to its volume therefore the volume of sample used = volume of helium displaced.

Volume of clay sample used = 5.00 cm^3

Also since Hg will not fill the pores of the clay particles at atmospheric pressure, volume of mercury displaced is equal to the actual volume of mercury.

Particle porosity (ξp)= $V g \rho_s / (V g \rho_s + 1)$

Where Vg is void volume per grammes of particles = volume of mercury displaced – volume of helium displace / mass of sample used

ρ_s = mass of sample used / volume of sample

Also ρ_p = mass of sample used / volume of mercury displaced

SAMPLE 1

Vg = 9-5/10 =0.40 cm^3/g

ρ_s =10/ 5 = 2 g/cm^3

ρ_p = 10/ 9= 1.11 g/cm^3

ξp = 040 x 2.00 / (0.40x 2)+1

ξp = 0.444

The same procedure was applied to samples 2- 5 and the results are presented in chapter 4.

APPENDIX 2

Tables of Standard

Table A2.1 shows the standard values of Peroxide Value in relation to mass of oil samples used while Table A2.2 shows the summary of values for index of quality from literatures.

TABLE A2.1: PV STANDARD IN RELATION TO MASS

Expected PV (Milliequivalent/Kg)	*Mass of Test Sample (g)*
0 – 12	5.0 – 2.0
12 – 20	2.0 – 1.2
20 – 30	1.2 – 0.8
30 – 50	0.8 – 0.5
50 – 90	0.5 – 0.3

Adapted from 1S0 3960 (1977).

TABLE A2.2: VALUES FOR INDEX OF QUALITY OF PALM OIL.

Index of Quality	*Value*
SV	196 – 205
AV	1 – 32.95
IV	46 – 60

Adapted from Cocks and Van Rede (1966)

APPENDIX 3

Statistical Analysis

						95% Confidence Interval for Mean	
		N	Mean	Std. Deviation	Std. Error	Lower bond	Upper bound
O	1.00	2	.0000	.0000	.0000	.0000	.0000
	2.00	2	.0000	.0000	.0000	.0000	.0000
	3.00	2	.0000	.0000	.0000	.0000	.0000
	4.00	2	.0000	.0000	.0000	.0000	.0000
	5.00	2	1.000E-02	.0000	.0000	1.000E-02	1.000E-02
	Total	10	2.000E-03	4.216E-03	1.333E-03	-1.0162E-03	5.016E-03
GO	1.00	2	3.000E-02	1.414E-02	1.000E-02	-9.7062E-02	.1571
	2.00	2	1.000E-02	.000	.0000	1.000E-02	1.000E-02
	3.00	2	4.500E-02	7.071E-03	5.000E-03	-1.8531E-02	0.1085
	4.00	2	1.000E-02	.0000	.0000	1.000E-02	1.000E-02
	5.00	2	0.300	.0000	.0000	0.3000	.3000
	Total	10	7.900E-02	0.1174	3.713E-02	-4.9982E-03	0.1630
2O3	1.00	2	3.30000	.0000	.0000	3.3000	3.000
	2.00	2	3.13000	1.414E-02	1.000E-02	3.00029	3.2571
	3.00	2	3.12000	.0000	.0000	3.1200	3.1200
	4.00	2	10.8000	1.414E-02	1.000E-02	10.6729	10.9271
	5.00	2	2.52000	1.414E-02	1.000E-02	2.3929	2.6471
	Total	10	4.57400	3.2932	1.0414	2.2182	6.9298
2O3	1.00	2	5.22000	.0000	.0000	5.22000	5.2200
	2.00	2	6.22000	1.414E-02	1.000E-02	6.0929	6.3471
	3.00	2	8.04000	2.28E-02	2.000E-02	7.7859	8.2941
	4.00	2	6.51000	1.414E-02	1.000E-02	6.3829	6.6371
	5.00	2	5.18000	2.828E-02	2.000E-02	4.9259	5.4341
	Total	10	6.2340	1.1033	0.3489	5.4447	7.0233
O2	1.00	2	9.3600	1.414E-02	1.000E-02	4.2329	90.4841
	2.00	2	90.0900	1.414E-02	1.000E-02	8.9629	90.2171
	3.00	2	88.2200	2.828E-02	2.000E-02	87.9659	88.4741
	4.00	2	81.8900	1.414E-02	1.000E-02	81.7629	82.0171
	5.00	2	91.2900	1.414E-02	1.000E-02	91.1629	91.4171
	Total	10	88.3700	3.5733	1.1300	85.8138	90.9262
ORVOL	1.00	2	0.4000	1.414E-02	1.000E-02	.2729	.5271
	2.00	2	0.6000	1.414E-02	1.000E-02	.4729	.7271
	3.00	2	0.4500	1.414E-02	1.000E-02	.3229	.5771
	4.00	2	0.3000	1.414E-02	1.000E-02	.1729	.4271
	5.00	2	0.4000	1.414E-02	1.000E-02	.2729	.5271
	Total	10	0.4300	0.1038	3.283E-02	.3557	.5043
OLIDEN	1.00	2	2.0000	0.1414	0.1000	0.7294	3.2706
	2.00	2	1.6700	0.1414	1.000E-01	.3994	2.9406
	3.00	2	1.5400	1.414E-02	1.000E-02	1.4129	1.6671
	4.00	2	2.0000	0.1414	0.1000	0.7294	3.2706
	5.00	2	2.0000	0.1414	0.1000	0.7294	3.2706
	Total	10	1.8400	0.2289	7.238E-02	1.6783	2.0057

Descriptives

		N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean	
						Lower Bound	Upper Bound
PARTICLE	1.00	2	.9000	.1414	1.000E-01	-.3706	2.1706
	2.00	2	.8330	.1414	.1000	-.4376	2.1036
	3.00	2	1.0000	.1414	.1000	-.2706	2.2706
	4.00	2	1.2500	.1414	.1000	-2.0620E-02	2.5206
	5.00	2	1.1100	.1414	1.000E-01	-.1606	2.3806
	Total	10	1.0186	.1890	5.977E-02	.8834	1.1538
POROSITY	1.00	2	.4440	.1414	.1000	-.8266	1.7146
	2.00	2	.5000	.1414	1.000E-01	-.7706	1.7706
	3.00	2	.4100	.1414	.1000	-.8606	1.6806
	4.00	2	.3750	.1414	1.000E-01	-.8956	1.6456
	5.00	2	.4440	.1414	.1000	-.8266	1.7146
	Total	10	.4346	.1141	3.609E-02	.3530	.5162
CLAYAU	1.00	2	12.2850	.3323	.2350	9.2990	15.2710
	2.00	2	12.5600	.0000	.0000	12.5600	12.5600
	3.00	2	12.7300	.7071	.5000	6.3769	19.0831
	4.00	2	12.3400	2.828E-02	2.000E-02	12.0859	12.5941
	5.00	2	12.6700	1.414E-02	1.000E-02	12.5429	12.7971
	Total	10	12.5170	.3202	.1013	12.2879	12.7461
CLAYFFA	1.00	2	6.2850	7.071E-03	5.000E-03	6.2215	6.3485
	2.00	2	6.3200	.0000	.0000	6.3200	6.3200
	3.00	2	6.6500	.0000	.0000	6.6500	6.6500
	4.00	2	6.2050	2.121E-02	1.500E-02	6.0144	6.3956
	5.00	2	6.3700	1.414E-02	1.000E-02	6.2429	6.4971
	Total	10	6.3660	.1603	5.069E-02	6.2513	6.4807
CLAYSU	1.00	2	160.4200	1.414E-02	1.000E-02	160.2929	160.5471
	2.00	2	142.5300	4.243E-02	3.000E-02	142.1488	142.9112
	3.00	2	162.4200	2.828E-02	2.000E-02	162.1659	162.6741
	4.00	2	160.2700	2.828E-02	2.000E-02	160.0159	160.5241
	5.00	2	144.1300	4.243E-02	3.000E-02	143.7488	144.5112
	Total	10	153.9540	9.1941	2.9074	147.3769	160.5311
CLAYIU	1.00	2	58.2600	2.828E-02	2.000E-02	58.0059	58.5141
	2.00	2	58.2300	1.414E-02	1.000E-02	58.1029	58.3571
	3.00	2	58.3100	1.414E-02	1.000E-02	58.1829	58.4371
	4.00	2	57.9800	1.414E-02	1.000E-02	57.8529	58.1071
	5.00	2	58.1200	2.828E-02	2.000E-02	57.8659	58.3741
	Total	10	58.1800	.1252	3.958E-02	58.0905	58.2695
CLAYEU	1.00	2	147.9100	2.828E-02	2.000E-02	147.6559	148.1641
	2.00	2	129.9700	.0000	.0000	129.9700	129.9700
	3.00	2	149.2000	4.243E-02	3.000E-02	148.8188	149.5812
	4.00	2	147.9300	.0000	.0000	147.9300	147.9300
	5.00	2	131.5000	1.414E-02	1.000E-02	131.3729	131.6271
	Total	10	141.3020	9.1222	2.8847	134.7763	147.8277

Descriptives

		N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean	
						Lower Bound	Upper Bound
CLAYPV	1.00	2	.9800	1.414E-02	1.000E-02	.8529	1.1071
	2.00	2	1.0400	.0000	.0000	1.0400	1.0400
	3.00	2	.9600	.0000	.0000	.9600	.9600
	4.00	2	.9600	.0000	.0000	.9600	.9600
	5.00	2	1.2600	2.828E-02	2.000E-02	1.0059	1.5141
	Total	10	1.0400	.1205	3.809E-02	.9538	1.1262
CLAYPERC	1.00	2	45.0000	.0000	.0000	45.0000	45.0000
	2.00	2	45.5300	.0000	.0000	45.5300	45.5300
	3.00	2	41.6300	1.414E-02	1.000E-02	41.5029	41.7571
	4.00	2	43.2000	.0000	.0000	43.2000	43.2000
	5.00	2	45.1400	1.414E-02	1.000E-02	45.0129	45.2671
	Total	10	44.1000	1.5526	.4910	42.9893	45.2107

omogeneous Subsets

CAO

uncan[a]

		Subset for alpha = .05				
TREAT5	N	1	2	3	4	5
1.00	2	.0000				
2.00	2		.0000			
3.00	2			.0000		
4.00	2				.0000	
5.00	2					1.000E-02
Sig.		1.000	1.000	1.000	1.000	1.000

leans for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 2.000.

MGO

uncan[a]

		Subset for alpha = .05		
TREAT5	N	1	2	3
2.00	2	1.000E-02		
4.00	2	1.000E-02		
1.00	2		3.000E-02	
3.00	2		4.500E-02	
5.00	2			.3000
Sig.		1.000	.087	1.000

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 2.000.

FE2O3

Duncan[a]

		Subset for alpha = .05			
TREAT5	N	1	2	3	4
5.00	2	2.5200			
3.00	2		3.1200		
2.00	2		3.1300		
1.00	2			3.3000	
4.00	2				10.8000
Sig.		1.000	.403	1.000	1.000

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 2.000.

AL2O3

Duncan[a]

TREAT5	N	Subset for alpha = .05			
		1	2	3	4
5.00	2	5.1800			
1.00	2	5.2200			
2.00	2		6.2200		
4.00	2			6.5100	
3.00	2				8.0400
Sig.		.102	1.000	1.000	1.000

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 2.000.

SIO2

Duncan[a]

TREAT5	N	Subset for alpha = .05				
		1	2	3	4	5
4.00	2	81.8900				
3.00	2		88.2200			
2.00	2			90.0900		
1.00	2				90.3600	
5.00	2					91.2900
Sig.		1.000	1.000	1.000	1.000	1.000

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 2.000.

POREVOL

Duncan[a]

TREAT5	N	Subset for alpha = .05			
		1	2	3	4
4.00	2	.3000			
1.00	2		.4000		
5.00	2		.4000		
3.00	2			.4500	
2.00	2				.6000
Sig.		1.000	1.000	1.000	1.000

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 2.000.

SOLIDEN

Duncan[a]

TREAT5	N	Subset for alpha = .05 1	 2
3.00	2	1.5400	
2.00	2	1.6700	1.6700
1.00	2		2.0000
4.00	2		2.0000
5.00	2		2.0000
Sig.		.352	.055

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 2.000.

PARTICLE

Duncan[a]

TREAT5	N	Subset for alpha = .05 1	 2
2.00	2	.8330	
1.00	2	.9000	.9000
3.00	2	1.0000	1.0000
5.00	2	1.1100	1.1100
4.00	2		1.2500
Sig.		.118	.064

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 2.000.

POROSITY

Duncan[a]

TREAT5	N	Subset for alpha = .05 1
4.00	2	.3750
3.00	2	.4100
1.00	2	.4440
5.00	2	.4440
2.00	2	.5000
Sig.		.426

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 2.000.

CLAYAU

Duncan[a]

		Subset for alpha = .05
TREAT5	N	1
1.00	2	12.2850
4.00	2	12.3400
2.00	2	12.5600
5.00	2	12.6700
3.00	2	12.7300
Sig.		.271

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 2.000.

CLAYFFA

Duncan[a]

		Subset for alpha = .05				
TREAT5	N	1	2	3	4	5
4.00	2	6.2050				
1.00	2		6.2850			
2.00	2			6.3200		
5.00	2				6.3700	
3.00	2					6.6500
Sig.		1.000	1.000	1.000	1.000	1.000

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 2.000.

CLAYSU

Duncan[a]

		Subset for alpha = .05				
TREAT5	N	1	2	3	4	5
2.00	2	142.5300				
5.00	2		144.1300			
4.00	2			160.2700		
1.00	2				160.4200	
3.00	2					162.4200
Sig.		1.000	1.000	1.000	1.000	1.000

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 2.000.

CLAYIU

Duncan[a]

		Subset for alpha = .05			
TREAT5	N	1	2	3	4
4.00	2	57.9800			
5.00	2		58.1200		
2.00	2			58.2300	
1.00	2			58.2600	58.2600
3.00	2				58.3100
Sig.		1.000	1.000	.212	.063

Means for groups in homogeneous subsets are displayed.

a Uses Harmonic Mean Sample Size = 2.000.

CLAYEU

Duncan[a]

		Subset for alpha = .05			
TREAT5	N	1	2	3	4
2.00	2	129.9700			
5.00	2		131.5000		
1.00	2			147.9100	
4.00	2			147.9300	
3.00	2				149.2000
Sig.		1.000	1.000	.437	1.000

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 2.000.

CLAYPV

Duncan[a]

		Subset for alpha = .05		
TREAT5	N	1	2	3
3.00	2	.9600		
4.00	2	.9600		
1.00	2	.9800		
2.00	2		1.0400	
5.00	2			1.2600
Sig.		.227	1.000	1.000

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 2.000.

CLAYPERC

Duncan[a]

TREAT5	N	Subset for alpha = .05				
		1	2	3	4	5
3.00	2	41.6300				
4.00	2		43.2000			
1.00	2			45.0000		
5.00	2				45.1400	
2.00	2					45.5300
Sig.		1.000	1.000	1.000	1.000	1.000

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 2.000.