STUDIES ON THE BLEACHING CHARACTERISTICS OF SOME NIGERIAN CLAY

BY:

OLAGUNJU, NURUDEEN OLUWAGBEMIGA

DECEMBER, 1997

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B.Sc CHEMISTRY (A.B.U, 1991)

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DEPARTMENT OF CHEMISTRY
FACULTY OF SCIENCE
AHMADU BELLO UNIVERSITY
ZARIA - NIGERIA

DECEMBER, 1997.

DECLARATION

I hereby declare that this thesis contains the report of my research work and has not been presented in any previous application for a higher degree. All information from other sources have been acknowledged by means of references.



OLAGUNJU, NURUDEEN OLUWAGBEMIGA

24th Feb, 1998

DATE

CERTIFICATION

This thesis entailed "studies on the bleaching characteristics of some Nigerian clay" by OLAGUNJU, Nurudeen Oluwagbemiga, meets the regulation governing the award of the degree of master of science of Ahmadu Bello University, Zaria, Nigeria and is approved for its contribution to knowledge and literary presentation.

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DEDICATION

This work is dedicated to the memory of my late grannies madam Rabiat Olagunju and madam Dorcas Aina Ibéyemi; my parents Mr. and Mrs. S.O Olagunju; and to all parents who have laboured to educate their children.

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I wish to express my profound gratitude to my supervisor, Professor J.Y Olayemi and Dr. J.F Iyun for their valuable assistance, suggestion and constructive critisms throughout the course of my work.

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Finally and above all, I am immensely grateful to Almighty Allah for the strength and wisdom accorded to me to accomplish this study.

ABSTRACT

This study evaluated the natural and activated bleaching powers of some selected Nigerian clays with a view to initiating their utilization for bleaching earth manufacture. Fourteen clay samples were collected from eleven different locations in Nigeria: [Ilorin, Igbaja, Moniya, Omiadio, Ogbomosho. Ile Ife, Osogbo, llesha, Kankara, Alexander Hall (ABU) and Bomo.]

The chemical analyses were carried out to determine their elemental composition. They were activated by (three) different acid treatments [using Hydrochloric acid (HC1). Method I consist of the use of 5.5MHC1 on clay sample on a 5:1 ratio; Method II consist of the use of 5MHC1 on clay sample on a 2:1 ratio; and method III consist of the use of 1M, 3M and 5MHC1 on clay samples in a slurry form in a ratio of 4:1 1 . Palm oil was use as the adsorbate and the clay as the adsorbent. Standard clay was used in the bleaching comparism, and their extent of bleaching was monitored spectrophotometrically.

Four of the samples were found to have good bleaching properties taking 60% colour reduction as a good performance index. S_5 69.19%, S_{10} 66.09%, $S_{2(II)}$ 61.76%, and 60.68%) S_8; Seven samples $S_{l(B)}$, $S_{2(1)}$, $S_{3(II)}$, S_6, S_7, S_9, and S_{II} have bleaching performance above 50% and below 60% while three samples $S_{1(A)}$, S_4, and $S_{3(1)}$ have bleaching performance below 50% in their natural state.

After acid activation of the clay samples the second acid activation of the clay gave the best bleaching performance compared to the other two methods.
The acid to clay ratio as exemplified in the second activation method; the bleaching temperature; volume of the acid used; and the percentage mass of the had pronounced effect on the bleaching performance of the clays.

Among the local clays used S_5 clay in both the natural and activated state was found to be superior in its bleaching ability over all the other clays and in comparism with the fuller's earth at 105^{o}C. Fuller's earth used at S2°C had a better bleaching ability over the local clays. Activated S_5 followed very closely.

The higher bleaching ability of the clays in the activated state was related to the percentage sum of the oxide of aluminium, silicon and sodium present in the clays and also lost on ignition in their natural states. It was found that alkali refining of the crude oil reduced part of the colours from the crude oil and thus increasing the percentage of colour reduction when the local clay were used on them. Also some of the activated Nigerian clays showed higher apparent bulk densities and consequently a corresponding lower oil retention than the fuller's earth.

TABLE OF CONTENTS

		Page
DECLARATION		i
CERTIFICATION		ii
DEDICATION		iii
ACKNOWLEDGEMENT		iv
ABSTRACT		v - vi
TABLE OF CONTENTS		vii - ix
LIST OF TABLES		x
LIST OF FIGURES		xi
LIST OF APPENDICES		xii
CHAPTER 1		
1.0	INTRODUCTION	1
1.1	General introduction	1
1.2	Objective of research	2
CHAPTER 2		4
2.0	LITERATURE REVIEW	4
2.1	Bleaching	4
2.2	Colour pigment of vegetable oil	6
2.2.1	Carotenoids	6
2.2.2	Chlorophyll	8
2.2.3	Tocopherols	9
2.2.4	Gossypol	10
2.3	Classification and mineral composition of bleaching earths	11
2.3.1	Fuller's earth	11
2.3.2	Bentonites	12
2.4	Geology of bleaching earth	13
2.5	Composition and structure of clay minerals	14
2.6	Activation of bleaching earth	17
2.6.1	Acid activation	18
2.6.2	Heat activation and extrusion	20
2.7	Effect of acid activation of clay on bleaching	21
2.8	Mechanism of bleaching	21

2.9 Effects of clay properties on its bleaching performance 23
2.9.1 Acidity 23
2.9.2 Volatile matter 24
2.9.3 Apparent bulk density 24
2.9.4 Moisture 24
2.9.5 Particle size 24
2.10 Review of method used for clay acid activation 25
CHAPTER 3 28
3.0 MATERIALS AND METHODS 28
3.1 Sample collection and Description 28
3.2 Preparation of clay sample 30
3.3 Determination of moisture content 31
3.4 Determination of loss on ignition 31
3.5 Decomposition of clay sample 31
3.6 Determination of silica 33
3.7 Decomposition of clay sample by the perchloric-hydrofluoric acid digestion mixture for the determination of alkali oxide 35
3.8 Determination of alkali oxides 36
3.9 Determination of ferric oxides 39
3.10 Determination of titania 41
3.11 Determination of alumina 42
3.12 Determination of lime and magnesia by atomic absorption spectroscopy 44
3.13 Determination of pH of clay samples 46
3.14 Determination of titra table acidity 47
3.15 Measurement of apparent bulk density 47
3.16 Assessment of the bleaching performance of Clay sample in their natural state 47
3.17 Method state of activation of clay samples 48
3.18 Assessment of the bleaching performance of the activated clay sample . 49
3.19 Determination of free fatty acid 49

3.20 Alkali refining of palm, groundnut and permkernel oil 50

3.21 Assessment of the bleaching performance of the activated Clay sample on alkali refined palm, palm kernel and groundnut oil 51

3.22 Determination of oil retention 52

CHAPTER 4 53

RESULT AND DISCUSSION 53

4.1 Sample preparation 53

4.2 Chemical composition and some characteristic parameters of the clays studied 53

4.3 Bleaching performance of unactivated clay samples 58

4.4.1 Activation of clay sample and their bleaching performance 63

4.4.2 Effect of activation time, volume of acid and time Of drying of activated clay on method II 73

4.4.3 Effect of activation on clay with low performance index In the natural state 74

4.4.4 Effect of successive addition of clay on the colour reduction 74

4.5 Effect of alumina, silica, sodium oxide and loss on ignition On the bleaching power 74

4.6 Refining of oil and bleaching with activated clays 81

4.7 Effect of bleaching on the solid formation rate of palm oil 86

4.8 Oil retention of the clay samples 86

CHAPTER 5 88

5.0 CONCLUSION AND SUGGESTION FOR FURTHER WORK 88

REFERENCES 90

APPENDICES 96

LIST OF TABLES

Table — Pages

4.1: Summary of chemical composition of clay samples in percentages 55

4.2: Some characteristic parameters of clays studied in their natural form . . . 56

4.3: Bleaching of natural clay samples at different percentage clay 57

4.4: Bleaching performance (in percentage) of natural S_5, S_8, S_{10}, S_{200} and F on top and bottom layer of palm oil 60

4.5: Bleaching performance (in percentage) of S_8 clay activated By various methods on top and bottom layers of palm oil 62

4.6: Bleaching performance (in percentage) of S_{200} clay actuated By various methods on top and bottom layers of palm oil 64

4.7: Bleaching performance (in percentage) of S_5 clay activated By various methods on top and bottom layers of palm oil 65

4.8: Bleaching performance (in percentage) of S_{10} clay activated By various methods on top and bottom layers of palm oil 65

4.0: Some characteristic parameters of clays studied in their activated form . . 66

4.10: Bleaching action of S_5, S_{10}, S_8, and S_{200} clay in their natural Form as compared to fuller's earth on top layer of palm oil 76

4.11: Table of silica, sodium oxide, loss on ignition (in percentage) And percentage bleaching of activated S_5, S_8 and S_4 clay 76

4.12: Evaluation of the bleaching ability of activated S_8, S_5, S_4 clay And F on alkali refined palm, palm kernel And ground nut oil spectrophotometrically 82

4.13: Evaluation of bleaching ability of activated S_8, S_5, S4 clay And F on alkali refined palm, palm kernel and Groundnut oil using the lovibond tintometer 84

4.14: Table of percentage bleaching of activated S_5, S_8, S_4 clay And F on groundnut and palm kernel oil 87

4.15: Table of oil retention (in percentage) and Apparent bulk density Of activated S_5, S_8, S_4 clay and F 87

LIST OF FIGURES

Figure		Page
2.1	Structure of β - carotene	8
2.2	Structure of Lycopene	8
2.3	Structure of Chlorophyll	9
2.4	Structure of Gossypol	11
2.5	The structure of Kaolinite viewed along the a - axis	14
2.6	The structure of montmorillonite viewed along the a - axis	15
2.7	The structure of illite viewed along the a - axis	16
2.8	The idealized structure of acid activated montmorillonite	20
4.1:	Graph of percentage bleaching against apparent bulk densities Of all natural clay samples at varied percentage clay	61
4.2:	Graph of percentage bleaching against time of bleaching For the different methods of activation of S_8 clay	69
4.3:	Graph of percentage bleaching against time of bleaching For the different methods of activation of S_5 clay	70
4.4:	Graph of percentage bleaching against time of bleaching for the different methods of activation of S_{200} clay	71
4.5:	Graph of percentage bleaching against time of bleaching For the different methods of activation of 5_{10} clay	72
4.6:	Graph of percentage bleaching against clay activation Time of S_8 clay by activation method II	77
4.7:	Graph of percentage bleaching against volume of acid used In the activation of S_5, S_8, and S_4 clay	78
4.8:	Graph of bleaching activity in percentage against (Al_2O_3 + SiO_2 + Na_2O) percentage for S_5, S_8, and S_4 Clays activated with 200cm^3, 5M Hcl	79
4.9:	Graph of percentage bleaching against time of bleaching For activated S_8 clay	80

LIST OF APPENDICES

Appendix		Page
A.	Calibration curve for determination of lithium oxide	96
B.	Calibration curve for determination of potassium oxide	97
C.	Calibration curve for determination of sodium oxide	98
D.	Calibration curve for determination of Iron (II) oxide	99
E.	Calibration curve for determination of titanium (IV) oxide	100
F.	Calibration curve for determination of calcium oxide	101
G.	Calibration curve for determination of magnesium oxide	102
H.	Plates showing the physical appearance of the various clays In their natural form	103
I.	Plate showing clay in their natural and activated form	106
J.	Plate showing crude, refined and bleached palm oil by some activated clay	106
K.	Plate showing the effect of bleaching on the rate of solid formation of palm oil bleached with some activated clay	107

CHAPTER ONE

1.0 INTRODUCTION

1.1 The use of bleaching (or decolouring) earths is common and enormous in industries that use or process mineral, vegetable and animal oils, petroleum and sugar products etc. such industries in Nigeria still import substantial amounts of these bleaching agents at high (foreign exchange) cost (Ibemesi *et al*, 1990).

The removal of colouring matter using clay is an adsorptive process which is essentially a surface phenomenon whereby colouring pigments are removed from the adsorbate through the adherence of the colour pigments to the surface of the adsorbent. The extent of colour removal achieved depends on the specific affinity between the adsorbent and the adsorbate, nature and quantity of the earth used, temperature of mixing and contact time between the oil and earth (Sanelli, 1981; Ibemesi, 1986; Anozie 1993).

Bleaching earths are hydrated aluminium silicate which are usually montimorillonite clays that exhibit adsorptive properties in their natural or activated state (Hawley, 1977). Some clays are known to bleach well in their natural form while others are either inactive or have poor decolouring effect. However, some clays after suitable treatment, exhibit enhanced bleaching ability. Such treatment is known as activation and the most common treatment is acid activation using either hydrochloric or tetraoxosulphate (VI) acid. The enhanced bleaching power of the clay after activation is attributed to the opening up of the inner structure and intergranular space of the clays, thereby making a larger surface area available for adsorption (Fogle *et al*; 1933; Thomas *et al;* (1950).

The natural bleaching earths are made from clays possessing a natural ability to bleach oil or remove colour bodies by adsorption. Such clays are dried and milled to a powder of the required particle size distribution (Rich, 1964). Usually, clays exhibiting high natural bleaching power are not suitable for activation, and most clays used for activated clay manufacture are poor in Natural bleaching activity (Richardson,

1978). There is not always a correlation between the chemical composition of clays and their adsorptive power. An earth that is almost devoid of adsorptive capacity may be identical in composition with the active earth, hence bleaching power of clays can only be assessed by actual testing (Nutting, 1933).

Mining of bleaching earth dates back to the middle ages in England and in the United States to late 19th Century. Bleaching earths have also been mined and produced in Canada, France, Italy, USSR, West Germany, Japan, Hungary, Rumania, Spain, Morocco, Syria, Argentina, Australia and India. This has resulted in the marketing of the earths with different trade names such as Tonsil, Fuller's, Floriden, Greede, Laurel, Saunder's, Vega, Filtrol, Impact, Supact, Prolite and a host of others. All these developed from clay deposits in various countries (Mansfield, 1937; Oboh, 1987).

Abundant clay mineral deposits exist in Omiadio, Iperindo Ijesha, Akinlabi, Igbetti, Benin City and Uhumora in the West, Owerri and Onitsha in the east, Bukuru, Ganuwuri, Kankara and Minna in the North. Some of these deposits are already being mined for the production of cement, bricks, pottery and ceramics.

The demand for edible vegetable oils has increased worldwide due to population growth, rising standard of living as well as consumer preference for light coloured fats and oils, arising partly from health consideration (N.gsk, 1981). Apart from their use as frying oils, edible oils are used in the manufacture of a vast number of products such as margarines, shortenings, bakery fats, confectionery fats, ice cream, emulsifier, filled milk and coffee whitener (Wood *et al* 1981; Berger, 1986).

Most oils are bleached to a very light colour for use as edible product. Our increasing dependence on imported refined lubricants and edible oils from the far East emphasises the need for Nigerian to refine her own vegetable oils particularly palm oil.

1.2 Objective of the Research:

In view of Nigeria's overdependence on imported edible oils there is the need to exploit our clay deposits for the production of bleaching earths for vegetable oil

industries. The aims of this project are therefore to

i. Assess the bleaching power of some of the local Nigerian clays in the natural states and after activation.

ii. Develop a workable procedure for activating the clays.

iii. Work out the optimum conditions for using these clays for commercial bleaching of vegetable oils and lubricants.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Bleaching

Bleaching is the partial or complete removal of colour of a substance. This is achieved in liquid substances through the application of heat or the use of bleaching material such as clay or carbon (Patterson, 1976). With respect to the bleaching of oil, the term bleaching is too narrow a description. "Adsorptive cleansing or adsorptive bleaching" is regarded to be more accurate. Adsorption bleaching is a surface phenomenon whereby colouring pigments are removed from the adsorbate (oil) through the adherence of the colour pigment to the surface of the adsorbent (Patterson, 1976; Anozie, *et al* 1993).

The bleaching of oil is essential in that the crude is not a stable chemical composition with fixed properties, it is an ever changing material which refining and bleaching stabilize and transform into a more durable product. Bleaching of oils by heat is not encouraged because it can destroy the pigment in the oil and also cause the production of other colours due to presence of degradation products e.g chroman 5, 6, quinone from gamma tocopherol, in the presence of air which often resists further attempt or removal (King *et al*; 1949; Rich, 1964; and Patterson, 1976).

In the adsorptive bleaching of oils, the clays used are either in their natural or activated forms. The extent of colour removal achieved by the clay depends on the specific affinity between the clay and the pigment. Some clays are known to bleach very well in their natural states while others are either inactive or have poor bleaching effect in their natural form. However, clays that have poor bleaching power in the natural form if suitably treated (acid-activation), exhibit enhanced bleaching ability. The enhanced bleaching power of the clays, after activation is due to the opening up of the inner structure and intragranular space of the clays, thereby making a larger surface area available for adsorption (Thomas, 1950).

Several other materials compete with the pigment for space on the surface of the clays. Important non-pigments are residue of soap stocks after alkali refining, which would hinder filtration or later generate an off-flavour; gums, including phosphatides and related substances which above a certain level are associated with flavour instability; and traces of pro-oxidant metals arising from their previous use as catalyst or simply contamination from tanks, vessels, and pipelines.

Natural clays are said to be very good when they are capable of adsorbing from suitably strong solutions of pigments up to 15% of their own weight of such pigment and they easily retain about 30% of their own weight of oil. The acid activated clay can retain up to 70% of its own weight of oil since the activation has greatly increased the void space (Siddiqui, 1968). The activated carbon has the best bleaching power, but can retain up to 150% of its own weight of oil. Because of this and their expensive nature, their use have been discouraged except when the required bleaching is not obtained with activated clay only. They are then mixed with clay in the proportion of 10:90 and 40:60 carbon to clay in extreme cases (Baker *et al*; 1968; Patterson, 1976).

In addition, when natural clays are used in bleaching they remove or greatly diminish traces of soap and do not elevate free fatty acids or Isomerize unsaturated fatty acid groups. Acid activated clays, depending on the degree of acidification, are likely to split soap residue and also elevate the free fatty acid constituents of the oil. They also destroy peroxides and promote Isomerization of the unsaturated fatty acid (Patterson, 1976).

The bleacheability of an oil is affected by age, climate, season and the region of the world in which it is extracted. It is reported that oils which are extracted and bleached at the beginning of the season are easily bleached compared to those extracted and bleached at the end of the cropping season. With regards to age, aged oil may have been exposed for months to all kinds of storing and climatic conditions which tend to increase and fix the colour of the oil (Goebel, 1976). Consequently, the requirements for the bleaching process increase with respect to temperature, type and amount of bleaching clay applied. On the basis of regional differences, colour of oil and colour fixings are different. Colours are darkest from the north towards the

equator and lighter again when going further south, thus their bleaching conditions vary accordingly (Goebel, 1976; Patterson, 1976).

A number of factors have been stated to influence the bleaching ability of clays, they include:

i. The acid to clay ratio.

ii. The concentration of the acid.

iii. The bleaching temperature.

iv. The holding time and

v. The percentage mass of clay in oil.

The efficiency of an adsorbent is often measured by the minimum dose required to reduce the concentration of the adsorbate (pigment) to the required level.

2.2 Colour Pigment of Vegetable Oil:

Fresh oils derive their colour from naturally occurring seeds and nuts. These seeds and nuts contain plants pigment which is impacted onto the oil during extraction (Baidwin, 1949). The extent of colour in the oil, depends on the quantity and characteristics of the colouring matters present and the processes of extraction employed. Various natural colour pigments are known to be present in vegetable oils. These include carotenoids, chlorophyll, tocopherol, gossoypol etc (Cowan, 1976).

2.2.1 Carotenoids:

Carotenoids also referred to as liprochromes, are the yellow and red pigments of fats. They are tetraterpenes derived from acyclic conjugated polyene lycopene which function as photosynthetic pigments in many plants and bacteria. This class of

compounds includes hydrocarbons (carotenes), and their corresponding hydroxyl, epoxy and oxy derivatives and the xanthophyll. Carotenoids are highly unsaturated and owe their colour to a long conjugated system of double bonds. Carotenes ($C_{40}H_{56}$), occurs in the lipoid fraction of the green and yellow vegetables, palm oil, and in certain animals oils and fats. Three Isomers of this hydrocarbon are known $\propto$, β and δ - carotene (Hiu, 1992).

Crude palm oils from Malaysia and Zaire vary in carotene content from 50 - 700ppm, while larger amounts 800 - 2000ppm have been reported in Dura species from Nigeria (Ames, 1960).

The most important of the carotene, β - carotene contains two β - ionone rings while the $\propto$ and δ carotenes contain one each. (Figure 2.1) They are all precursors of vitamin A but β - carotene is the most potent.

Xanthophyll are hydroxy and carbonyl derivatives of the carotenes. The term xanthophyll is now more commonly used to designate one individual carotenoid, 3, 3 - dioxy $\propto$ - carotene found in palm oil.

Lycopenes which is an important pigment of tomato is also grouped under carotenoids and has the same formula as carotene ($C_{40}H_{56}$), but is devoid of ionone rings. (Figure 2.2) Carotenoids pigments range in colour from yellow to deep red and are generally fat soluble and water insoluble, stable to alkali but unstable to acid and oxidizing agents. The colours are easily destroyed by heat, hydrogenation or by oxidation.

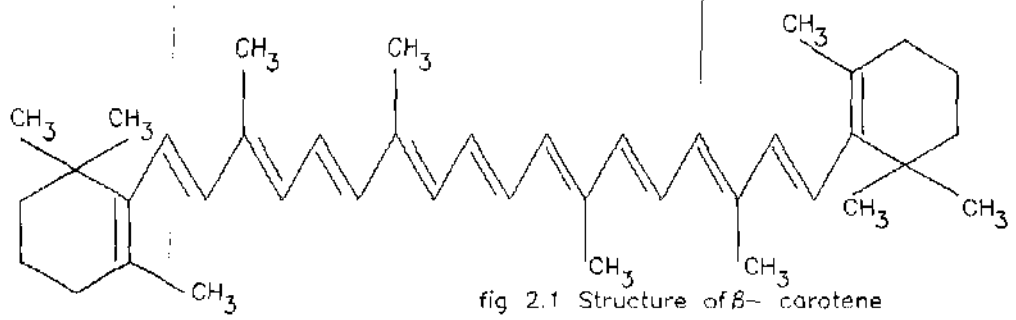


fig 2.1 Structure of β– carotene

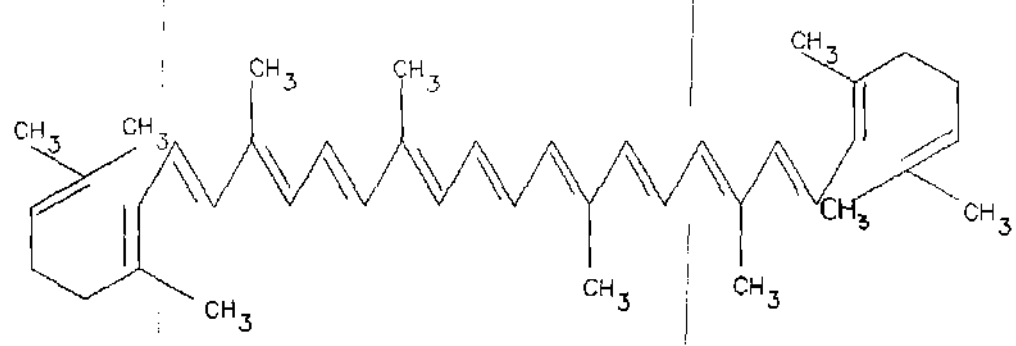
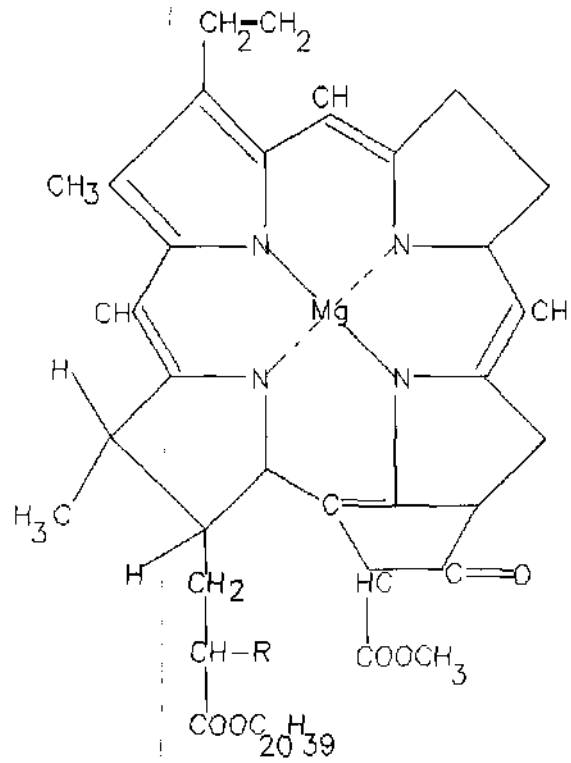


fig 2.2 Structure of lycopene

2.2.2 Chlorophyll:

This is a pigment of characteristic green colour carrying nitrogen in four pyrole rings. It contains magnesium at the centre of the molecule and two ester groups. (Figure 2.3) The green colour of certain oils like olive is due to chlorophyll. Several forms of chlorophyll exit. Higher plants contain a mixture of chlorophyll (a) with empirical formula ($C_{55}H_{72}N_4O_5Mg$) and chlorophyll (b) with one more oxygen atom and less two hydrogen atoms ($C_{55}H_{70}O_6N_4Mg$). These pigments are resistant to refining, bleaching and hydrogenation. Chlorophyll are not readily degraded by heat. They tend to be stabilized by alkali and decompose more readily in acid. Hence they are readily adsorbed in clays of low pH at the expense of increase in free fatty acid in the oil (Pritchett *et at*; 1947; Cowan, 1976).



If $R = CH_3$ = Chlorophyll *a*

$R = CHO$ = Chlorophyll b

fig 2.3 Structure of Chlorophyll

2.2.3 Tocopherols

Most vegetable oils contain tocopherols, the more unsaturated oils containing higher concentrations up to 1000mg/kg or more. While saturated vegetable oils like coconut or palm kernel contain almost none. There are several types of tocopherols, the alpha (α), Beta (β), gamma (δ) and delta - form (Rossel, 1991). They differ from one another in the position and number of methyl groups on the phenol ring. There is also a series of corresponding tocotrienols in which the 16 carbon side chain is unsaturated. The eight compounds, collectively known as tocols, are sometimes called tocopherol isomers, but this is not strictly accurate as the compounds have different molecular formulae (Rossel, 1991).

Tocols are natural antioxidant, the higher levels in unsaturated vegetable oils thus offering greater protection. Animals fats, in contrast, have no natural tocopherol content, whilst fish oils may contain small amounts (Young *et al*; 1986). The

tocotrienols have greater antioxidant potential than the tocopherols, while delta tocopherol is more potent than the alpha tocopherol. Tocols also have vitamin E potency, and in contrast with their antioxidant potential, alpha tocopherol has the greatest activity.

In purified forms tocopherols are light yellow or colourless liquids. A red pigment chroman-5,6 - quinone is formed by atmospheric oxidation of gamma tocopherol. This pigment is responsible for the dark colour of some processed vegetable oils.

2.2.4 Gossypol:

Gossypol is the predominant yellow toxic pigment, with the formula $C_{30}H_{30}O_8$, occuring in cotton seed. (Figure 2.4) It is a very reactive polyphenolic binaphthaldehyde and exhibit strongly acidic properties. Gossypol can be readily removed from cotton seed oil by alkali washing. It is the pigment in the pigment glands of cottonseed and during the processing of the seed, the glands may be ruptured by water, aqueous solvents or the shearing forces of rolls and presses. When present in glands or released, gossypol is designated as free and is toxic. Certain processing conditions can cause the free gossypol to react with protein amino groups, thus binding the gossypol in a non-toxic form (Pritchard, 1991)

Other colouring matter found in oils may be degradation products of the natural colours that arise as a result of processing of the oil bearing material, unsuitable storage, oxidation etc. Oxidation of oils may convert unsaturated fatty acid and glycerides to coloured compounds having a quinonoid structure. These colours are difficult to remove by bleaching agent and are said to be fixed (Bailey, 1964).

The brown colour components of many vegetable oils result from damaged seeds and consists of degraded proteins, carbohydrates, mucilaginous materials, phospholipids etc. These may be present as colloidal dispersions rather than in solution as are most of the other pigments. These compound are however not present in high quality oil.

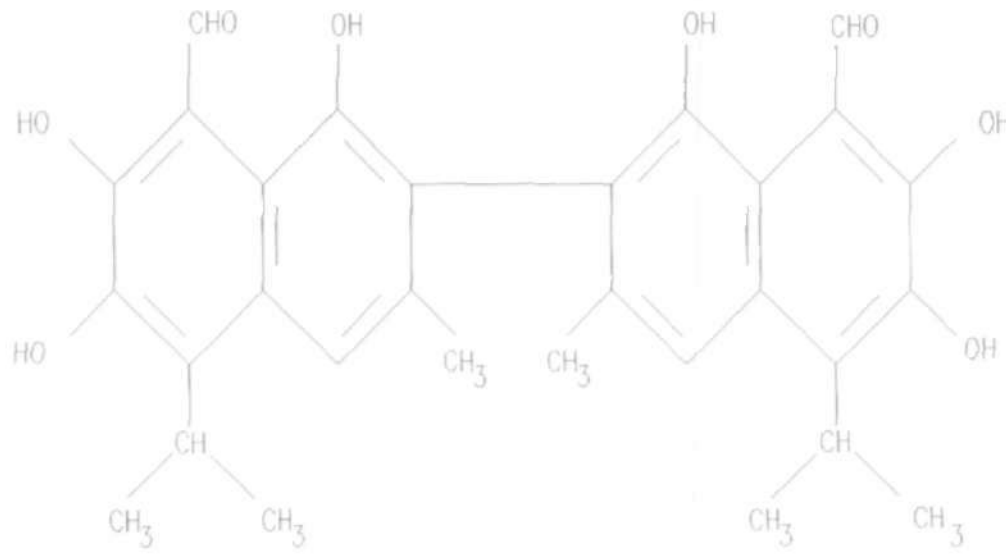


Fig 2.4 Structure of Gossypol

2.3 Classification and Mineral Composition of Bleaching Earths:

Bleaching earths are clays that, in their natural state or after chemical or physical activation have the capacity to adsorb colouring matter from oils (Rich, 1949). They are finely crystalline silicates of aluminium and/or magnesium with variable amount of lime, alkali and iron with a large proportion of water of hydration (Searle *et al*; 1959). Bleaching clays are often classed as Fuller's earth and benttonites according to their inherent properties (Siddiqui, 1968a).

2.3.1 Fuller's Earth:

Fuller's earth is a type of clay which in its natural form has the power to decolourize oils, fats and grease (Anon, 1953). The name has no geological significance, but owes its origin to the use of certain types of adsorbent clays in the archaic procedure of removing grease and fat from woolen cloth during the process of scouring or filling (Mansfield, 1936; Grim, 1953).

Clay is characterized by high water content, low plasticity and foliated structure. Most show a high silica to alumina ratio, lower apparent bulk density than acid-activable or other clays and have a pH of 6.5 - 7.5. The colour and texture of the Fuller's earth are so varied that it is not possible to make generalization (Siddiqui, 1968a). However, the best grades are light grey to brown in raw wet state and nearly white after drying. These earths are not activable commercially. Infact, earths of this type do not respond satisfactorily to acid activation (siddiqui, 1968a). Fuller's earth are made up predominantly of attapulgites and montmorillonite, more than 90% with small quantities of kaolinite, halloysite and illite, (Amon 1953; Gillson, 1960; Hallam *et al*; 1968). Sometimes, the attapulgites which is itself a distinct mineral is referred to as Fuller's earth (Siddiqui, 1968a).

Non clay constituents of Fuller's earth include quartz, amorphous silica, microline, orthoclase, albite, amphibole and biotite. All these minor constituents are not necessarily found in any one deposit nor are Fuller's earths always composed entirely of clay. Some materials which have been used for decolourizing are primarily silts with relatively low clay content and low decolourizing ability.

2.3.2 Bentonites:

Bentonites are clays produced from the alteration insitu of volcanic ash (Hallam *et al*; 1968). They are in general characterized by the power to absorb water to a greater extent than other plastic clays. However, bentonites vary in their ability to absorb water and those with lower swelling capacity have greater decolourizing ability after acid treatment.

Bentonites vary in colour and are often found in many shades of grey, blue, yellow, red and brown. They have a pH of 4 - 9.8. The diverse characteristics of bentonites make it difficult to assign general physical properties in all varieties according to siddiqui (1968a).

Bentonites are usually composed mainly of montmorillonites. Although, some may consist of the rarer clay minerals beidellites, saponite, hectorites and nontronite.

Minerallogically, bentonites are 75% or more of montmorillonites with fragments of kaolinites, illite, felspar, gypsum, unweathered volcanic ash, quartz and traces of other minerals (Siddiqui, 1968a).

2.4 Geology of Bleaching Earths:

Based on recent studies on the synthesis of clay minerals, various mechanism for the formation of orgillaceaus materials have been put forward. Terrestial weathering of basic igneous rock, hydrothermal alterations, and marine sedimentation have been suggested as possible mode of clay formation (Hallam *et al*; 1968). In all, the factors controlling the formation of clay minerals are the chemical characteristsics of the parent materials from which they are derived and the chemistry of the environment in which the change takes place (Siddiqui, 1968a). Bentonites occur in the younger geological formations because both montmorillonite and kaolinite tend to disappear in sediments of increasing age while the very ancient sediments are largely composed of illite or micaceaus types of clay minerals.

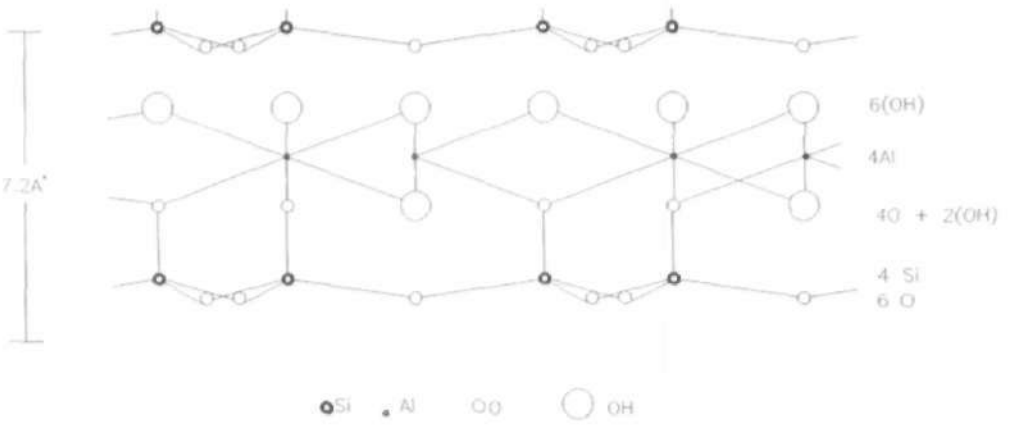
The abundance of montmorillonites in some ancient sediments vary geographically because of peculiar, relatively local conditions favourable for the persistence of the mineral. For example, the cretaceous formation of the United States of America contains large amount of bentonites and montomrillonites, whereas the sediments of the same age in France possess less montmorillonite (Grim, 1953). Except for a few such cases, montmorillonite is found abundantly in many mesozoic, tertiary or kainozoic sediments, recent marine sediments and in present day weathering products. It is generally absent in sediments older than mesozoic (Siddiqui, 1968a, Hallam *et al*; 1968).

In general, montomonillonites and attapulgites are geologically of recent origin. Illites are abundant in ancient sediments while kaolinites occur in older formation (Siddiqui, 1968a).

2.5 Composition and Structure of Clay Mineral:

Clay minerals are aluminosilicates, most of which are in the form of platey sheets. They consist of aggregates of minute crystal particles, usually 0.1 - 100μm. their dimensions in terms of length and breath may be large compared to the thickness of the sheets, like a piece of paper. They are hydrous aluminosilicates with 2 or 3 layer crystal structure. Many of the physical properties of colloids such as swelling when moists, shrinking on drying and flocculation in a water suspension are typical of clay minerals (Drapple, 1959).

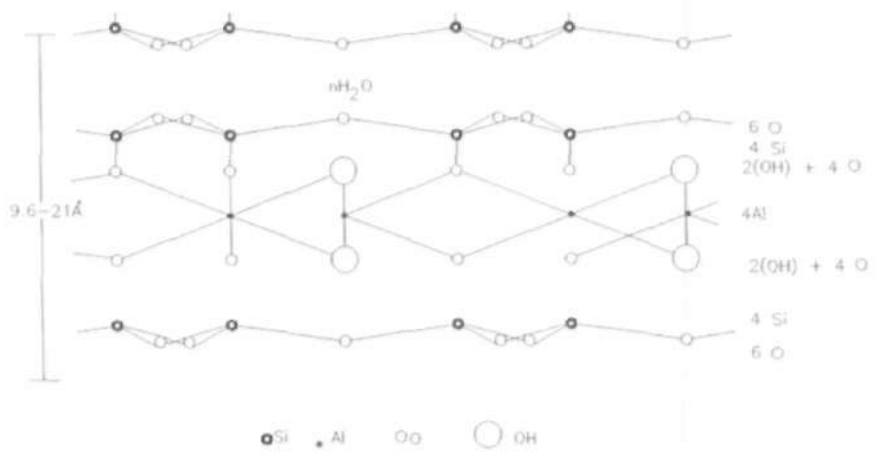
Common elements in the clay crystals are aluminium, silicon and oxygen. Almost all clay minerals are related to the three major groups kaolinites, illites and montmorillonites. Their lattice structure is best understood by considering it to be composed of sheets of tetrahedrally coordinated silica in units of si_4o_{10}, separated by aluminium hydroxyl units arranged so that each aluminium is surrounded by six oxygen and hydroxyl group.



Kaolinite $(OH)_8Al_4Si_4O_{10}$

Fig 2.5 The Structure of Kaolinite viewed along the a– axis Grunner (1932)

Kaolinites consist of 2 layers, one of silica tetrahedral and the other of aluminium hydroxyl (Figure 2.5) whilst montonorillonite consists of two basic sheets of silica tetrahedrally arranged as layers and with unshared oxygen directed towards one another. (Figure 2.6) The montmorillonite silica sheets are held together by aluminium hydroxyl units referred to as gibbsite units, fitted into position so that each aluminium is surrounded by four oxygen and two hydroxyl ions.

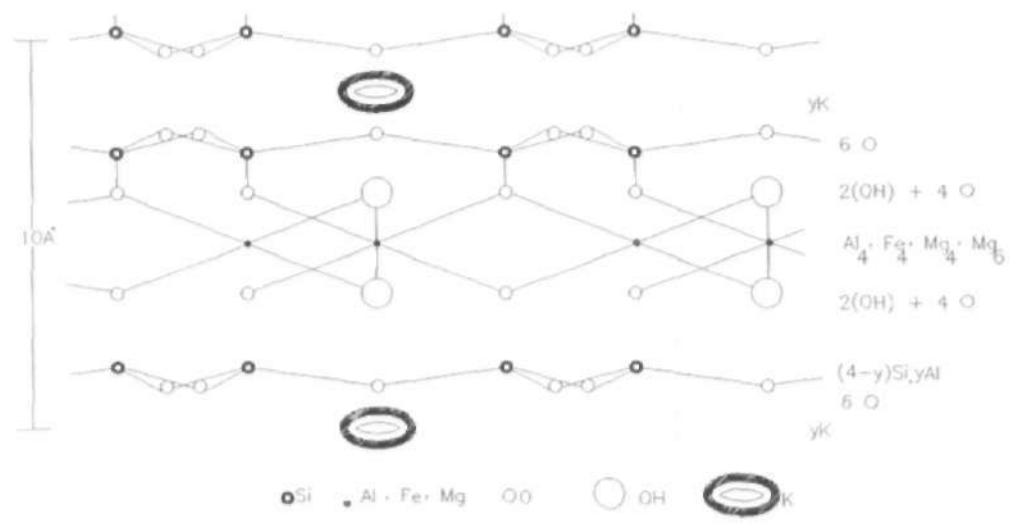


Montmorillonite $(OH)_4Al_4Si_8O_{20}.nH_2O$

Fig 2.6 The Structure of Montmorillonite viewed along the a– axis after Hofman, Endell and Wilm (1933)

Composite layers of the type described are bound loosely to each other by water in layers of variable thickness (9.6 - 21.4A°). Different amounts of water are introduced as the lattice expands while water is loss as the lattice contracts. Hence montmorillonite is said to have an expanding lattice whilst kaolinites does not expand with increasing water content, probably because of the juxta-position of hyydroxyl and oxygen layers when the sheets are stacked one above the other (Siddiqui, 1968a).

Isomorphic substitution of elements in the montmorillonite structure occurs mainly within the octahedral layer where Mg^{2+} or Fe^{3} or Zn^{2+} replaces Al^{3+} and to a much less extent within the silicate layer Al^{3+} replaces Si^{4+}. Extensive replacements give rise to a number of modifications resulting in new mineral forms such as nontronites and bridellites. Illite has a basic lattice much like that of montmorillonite except that K^{+} ions replace water in the lattice structure (Figure 2.7)



Illite $OH_4 K_y (Al_4 Fe_4 Mg_4 Mg_6)(Si_{8-y} Al_y)O$ y = 1–1.5

Fig 2.7 The Structure of illite viewed along the a– axis after Grim, Bray and Bradley (1942)

Water in clays exist in intergranular openings and within the space lattice. Much of this water held in pores are removed by ordinary air drying and in the process, bulk properties such as plasticity are altered appreciably. Some clays tend to retain more of the pore water on heating than others. While montmorillonites will loose 15%

of its air dry weight at 105°C, kaolinite will loose only about 2.5%. The bulk of kaolinite water is released at much higher temperatures about 430°C, accompanied by reorganization of the Al_2O_3 and Si_2O_5 layers into a new lattice of anhydrous silicate.

2.6 Activation of Bleaching Earth:

Activation is the process whereby clays intended for bleaching are subjected to various physical and chemical treatments to enhance their adsorption capacity and to give them certain desirable properties with respect to their applicability. Most bentonite are readily converted to bleaching earths by simply treating the ground material with dilute hydrochloric, tetraoxosulphate (VI) or organic acids. Some bentonites are activated by alternately drying and moisturing with water alone (Nutting, 1935). Several activation processes have been patented, they include:

i. Simple heat treatment with acid activation (Ollano, 1954).

ii. Extrusion activation before heat activation (Anon, 1957).

iii. Acid activation and modification of acid treatment. (Green and Allegrini, 1957).

The common patents are based on direct acid activation using varying concentrations of Hydrochloric or tetraoxosulphate (VI) acid for various times at elevated temperatures. The acid treated clay is then washed with water, dried and milled (Sodafabrik, 1922; Burghart, 1930 and 1931). Some are heated to temperatures as high as 180°C before drying, washing and milling. Pretreatment with water glass and/or alkali prior to activation has been suggested (Mailleraye, 1935) whilst other workers have recommended a post activation solvent wash (preston, 1953; Kagaanova, 1959). Post acid activation treatments that have been suggested include:

i. Treatment with dilute acid (HCl) to remove $FeSO_4$ and $Al_2(SO_4)_3$ before washing with water (Kuwada *et al*; 1953).

ii. Aluminium salt solution wash before ammonium hydroxide neutralization (Midzuno *et al*; 1955).

iii. *Calcining after activation* (Sauret, 1965).

Other activation methods that have also been recommended include the use of gases and bleaching agents like carbondioxide, hydrochloric acid, chlorine, sulphur (IV) oxide (Endell, 1935), alkali boiling (Rikagaku, 1933), electrodialysis and electroultrafiltration (Anon, 1934).

2.6.1 Acid Activtaion:

Studies have shown that activated clays consist mostly of low and non-swelling type montmorillonites with appreciable base exchange capacity (Siddiqui, 1968a). Acid treatment replaces exchangeable K^+, Na^+ and Ca^{2+} by H^+ in the inter-lamellar space and also leaches out a part of the Al^{3+}, Fe^{3+} and Mg^{2+} from the lattice structure, thus rendering the clays more porous and electrochemically more active (Winners, 1954; Oboh *et al*; 1987).

The ease with which the bases may be removed or replaced varies with the type of structure as well as the particular base affected. Hydrochloric acid and tetraoxosulphate (VI) acid are commonly used as activating agents, because they are effective than Trioxonitrate (V) acid and organic acids which are inferior in dissolving out lime and alumina (Eckart, 1929).

The solubility of clay minerals in acid varies with the nature of the acid, concentration, acid/clay ratio, temperature and duration of treatment. Different types of clays have different solubilities and there are great variations in solubilities within a group. Thus, a magnesuim rich montmorillonite is generally more soluble than that is rich in aluminium, with iron rich monitimonillonite in between (Grim, 1953).

During acid leaching, the basic components of the clays are attacked first at the edges of the platelets, with penetration then proceeding inwards. Mg^{2+}, Al^{3+} and Fe^{3+}

proceed from octahedral position to exchange sites and then into solution (Grim, 1962). The acid penetration thus proceeds into the interior of the structure from the edges, leaving the frame work possessing a large area (Siddiqui, 1968). The changes taking place during acid leaching of an idealized montmorillonite may be expressed as

$$(Al_4)(Si_8)O_{20}(OH)_4 + 3H^+ \xrightarrow{H^+} (Al_3)(Si_8)O_{20}(OH)_2 + Al^{3+} + 2H_2O$$

$$(Al_4)(Si_8)O_{20}(OH)_4 + 6H^+ \xrightarrow{2H^+} (Al_2)(Si_8)O_{20} + 2Al^{3+} + 4H_2O$$

At this stage, half the Al atom has been removed from the structure together with 2 hydroxyl groups as postulated by Thomas, *et al*; (1950) (figure 2.8). The remaining Al atoms are tetrahedrally coordinated with four oxygen atoms. This change from octahedral to tetrahedral coordination leaves the crystal lattice with a negative charge balanced by hydrogen ions. As the acid treatment proceeds further, greater dissolution of octahedral aluminium occurs and a silica tetrahedral skeleton is left at the end.

$$(Al_2)(Si_8)O_{20} + 3H^+ \xrightarrow{2H^+} Al^{3+} + (Al)(Si_8H_4)O_{20}$$

$$(Al_2)(Si_8)O_{20} + 6H^+ \xrightarrow{H^+} Al^{3+} + (Si_8H_8)O_{20}$$

However, the idealized state is not reached in activable bentonites and some cations in the octahedral layers linger to support the silica sheets, though in a poorly orderly fashion. The action can be controlled to give an optimum amount of alumina to keep the structure intact, which maximizes the selective sorption capacity (Siddiqui, 1968a).

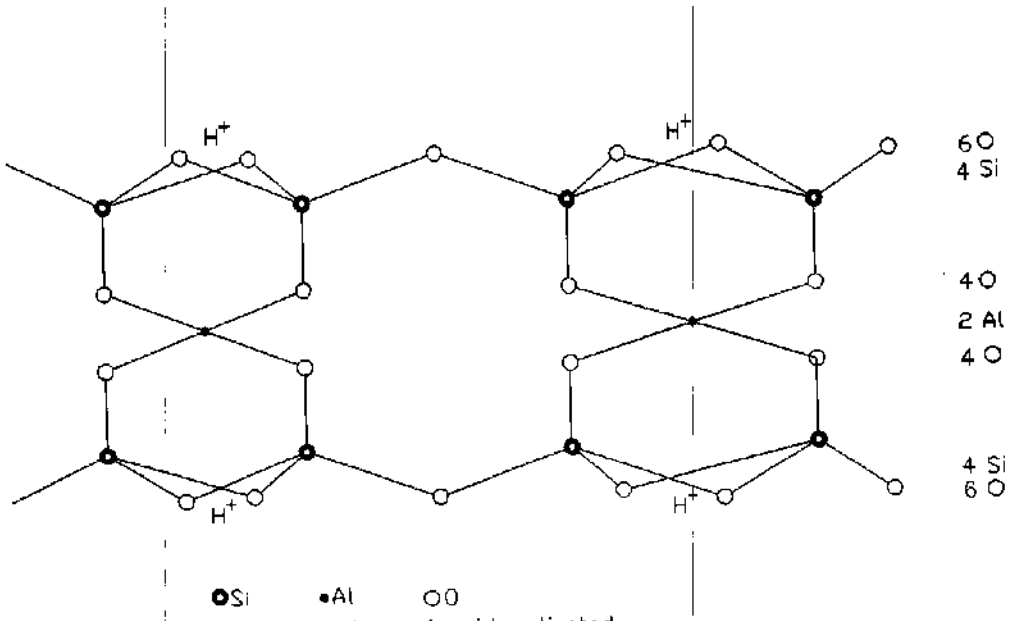


Fig 2.8 The Idealised structure of acid activated Montmorillonite as postulated by Thomas,Hickey and Stecker,(1950)

Acid activation serves to produce flat silicates sheets free of adsorbed cations, except hydrogen and some aluminium and thus gives an extended surface useful for adsorption. It also causes enlargement of capillaries and increases the inner pore surface by leaching out various mineral constituents. The structure is opened up and active surfaces set free which in their natural condtion were sealed with metal salts. Excessive acid treatment of clays may eventually leach out too much of the basic constituents with detrimental effect on their selectivity. For maximum activation, the structure of the elementary unit should be retained and drastic conditions of activation avoided (Siddiqui, 1968).

2.6.2 Heat Activation and Extrusion:

Some clays such as attapulgite and sapiolite are heat activated as compared to illites and montmorillonite which are usually acid activated. This is attributed to the fact that they contain water molecules in their structural channels, thus may be activated by drying at 300 - 350°C. The loss of water from the channels result in a large increase in their internal surface area. It is important to note that Fuller's earth containing their minerals are thus activated by heat (Dandy, 1967; Siddiqui, 1968a).

The adsorption capacity of a Fuller's earth may also be increased by an extrusion process in which the clay is pugged and forced through slots under high pressure. The treatment causes a large increase in surface area and attapulgite and sapiolite fibres occuring as bundles bound to one end are separated into individual fibres, exposing new surface to action.

2.7 Effect of Acid Activation of Clay on Bleaching:

The oil retention of acid activated clays are often greater than those of the natural bleaching clays of the same particle size. This is attributed to the apparent bulk density of the acid activated clay which are usually lower than those of the natural bleaching clays. But literatures have reported that acid activated clays have a higher bleaching ability than the natural ones. This could be traced to the fact that bleaching is essentially an intracrystalline property of clay (Siddiqui, 1968).

In general, acid activated clays with a high degree of moisture desorption have better bleaching qualities (Nadirov *et al*; 1967). Maximum bleaching is achieved with clay containing 15-18% moisture for bleaching animal fats and fish oil or 12-15% moisture for vegetable oil (Nadirov 1963; Bakr *et al*, 1968). It is also observed that predried clay samples were better adsorbent than those not predried, but the optimum contact temperature varied from sample to sample (Ezdakov, 1966; Oboh, 1988; Anozie, 1993).

Acid activated clay samples heated to very high temperatures are known to exhibit lower decolourizing power (Rich, 1964; Oboh, 1987).

Acid treatment increases bleaching activity of clays by replacing the exchangeable aluminium (Al^{3+}) and other metallic ions by hydrogen (H^{+}) in the interlamellar space. The bleaching activity of acid activated clay is also attributed to the non crystalline silicic acid liberated during the acid treatment (Koegler, 1963).

Studies have also shown that at specific particle size of the activated clay bleaching power increases with time (10 - 60 minutes) and it starts to decrease for a

particular percentage of the clay. Moreover, the ratio of the clay to acid used have been shown to be of importance when activating the clays, and the activated clay with the best bleaching efficiency are obtained when one part of clay is mixed with two or three parts of acid (3MHCl) (Oboh, 1988; Anozie, 1993).

2.8 Mechanism of Bleaching:

Bleaching earth, by virtue of their structure, history of formation and the processes subjected to during activation possess large surface areas for adsorption of colouring matter (Rich, 1964). The mechanism of decolourization is not yet fully understood, but is known to be a selective adsorption process of colouring matter on exposed solid surfaces in contact with the liquid to be decoloured (Nutting, 1933) Any solid adsorbs only fluid that wets it, in the sense that near the boundry surface internal pressure, density and viscosity are increased. In certain cases these effects are heightened by chemical affinity (Nutting, 1933). The presence of open bounds or free valencies on the surface results in selective adsorption which is referred to as chemical adsorption or chemisorption (Mantel, 1951)

According to Nutting, (1935), clay particles are potential bleaching earths for oils when their surface hold H^+ or OH^- radicals adsorbed in a thin layer. When these are driven off by heating, open bond are left which select from the oils, the darker and more basic constituents. At elevated temperatures (100 - 160°C) dark oil particles directly replace hydrogen and hydroxyl ions without previous drying. Certain clays are not active because bases such as iron, alumina, calcium etc already occupy the surface bonds. Such clays may be activated by replacing such bases by hydrogen of an acid. This open bond hypothesis is fundamental in understanding the behaviour of bleaching clays.

The process of adsorption was believed to be purely one of base exchange in which an equivalent quality of the base was displaced by colourants. However, Kayser and Blosch, (1953) and Khoo *et al*; (1979) have shown that there are evidences indicating that the adsorption may not be purely physical and, infact, that two distinct mechanisms of adsorption operate simultaneously. One is the electrochemical nature

whilst the other is purely physical. This physical adsorption could be explained using the Freundlich's theory (Cowan, 1976).

Mathematically, this theory relates adsorption to residual solute concentration at a single temperature.

$$\text{Freundlich's equation} = \frac{X}{M} = KC^{n}$$

where X = amount of substance adsorbed
M = amount of adsorbent
K and n are constants

This is also expressed as

$$\log\left(\frac{X}{M}\right) = \log K + n \log c$$

A plot of log ($^{x}/_{m}$) versus log c will produce an adsorption isotherm which is a straight line with a slope equal to n and $^{x}/_{m}$ will be equal to K when c equal 1. Practically, K is a measure of the activity or decolourizing power of the adsorbent, whereas n is an indication of its characteristic manner of adsorption (Bailey's, 1964).

2.9 Effects of Clay Properties on its Bleaching Performance:

2.9.1 Acidity:

Natural clays have a pH between 4 - 7 and activated clays 2.5 - 4.0. Chlorophyll pigments are readily removed by clays of low pH. (Pritchet *et al*; 1947; Rich, 1964). Hence chlorophyll rich oils such as soyabean require bleaching earths of substantial acidity for optimum adsorption. However low pH has a detrimental effect on oils. It causes an increase in the free fatty acid content of the oils because of H^{+} causes some hydrohysis of the glyceride to free fatty acid and glycerine (Richardson, 1978; Oboh *et al*; 1988)

2.9.2 Volatile Matter:

After washing and filtering, activated clays must be dried to facilitate handling and to maximize its bleaching power. It has been determined that maximum bleaching power of clay lies between 19-22% by weight of volatile matter (Richardson, 1978). In addition to drying speed affects bleaching power. Therefore, flash drying equipment are widely utilized in the industry.

2.9.3 Apparent Bulk Density:

Apparent bulk density (ABD) is referred to as the weight per unit volume of clay when it is tapped to constant volume in a graduated cylinder (Rich, 1960). ABD of a clay is inversely proportional to its adsorptive capacity and filtration rate (Rich, 1964) since ABD of a clay depends on the void space, ABD is inversely proportional to the amounts of oil retained by the clay (Rich, 1960; Oboh *et al*; 1988).

2.9.4 Moisture:

Bleaching clays normally contain from 10-18% free moisture. When a clay is dried, the water molecules escape and the layer collapses. This reduces the active surface area, thereby reducing the adsorptive capacity of the clay (Rich, 1964). However, when used for bleaching oil, it is necessary to remove the moisture from the clay to obtain optimum adsorptive capacity. The colouring materials cannot be maximally adsorbed until all the water has been removed. to achieve this, the clay must be added to the oil at a temperaturre below the boiling point of water at the pressure employed in the bleaching. The temperature of the oil is then increased gradually to a point somewhat above the boiling point for maximum adsorption.

2.9.5 Particle Size:

The sizing of the clay (bleaching earth) is important in its bleaching power. Grinding to a very fine state will increase the bleaching power of clays markedly. However, this reduces the filtration rate and increases oil retention. Thus the particle

size distribution of the clays should be maintained at an average so that the clays would have good adsorptive capacity (Slisarenko *et al*; 1958; Rich, 1964; Richardson, 1978).

2.10 Review of Methods used for Clay Acid Activation:

A number of acids have been used in the acid activation of clays, but HCl and H_2SO_4 are frequently used since they give the best bleaching effects. Most of the methods employed are the wet activation type with modification on the various conditions. Also, the dry activation method is used, but because of the complexity in the activation process it is not common.

Heating the clays to 380°C then treating them with 3% HCl for two hours with a contact time of 30 minutes at 100°C furnished a clay which gives the best bleaching results (El-Nockrashy, 1970). In the decolouration of some oils this temperature (100°C) is too high, thus darkening occurs (Peanut oil). In this case holding for 20 minute at 60°C is reported to be satisfactory (Novak, Ivan, 1970).

Also, 2 - 3 weight part of water could be added to one part of clay, after grinding and drying, then followed by concentrated H_2SO_4 so that the mixture would contain 50 - 55% H_2SO_4 in relation to the air dry clay. This sample is then heated at 120-130°C and then at 170-190°C for 1.30 - 2.00 hours. It was observed that this gave a good bleaching effect at the sample temperature (85 - 90°C) and time (30 minutes) (Kamaletdinoval *et al*,1966; Ganchev *et al*, 1971).

Kauspedas, (1962) heated clay sample of a particular particle size to a temperature of 200 - 220°C for 2 hours before activating with 20% H_2SO_4 or HCl until all carbondioxide (CO_2) was removed, washed until neutral, dried at 105 -110°C, powdered again and passed through the seize.

Joshi *et al*; (1953, 1957) prepared acid activated clay by activating with 5M HCl, 200cm^3/100g for 3 hours, washed free of acid, dried and heated at 350°C with particle size 100 - 200 mesh. They also reactivated a powdered clay sample previously activated by treatment with HCl with H_2SO_4 by slurrying 100g in 200cm^3 water and

adding up to 37 - 40% acid slowly to the mixture. Then this was washed free of acid, filtered and dried.

Folliet, (1951) activated clay samples by first removing calcium and iron salt with HCl then any sand and gravel is separated by washing the slurry and decanting. The slurry is mixed with 40 - 60% weight of concentrated H_2SO_4, stirred and heated for 24 - 72 hours.

Winner, (1954) in his own case activated clay samples by leaching with varying concentrations of HCl for $2^1/_2$ hours with the best bleaching at 10% HCl. This corresponds to the leaching of 36.5 - 42.5% of iron originally present in the clay.

Battalova *et al*; (1963) used three different concentrations of H_2SO_4, temperature and time to activate clay samples

(i) 30% H_2SO_4 for 6 days at room temperature

(ii) 20% H_2SO_4 for 6 hours at 97 - 98°C

(iii) 13% H_2SO_4 for 6 hours at 97 - 98°C.

They found that clay activated with 20% H_2SO_4 for 6 hours at 97 - 98°C gave the best bleaching ability. The clay was active and stable.

Jacque Saurel, (1964) prepared acid activated clay be adding concentrated H_2SO_4 (135g/L) to a paste containing 300g montimorillonite/L water. This slurry was then filtered and the filter cake heated to 160 - 180°C for 1 - 2 hours. The activated clay was then ground, washed free for acid with water, filtered, dried and granulated.

Oboh *et al*; (1987, 1988) activated clay samples by drying in oven at 105 - 110°C for 1 - 2 hours, milled and sieved with a 180μm standard canadian sieve. 50g samples were mixed with various quantities of HCl (0.3 - 8.2M) and H_2SO_4 (0.1 - 5.1M) and refluxed by boiling for various durations 1 - 6 hours. After slight cooling,

the slurry was filtered and washed free of acid as indicated by litmus paper. The clays were then dried at 110°C for 2 - 3 hours, ground using a mortar and pestle, and sieved with 180μm canadian standard Tyler Sieve again.

Ibemesi *et al*; (1990) activated clay samples by mixing thoroughly 200g of 230 mesh sized clay with 400cm^3 of 30% H_2SO_4 in a 2 necked, 2 - litre, round bottom flask, heating under reflux for 3 hours at 104 - 107°C. The mixture was then filtered under suction and washed with distilled water till the clay was acid free. The clays were then dried in an oven for two and a half hours at 150°C and reground to the 230 mesh size before use.

Anozie *et al*; (1993), activated their own clay samples by measuring different quantitites of 1.0 - 5.0M HCl and adding each to a slurry of the clay. The mixture was then boiled at 105°C for two and a half hours, cooled, washed, filtered, dried and ground into fine powder.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Sample Collection and Description:

The clay samples used in this work were collected from different locations in Nigeria. The sources of the clays varied from location to location. However, within each location the sample taken was representative of the predominant clay formation in the location. About 6 kg each of the clays from different location were collected.

(i) Bomo Clay (S_1)

Bomo is a village close to Samaru where Ahmadu Bello University is located. The clay sample was obtained from the Bomo Dam.

(ii) Osogbo Clay (S_2)

Osogbo is the capital of Osun State. It is, located in the centre of the state. The clay samples were collect at two different sites based on the colours of the clays. Osogbo (I) clay was collected at a site close to the state sport complex along Ikirun road. It is brown in colour. Osogbo (II) clay was collected at a site after the State Governor's Lodge before the School of Nursing on the way to Ilobu. It is creamy in colour.

(iii) Omiadio Clay (S_3)

Omi adio is a town in Oyo State, which is also not far from Ibadan along Abeokuta Road. The clay samples are Omiadio (I) and Omiadio (II) were collected from the Nigerian Mining Cooperation. These clays were used by them in making brick for house construction.

(iv) Igbaja Clay (S_4)

Igbaja is a town in Ifedodun Local Government Area of Kwara State. A clay sample was collected from the valley after the muslim prayer ground along Igbaja-Obin road. The clay sample was grey in colour.

(v) Ilorin Clay (S_5)

Ilorin is the capital of Kwara State. It is located in the central - west region of Nigeria west of the river Niger. The clay sample is ash colour and this was collected at the stream passing through Sabo-Oke and GRA by the Love garden near the Nigerian Hearld.

(vi) Ile Ife clay (S_6)

Ile Ife is in Osun State in the Southern part of Nigeria. The clay was actually collected from Ajabamidele, close to the bridge at the outskirt of Ile Ife when coming from Ibadan. The clay is brown in colour.

(vii) Ogbomosho Clay (S_7)

Ogbomosho is a town in Oyo State. It is the second largest town in Oyo State. The clay sample was obtained from a site on the way to Federal Government College about 700 meter from the school. It is a brown coloured clay.

(viii) Kankara Clay (S_8)

Kankara is a town in Kastina State and the clays obtained from there are often used in the making of ceramics and pottery. Clay sample was collected from the department of industrial design (Ceramic section). It is Biege in colour.

(ix) Alex Clay (S_9)

Alexander (Alex) is one of the hostel in the Ahmadu Bello University and the clay sample was obtained by the E. E Block on the way to the University library.

(x) Moniya Clay (S_{10})

Moniya is a town at the outskirt of Ibadan. It is the Headquarters of Akinyele local government along Ibadan Ilorin road. The clay sample was collected from a clay deposit behind the Federal Road Safety Commission Office. It is a lilac coloured clay.

(xi) Ilesha Clay (S_{11})

Ilesha is a town in Osun State. It is about 70km from the state capital Osogbo. The clay sample was collected from a site after the International breweries before the junction to Akure. It is brown in colour.

(xii) Fuller's Earth (**F**)

BDH chemical limited poole England.

3.2 Preparation of Clay Sample:

The various clay samples were suspended in tap water and washed repeated to remove non-clay particulate. Each was then sieved with a 425μm Endocott Sieve grade followed by a 150μm grade again to bring out the actual clay particles. These were then allowed to sediment which took about three days for proper sedimentation. Then distilled water was also used to wash sedimented clay again before final the sedimentation. These clays were dried in the open air in the laboratory on large polyethene sheet for ten days. After the drying they were pounded in a wooden mortar with a pestle each, then sieved with a 250μm size Endocott sieve grade.

3.3 Determination of Moisture Content:

This involves the measurement of the weight loss due to evaporation of water from the sample. Approximately 5g of each clay sample was accurately weighed into separate dried preweighed crucibles. The samples were heated to constant weight in an air oven at 100°C. After cooling in a dessicator, the loss in weight was determinated and expressed as a percentage of the unheated sample (Jackson, 1958; Hesse, 1971).

$$\text{percent moisture content} = \frac{\text{Total loss in weight}}{\text{weight of original sample}} \times \frac{100}{1}$$

3.4 Determination of Loss on Ignition

Loss on Ignition is conventionally taken as the equilibruim weight loss on heating at 1000°C This weight loss consist of bound or chemically adsorbed water, water formed by dehydroxylation of initially hydrous or hydroxylated silicate structure (Particularly applicable to clays), carbon (IV) oxide and sulphur (VI) oxide from the decomposition of carbonates and sulphates respectively. (Cluton, *et al*; 1970). Loss on ignition is determined gravimetrically.

Method:

1.00g of the finely grounded and dried (110°C) clay samples were weighed in clean preweighed porcelain crucibles. The crucibles were partially covered with their lids and placed in a muffle furnace. The temperature of the muffle furnace was slowly raised to 1000± 10°C and the samples were ignited at this temperature for 30 minutes. Then the crucibles were removed from the furnance completely covered with the lids, cooled in a dessicator and weighed. Loss on ignition was calculated as a percentage of the weight of the sample used. This determination was carried out in triplicate for each sample (Cluton et al, 1970; Hesse, 1971). Loss on ignition was then calculated as follows. weight of crucible + sample . . . . . a

weight of crucible + residue after ignition . . . . . b

Loss in weight of sample . . . . . (a-b)

(All weights are in g)

$\therefore$ Loss on Ignition at 1000°c = (a -b) x 100

$$\text{Percentage weight loss} = \frac{\text{Total loss on Ignition}}{\text{weight of Ignition sample}} \times \frac{100}{1}$$

3.5 Decomposition of Clay Sample:

In analysing complex materials like clay which is only slightly soluble in water, one of the most crucial decision of the analyst is that of method of decomposing the sample as this sets the course of subsequent analytical work and can save unnecessary steps. The various methods of decomposing a sample fall into four categories: acid digestion, acid fusion, alkaline fusion and ammonium salt attack. The analyst has to choose the method that, taking everything into consideration, is best adopted to the material to be analysed.

No general rule can be applied regarding the advantages to be gained by employing any particular method as this is determined by the nature of the material and subsequent analytical procddures.

Many questions however, (williard *et al*; 1961) have to be answered. Such questions include, Does the process attack the vessel in which it is conducted?. How effective is it?. Will the reagents interfere in any analysis?. Will the excess reagents be removed, if necessary? Will any loss of material be involved?.

The decomposition method employed for all these samples was the alkaline fusion (K_2CO_3/Na_2CO_3) followed by the dissolution of the cake in hydrochloric acid.

Method:

About 1g quantities of each finely ground dried (at 110°C) samples were accurately weighed in platinuim crucibles. 6.0g of anhydrous sodium carbonate and 0.8g of boric acid were added and the mixture thoroughly mixed to form a charge at the bottom of the crucible. A little more carbonate was added as a layer on top of the mixture. The crucible was covered with the lid and heated over the Bunsen flame, gently at first and then gradually raising the temperature to the full heat for 10 minutes. The crucible was then transfered to a muffle furnace at about 1200°C and the contents fused for 15 minutes.

After cooling, if the fusion appeared blue or blue green, indicating the presence of manganese. $2cm^3$ of ethanol (95%) was added to it before dissolution.

$15cm^3$ of hydrochloric acid (36 percent), $1cm^3$ of tetraoxosulphate (VI) acid (50% $^{v}/_{v}$) and $10cm^3$ of water were added and the crucible transfered to a steam bath to facilitate dissociation of the melt. In a situation when the solution jelled before dissolution was complete the gel was stirred with a glass rod. After dissociation was complete the lid was removed and any spray adhering to it washed into the crucible with minimum amount of water (Hesse, 1971 and Vogel, 1978).

3.6 Determination of Silica:

Silica or silicon (IV) oxide can be determined by gravimetric, colorimetric and spectrographic methods. In the present work gravimetric method was used.

Method:

The contents from the decomposition of the clay sample was digested in the platinium crucible over the steam until a stiff gel formed. Any loss of hydrochloric acid during digestion was replaced by adding appropriate amount of diluted hudrochloric acid (50% $^{v}/_{v}$). After the gel had formed, 10cm^3 of water was added and the mixture allowed to stand for 5 minutes.

The gel was filtered using Whatman 541 filter paper transfering the gelled silica to the filter paper with hot dilute hydrchloric acid (50% $^{v}/_{v}$) and scrubbing the crucible with a glass rod. The percipitate was washed four times with hot dilute hydrochoric acid (5% $^{v}/_{v}$) and then with hot water until practically free from chloride.

The percipitate and washing were reserved. The filter paper containing the percipitate was transfered to a preweighed platinum crucible, charred over the Bunsen flame, until free from carbonaceous matter, and was ignited in a Muffle furnace at 1200°C for 30 minutes. After cooling in a dessicator, the crucible and contents were weighed. This gave the weight of silica and impurities (crude silica).

The contents of the crucible were moistened with water, 5 drops of dilute tetraoxosulphate (VI) acid (50% $^{v}/_{v}$) added in turn, and the mixture evaporated over a low temperature hot plate in a fume cupboard. Finally the crucible with the residue was ignited in a muffle furnace at 1200°C for 5 minutes. After cooling, the crucible was weighed to obtain the weight of impurities. The differnce between the two weights represented the gravimetric silica. This determination was carried out in triplicate.

weight of platinuim crucible	=	a
crucible x silica x impurities	=	b
crucible x impurities	=	c
weight of silica	= d = (b - c)	

(All weights are in g)

$$\text{percentage weight of silica} = \frac{b - c}{1.00} \times \frac{100}{1}$$

3.7 Decomposition of Clay Samples by the Perchloric - Hydrofluoric Acid Digestion Mixture for the Determination of Alkali Oxides:

About 0.1g of oven dried (100°C) clay sample was accurately weighed in a platinum crucible. This was moistened with a drop of two or water. 5cm^3 of hydrofluoric acid (40% $^{w}/_{v}$), 0.5cm^3 of perchloric acid (60% $^{w}/_{v}$) were added and the crucible was nearly covered with its lid and heated on a hot plate at about 200°C until the liquid had evaporated. On cooling, 5cm^3 of 6M hydrochloric acid was added followed by distilled water so that the crucible was half filled. The crucible with the mixture was then heated on the hot plate to boiling for 5 minutes. After the residue had disolved, it was transfered to a 100cm^3 volumetric flask and was diluted to volume (Hasse, 1971).

3.8 Determination of Alkali Oxides

Solution Preparation:

i. Aluminium Sulphate (10,000 ppm Al_2O_3) Aluminium metal was cleaned with hydrochloric acid (50% $^v/_v$), ethanol (95%) and ether.

To 2.645g of the clean dry metal 10cm^3 of tetraoxosulphate (VI) acid (d = 1.84), 3.0cm^3 of trioxonitrate (V) acid (d = 1.42) and approximately 12.5cm^3 of water were added. After reacting in the cold, the mixture was gently heated until the metal dissolved and the trioxonitrate (V) oxide were expelled while the tetraoxosulphate (VI) acid fumed strongly. The solution was cooled and the crystalline melt dissolved in water and diluted to 500cm^3 in a volumetric flask.

ii. Aluminium Sulphate (2,000 ppm Al_2O_3).

50cm^3 of the Aluminium sulphate solution above were diluted to 250cm^3 in a volumetric flask.

iii. Lithium, Sodium and Potassium concentrated standard solution (A) (400 ppm Li_2O, 100 ppm Na_2O, 400 ppm K_2O). 0.608g of lithium chloride, 0.2543g sodium chloride and 0.191g of potassium chloride salts dried at 150°C, were each dissolved in water and diluted to 250cm^3 in a volumetic flask.

iv. Lithium/Potassium standard solution (B) (40 ppm Li_2O, 40 ppm K_2O) and sodium standard solution (20 ppm Na_2O):

25cm^2 of concentrated potassium/lithium standard solution (A) were diluted to 250cm^3 in a volumetric flask. Also 50cm^3 of concentrated sodium standard solution (A) was diluted to 250cm^3 in a volumetric flask.

v. Lithium/Potassium top standard (30ppm Li_2O, 30ppm K_2O).

7.5cm^3 of lithium/potassium concentrated standard solution, 4.0cm^3 of dilute trioxonitrate (V) acid (5% $^v/_v$) and 3.0cm^3 of aluminium sulphate solution (10,00ppm Al_2O_3) were transfered to 100cm^3 volumetric flask, diluted to volume with water and mixed.

vi. Sodium top standard (15ppm Na_2O).

1.5cm^3 of sodium concentrated solution, 4.0cm^3 of dilute trioxonitrate (V) acid (5% $^v/_v$) and 3.0cm^3 of aluminium sulphate solution (10,000ppm Al_2O_3) were transfered to 100cm^3 volumetric flask, diluted to volume with water and mixed.

vii. Lithium, Potassium and Sodium Zero Standard.

4.0cm^3 of trioxonitrate (V) acid (5% $^v/_v$) and 3.0cm^3 of Aluminium sulphate solution (10,000ppm Al_2O_3) were transfered to 100cm^3 volumetric flask, diluted to volume and mixed.

3.8.1 Preparation of Calibration Standards:

1.25, 2.5, 50, 10.0, 15.0, 25.0 and 31.25cm^3 aliquot respectively of lithuim, sodium an potassium standard solution (B) were transfered to 50cm^3 volumetric flasks containing 2.0cm^3 trioxonitrate (V) acid (5% $^v/_v$) and 1.5cm^3 of aluminium solution (10,000ppm Al_2O_3) and diluted to volume. This gave 1, 2, 4, 8, 12, 16, 20 and 25ppm Li_2O and K_2O and 0.5, 1, 2, 4, 6, 8, 10 and 12.5ppm Na_2O respectively.

3.8.2 Preparation of Samples:

25cm^3 of the stock solution from the perchloric - hydrofluoric acid digestion were transfered to a 50cm^3 volumetric flask containing 5.0cm^3 of aluminium sulphate (2000ppm Al_2O_3) and 2.0 cm^3 Trioxonitrate (V) acid (5% $^v/_v$) and diluted to mark with distilled water.

Method:

A flame photometer was lit and air turned on and adjusted to 10lb/1n^2. Water was sprayed and the gas flow adjusted to give a well defined blue cone. The appropriate filter was fitted. The full scale for lithium and potassium was set with the potassium/lithium top standard (30ppm Li_2O, 30ppm K_2O), and the zero on potassium/lithium zero standard. The calibration standards were then sprayed noting the readings and checking the full scale and zero frequently. From these readings a calibration curve was prepared (Appendix A and B). For sodium also the full scale was set with the top standard (15ppm Na_2O) and the zero on the sodium zero standard. The standards were again sprayed as above and calibration curve similarly obtained (Appendix C).

The sample solutions were sprayed, the reading were noted and the concentrations of lithium, sodium and potassium in the original clay samples calculated with reference to the calibration curves. (Dvorak et al, 1971; Vogel, 1978; Chia, 1980). Formula used in the calculation of the concentration in the original sample.

$$\text{Mg/100g clay} = \frac{\text{ppm graph} \times \text{V.E} \times \text{D.F} \times 100}{1000 \times \text{W} \times \text{Eq.wt of element}}$$

where

V.E = Volume of extract

D.F. = Dilution Factor

W = Weight of sample used for digestion

Eq.wt = Equivalent weight of element

$$\text{Dilution Factor} = \frac{\text{Volume of Volumetric Flask used}}{\text{volume of aliquot taken.}}$$

In a solution where further dilution was done the dilution factor was multiplied by 10.

3.9 Determination of Ferric Oxide:

The colorimetric method of analysis was employed for the determination of the ferric oxide. This was to ensure that the iron content of the clay sample which could be in the ferric or ferrous state was quantitatively determined. In the colorimetric procedure used hydroxylamine (as the hydrochloride salt) was added to sample solution to reduce any Fe^{3+} to Fe^{2+}. The latter is then completed with 1,10 phenanthroline reagent giving a strongly coloured reddish-range complex identified as (Tris (1,10 phenanthroline) iron II). The complex is quite stable and conforms to beer's law over a concentration range of 0-4ppm, its colour intensity being constant in weakly acidic, neutral or weakly alkaline medium (pH 4 - 9) and has a maximum absorbance at 510nm.

Solution Preparation:

(a) 1, 10 - phenanthroline (0.1%): - 250mg of 1, 10 phenanthroline monohydrate were dissolved in $5cm^3$ of ethanolic acid and diluted to $250cm^3$ with water in a volumetric flask.

(b) Sodium acetate (10%): 25g of sodium acetate was dissolved in water and diluted to $250cm^3$.

(c) Hydroxylamine (10%): 25g of hydroxylamine hydrochloride was dissolved in water and diluted to $250cm^3$.

(d) Standard Iron II solution (100mg Fe_2O_3/dm^3): 0.3511g of ferrous ammonium sulphate, $Fe(NH_4)_2(SO_4)_2.6H_2O$ were dissolved in $5cm^3$ of hydrochloric acid and then diluted to volume $500cm^3$ in a volumetric flask.

(e) Diluted Standard Iron II solution (10mg Fe_2O_3/dm^3): $50cm^3$ of the standard Iron II solution (100mg Fe_2O_3/dm^3) were diluted to $500cm^3$ in a volumetric flask when required.

Method:

Various aliquots (0 - $20cm^3$) of the diluted standard Iron II solution (10mg Fe_2O_3/dm^3) were pipetted into $50cm^3$ volumetric flasks. $0.5cm^3$ 1,10 phenanthroline solution (0.1% $^w/_v$) and $2.0cm^3$ of sodium acetate solution (10%) were added in turn. After standing for 15 minutes the solution in each flask was diluted to volume with distilled water.

The absorbance of each solution was measured against the reagent blank in a 10mm cell at 510nm using a Corning colorimeter 253. A plot of absorbance against the concentration of iron oxide in each flask yield the calibration curve (Appendix D).

$1.0cm^3$ aliquot of the stock solution from the perchloric-hydroflouric acid digestion was transfered to $50cm^3$ volumetric flask. The colour was developed and the absorbance measured as outlined above. The ferric oxide content of the solution was then determined by reference to the calibration curve. The absorbance measurement for both the standard and the sample were carried out in triplicates.

Calculation:

$$\text{Concentration in (ppm)} = \frac{\text{Absorbance}}{\text{slope} \times 1.79 \times 10^{-5} \text{ (molar absorption coefficient)}}$$

$$\text{Percentage } Fe_2O_3 = \frac{\text{Concentration (ppm)} \times \text{volume of dilution}}{10 \times \text{volume of aliquot} \times \text{sample weight.}} \times \frac{100}{1}$$

3.10. Determination of Titania:

The colorimetric method was employed in the determination of Titania. This is a fast and reliable method. It depends on the formation of intensely yellow peritanic acid when hydrogen peroxide is added to the acidified solution of titanium sulphate (Allport et al, 1963)

Solution:

i. Orthophosphoric acid (40% $^{v}/_{v}$)

ii. Hydrogen peroxide (6% $^{v}/_{v}$)

iii. Standard titanium solution (1.0mg TiO_2/cm^3): 0.500g of titanium oxide was mixed with 16g ammonium sulphate and $40cm^3$ of concentrated tetraoxosulphate (VI) acid and heated until the mixture dissolved. On cooling, about $100cm^3$ of water was added and the solution quantitatively transfered to a $500cm^3$ volumetric flask and diluted to volume.

iv. Diluted standard titanium solution (0.08mg TiO_2/cm^3): $20cm^3$ of the standard titanium solution (1.0mg TiO_2/cm^3) was diluted to $500cm^3$ in a volumetric flask whenever this solution was required.

Method:

Eight duplicate aliquots between O to $25cm^3$ respectively of the diluted standard titanium solution (0.08mg TiO_2/cm^3) were transfered each to $50cm^3$ volumetric flasks. To each, $10cm^3$ of orthophosphoric acid (40% $^{v}/_{v}$) were added and to one of each pair, only $10cm^3$ of hydrogen peroxide solution (6% $^{v}/_{v}$) was added. The solution in each flask was diluted to volume and thoroughly mixed.

The absorbance of the complex formed from peritanic acid was measured against the appropriate control solution in a 10mm cell at 398nm using a Bausch and lamb spectronic 70 spectrophotometer. The colour of the solution was stable for over 24 hours. The calibration curve of TiO_2 was obtained by plotting absorbance against concentration of TiO_2 (Appendix E).

20.0cm^3 aliquots of the stock solution of the perchloric-hydrofloric acid digestion were transfered to each of the two 50cm^3 volumetric flasks, followed by the addition of 10cm^3 orthophosphoric acid (40% $^v/_v$). 10cm^3 of hydrogen peroxide (6% $^v/_v$) was added to only one of the two flasks. Each solution was then diluted to 50cm^3 and thoroughly mixed. The absorbance of the solution in the first flask was measured against that of the second as carried out for the standard. The titania content of the original sample was calculated by reference to the calibration curve. The absorbance measurements were carried out in triplicates.

Calculation:

$$\text{concentration in (ppm)} = \frac{\text{Absorbance}}{\text{Slope} \times 1.25 \times 10^{-5}\text{M}}$$ (molar absorption coefficient)

$$\text{percentage Titania } (TiO_2) = \frac{\text{Concentration x Vol. of dilution}}{10 \times \text{vol of aliquot x sample weight}} \times \frac{100}{1}$$

3.11 Determination of Alumina:

In the absence of interfering substances, aluminium can be accurately determined by many different methods. But in the presence of other ions some of which are present in clays, the exact determination of aluminium is difficult (Akanya, 1980). In this study, aluminium was separated from some other methods by percipitating it together with some other metals in the clays in the form of hydroxides (Iron and Titanium). This percipitate was then filtered out and ignited in a muffle furnace to obtain the metals in the oxide form. After this, the oxides of iron and titanium were substracted out from the total oxide obtained.

Reagents and Solution Pereparation:

i. Tetraoxosulphate (VI) acid

ii. Trioxonitrate (V) acid

iii. Ammonium chloride salt

iv. Ammonical ammonium nitrate (10g/dm^3): 10cm^3 of trioxonitrate (V) acid was diluted to 200cm^3 with distilled water. Ammonia solution (50% $^v/_v$) was added until the solution was just alkaline to bromophenol blue.

After cooling the solution was diluted to $1dm^3$.

v. Concentrated Ammonia solution.

Method:

$100cm^3$ of the stock solution from the sodium carbonate fusion/hydrochloric acid digestison was pipetted into a $500cm^3$ beaker. $10cm^3$ of tetraoxosulphate (VI) acid was added and excess sulphur (IV) oxide boiled off. This action reduced Cr^{4l} which interferes quantitatively with aluminium to cr^{3+}. The solution was cooled slightly, $5cm^3$ of trioxonitrate (V) acid was added and the solution boiled again for 15 minutes to oxidize any Fe^{2+} to Fe^{3+}. On cooling to about 80°C.5g of ammonium chloride was added, this is to reduce to a minimum the co-precipitation of the divalent metals such as calcium and Magnesium followed by ammonia solution with stirring until the solution was just alkaline to bromophenol blue. This action precipitated aluminium, Iron and Titanium as their hydroxides. The excess ammonia was boiled off, the precipitate allowed to settle for about 5 minutes and quantitatively transferred to a whatman filter paper (No. 541) and thoroughly washed with hot ammonical ammonium nitrate ($10g/dm^3$). The precipitate obtained in the filter paper was then ignited in a muffle furnace in a platinium crucible to convert the hydroxides to the oxide from at a temperature of 1200°C. The platinium crucible was then cooled in a dessicator before weighing on an analytical balance. This was carried out in triplicates.

Calculation:

weight of oxide in 1g clay sample = weight obtained on weighing x 2.5

The weight of the oxide obtained was multiplied by 2.5 because the solution fro which the $100cm^3$ was pipetted is a $250cm^3$ solution of the 1g digestion of the clay sample.

percentage weight of alumina = percentage weight of oxide obtained - percentage-weight Fe_2O_3 and TiO_2

Weight of empty platinium crucible = I

Weight of crucible + oxide = II

Weight of oxide after Igniting at 1200°C for 20 minutes.	=	(II - I) = III.

3.12 Determination of Lime (CaO) and Magnesia (MgO) by Atomic Absorption Spectroscopy:

Lime and Magnesia can be determined either titrimetrically or spectrometrically using the atomic absorption spectroscopy. The atomic absorption spectroscopic method of lime and magnesia determination was used in this analysis based on its accuracy and fastness. The determination of the magnesia is often straight forward and the very few interferences (chemical) encountered when using an acetylene air flame for the lime determination were overcome by using "releasing agent". Lanthanum chloride solution (Hesse 1971; Vogel; 1978).

Solution Preparation:

i. Standard calcium solution (1.0 mg/cm^3): 2.4973g of calcium carbonate were dissolved in a little dilute hydrochloric acid which was then transfered into a 1dm^3 volumetic flask and diluted with distilled water.

ii. Diluted standard calcium solution (0.05mg/cm^3) 50cm^3 of the standard calcium solution (1.0mg/cm^3) was diluted to 1000cm^3 in a volumetic flask when required.

iii. Lanthanium chloride (50,000mg/cm^3): 33.5g of lanthanium chloride ($LiCl_3.7H_2O$) was dissolved in 50cm^3 of 1m trioxonitrate (V) acid. This was warmed gently to dissolve the salt, then cooled, after cooling it was made up to 250cm^3 in a volumetric flask.

iv. Standard Magnesium solution (1.00mg/cm^3): 1000g magnesium metal (AR grade) was dissolved in 50cm^3 of 5M Hydrochloric acid. This was then diluted to 1dm^3 in a volumetric flask.

v. Diluted standard magnesium solution (0.01mg/cm^3) 10.0cm^3 of the standard magnesium solution (1.0mg/cm^3) was diluted to 1000cm^3 in a volumetric flask when required.

Method for Lime (CaO)

Aliquot of 0 - 15cm^3 of the diluted standard calcium (0.05mg/cm^3) were transfered to 50cm^3 volumetric flasks.

To each 5.0cm^3 of the lanthanum stock (50,100mg/cm^3) was added. The solution in each flask was diluted to volume and vigorously mixed. The absorbance was measured by aspirating the various standards into the burner, at a wavelength of 423nm for the calcium hallow cathode lamp starting with the lowest co ncentration and aspirating distilled water after taking the reading for each solution on a unicam sp 1900 atomic absorption spectrophotometer. A calibration curve of lime (CaO) was obtained by plotting absorbance against concentration of lime. (Appendix F).

2.5cm^3 aliquot of the stock solution of the perchloric-hydroflouric acid digestion were transfered to 50-0cm^3 volumetric flask and 5.0cm^3 lanthanum stock (50,000mg/cm^3) was added. It was then made up to volume. The absorbene was measured as above and the lime (CaO) content of the solution determined by reference to the calibration curve.

Calculation:

$$\text{Meq/100g clay} = \frac{\text{ppm graph x vol. of extract x dilution factor x 100}}{1000 \times \text{weight of sample used for digestion} \times \text{Equivalent weight of element}}$$

$$\text{Percentage calcium} = \frac{\text{Meq/100g clay}}{100,000} \times \frac{100}{1}$$

Converting to CaO = Percentage calcium x 1.4.

Method for Magnesia (MgO)

Aliquots of 0 - 10.0cm^3 of the dilute standard magnesium (0.01mg/cm^3) were transfered to 50cm^3 volumetric flask.

To each 5.0cm^3 of a lanthanium stock (50,000mg/cm^3) was added. The solution in each flask was diluted to volume and thoroughly mixed. The absorbance was measured by aspirating the various standards into the burner, at a wavelength of 285nm for magnesium hollow cathode lamp, starting with the lowest concentration and aspirating distilled water after taking the reading for each solution, on a Unicam Sp 1900 atomic absorption spectrohotometer. A calibration curve of magnesia (MgO) was obtained by plotting absorbance against concentration for magnesia MgO (Appendix G).

2.5cm^3 aliquot of the stock solution of the perchloric-hydrofloric acid digestion was transfered to 50cm^3 volumetric flask and 50cm^3 of lanthamum stock (50,000 mg/cm^3) was added. The solution was then made up to volume. The absorbance was measured as above and the magnesia (MgO) content of the solution was determined by reference to the calibration curve.

Calculation:

Formula same as that in calcium except that the equivalent weight is different.

$$\text{Percentage Magnesium} = \frac{\text{Meq/100g clay}}{100{,}000} \times \frac{100}{1}$$

Converting to MgO = Percentage calcium x 1.66.

3.13 Measurement of pH of Clay Sample

5g of each of the various clay samples was soaked in distilled water in a 100cm^3 standard volumetric flask for at least 12 hours. After thorough mixing, the pH of a 25cm^3 aliquot of the suspension was determined using a crison micro pH 2000 pH meter as described by Oboh, (1987).

3.14 Determination of Filtrable Acidity

25cm^3 of clay suspension from the one used for the pH determination was taken and titrated against standard 0.1M NaoH using 1% phenolpthalein as indicator. The mg of NaoH consumed per gramme of clay sample was calculated (Oboh, 1987).

3.15 Measurement of Apparent bulk density of clay samples in their Natural Form

Each of ground and sieved clay sample was transfered to weighed 100cm^3 graudated cylinders to the 100cm^3 mark. The clay and cylinder were weighed to obtain the weight of the clays by difference. The cylinders were tapped vigorously on a horizontal surface to constant clay volume. To determine constant clay volume, the volume after every 50 taps was measured and the volume was taken as constant when five successive 50 taps readings showed no further decrease in volume. The apparent bulk density was expressed as g/cm^3 (Rich, 1964).

Calculation:

$$\text{Apparent Bulk Density (g/cm}^3\text{)} = \frac{\text{Weight of Clay (g) x 0.6253}}{\text{Tapped volume of clay (cm}^3\text{)}}$$

3.16 Assessment of the Bleaching Performance of Clay Sample in their Natural State

1.25% (0.625g), 2.5% (1.25g) and 5.0% (2.50g) of oven dried clays in their natural form with particle size 250μm, were mixed with 50cm^3 of filtered crude palm oil in separated 250cm^3 beakers. The beakers and contents were heated on a hot plate with constant stirring at 105 $\pm$ 05°C for 30 minutes. Each bleached oil was filtered under section with a sinta funnel when cooled to a temperature of about 70°C to remove the clay absorbent.

The evaluation of the bleaching performance of each clay was carried out by spectral analysis using a ultraviolet visible spectrophotometer (spectronic 21D milton Ray). The amount of carotene in the oil was evaluated.

A solution of both the unbleached and the bleached palm oil in carbontetrachloride was used. The solution of the unbleached palm oil in carbontetrachloride was used to obtain the wavelength of maximum absorbance (Van Redes, 1966). This wavelength (460nm) was then used to assess the bleaching of the palm oil with the clay samples. Various percentages of clay were used. 0.03g palm oil was dissolved in 5.0cm^3 of carbontetrachloride. Carotene is given in mg/kg β-carotene and the amount of β-carotene in the oil was evaluated from the expression given by BS 1, (1977) as

$$\beta\text{-carotene (mg/kg)} = \frac{\text{Absorbence x Volume of solvent used}}{\text{Weight of sample(g) x 100}} \times 383$$

$$E_{1cm}^{1\%} \text{ at } 460nm = 2610 \text{ in carbontetrachloride}$$

$$\frac{1000,000}{2610} = 383.14$$

$$\text{Percentage bleaching Performance} = \frac{\text{(Carotene in unbleached oil) - (Carotene in bleached oil)}}{\text{Carotene in Unbleached oil}} \times \frac{100}{1}$$

3.17 Methods Used in the Activation of Clay Samples:

Three different variations (methods) were tried in the activation of the clay samples using hydrochloric acid.

3.17a Method 1

50g of each selected clay sample of particle size 250μm was weighed, and mixed with 250cm^3 of 5.5HCl. The mixture was boiled for 2 hours and after slight cooling the slurry was washed free of acid by allowing to remain in distilled water for sufficient length of time and repeatedly. It was ensured that all residual traces of acid were removed by testing with pH paper. Then the activated clay was filtered out and dried at 110°C for 3 hours. After drying, grinding of the sample was done using a mortar and pestle. The powder was sieved back to the 250μm with Endocott standard sieved (Mansfield, 1936).

3.17b Method II

To 100g each of the selected clay samples of the same particle size as in method I, 200cm^3 of 5M HCl was added. The mixture was boiled for 3 hours. The clay was washed free of acid by soaking in distilled water overnight, stir, and tested with pH paper repeatedly to ensure that all residual traces of acid were removed. It was filtered and dried in an oven at 105°C for 2½ hours. It was then sieved back to the former particle size (Joshi *et al*, 1953).

3.17c Method III

Slurry of selected clay samples were made by mixing 50g of clay with 50cm^3 of distilled water.

To each clay slurry, was added 200cm^3 of 1.0M, 3.0M or 5.0M HCl. The mixture was boiled at 105°C for 2½ hours. Each mixture was cooled, washed acid free by soaking in distilled water overnight, stir and tested with pH paper repeatedly. It was then filtered, dried and ground into 250μm particle size (Anozie *et al*, 1993).

3.18 Assessment of the bleaching performance of the Activated Clay Sample:

Refer to section 3.16.

3.19 Determination of Free Fatty Acid (FFa)

Free fatty acid was determined using a modification of the standard Association of Official Analytical Chemist method (1973).

3g of oil was dissolved in 50cm^3 of ethanol and titrated, while swirling, with 0.1M NaoH using 1% phenolphthalein as indicator (Tam, 1977).

Calculation:

$$\text{Percentage Free Fatty Acid} = \frac{V \times N \times M}{100\ W}$$

Where W = Weight (gramme) of sample

V = Volume of O.IM NaoH used

M = Molecular weight of fatty acid, which in most predominant in oil.

N = Molarity of NaoH.

3.20 Alkali Refining of Palmoil, Groundnut Oil and Palmkernel oil Solution Prepartion

(i) 14° Be/ lye (2.375M NaoH) - This was prepared by dissolving 9.50g of NaoH pellets in 100cm^3 of distilled water.

(ii) 16° Be/ lye (2.765M NaoH) - Prepared by dissolving 11.06g of NaoH pellet in 100cm^3 of distilled water.

Method:

To 1kg of each of crude filtered palm kernel oil and groundnut oil calculated amount of 14° Be/lye with sodium hydroxide excess amounting to about 0.20% excess was added to the oil based on the % FFa of the oil initially calculated. This addition was carried out rapidly with the continous stirring of the oil at a temperature of about 50 - 55°C on a water bath. The mixing was for about 15 minutes. At the end of the mixing the stirring rate was reduced and the heat was increased rapidly to bring the temperature to 63°C. Under the influence of heat, the emulsion broke and the soap stock separated from the clear oil in the form of small flocculent particles which tended to coalesce as stirring was continued. The heat was then turned off and thorough setting of the soapstock formed allowed for a period of about 12 hours. Then the oil was drained off and washed with hot water repeatedly in separatory funnel until the oil was free of soap. The washed oil was then dried on a water bath.

The same procedure was repeated for palm oil but using 16° Be' lye with sodium hydroxide excess of about 0.20% (Bailey, 1964).

3.21 Assessment of the bleaching performance of the Activated Clay samples on Alkali refined palm oil, palm kernel and groundnut oil

2.5% (1.25g) of oven dried activated clay with particle size 250Nm, was mixed with 50cm^3 of refined palmoil in a 250cm^3 beaker. The beaker and content was heated on a hot plate with constant stirring at 105 $\pm$ 05°C for 30 minutes. For palm kernel and groundnut oil 2.5% of oven dried activated caly with particle size 250μm were mixed with 50cm^3 each in separate 250cm^3 beaker. The beaker and content were heated on a water bath with constant stirring at 82 $\pm$ 02°C for 30 minutes also.

Each bleached oil was filtered under suction with a sinta funnel when cooled to a temperature of about 60 - 70°C to remove the clay adsorbent.

The evaluation of the bleaching performance of each clay was carried out by spectral analysis using a ultraviolet visible spectrophotometer (spectronic 21D milton Ray). The amount of cerotene in the oil was evaluated.

A solution of the crude filtered, refined and the bleached oils were made in carbontetrachloride. The solution of the unbleached (crude filtered) oil in carbontetrachloride was used in obtain the wavelength of maximum absorbance. This wavelength (460nm) was then used to assess the bleaching of the oils with the clay samples. 0.03g palm oil was dissolved in 5.0cm^3 in carbontetrachloride while 2g of palm kernel and groundnut oil were each dissolved in 5.0cm^3 carbontetrachloride. The amount of 6-carotene in the oil was evaluated from the expression given by BS1, (1977) (refer to 3.16).

Also the bleaching for all the oils was assessed individually uisng the lovibond tintometer. The percent colour reduction was calculated using the equation of Krishnan (1975).

$$\text{Percentage colour} = 100 \times \frac{10(R + Y) - 10(R_1 + Y_1)}{10 (R + Y)}$$

where $10(R + Y)$ = Total colour of initial oil

$10(R_1 + Y_1)$ = Total colour of bleached oil

Fuller's earth was also included in the assessment for comparism.

3.22 Determination of Oil Rctention

50g of the refined oil (palm oil, palm kernel oil and groundnut oil) each was heated with 1.25g of the activated clay and the temperatute was brought to 105 $\pm$ 05°C palmoil and 82 $\pm$ 02°C for palm kernel oil and groundnut oil for 30 minutes with constant stirring.

After allowing the oil to cool to about 60°C the mixture was vaccum filtered through a sinta funnel which was been wetted with the same oil and weighed prior to filtration by suction, then the suction filtration was continued on the cake for an addition of 30 minutes. The funnel and cake weighed were together. The amount of oil retained by the cake was then obtain by differnece in weight.

CHAPTER FOUR

4.0 RESULT AND DISCUSSION

4.1 Sample Preparation

In the preparation of the clays the initial washing and sieving using sieve sizes of 425μm and 150μm separated out the sand particle from the actual clay sample with the sand the first sieving giving coarse sand particle compared to the second sieving which gave very fine sand particles. Drying of the actual clay gave a homogenous phase, but the S_1 clay gave two phase, which were tagged. $S_{1(A)}$ for the top phase and S_1 (B) for the lower phase. The water absorption on the sheets of the clays after drying varied from sample to sample, S_4 clay was the least porous then followed by $S_{1(A)}$, S_9, $S_{3(II)}$, S_7, S_5, S_6, $S_{1(B)}$, $S_{2(I)}$, S_{10}, S_8, $S_{3(I)}$, and S_{11} was the most porous of all the clays. In addition the brittleness follows the same order as the porosity. It was observed that as the colour of clays move from Grey to lighter ones their porosity increases. Appendix H plate (I), (III) and (III).

4.2 Chemical Composition and Some Characteristic Parameters of the Clays Studied

The clays from the different sources in their natural state varied in chemical composition (Table 4.1). From the data on the clays, silica (SiO_2) appears to be the predominant component of each clay. The values obtained ranged from 32.09% for S_6 to 74.49% for S_1(B). It was followed by alumina (Al_2O_3) whose values range from 15.11% for S_1(B) to 37.80% for S_6. The combination of percentage silica and Alumina varied from 66.13% for S_3(II) to 89.60% for S_1(B) with most of the clays having a percentage of 70 above. The presence of Iron oxide (Fe_2O_3) is also fairly high 1.23% to 13.69% and this may be responsible for the reddish/brown colur of some of these clays. (Chia 1980). The titania (TiO_2) content range from 0.20% to 1.55%. The lime (CaO) shows a narrow range in its concentration 3.8 - 7.47 x 10^{-1}%, while the magnesia (MgO) is from 0.51 - 3.32 x 10^{-1}%. The alkali oxides occur in concentrations ranging from 0.027 - 1.32% for Na_2O, 0.19 - 1.81 x 10^{-1}% for K_2O and 0.61 - 5.26 x 10^{-1}% for Li_2O. In the alkali oxides it shows that Na_2O exist in higher concentrations.

The loss on ignition, which is due to loss of water, sulphur (VI) oxide and carbon (IV) oxide, has a range of values from 2.93 to 16.62%. There was a fairly large variation in the apparent bulk density (ABD) 0.54 - 0.87g/cm^3 and moisture content 0.78 - 6.35% while the variation in their pH was between 5.34 to 8.48 and their titratable acidity was within the range of 0.16 - 32 mg NaoH/g. (Table 4.2)

TABLE 4.1: SUMMARY OF CHEMICAL COMPOSTION OF CLAY SAMPLES IN PERCENTAGE

SAMPLE	SiO_2 (%)	Al_2O_3 (%)	SiO_2 + Al_2O_3 (%)	Fe_2O_3 (%)	TiO_2 (%)	10 (% CaO)	10 (% MgO)	10 (% Na_2O)	10 (% K_2O)	10 (% Li_2O)	Loss on Ignition
S_1(A)	53.00 ± 0.26	24.17 ± 0.053	77.17	4.48 ± 0.051	1.02 ± 0.026	4.82	1.94	4.93	0.99	4.04	9.56 ± 0.19
S_1 (B)	74.49 ± 0.24	15.11 ± 0.61	89.60	1.23 ± 0.031	0.57 ± 0.019	5.03	1.86	8.22	1.81	4.20	2.93 ± 0.16
S_2(I)	43.07 ± 0.11	31.86 ± 0.06	74.93	5.34 ± 5.050	1.22 ± 0.031	4.54	1.73	12.10	1.21	5.26	12.51 ± 0.18
S_2(II)	49.17 ± 0.09	29.43 ± 0.10	78.60	3.93 ± 0.031	0.52 ± 0.040	4.12	0.82	1.21	0.52	3.06	12.92 ± 0.22
S_3(I)	45.29 ± 0.47	33.44 ± 0.12	78.73	3.69 ± 0.031	0.27 ± 0.014	3.91	0.62	0.82	0.20	0.61	14.14 ± 0.47
S_3(II)	39.69 ± 0.31	26.44 ± 0.07	66.13	13.69 ± 0.023	0.78 ± 0.025	4.38	1.20	4.23	0.45	3.67	16.08 ± 0.54
S_4	36.81 ± 0.19	29.88 ± 0.024	66.70	7.25 ± 0.061	0.90 ± 0.033	4.96	2.60	13.20	1.06	5.26	14.56 ± 0.29
S_5	56.84 ± 0.22	25.24 ± 0.10	82.08	2.92 ± 0.040	1.00 ± 0.032	4.82	2.22	7.98	1.39	5.04	10.21 ± 0.38
S_6	32.09 ± 0.28	37.80 ± 0.01	69.89	9.04 ± 0.080	1.03 ± 0.032	4.05	0.78	0.92	0.25	0.86	14.71 ± 0.22
S_7	49.18 ± 0.22	26.19 ± 0.073	75.37	8.13 ± 0.030	0.63 ± 0.025	3.82	0.64	0.59	0.19	0.61	12.50 ± 0.28
S_8	42.46 ± 0.18	36.73 ± 0.11	79.19	1.46 ± 0.023	0.20 ± 0.019	5.17	0.68	11.40	1.44	5.26	12.38 ± 0.37
S_9	65.42 ± 0.46	18.29 ± 0.11	83.71	1.98 ± 0.026	0.31 ± 0.022	4.17	0.54	0.31	0.55	2.57	6.56 ± 0.47
S_{10}	34.76 ± 0.30	32.87 ± 0.18	67.63	11.00 ± 0.024	0.63 ± 0.032	3.96	0.51	0.27	0.50	2.81	16.62 ± 0.19
S_{11}	44.40 ± 0.26	28.24 ± 0.22	72.64	10.42 ± 0.040	1.55 ± 0.045	4.42	1.29	6.22	0.73	3.06	11.44 ± 0.33
F	70.33 ± 0.46	13.41 ± 0.25	83.74	5.34 ± 0.120	0.81 ± 0.063	7.47	3.32	1.66	0.55	2.02	6.96 ± 0.34

Table 4.2 Some Characteristic parameters of clays studied in their natural form

SAMPLE	pH	TITRATABLE ACIDITY (mgNaoH/g)	APPARENT BULK DENSITY (g/cm^3)	MOISTURE CONTENT (%)
S_1 (A)	8.48	0.160	0.83	5.06
S_1 (B)	8.28	0.160	0.87	1.21
S_2 (I)	7.27	0.123	0.64	2.64
S_2 (II)	6.00	0.320	0.62	1.68
S_3 (I)	6.38	0.256	0.62	0.85
S_3 (II)	5.95	0.192	0.72	2.81
S_4	7.11	0.224	0.78	6.35
S_5	5.34	0.192	0.79	2.06
S_6	6.78	0.272	0.60	2.35
S_7	6.88	0.224	0.71	1.76
S_8	7.01	0.128	0.68	0.78
S_9	7.87	0.160	0.86	2.73
S_{10}	7.48	0.160	0.70	1.52
S_{11}	7.84	0.192	0.54	1.10
F	6.91	0.256	0.65	11.68

Table 4.3: Bleaching of Natural clay samples at different percentage clay

SAMPLE	1.25%	2.5%	5.0%
S_1 (A)	38.00	61.11	97.22
S_1 (B)	54.00	69.76	92.22
S_2 (I)	55.52	84.72	51.25
S_2 (II)	61.76	89.11	83.54
S_3 (I)	45.81	79.41	74.64
S_3 (II)	59.73	78.64	94.12
S_4	36.95	70.86	94.42
S_5	69.19	93.54	85.57
S_6	52.86	89.26	80.08
S_7	59.14	78.97	86.04
S_8	60.14	92.11	91.60
S_9	54.86	85.98	79.06
S_{10}	66.09	91.74	69.37
S_{11}	59.05	79.51	78.65

4.3 Bleaching Performance of Unactivated Clay Samples:

The result of the bleaching performance of the clays in their natural (unactivated) forms are shown in Table 4.3 for 1.25%, 2.5% and 5.0% clay respectively on palmoil at a tempertaure of 105 $\pm$ 05°C and 30 minutes. It was observed that the bleaching percentage varies from 36.93% for S_4 clay to 69.19% for S_5 at 1.25% clay; between 61.11% for $S_{1(A)}$ to 93.54% for S_5 at 2.5% clay; and between the range of 51.25% for S_2(i) to 97.40% for $S_{1(A)}$ at 5.0% clay. It shows that some Nigerian clays in thier natural forms have a better bleaching ability than the commercial fuller's earth. It appears clays with apparent bulk density greater than 0.8g/cm^3 do not display very good bleaching characteristics, when not activated (Fig. 4.1). Generally, it appears that ability to bleach by the unactivated clays increases with apparent bulk density reaching peak values around 0.70g/cm^3.

Using 1.25% clay to oil, it was observed that four of the clays have good bleaching performance in their natural form using a performance index of 60% colour removal as good performance. S_5 69.19%, S_{10} 66.09%, $S_{2(II)}$ 61.76% and S_8 60.68%. With fuller's earth also having a bleaching performance of 61.08%. Seven samples ($S_{1(B)}$, $S_{2\ (I)}$, $S_{3(II)}$, S_6, S_7, S_9 and S_{11} have a bleaching performance above 50% and 60% while $S_{1(A)}$, S_4, and $S_{3(I)}$ had bleaching performance below 50% in their natural state.

The bleaching ability of the natural S_5, S_8, $S_{2(II)}$ and S_{10} clays at 2.5% clay was again tried on separated portions of the top and bottom layers of palm oil. It was observed that the bleaching performance ranged between 65.11% for S_8 clay to 79.37% for S_5 clay for the top layer oil. 54.53% for S_8 clay again to 58.39% for S_{10} clay for bottom layer. This was also compared with F clay which gave 66.46% for the top layer and 55.21% for bottom layer (table 4.4). The colour removal was more on the top layer as compared to the bottom layer with regards to their carotene contents, implying that the clays exert a higher adsorptive force on the top layer (Morgan *et al*, 1985).

The colour reduction of S_5, S_{10}, S_{20}, and S_8 clay in their natural (unactivated) state were also tried at a temperature of 82 $\pm$ 02°C for 30 minutes with 2.5% clay. These were compared with that of F clay (Table 4.10). Results showed that at lower temperatures F clay has a better bleaching ability than the other clays in comparism with that at 105 $\pm$ 05°C (Table 4.10) in which S_5, S_{10}, and S_{20} clays gave better results than the F clay. This might be due to the fact that at lower temperature F clay exert a higher adsorptive power on the colour pigment in the oil which then decrease with temperature increase while for the Nigerian clays their adsorptive power increase with temperature increase.

Table 4.4 **Bleaching Performance (in percentage) of natural S_5, S_8, S_{10}, S_{20} and F on top and bottom layers of palm oil.**

SAMPLE	% TOP LAYER BLEACHING	% BOTTOM LAYER BLEACHING
S_5	79.37	57.07
S_8	65.11	54.53
S_{10}	69.60	58.39
S_{20}	67.89	56.91
F	66.46	55.21

Bleaching Temperature = 105 ± 05°C

Bleaching Time = 30 minutes

Percentage Clay = 2.5%

Carotene in top layer before bleaching = 711.74mg/kg

Carotene in bottom layer before bleaching = 563.01mg/kg

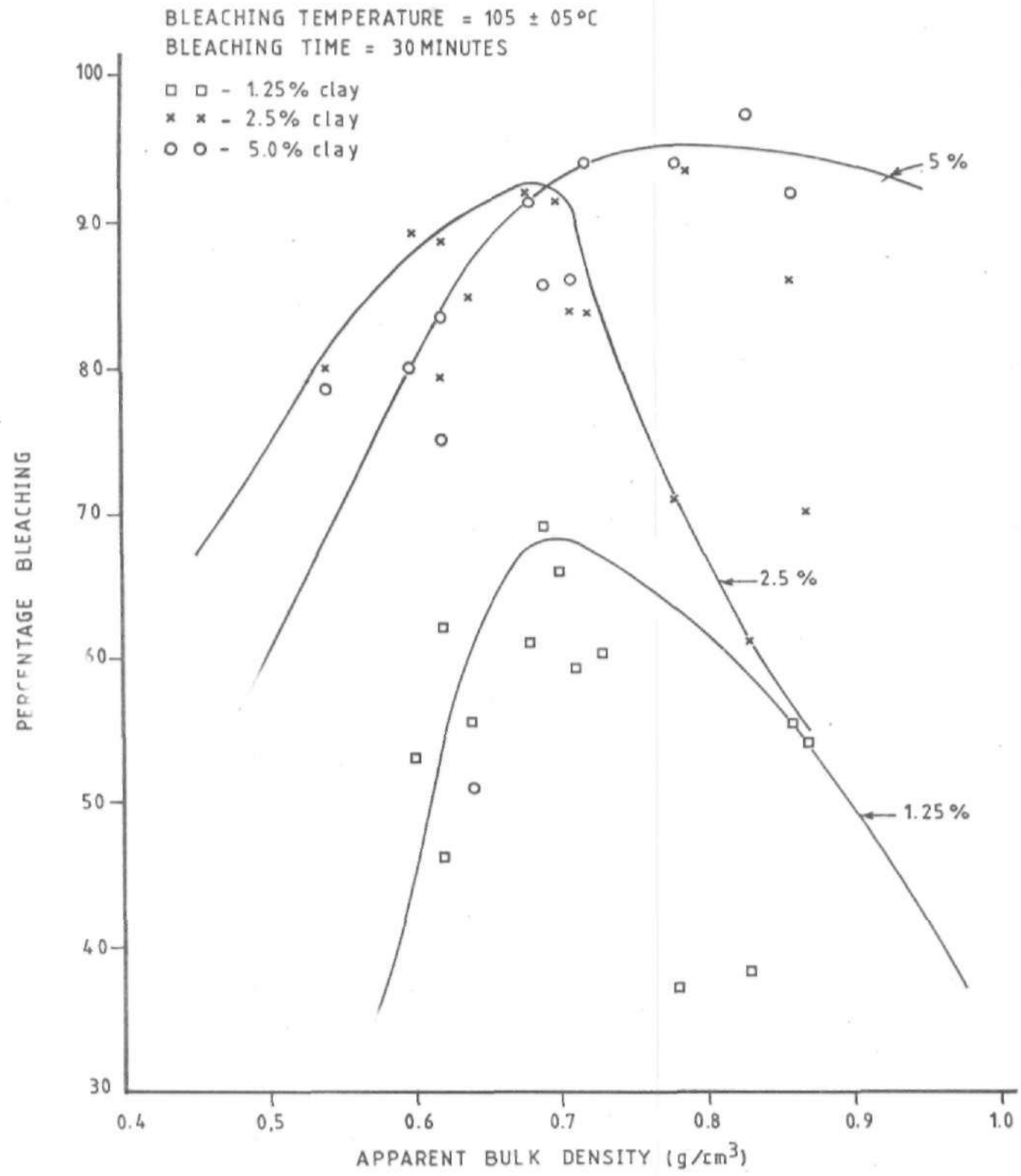


Fig. 4.1. Graph of percentage bleaching against apparent bulk densities of all natural clay samples at varied percentage clay.

Table 4.5 Bleaching Performance (in percentage) of Sample S_8 Clay Activated by Various Methods on top and bottom layers of palm oil:

Method of Activation	% Top Layer Bleching	Improvement in Bleaching due to Activation	% Bottom Layer Bleaching	Improvement in Bleaching due to activation
Method I	78.39	78.39 - 65.11 = 13.28	72.97	72.97 - 54.53 = 18.39
Method II	87.41	87.41 - 65.11 = 22.30	80.51	80.51 - 54.53 = 25.98
Method III, (a)	80.23	80.23 - 65.11 = 15.12	72.62	72.62 - 54.53 = 18.09
Method III, (b)	84.94	84.94 - 65.11 = 19.83	76.79	76.79 - 54.53 = 22.17
Method III, (c)	89.42	89.42 - 65.11 = 24.31	81.55	81.55 - 54.53 = 27.02

Bleaching Temperature = 105 $\pm$ 05°C

Bleaching Time = 30 minutes

Percentage Clay = 2.5%

Carotene in top layer before bleaching = 555.35mg/kg

Carotene in bottom layer before bleaching = 428.96mg/kg

4.4 Activation of Clay Samples and Their Bleaching Performance:

Activation of selected clay samples (with performance index of 60% and above) was done using hydrochloric acid activation. Three different methods were basically used which depend on the acid concentration, volume of acid and time of drying after washing acid free (section to 3.17). Activation of the clay sample carried out caused a change in colour of the clay sample to lighter ones (Appendix I plate IV). This implies that acid treatment and the resultant refluxing for sometimes at boiling point has a remarking effect on the colour and texture of the clay. It was also observed that the clays were less compact, more "fluffy" and contain more air void spaces. In addition, activation of the clay samples leads to a decrease in their apparent bulk density and pH while their titratable acidity and moisture content increased (Table 4.9).

Generally, there was a better bleaching performance for the clays when tried on separate portion of top and bottom layer of palm oil at 2.5% clay, for 30 minutes at 105 $\pm$ 05°C. The method I activation gave a colour removal of between 78.37 to 84.21% for the top layer and 72.92 to 75.49% for the bottom layer. Method II gave a colour reduction of 86.73 to 88.55% for the top layer and 78.64 to 81.17% for the bottom layer. While in the case of method III, Method IIIa, (1MHCl) produced a colour reduction of 71.95 to 80.25% for the top layer and 66.79% to 80.25% for the botom layer. Method IIIb (3MHCl) produced a colour reduction of 78.86 to 84.94% for the top layer and 71.26 to 79.79% for the bottom layer. Method IIIc (5MHCl) produced a colour reduction of 83.86 to 89.42% for the top layer and 75.49% to 81.42% for the bottom layer (Tables 4.5, 4.6, 4.7 and 4.8).

There was an improvement in the bleaching ability of the clays after their activation with the clays exerting a higher adsorptive power on the bottom layer of the palm oil than the top layer with an improvemnet in percentage colour reduction in the range 8.4 - 27.02% while for the top layer between 1.64 - 24.31% for all the three methods used (Table 4.5, 4.6, 4.7 and 4.8). The strong bleaching power of activated clay relative to their natural clays is attributable to the replacement of the exchangeable Al^{3+} and other metallic ions by H^{+} in the interlamellar space. In addition, mineral salt constituent are leached from the lattice structure thus rendering the clay more porous and electrochemically more active (Nutting, 1935; Rich 1964; Siddiqui, 1968a).

Table 4.6 Bleaching Performance (in percentage) of Sample S_{2D} Clay Activated by Various Methods on top and bottom layers of palm oil:

Method of Activation	% Top Layer Bleaching	Improvement in Bleaching due to Activation	% Bottom Layer Bleaching	Improvement in Bleaching due to activation
Method I	84.21	84.21 - 67.89 = 16.32	74.19	74.19 - 56.91 = 17.28
Method II	86.73	86.73 - 67.89 = 18.84	77.58	77.58 - 56.91 = 20.67
Method III, (a)	78.03	78.03 - 67.89 = 10.14	70.81	70.81 - 56.91 = 14.90
Method III, (b)	80.00	80.00 - 67.89 = 12.11	75.16	75.16 - 56.91 = 18.25
Method III, (c)	83.86	83.86 - 67.89 = 15.97	76.13	76.13 - 56.91 = 19.22

Bleaching Temperature = 105 $\pm$ 05°C

Bleaching Time = 30 minutes

Percentage Clay = 2.5%

Carotene in top layer before bleaching = 557.91mg/kg

Carotene in bottom layer before bleaching = 395.77mg/kg

Table 4.7 Bleaching Performance (in percentage) of Sample S_5 Clay Activated by Various Methods on top and bottom layers of palm oil:

Method of Activation	% Top Layer Bleaching	Improvement in Bleaching due to Activation	% Bottom Layer Bleaching	Improvement in Bleaching due to activation
Method I	82.90	82.90 - 79.37 = 3.53	75.49	75.49 - 57.07 = 18.42
Method II	88.55	88.55 - 79.37 = 9.18	81.17	81.17 - 57.07 = 24.10
Method III, (a)	75.34	75.34 - 79.37 = -4.03	69.02	69.02 - 57.07 = 11.95
Method III, (b)	81.01	81.01 - 79.37 = 1.64	73.71	73.71 - 57.07 = 16.64
Method III, (c)	85.03	85.03 - 79.37 = 5.66	78.55	78.55 - 57.07 = 21.48

Bleaching Temperature = 105 $\pm$ 05°C

Bleaching Time = 30 minutes

Percentage Clay = 2.5%

Carotene in top layer before bleaching = 507.47mg/kg

Carotene in bottom layer before bleaching = 359.39mg/kg

Table 4.8 Bleaching Performance (in percentage) of Sample S_{10} Clay Activated by Various Methods on top and bottom layers of palm oil:

Method of Activation	% Top Layer Bleching	Improvement in Bleaching due to Activation	% Bottom Layer Bleaching	Improvement in Bleaching due to activation
Method I	82.39	82.39 - 69.60 = 12.79	74.78	74.78 - 58.39 = 16.39
Method II	87.04	87.04 - 69.60 = 17.44	78.67	78.67 - 58.39 = 20.28
Method III, (a)	71.95	71.95 - 69.60 = 2.35	66.79	66.79 - 58.39 = 8.40
Method III, (b)	78.86	78.86 - 69.60 = 9.26	71.26	71.26 - 58.39 = 12.87
Method III, (c)	84.15	84.15 - 69.60 = 14.55	75.49	75.49 - 58.39 = 17.10

Bleaching Temperature = 105 $\pm$ 05°C

Bleaching Time = 30 minutes

Percentage Clay = 2.5%

Carotene in top layer before bleaching = 507.47mg/kg

Carotene in bottom layer before bleaching = 359.39mg/kg

Table 4.9 **Some Characteristic Parameters of Clays studied in their activated form.**

Sample	pH	Titratable Acidity mg NaoH/g	Apparent Bulk Density (g/cm^3)	% Relative Change in ABD	Moisture Content (%)
S_{10}	3.14	1.06	0.60 $\Delta = 0.10$	14.29	3.94
S_8	3.94	0.29	0.60 $\Delta = 0.08$	11.76	1.79
S_4	3.67	0.45	0.67 $\Delta = 0.11$	14.10	8.69
S_5	3.60	0.51	0.68 $\Delta = 0.11$	13.92	3.23
S_7	3.21	0.96	0.55 $\Delta = 0.07$	11.29	3.30

Δ = Change in Apparent bulk density (ABD) due to activation of clay.

The activation exerted a more pronounced effect on the S_8 clay with respect to the percentage colour reduction on the top and bottom layer which had the least perfromance among the chosen clays followed by S_{20}, then S_{10} clay. With the activation having the least improvement on the bleaching effect of S_5 clay which had the best colour reduction in the unactivated state, but on a general consideration the total colour reduction was higher for the S_5 clay.

The variation in the bleaching of the various acitivation could be related to the fact that the bleaching power of clays treated with hydrochloric acid increases with concentration of acid to a maximum and declines thereafter. Also in terms of acid to clay ratio one part of clay to two parts of acid which occured in the case of mehtod II activation gave the best bleaching efficiency for all the activated clay samples as compared to mehtod I and III activation which have a clay to acid ratio of one to five and one to four respectively. This shows that the bleaching performance of the activated clay is sensitive to the amount of acid used to activate it and the use of excess acid results in over activation which leads to a decrease in bleaching performance (Oboh, *et al*; 1988; Anozie *et al*; 1993).

In addition, the bleaching performance of the S_5, S_{10}, S_{20}, and S_8, clay in their activated forms with the three methods of activation were carried out at 82 $\pm$ 02°C, 2.5% clay to palm oil and at varied time of 15 to 60 minutes of bleaching. It was noticed that with an increase in temperature there was an increase in bleaching performance for all the clays with the percentage colour reduction lower than that at 105 $\pm$ 05°C but increase with time. The method II activation gave the general overall best colour removal (figure 4.2, 4.3, 4.4 and 4.5). This could be attributed to the fact that as the time of contact between the oil and the clay increases at a particular temperature the bleaching performance of the clay increases (Rich, 1964).

Also when the effect of time of bleaching on the bleaching performance of the activated clay was tried with S_8 clay at varied time within the range 15 - 90 minutes of bleaching at 2.5% and 105 $\pm$ 05°C. It was observed that as the time of bleaching increased initially there was a remarkable increase in the bleaching which later decrease (Fig. 4.9). This could probably be attributable to new colour formation which the clay

was unable to absorb (Rich, 1964) and also at a particular temperature the bleaching performance of that clay increases with time until the optimum time is reached that which their is no appriciable increase in the colour reduction (Richardson, 1978).

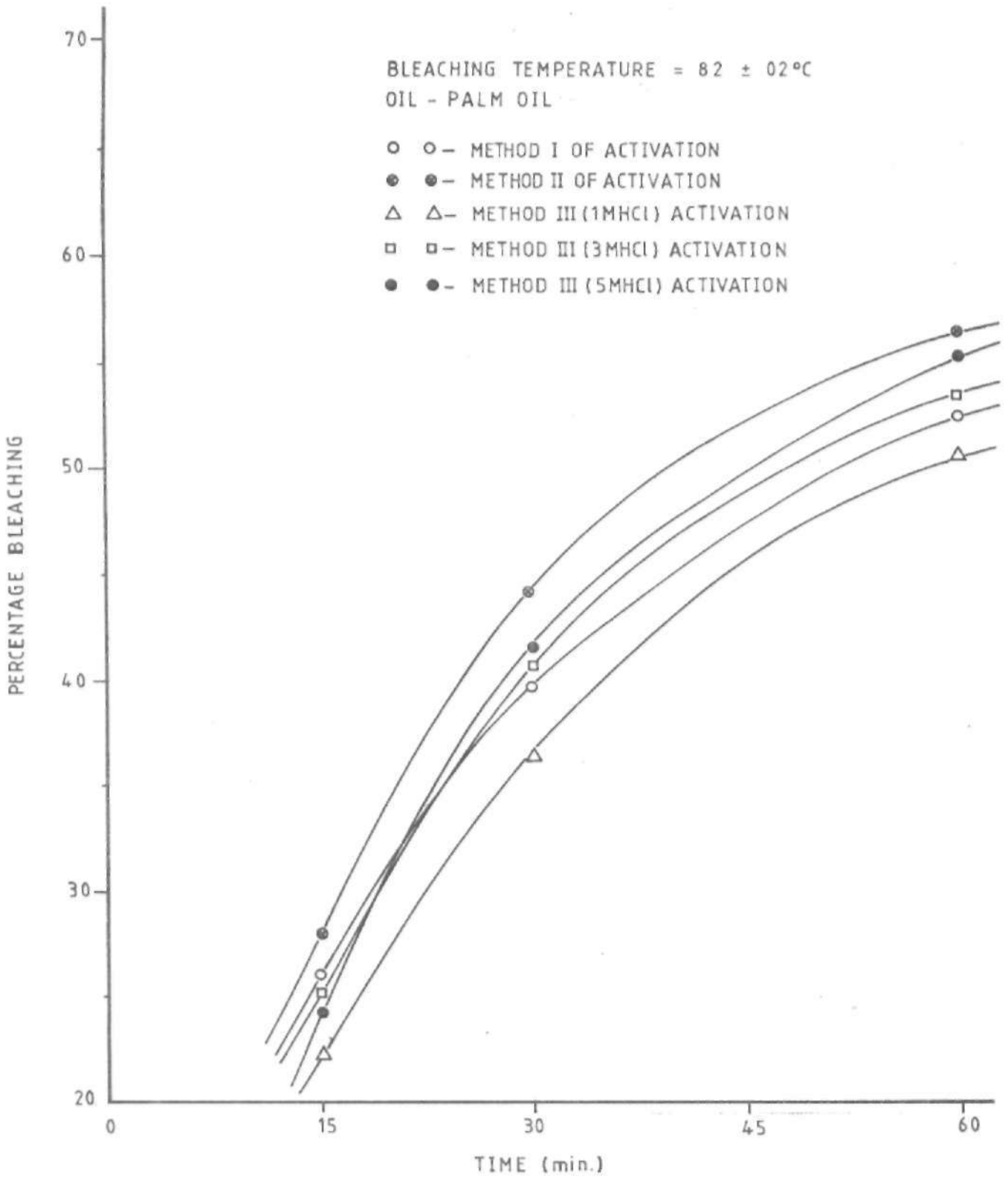


Fig. 4.2. Graph of percentage bleaching against time of bleaching for the different methods of activation of S_8 clay.

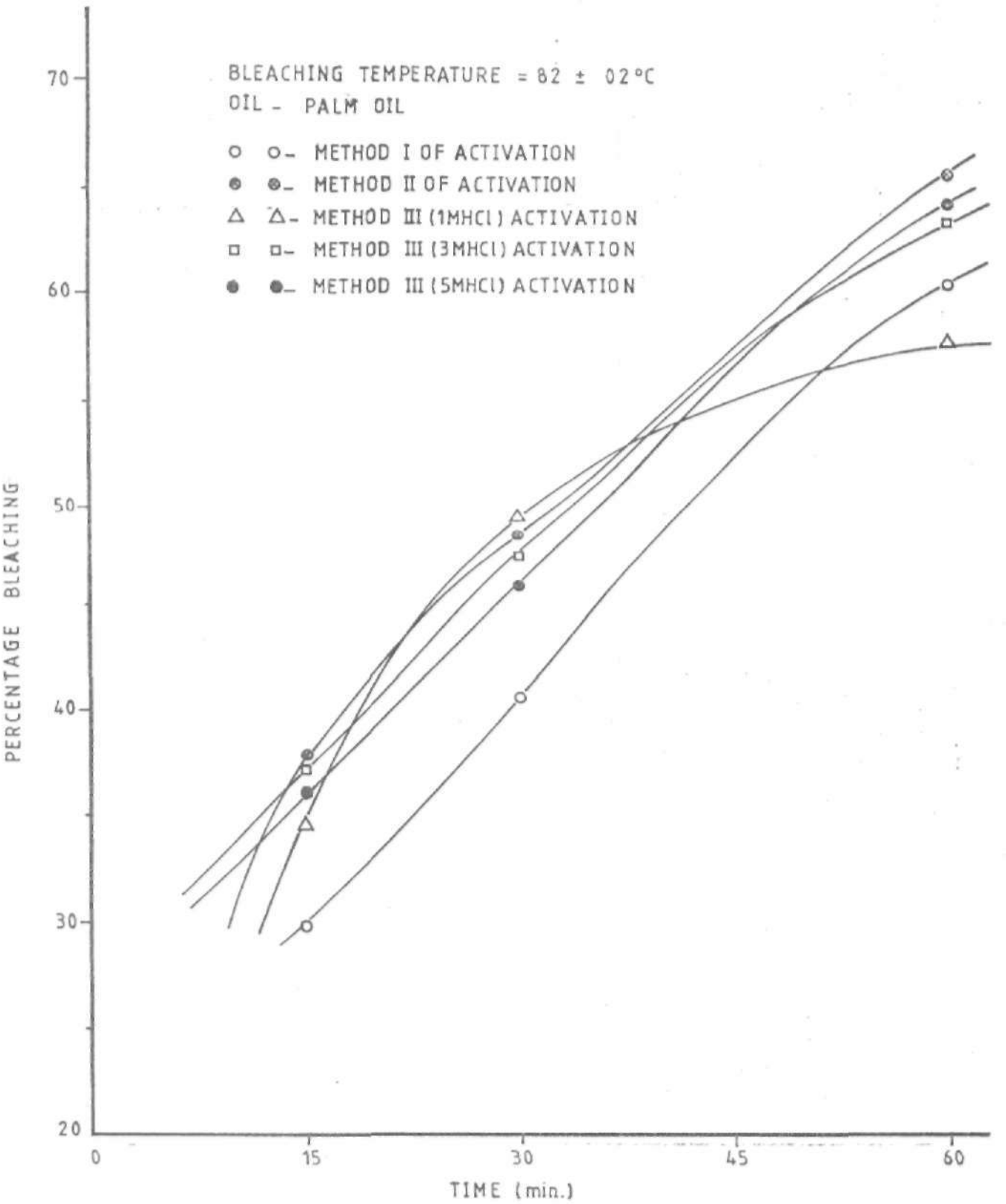


Fig. 4.3. Graph of percentage bleaching against time of bleaching for the different methods of activation of S_5 clay.

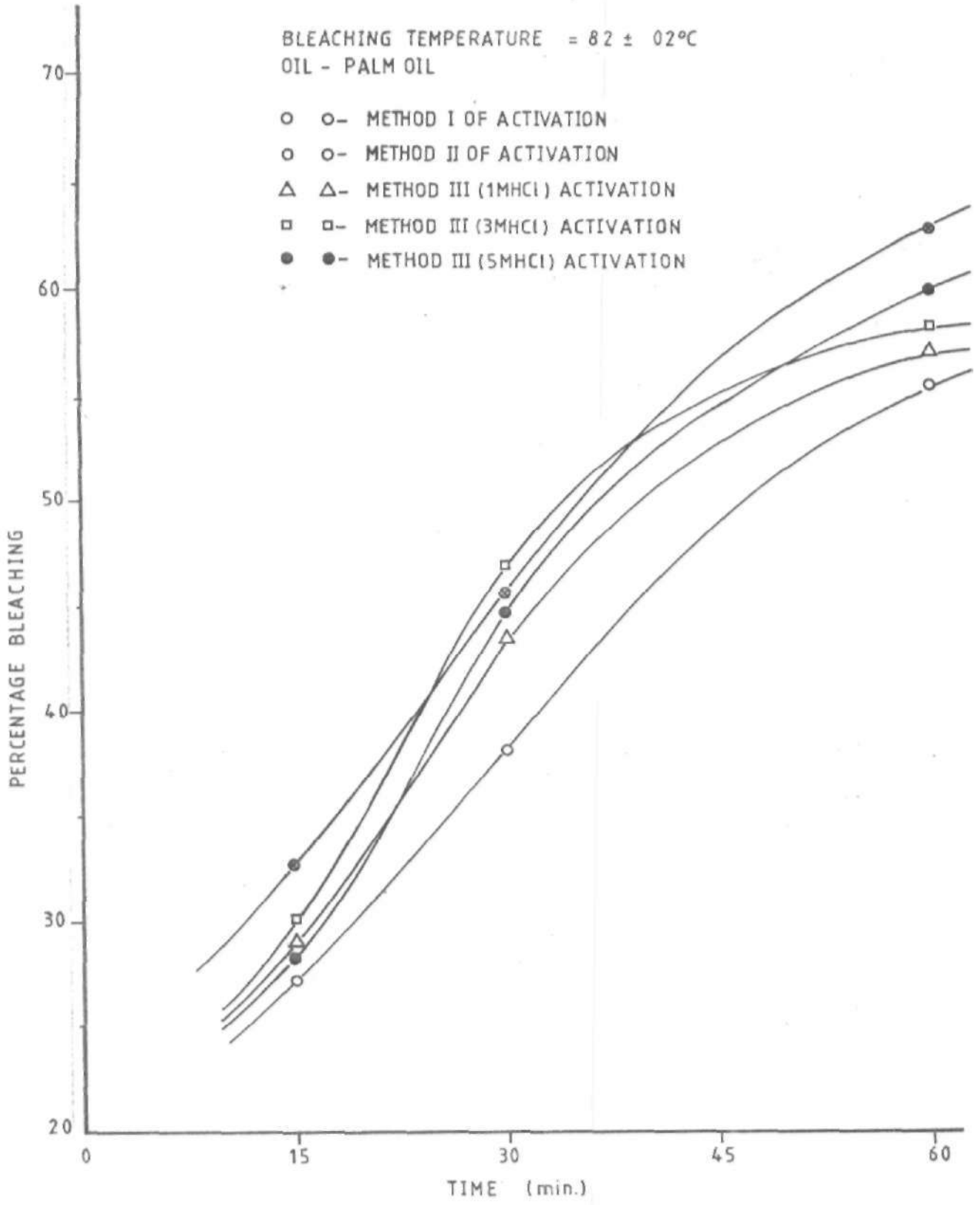


Fig. 4.4. Graph of percentage bleaching against time of bleaching for the different methods of activation of S_2 (II) clay .

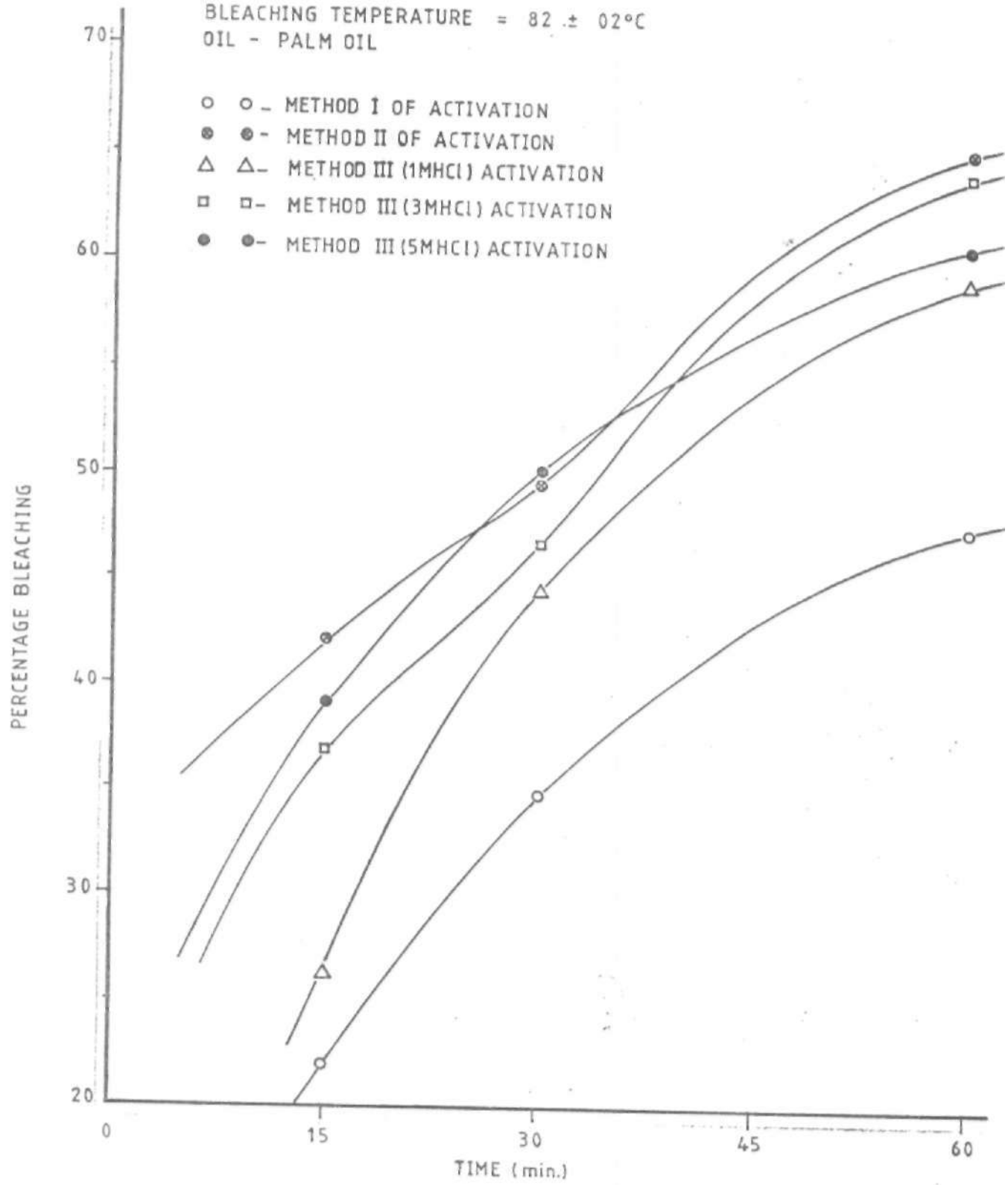


Fig. 4.5. Graph of percentage bleaching against time of bleaching for the different methods of activation of S_{10} clay.

4.4.2 Effect of Activation Time, Volume of Acid and Time of Drying of Activated Clay on Methed II:

The effect of time of activation of clay on addition of the 5MHCl in method II was demonstrated with S_8 clay by varying the length (2, 3, 4 and 5 hours) of activation. The activated samples were washed acid free and dried in the oven. These clays bleaching ability were then tried on palmoil at a temperature of 105 $\pm$ 05°C, 2.5% clay and 30 minutes. It was observed that the bleaching performance increased from 2 - 3 hours of activation, then decrease at 4 hours of activation to 5 hours (Fig. 4.6). This was correlated with the bleaching ability of the unactivated clay, which showed that the activation of the clay increased the rate of the colour removal. The result could be related to the fact that at higher activation above 3 hours there was excessive leaching of basic clay constituents with consequent loss in selectivity (Siddiqui, 1968 a, b).

When the volume of the 5MHCl used in the activation of sample was also varied between 150 to 300cm^3 on different sets of S_5, S_8 and S_4 clays. It was observed that the 150cm^3 of the 5MHCl, produced a colour reduction within the range of 61.25 to 81.71%, the 200cm^3 produced colour reduction within the range of 83.11% to 87.76% while the 300cm^3 of acid produced a colour reduction within the range of 54.20 to 78.40% (Fig. 4.7). This implies that for each clay bleaching activity depends on the volume of acid used for activation. It first increased to a maximum, for each clay at 200cm^3 of 5MHCl. S_5 and S_4 clays have a similar behaviour over the entire range of HCl volumes, with S_5 clay showing superiority throughout. S_5 clay is superior to S_8 throughout the 5MHCl volumes used. S_4 clay is inferior to S_8 clay only when the latter is activated with 6MHCl of between 175cm^3 and 237.5cm^3. At 200cm^3 of 5MHCl S_5 is greater than S_8 and S_8 grater than S_4 clay in their colour reduction.

Using S_8 clay the time of drying after activating was varied. It was observed that when 2½ hours of drying the activated clay at 105°C was used the bleaching performance was 86.84% at 2.5% clay to oil and 30 minutes. While when, 4 hours of drying the same clay after activating and using to bleach under the same condition gave a colour reduction of 92.16%. This shows that the longer time of drying the clay after activation has increased the bleaching activity of the clay. This could be related to the moisture content of both activated clays with the clay dried for 4 hours having a lower

moisture content thus enabling the clay to obtain a optimum adsorptive capacity than that which was dried for 3 hours (Rich, 1964).

4.4.3 Effect of Acitivation on Clay with Low Performance Index in the Natural State:

The best method of activation (method II) was used in activating clay S_4 which exhibited poor bleaching ability on palmoil at 1.25% clay in its natural form. It was observed that at 2.5% clay and bleaching time of 30 minutes at 105 $\pm$ 05°C, S_4 clay exhibited a better bleaching ability of about 83.11% colour reduction compared to that of 70.86% at the same percentage clay. This could be related to the fact that treatment with acid causes the Al^{3+} ion in the lattice structure to be replaced by H^+ ion and also the higher surface area which the clay S_4 now has compared to its natural form, has made it to possess a greater adsorptive capacity (Rich, 1964).

4.4.4 Effect of Successive Addition of Clay on the Colour Reduction:

Activated S_4 clay by mehtod II activation, was used in the bleaching using successively 1.25% of the clay on palmoil two times for a time duration of 30 minutes and a temperature of 105 $\pm$ 05°C. It was observed that the successive bleaching of the oil with the clay produced a better colour reduction than when 2.5% clay was just used directly on the palmoil. The first 1.25% clay produced a colour reduction of 49.20% and the second 1.25% clay produced a colour reduction of 88.70% as compared to 83.11% for using 2.5% clay at once. The first 1.25% clay could be referred to as a preliminary bleaching process and the second 1.25% clay is refered to as the main bleaching (Goebel, 1976).

4.5 Effect of Alumina, Silica, Sodium oxide and Loss on Ignition on the Bleaching Power

A plot of bleaching activated S_5, S_8, and S_4 clay samples against the sum of percentage alumina, silica and sodium oxide in the clays before activation and also percentage bleaching against sum alumina and silica was plotted on the same graph (Fig. 4.8). This showed that there is a linear and direct relationship between the

percentage sum Alumina, silica and sodium oxide, but it was observed that as the percentage sodium oxide increase in the clays their percentage colour reduction decreases showing an inverse relationship. A similar relationship is also shown with the increase on loss on ignition. (Table 4.11). While an increase in the silica content showed an increase in their bleaching power thus S_5 greater than S_8 and S_8 greater than S_4 clay. (Table 4.11) implying that there is a direct relationship between the percentage bleaching and silica content. In general bleaching acticity appears to be in decreasing order of percentage sodium oxide (Na_2O) and loss on ignition and increasing order of silica (SiO_2).

Table 4.10 Bleaching action of sample S_{20}, S_5, S_8, and S_{10}, in their natural form as compared to Fuller's earth on th top layer of palm oil

SAMPLE	% Bleaching at 82°c	% Bleaching at 105°c
F	39.20	66.46
S_5	35.59	79.37
S_{10}	30.04	69.60
S_8	25.21	65.11
S_{20}	27.14	67.89

Bleachi Time = 30 minutes

Percentage Clay = 2.5%

Carotene in top layer before bleaching = 529.19mg/kg.

Table 4.11 Silica, Sodium Oxide, Loss on Ignition (in percentage) and percentage bleaching of activated clay samples

Sample	SiO_2 %	Na_2O %	Loss on Ignition %	% Bleaching
S_5	56.84	0.798	10.21	81.16
S_8	42.46	1.140	12.38	78.75
S_4	36.81	1.320	14.56	72.10

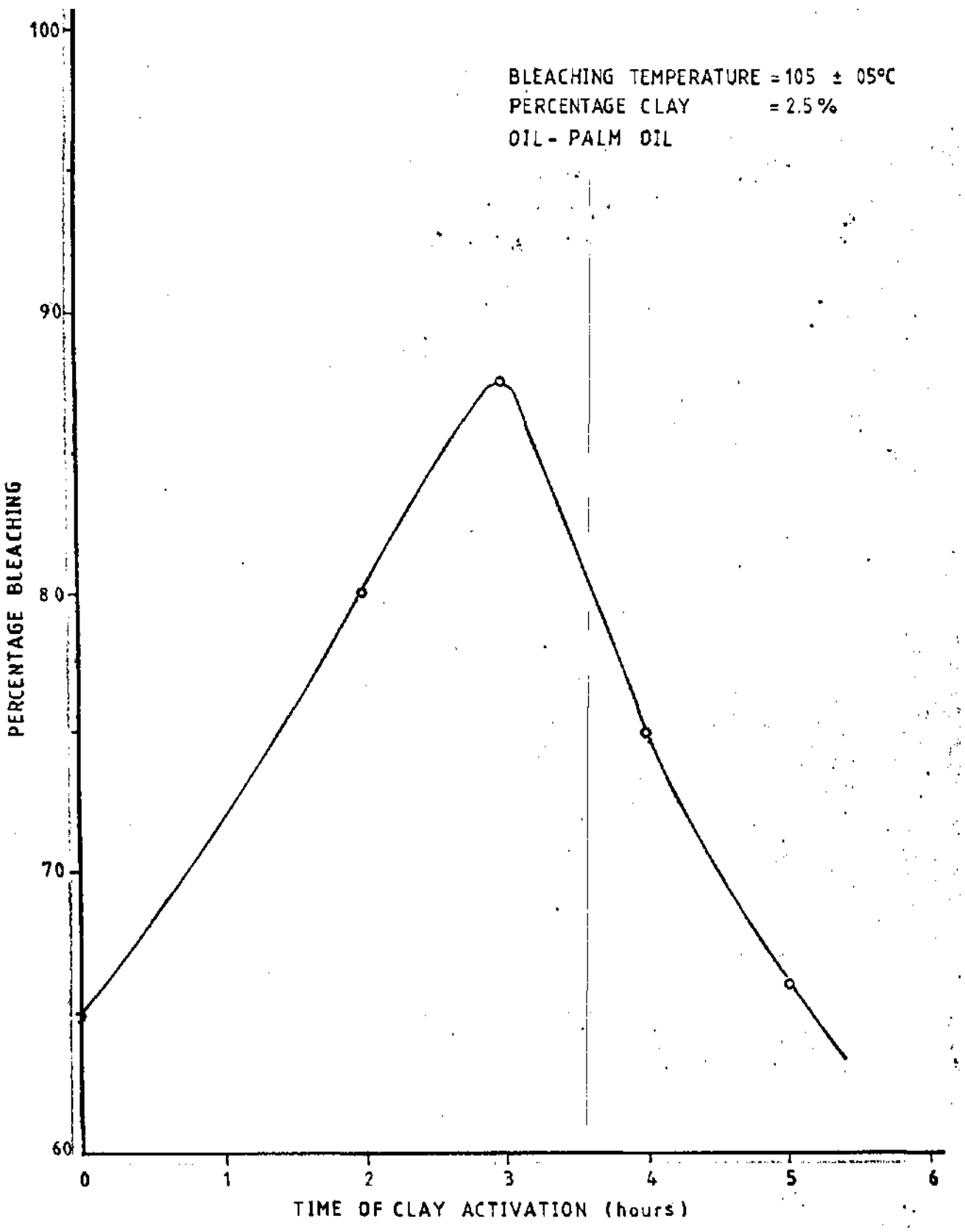


Fig. 4.6. Graph of percentage bleaching against clay activation time of S_8 clay by activation method II.

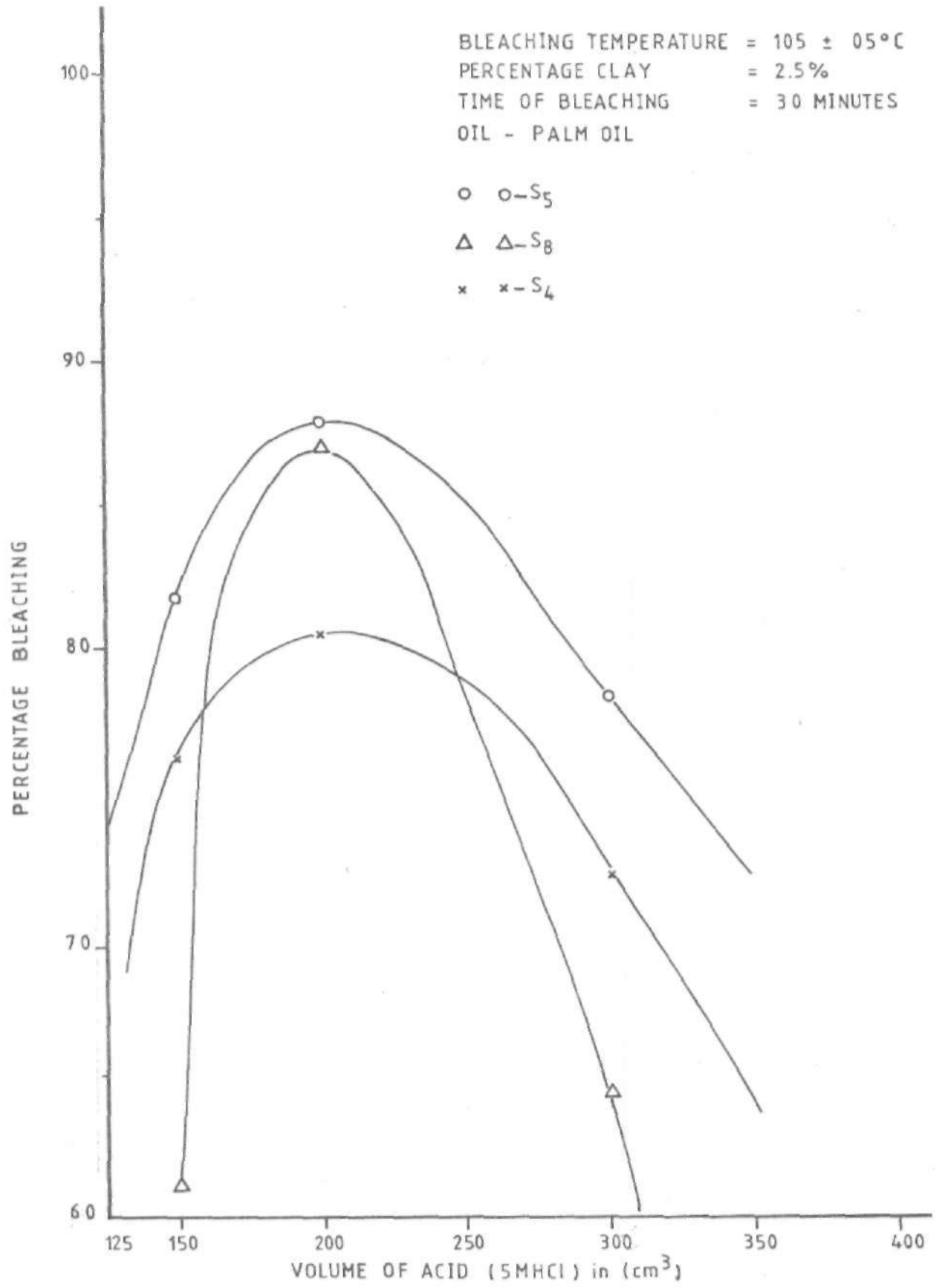


Fig. 4.7. Graph of percentage bleaching against volume of acid used in the activation of clay samples S_4, S_5, and S_8.

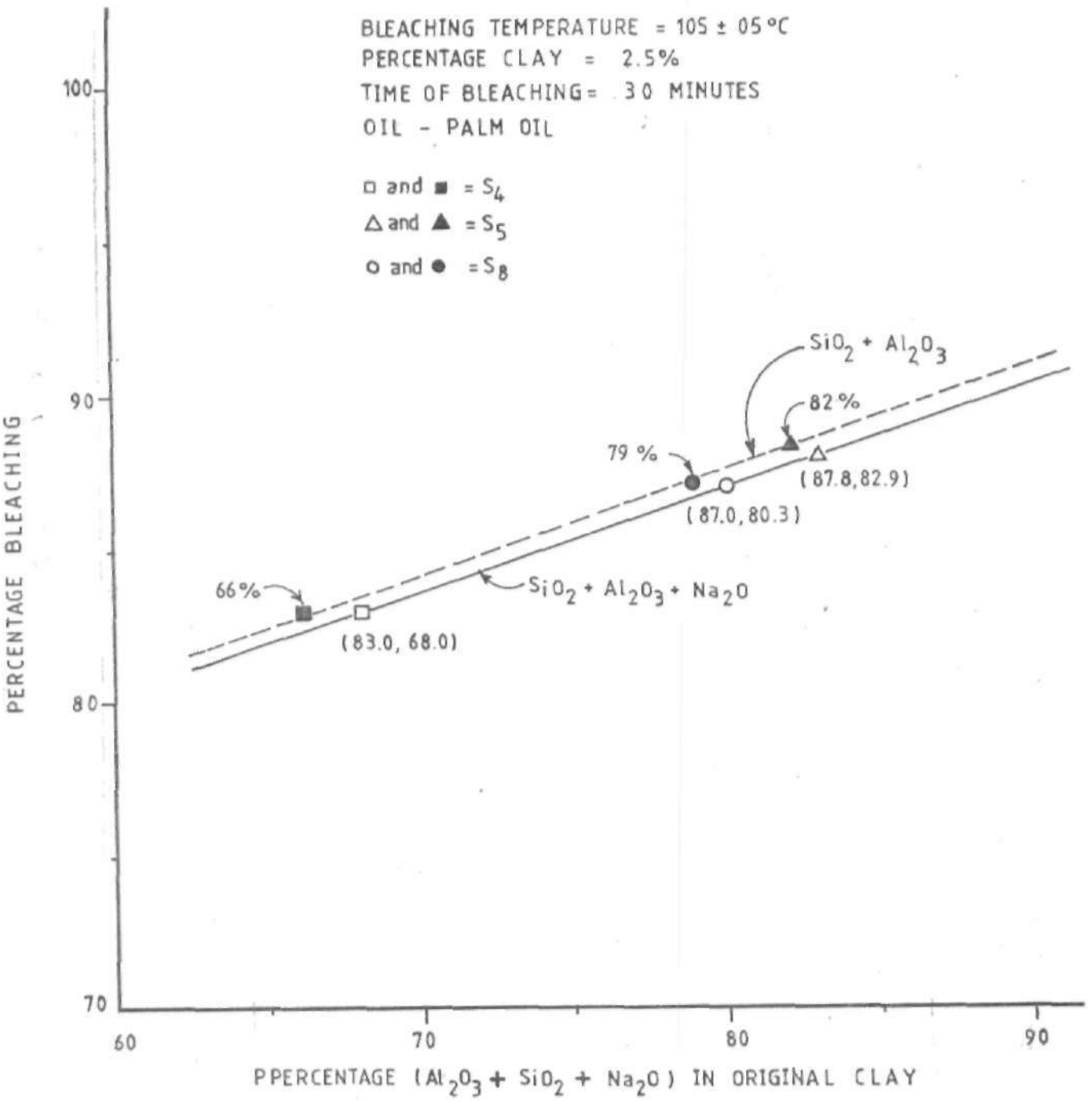


Fig. 4.8. Bleaching activity in percentage against (Al_2O_3 + SiO_2 · Na_2O) percentage for S_5, S_8, and S_4 clays activated with 200 cm^3, 5M Hcl.

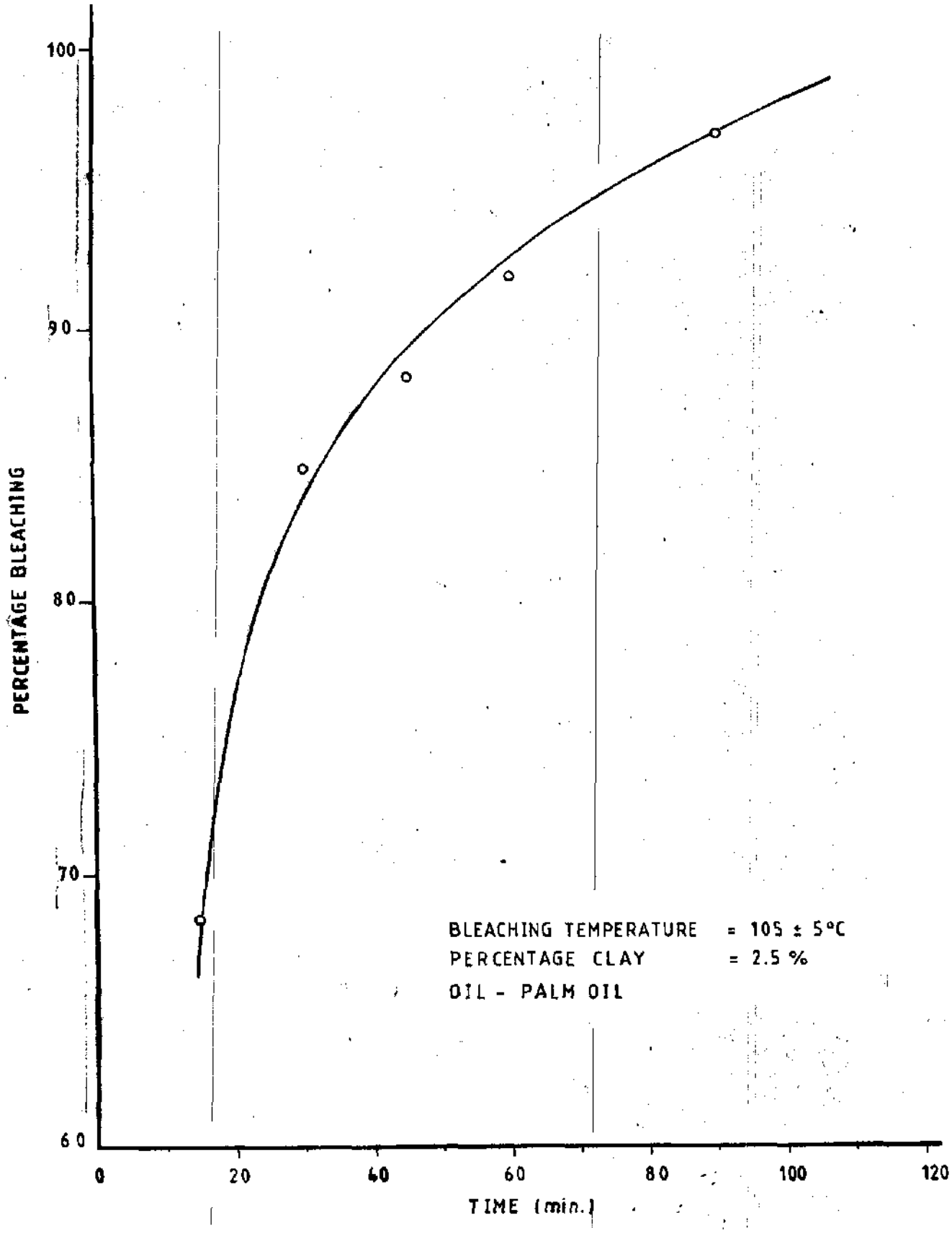


Fig. 4.9. Graph of percentage bleaching against time of bleaching for activated S_8 clay.

4.6 Refining of Oil and Bleaching with activated clays

Crude palm, groundnut and palm kernel oils were refined by alkali refining using different lye in Buame concentration. For palm kernel and groundnut oil 14° Be' lye was used and for the palm oil the 16° Be' lye was used. It was observed that the alkali refining of the oil removed the colour of the oils to some extent, odour and some undesirbale substance that may have adverse effect on the stability of the oils.

For palm oil the colour was reduced by about 50.5% when measured spectrophotometrically and 49.58% using the lovibond tintometer. For the groundnut oil it was redudced by 38.89% when measured spectrophotometrically and 36.75% using the lovibond tintometer. While for the palm kernel oil it was reduced by 27.27% spectrophotometrically and using the loviband tintometer 28.57% (Table 4.12 and 4.13) (Appendix J, Plate V).

Also with respect to the crude palm oil the rate of colour removal with various acid activated clays improved compared to when the acid activated clay were used on just the filtered crude palmoil. From the result of bleaching by the activated S_5, S_8, and S_4 clays in comparison with F clay at the temperature of bleaching 105 $\pm$ 05°C and 2.5% clay for 30 minutes showed that the clays out performed the F clay while at lower temperature of 82 $\pm$ 02°C and same condition of bleaching using the same clays on groundnut oil and palm kernel oil, the F clay performed better than all the clays (Table 4.12 and 4.13).

Bleaching of groundnut and palm kernel oil after refining at 97 $\pm$ 02°C has shown to decrease in their colour removal (Table 4.14). This deterioration in colour could be due to oxidation of colourless compounds or the existing colour pigments becoming fixed at high temperature. Rich, (1964), Cowan (1976) both reported that the chlorophyll pigment present in the oil tend to stabilize at elevated temperature and therefore harder to remove.

Table 4.12 Evaluation of the Bleaching Ability of Activated Clay Samples and Fuller's Earth on Alkali Refined Palm oil, Palm Kernel Oil and Groundnut Oil Spectrophotometrically

(1) Palm Oil (Whole)

Colour Reduction due to refining 50.5%

Clay	Colour Reduction with Respect to Crude oil (%)	Colour Reduction with Respect to Refined oil (%)
F	89.10	78.02
S_5	96.46	92.84
S_8	95.12	90.13
S_4	93.40	86.67

Bleaching Temperature = 105 ± 05°C

Bleaching Time = 30 minutes

Percentage Clay = 2.5%

Carotene in top layer before bleaching = 525.74mg/kg

Carotene in bottom layer before bleaching = 258.52mg/kg

(2) Groundnut oil

Colour Reduction due to refining 38.89%.

Clay	Colour Reduction with Respect to Crude oil (%)	Colour Reduction with Respect to Refined oil (%)
F	85.55	76.36
S_5	83.33	72.73
S_8	81.11	69.08
S_4	75.55	60.00

Bleaching Temperature = 82 ± 02°C

Bleaching Time = 30 minutes

Percentage Clay = 2.5%

Carotene in top layer before bleaching = 86.18mg/kg

Carotene in bottom layer before bleaching = 52.66mg/kg

(3) Palm Kernel oil

Colour Reduction due to refining 27.27%

Clay	Colour Reduction with Respect to Crude oil (%)	Colour Reduction with Respect to Refined oil (%)
F	51.52	33.33
S_5	48.49	29.16
S_8	42.43	20.84
S_4	36.36	12.49

Bleaching Temperature = 82 ± 02°C

Bleaching Time = 30 minutes

Percentage Clay = 2.5%

Carotene in top layer before bleaching = 31.60mg/kg

Carotene in bottom layer before bleaching = 22.98mg/kg

Table 4.13 Evaluation of the bleaching ability of activated clay samples and fuller's earth on Alkali refined palmoil, palm kernel oil and groundnut oil using the lovibond tintometer.

(1) Palm oil (whole)

Colour Reduction due to refining 49.58%

Clay	Colour Reduction with Respect to Crude oil (%)	Colour Reduction with Respect to Refined oil (%)
F	66.57	33.89
S_5	81.16	62.75
S_8	78.75	57.98
S_4	72.10	44.82

Bleaching Temperature = 105 ± 05°C

Bleaching Time = 30 minutes

Percentage Clay = 2.5%

Carotene in top layer before bleaching = 13.3Y, 57.3R

Carotene in bottom layer before bleaching = 13.2Y, 22.R

(2) Groundnut oil

Colour Reduction due to refining 36.74%

Clay	Colour Reduction with Respect to Crude oil (%)	Colour Reduction with Respect to Refined oil (%)
F	82.30	73.68
S_5	81.42	72.37
S_8	75.22	63.16
S_4	69.03	53.95

Bleaching Temperature = 82 ± 02°C

Bleaching Time = 30 minutes

Percentage Clay = 2.5%

Carotene in top layer before bleaching = 9.8Y, 1.5R

Carotene in bottom layer before bleaching = 6.5Y, 1.1R

(3) Palm Kernel oil

Colour Reduction due to refining 28.57%

Clay	Colour Reduction with Respect to Crude oil (%)	Colour Reduction with Respect to Refined oil (%)
F	57.14	40.00
S_5	53.06	34.29
S_8	46.94	25.71
S_4	44.90	22.86

Bleaching Temperature = 82 ± 02°C

Bleaching Time = 30 minutes

Percentage Clay = 2.5%

Carotene in top layer before bleaching = 3.6Y, 1.3R

Carotene in bottom layer before bleaching = 2.6Y, 0.9R

4.7 Effect of Bleaching on the Solid Formation Rate of Palm oil

It was observed that the rate of solid formation in palm oil increased with bleaching compared to the unbleached. This might be attributed to the reduction in the double bonds due to degradation or polymerization of some of the fatty acid in the oil consequent upon heating (Jawal, *et al*; 1983) (Appendix K, Plate VI). During the heating this polymers formed increases the viscosity of the palm oil and causes water to be entrapped in the oil.

This polymers are formed by oxidative (Emmanuel, *et al*; 1967) and thermal (Swern, 1964) mechanism during bleaching. In oxidative mechanism free radical are produced from the oxidation of the fatty acid moiety. This radical may terminate with other free radicals to produce R-o-o-R, or R-o-R or R-R, with the R-R predominantly in the terminal polymerization.

Possibly the presence of traces of colour pigments and metals such as iron and copper which as catalyst in the polymerization process accelerated the oxidative polymerization of the fatty acids in the oils thus aiding in the solid formation of the bleached oil (Patterson, 1978).

4.8 Oil Retention of the Clay Samples

The oil retention of activated samples varies from each other with S_5 clay having the least of 1.66%, S_4 clay 1.78% and S_8 clay 12.10% in comparism with 4.14% for F clay at 2.5% of the clay to oil. It could be inferred that the apparent bulk density of the clay samples have an effect on the oil retention of the clay sample during filtration. This relation could be observed as an inverse relationship which means the higher the apparent bulk density the lower the oil retention (Rich, 1960) (Table 4.15).

Table 4.14 Percentage Bleaching of Some Activated Clays on Groundnut and Palm Kernel oils.

SAMPLE	% Bleaching at 82°c	% Bleaching at 97°C	% Bleaching at 82°c	% Bleaching at 97°c
F	85.55	82.13	51.52	50.08
S_5	83.33	80.93	48.49	44.43
S_8	81.11	77.72	42.43	37.04
S_4	75.55	71.31	36.36	29.63

Bleaching Time = 30 minutes

Percentage Clay = 2.5%

Carotene in top layer before bleaching = 80.47mg/kg

Carotene in bottom layer before bleaching = 26.85mg/kg

Table 4.15 Oil retention (in percentage) and apparent bulk density of activated S_5, S_8, S_4 Clays and Fuller's Earth.

SAMPLE	Oil retention (%)	Apparent Bulk Density (g/cm^3)
S_5	1.66	0.68
S_8	12.10	0.60
S_4	1.78	0.67
F	4.14	0.65

CHAPTER FIVE

5.0 CONCLUSION AND SUGGESTION FOR FURTHER WORK

Drying of the actual clays during the sample preparation gave a homogenous phase, but the S_1, clay gave two phases which were tagged S_{1a} and S_{1b}. Also as the water absorption of the clays increases the lighter their colour; S_4 clay being the least porous and S_{11} clay the most porus.

The elemental composition of all the local clays studied vary from clay to clay and the bleaching ability/power of the clays were observed to be linearly related to the percentage sum of the oxide of aluminium, silicon and sodium present in the clay in their natural state.

In the bleaching of palm oil, the S_5, S_{10}, S_{2a} and S_8 clays show bleaching performance of 60% and above, in their natural form in comparism with F clay. On activation of the clays, it was found that the method II of activation offered the best result relative to the other methods considered. This was closely followed by the method IIIc.

The acid to clay ratio and the molar concentration of acid were found to affect the bleaching performances of the activated clays. Activation with 5MHCl to clay ratio of 2:1 produced the best result with respect to bleaching performance. Hence for optimum bleaching performance 5MHCl and acid to clay ratio of 2:1 are recommended for the activation of the clays in their natural state.

Clay samples such as S_4 clay that show poor bleaching ability in their natural form were found to show better bleaching ability when it was activated. In all cases, activation of the clays caused a decrease in pH and apparent bulk density, an increase in the titratable acidity and a marked increase in the bleaching ability of the clays. Bleaching activity of the clays studied appear to be in decreasing order of percentage sodium oxide and loss on ignition and increasing order of silica.

The bleaching performance of all the clays increase generally with increase in the bleaching time, until on optimum time is reached whereupon, a decrease in the bleaching ability is observed. For the local clays a drying time of 4 hours at a temperature of 105°C is recommended for clays after activation since it enhanced the bleachng ability of the clays very well.

Activitated local clays S_5, $S_{2.5}$, S_8, S_{10} and S_4 protrait a better bleaching ability than the commercial F clay at higher temperatures while the F clay perform better at lower temperature. Refining of the oil to be bleached before bleaching enhances the bleaching ability and the colour reduction of the oil with respect to the crude oil as compared to that of the unrefined oil.

S_5 clay and S_4 clay showed a lower oil retention as compared to the F clay in their activated state but in the case of S_8 clay the oil retention was higher than all the clays considered. This showed that for a clay to have lower oil retention the apparent bulk density should be high.

In other to progress in this research, it is suggested that other clay deposits in the country are exploited and tried for their bleaching ability on oils. Also the effect of these clays on the quality of the oils should be extensively researched into so that those with very good ability would be used in the bleaching and refining of oils industrially and thus discourage the importation of earths from overseas countries.

Futhermore, from the analysis of some clays, it is clear that some have high silica content. Additional study in this field would be valuable with respect to the imporance of silicate to the glass industries.

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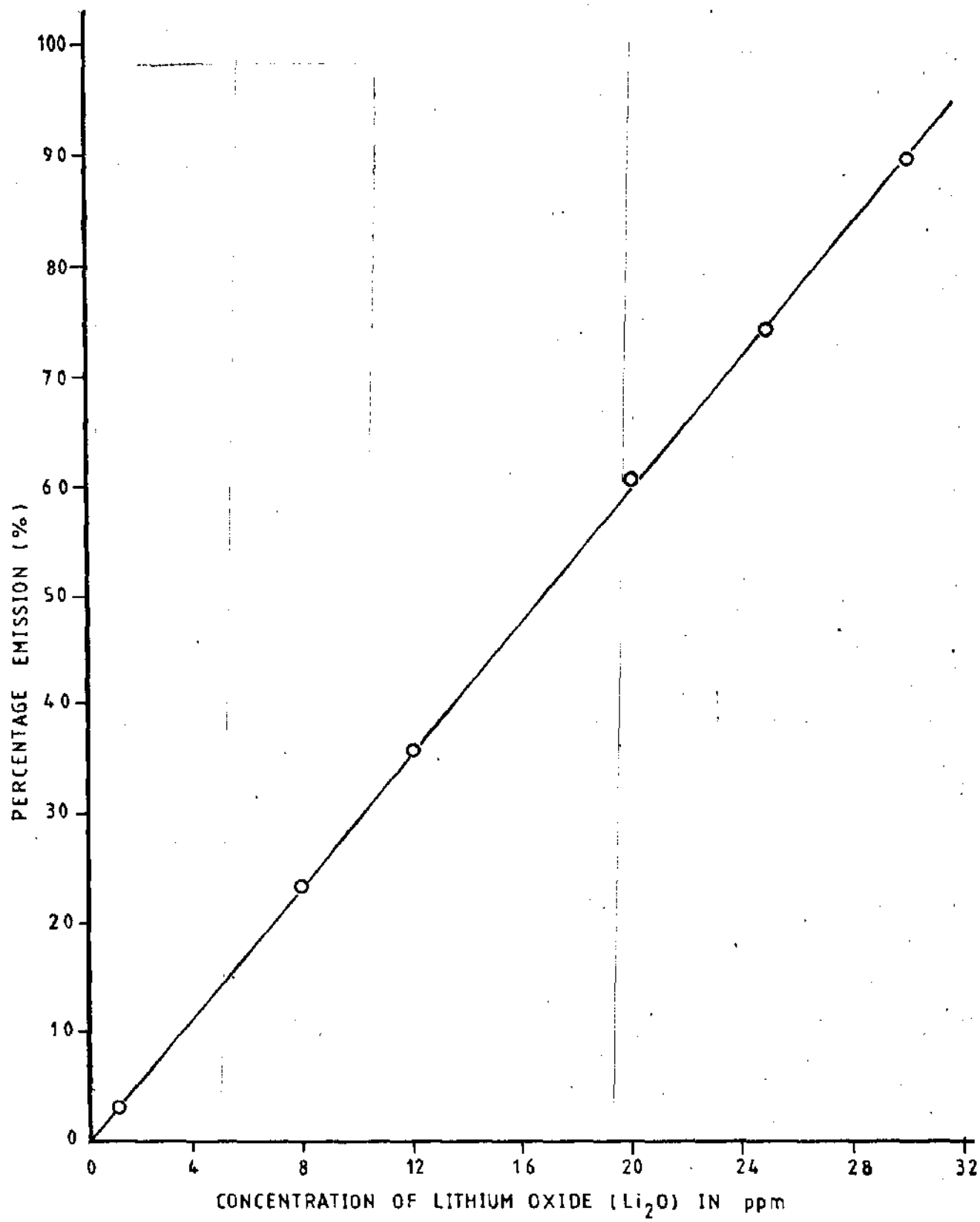
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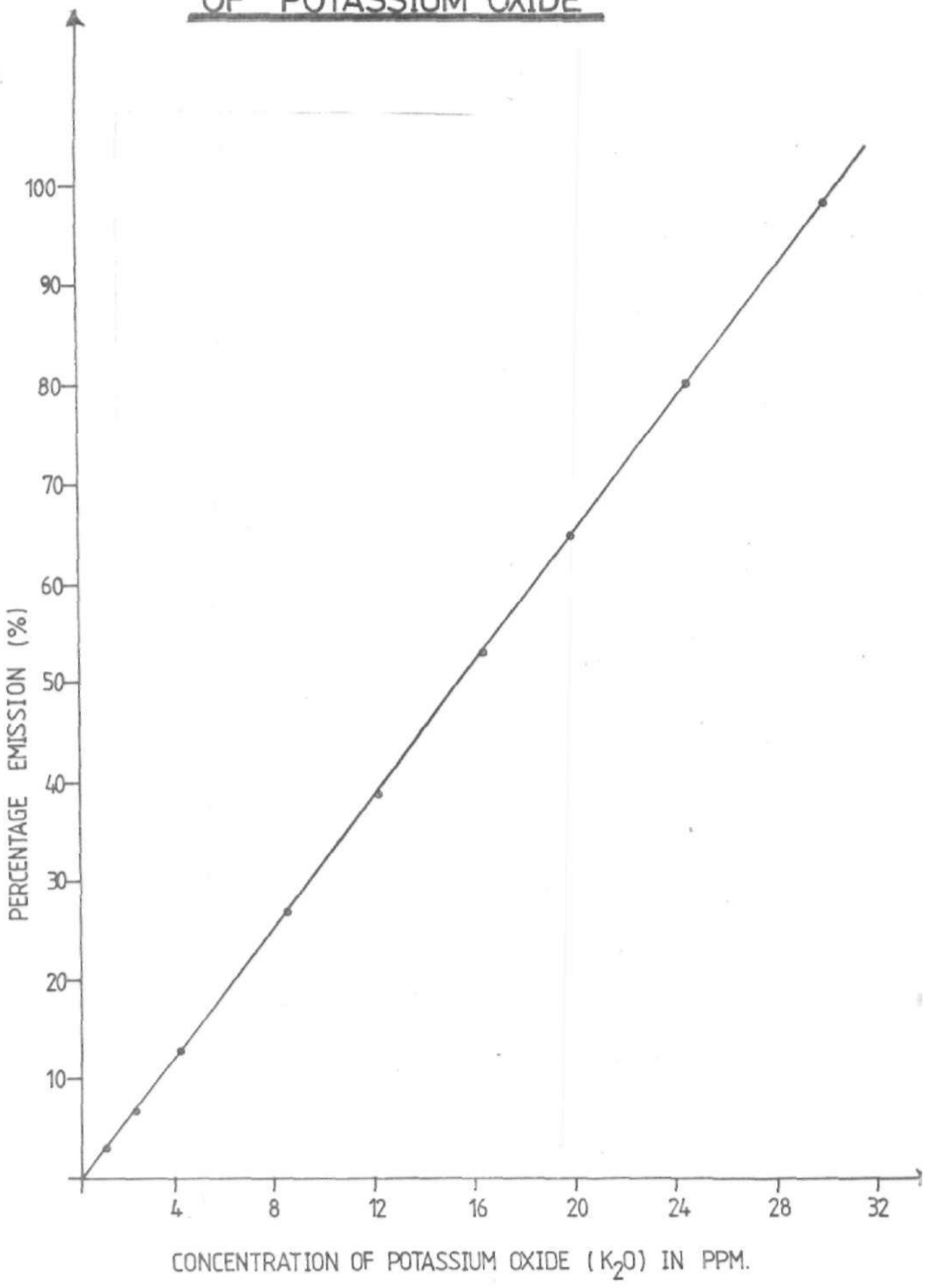
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CALIBRATION CURVE FOR DETERMINATION OF LITHIUM OXIDE.



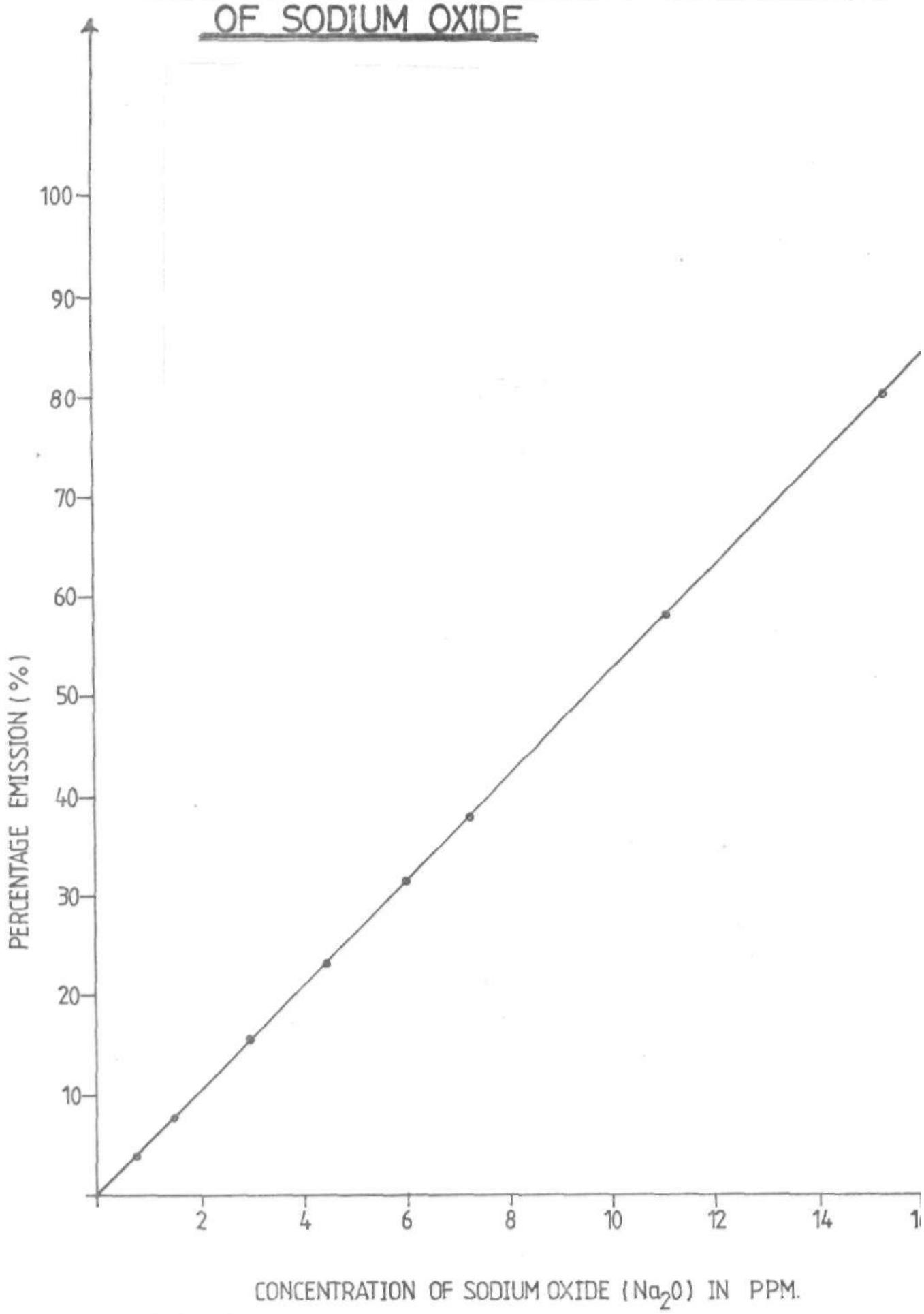
APPENDIX A

CALIBRATION CURVE FOR DETERMINATION OF POTASSIUM OXIDE



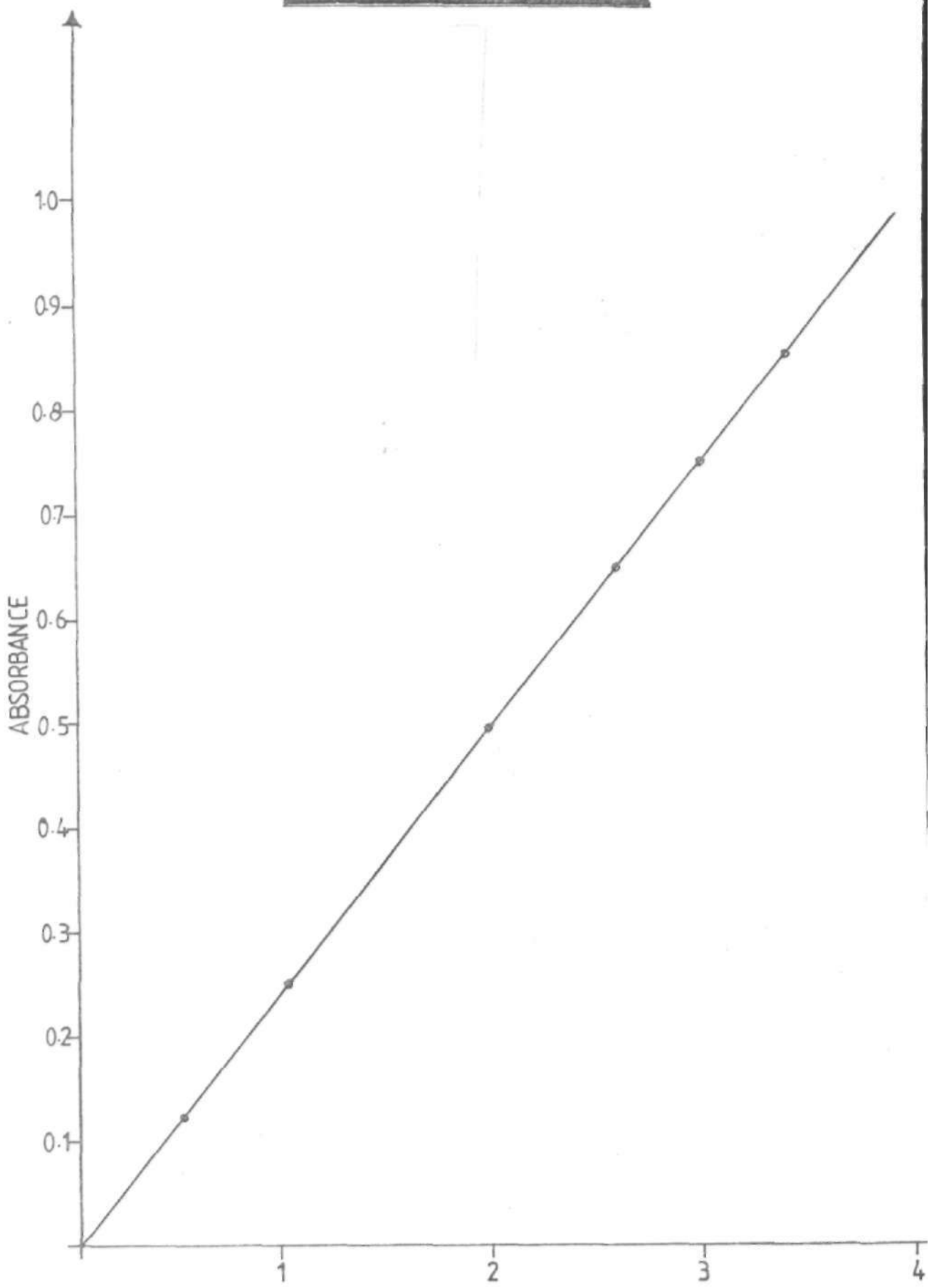
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CALIBRATION CURVE FOR DETERMINATION OF SODIUM OXIDE



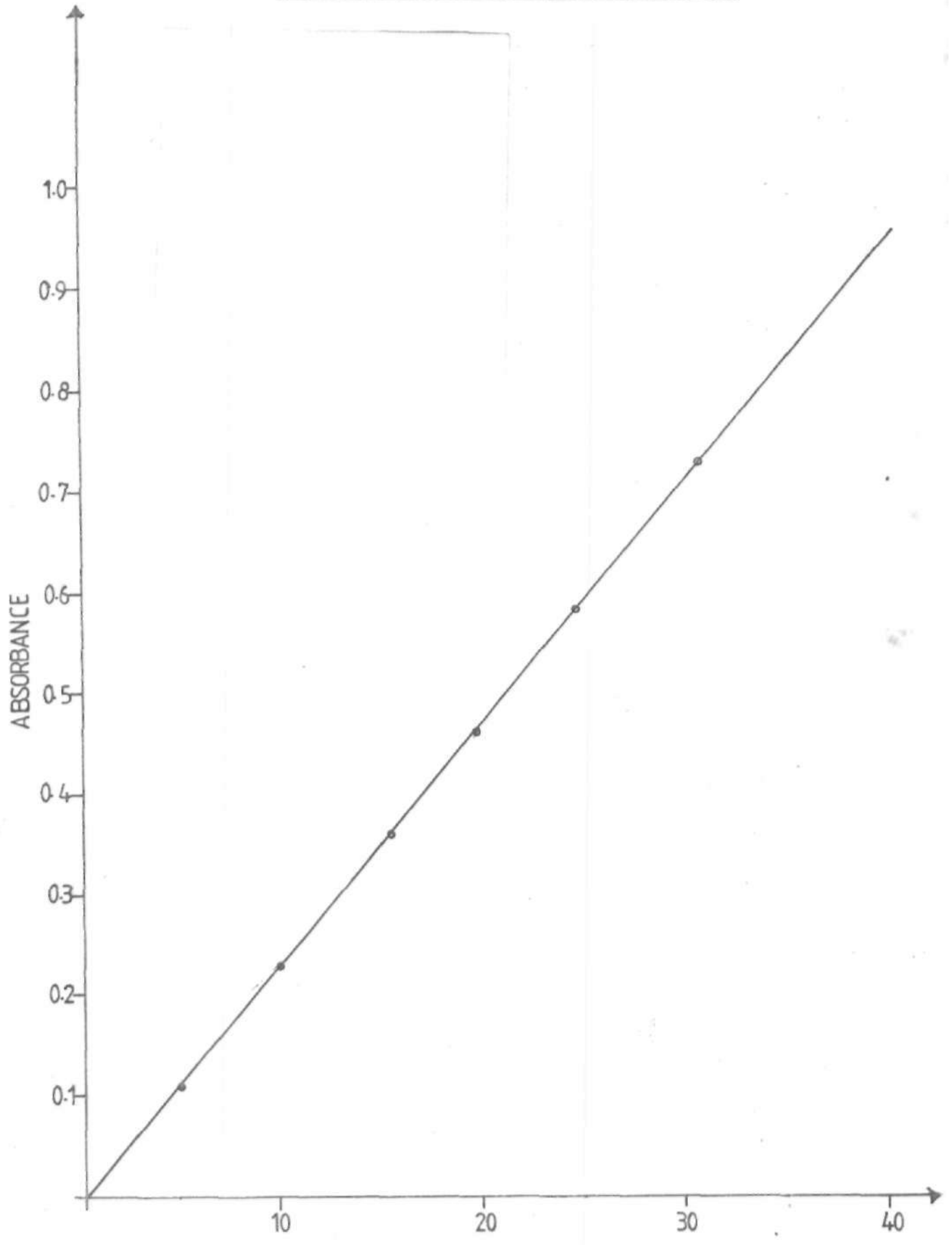
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CALIBRATION CURVE FOR DETERMINATION OF IRON III OXIDE



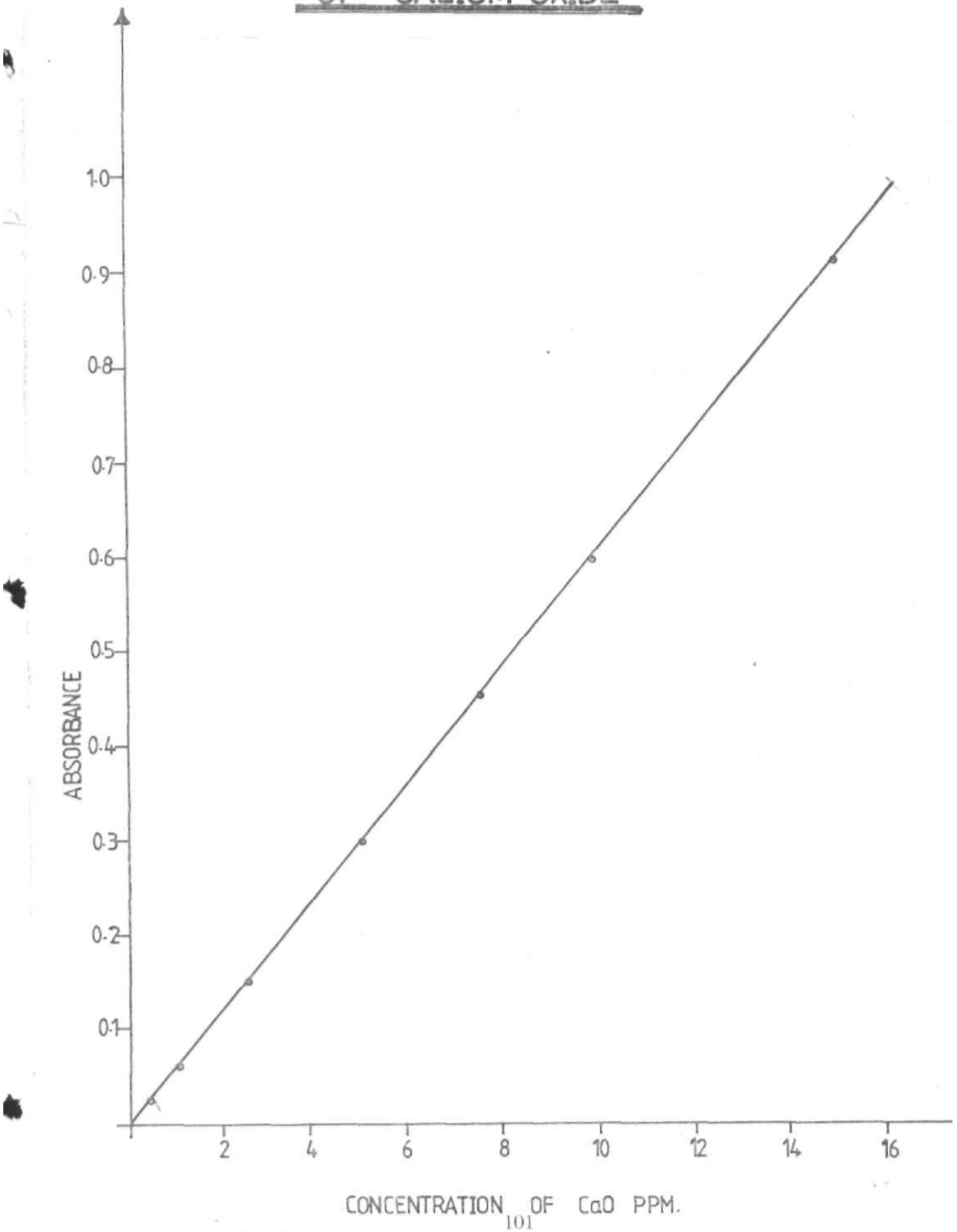
APPENDIX D

CALIBRATION CURVE FOR DETERMINATION OF TITANIUM (IV) OXIDE



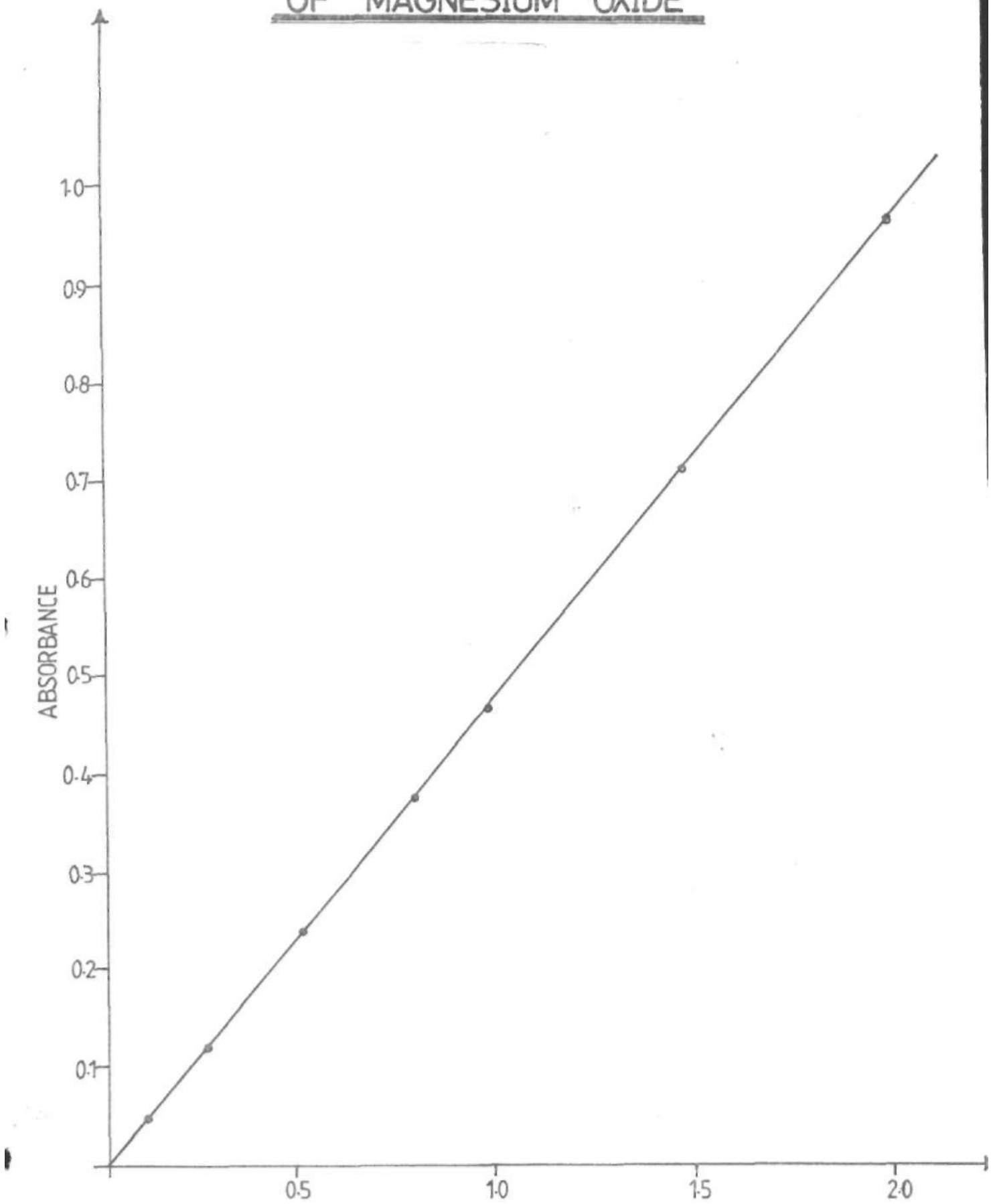
APPENDIX E

CALIBRATION CURVE FOR DETERMINATION OF CALIUM OXIDE

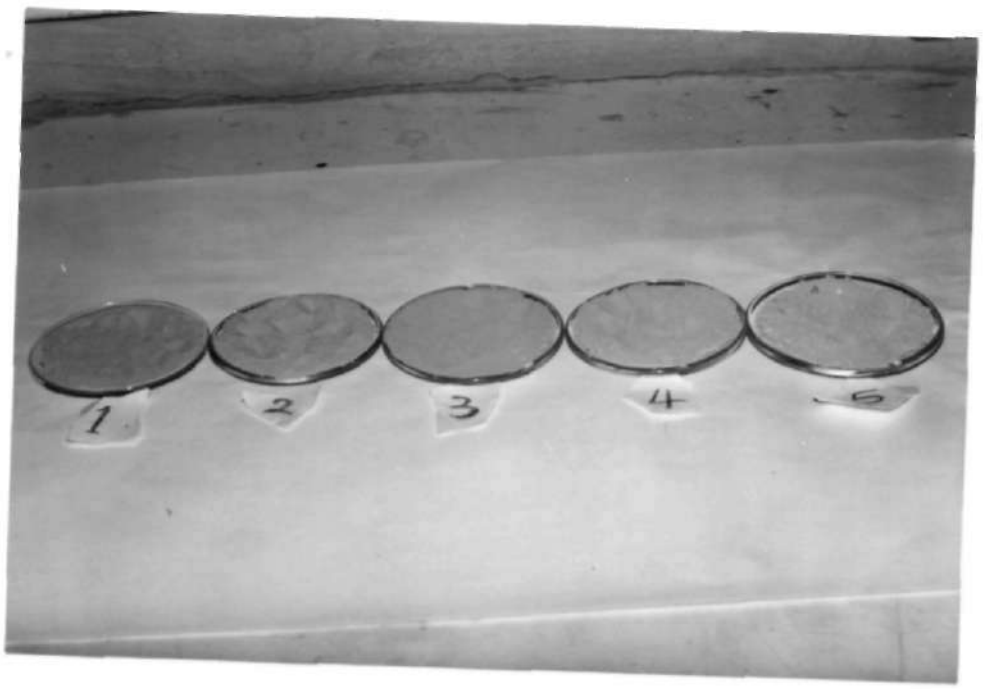


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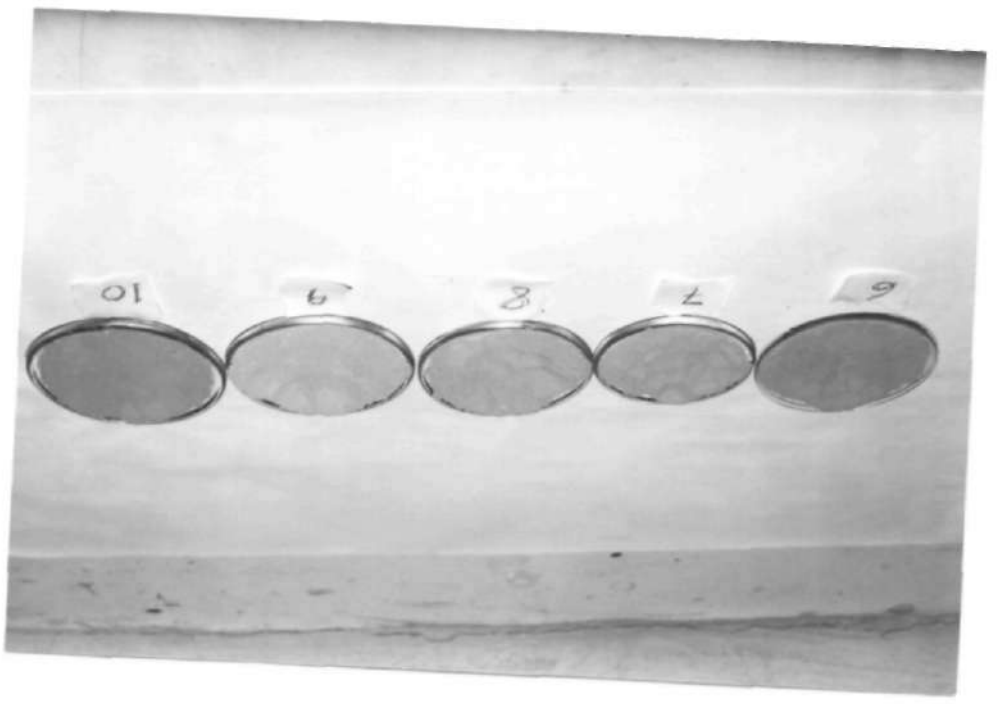
CALIBRATION CURVE FOR DETERMINATION OF MAGNESIUM OXIDE



APPENDIX G



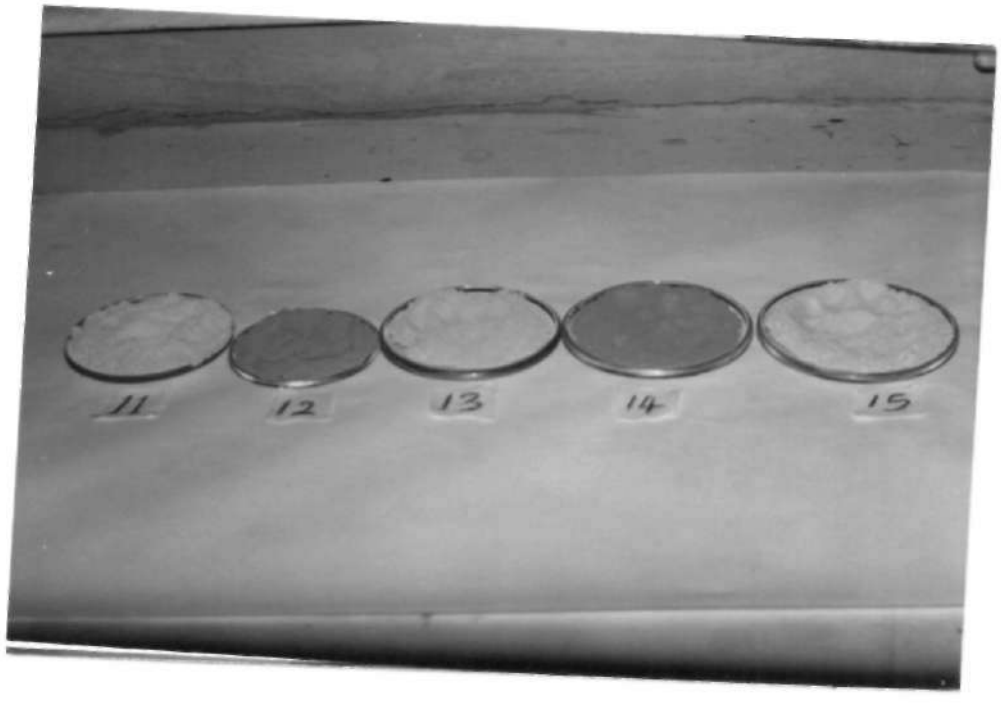
(1) S_2(A) (2) S_1(B) (3) S_2(I) (4) S_2(II) (5) S_3(1) in their natural form.



(6) S_3(II) (7) S_4 (8) S_5 (9) S_6 (10) S_7 in their natural form.

Plate III

APPENDIX H



(11) S_8 (12) S_9 (13) S_{10} (14) S_{11} (15) F in their natural form.

Plate III



Page IV Showing Clays in their Natural and Activated Form

(A) S_8 (B) S_5 (C) S_{20} (D) S_{10} (E) S_4

APPENDIX I

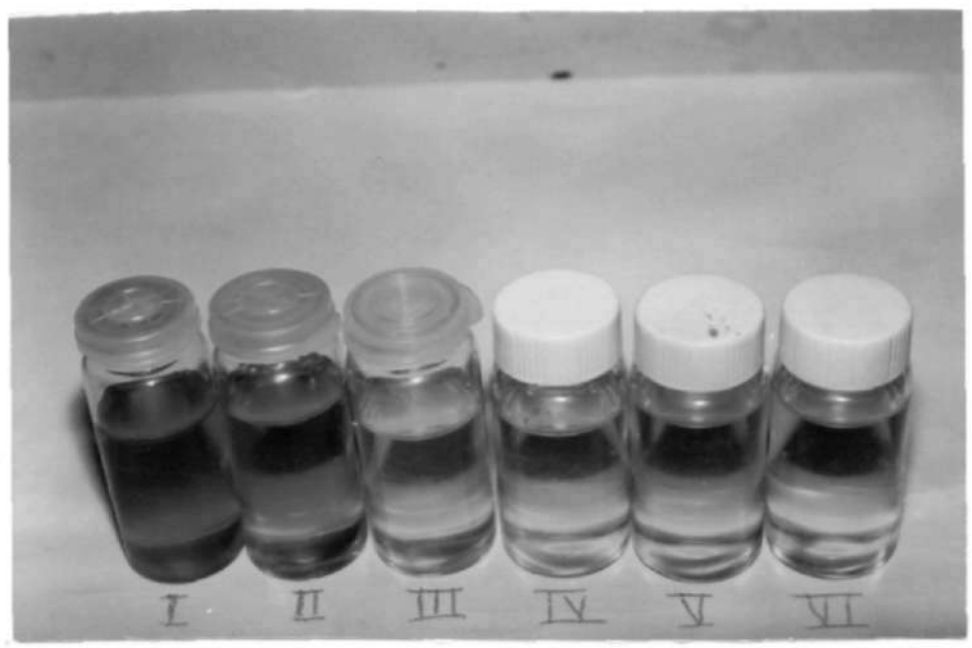


Plate V Showing Crude, Refined and Bleached Palm oil by some activated Clay:

(I) Crude Palm oil
(II) Refined Palm oil
(III) Palm oil bleached with Fuller's Earth (F)
(IV) Palm oil bleached with activated S_4
(V) Palm oil bleached with activated S_8
(VI) Palm oil bleached with activated S_5

APPENDIX J

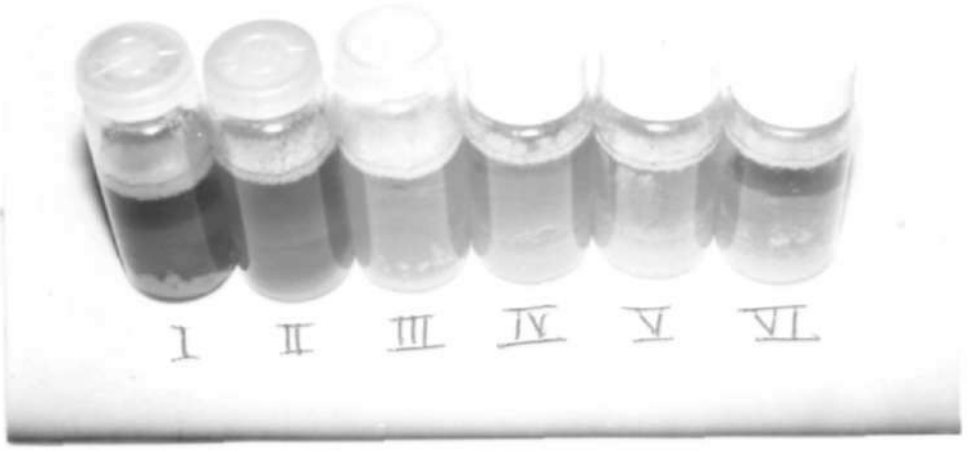


Plate VI Showing the effect of bleaching on the rate of solid formation of palm oil bleached with some activated clay.

(I) Crude Palm oil
(II) Refined Palm oil
(III) Palm oil bleached with Fuller's Earth (F)
(IV) Palm oil bleached with activated S_4
(V) Palm oil bleached with activated S_8
(VI) Palm oil bleached with activated S_5

APPENDIX K