MINERALOGICAL AND ELEMENTAL ANALYSIS OF CLAY SAMPLES FROM IMO STATE^SOUTH EASTERN NIGERIA

EXTERNAL DEFENCE PRESENTATION

BY

ANUMATA STANLEY E. (B.Sc. IMSU)
20184143148

PRESENTED TO THE DEPARTMENT OF CHEMISTRY, SCHOOL OF PHYSICAL SCIENCES, FEDERAL UNIVERSITY OF TECHNOLOGY OWERRI.

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IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF MASTER OF SCIENCE (M.Sc.) DEGREE IN MINERAL PROCESSING

JANUARY, 2022

CERTIFICATION

This Thesis; Mineralogical and Elemental Analysis of Clay Samples from lyinwaogbaUmuosodeAlikeIkenaiziObowoImo State Using Spectroscopic Techniques, is approved for the award of M.Sc. (Mineral Processing) in the Department of Chemistry, Federal University of Technology Owerrijmo State.

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DEDICATION

This Thesis is dedicated to my loving family. Wife; Lady Glory Akunna Anumata (Laux/KSJI), and my children; Miss Mary Claret Tobechi Stan- Anumata, Ekeoma Theophilus Valentine Stan-Anumata, Mmesoma Joan Stan- Anumata and JohnPaul Udochukwu Stan-Anumata.

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ABSTRACT

This thesis characterizes five clay samples from lyinwaogba Umuosode Alike Ikenanzizi Obowo, Imo State. The characterization is based on their physicochemical properties, mineralogy and elemental analysis using Scanning Electron Microscopy (SEM-EDS) for Morphological characterization, Fourier Transform Infra-Red Spectroscopy (FTIR) for chemical characterization, X-Ray Diffraction (XRD) and Energy Dispersive X-Ray Fluorescence (EDXRF). The pH ranged froml.91 to 2.89, loss on ignition ranged from 4.75 % -5.32 %, Cation Exchange Capacity ranged 24.11 meq/lOOg to 26.49 meq/lOOg. Refractive index ranged from 1.45 to 1.68 while the specific gravity ranged from 2.68 to 2.96. SEM-EDs images of clay fractions (A to E), depict a typical structure of conventional quartz and. Kaolinite. The FTIR analysis of the clay samples XA*®) showed Kaolinite, C-H stretching, Si-O stretching band at 3283.2 cm'^{1} to 3302.4 cm'^{1} 1638.9 cm'^{1} to 1710 cm'^{1} indicating the presence of Kaolinite. The EDXRF results of the clay samples (Atol?) shows, elements present, the highest metal in the clay -samples is Fe, and Sr, detected in trace amount are, Pb, Zn, Mn, and Ga. Ni was not detected, Cu was not detected except in sample D, where it was found in trace amount. The XRD mineralogical data indicates the presence of some mineral phases of characteristic peak of quartz, kaolinite, anatase and pyrite in the clay samples (A-E). The general data strongly suggest that the primary constituents of the clay were kaolinite with high quartz content and average SiO_2 of 58.30%. Altogether, the characteristics of the clay samples are good material for numerous industrial use.

Key words: Mineral, Elemental, Clay, Spectroscopic, Characterization.

CHAPTER ONE

INTRODUCTION

1.1 Background of Study

Clays are naturally occurring materials composed primarily of fine-grained minerals, which is generally plastic at appropriate water contents and will harden when dried or fired (Bauluz, et all, & Gonzalez 2003: Benea & Gorea, 2004). Clay deposits consist of the primary and secondary stages: while the primary clays are formed as a residual deposit in soil and trapped at the site of formation the Secondary clays rather have been transported by water erosion from their original location and deposited in a new sedimentary deposit (Baik&Lee, 2010). Clay deposits can be found in large lakes and marine basins because of its extremely low energy sedimentary environment. The formation of clay takes a long period of time which is as a result of what is known as chemical weathering of rocks which occurs gradually, usually the silicate-bearing ones, by low concentrations of diluted solvents like carbonic acid (Nyakairu & Koeberl, 2C j 1 The acidic solvent leaches the upper weathered layers and then move tr.r: _gh the weathering rock, and it is in this process of hydrothermal activity that s:~.; clay minerals are formed. They have varying chemical composition depending on both the physical and chemical changes in the environment where clay deposits are found (Ekosse et al., 2010; Ojo et. al., 2011).

Natural clay minerals are well known and familiar to mankind from the earliest days of civilization. Because of their low cost, abundance in most continents of the world, high sorption potential for ion exchange, clay materials are strong candidates as adsorbents (Buchwald, Hohmann, Posem & Brendler, 2009).Clay minerals share a basic set of structural and chemical characteristic and yet each clay mineral has its own unique set of properties that determine how it will interact with other chemical species. The variation in both chemistry and structure, among the clays leads to their applications in extremely diverse fields (Bundy, 1993; Celik, 2010; Balouga, 2012).

Clay is composed mainly of silica, alumina and water, frequently with appreciable quantities of iron, alkalies and alkali earths. Two structural units are involved in the atomic lattices of most clay minerals. One unit consists of closely packed oxygen and hydroxyls in which aluminium, iron and magnesium atoms are embedded in an octahedral combination so that they are equidistant from six »
oxygen or hydroxyls. The second unit is built of silica tetrahedrons. The silica tetrahedrons are arranged to form a hexagonal network that is repeated indefinitely to form a sheet of composition, $Si_4O_6(OH)_4$ (Buchwald et al., 2009). The formation of clay minerals is dependent on physicochemical conditions of the immediate weathering environment, nature of the starting materials and other related external environmental factors (Wilson, 1999), thus resulting into various types of clay materials. Consequently, the application potential of any clay mineral type in nature will depend on its chemical composition, structure and other inherent properties (Landouisi, 2013). The specific clay minerals are identified by several techniques including thermal differential analysis, elemental analysis by atomic absorption analysis, infrared spectrometry and X-ray diffraction. Chemical analysis is an essential step

to establish the nature of minerals. On this regard, clay minerals are classified into different groups as follows; Kaolinite, Smectite, Vermiculite, Illite and Chlorites (Agwu, Okon & Udoh, 2015).

In Alike Ikenazizi Obowo, the occurrence of the clay deposit at lyinwaogba is principally used by the community dwellers to celebrate Maternity (birth and arrival of new bom). It is obtained, crushed and mixed with common salt (Sodiumchloride) and offered as kola (gift) in appreciation for Maternity visit. Also, the traditional people of Alike Ikenazizi Obowo use the clay as anti-diarrhea, antiinflammatory, antiseptic and as medicine for the treatment of gastrointestinal conditions. It is often used to treat cases such as body idling and chicken pox by rubbing the ground clay mixed with water on the affected body part. The traditionalists equally used it with some herbs for wound, i.e for healing or soothing of wounds, cuts and bruises as well as for muscle damage.

Clay tablets were the first known writing medium (Ebert & John, 2011). It has a lot of useful application because of its negligible toxicity and the biocompatibility Grin. ... i... 2 ? . The medical pharmaceutical uses of clay dates back to the

prehistoric limes it could be used to soothe stomach upset and some animals such as Parrots and pigs ingest clay for similar reasons (Diamond & Jared, 1999). Kaolin and attapulgite clay have been used as anti-diarrhea medicines (Dadu, 2015).

Clay are used in a wide variety of industries, as soils they provide the environment for almost all plant growth and for nearly all life on the earth's surface (Murray, 2002). Clay provide porosity, aeration and water retention capacity and are reservoir for plants essential elements

(Boggs & Sam, 2006, Foley & Nora 1999). The use of clay in pottery making antedates recorded human history and provides a record of past civilizations. As building materials, bricks both baked and adobe have been used in construction since earliest time (Breuer & Stephen, 2012).

Impure forms have been used to make bricks, tiles and the cruder type of pottery while kaolin is required for the finer grades of ceramic materials (Breurer & Stephen, 2012). Another major use of kaolin is as paper coating and filler in paint making, it gives the paper a gloss and increases the opacity of the paper, for paints, kaolin increases the adhesion to wall properties of the paint and enhances the glossy properties (Nesse & William, 2000).

Refractory materials, including fire brick, chemical ware and melting pots for glass make use of kaolin together with other materials that increase resistance to heat (Foley & Nora K, 1999, Breuer & Stephen, 2012). Certain clays known as fuller earth have long been used in wool scouring (Boggs & Sam, 2006). In rubber compounding, the addition of clay increases resistance to wear and helps eliminate molding troubles (Ebert & John, 2011, Bergaya & Lagaly, 2006). Clay materials have a wide variety of uses in Engineering, Earth dams are made impermeable to water by adding suitable clay materials to porous soil, water loss in canals may be reduced by adding clay (Kockar, Mustafak, Akgun, Haluk & Akturk, 2005). Bentonite clay is widely used as a mold binder in the manufacture of sand casting (Eisenhour et al., 2009, Kockar et al., 2005).

Studies in the early 21st century have investigated clay's adsorption capabilities in various applications such as the removal of heavy metals from waste water and air purification

(Garcia-Sanchez, Alvarev-Ayuso, & Rodriguez-Martin, 2002, Churchman, Gates, Theng, Yuan, Faiza, Bergaya, Benny & Gerhard, 2006). The chemistry of clay minerals including their capacity to retain nutrient cations such as potassium and ammonium is important to soil fertility (Hodges, 2010).

Clay minerals are the most important industrial minerals. Millions of tons are utilized yearly in various applications. These applications include uses in geology, the process industries, agriculture, environmental remediation, construction and as catalyst in petroleum industry. The most generally used in the manufacture of catalysts are kaolin and montmorillonite (Benea & Gorea, 2004). In fact, catalysts gi • ±_ mmnh high octane gasoline in petroleum industry have been produced from clay s composed of halloysite, montmorillonite and kaolinites (Felhi, Tlili, gaied & Montacer, 2008), so that the quantity of kaolin used annually for production of petroleum cracking catalysts was estimated at more than 200,000 tons (Al-Ani, & Sarapaa, 2008; Richard, Afolabi, Oyinkepreye, Orodu, Vincent & Efeovbokhan, 2017).

The reason for utilization of certain clay minerals in specific application is that the physical and chemical properties of a particular clay mineral are dependent on its structure and composition. The structure and composition of kaolins, smectites, and palygorskite and sepiolite are very' different even though they each have octahedral and tetrahedral sheets as their basic building blocks. However, the arrangement and composition of these octahedral and tetrahedral sheets account for major and minor differences in the physical and chemical properties of kaolin, smectites and palygorskite (Loto & Omotosho, 1990; Richard et al., 2017).

Clays have received considerable attention especially as potential adsorbents for environmental research. Many researchers around the world, have beamed their search lights on the phase developments that occurred by sintering clay in the presence of some oxides (Nazile, 2018).

The most abundant, ubiquitous, and accessible material on the earth crust is clay O.o. Suraju, Adepoju & Nurudeen, 2014). It was observed that a great emphasis is placed on exploiting the abundant solid minerals endowments in Nigeria with a view to diversifying the economic base of the country, improving Gross Domestic Product (GDP) and industrial activity (Richard et al., 2017). One of these endowments with tremendous potential for economic utilization is clay (Enu & Adegoke, 1986; Richard et al., 2017).

In Nigeria, clay raw material deposits are widely distributed across the six geopolitical zones of the country (Oluwafemi, 2012). There are several industries which can utilize the readily available and cheap clay raw materials after beneficiation in order to support industrial growth and relieve the government off the burden of importing such products. The improved industrial utilization of clay minerals in the country will depend mainly on the quality and durability of the material, and for this to be realized, there is need for rigorous studies on this resource. Unfortunately, very little attention has been given to clay characterization and mineralogy in Nigeria (and in particular Imo state) despite the growing demand for clay products and the possibility of creating jobs through cottage industries. Currently, the local communities in Nigeria are relying on the indigenous knowledge to make some clay products whose quality is hard to determine and neither does it meet the export standards as shown in Figure 1.

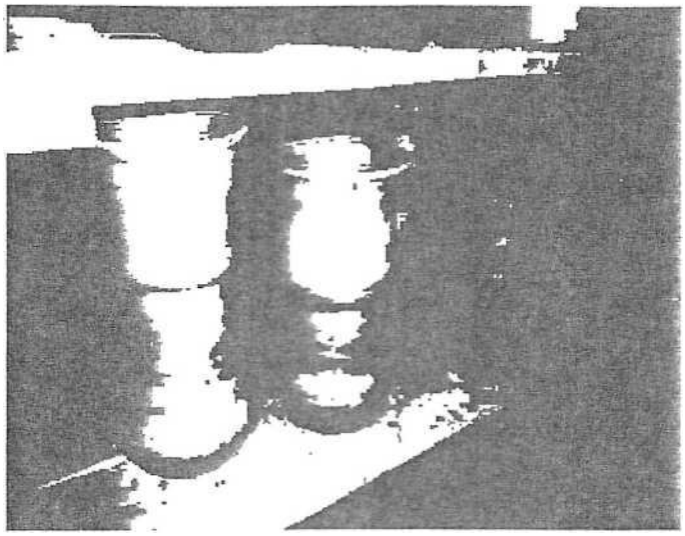


Figure 1.0 Locally made clay products (Source: Ombaka, 2016).

Despite the vast potentials, clay minerals are still grossly underutilized and the few pockets of existing clay-based industries have primarily harnessed the raw material for the production of ceramic wares and structural products. These clay deposits have the potential to be a major source of foreign income earning if properly harnessed. Therefore, in order to determine the profitability of utilizing clay from a particular deposit for any application, it is of paramount importance to examine the microstructural morphology, determine the mineralogical, elemental and functional group composition in such clay deposit.

1.2 Problem Statement

Clay raw material deposits have over the years presented man a means of economic beneficiation. The occurrence of clay mineral deposit, have equally presented the problem of characterization as to ascertain the economic benefits and industrial applications suitability. At lyinwaogba Umuosode Alike Hcenazizi Obowo L.G.A of Imo State, South-Eastern

Nigeria, the existence of clay mineral deposit there, are yet to be characterized as to establish the possible economic beneficiation to the Nigerian economic prospect.

- Characterization of the clay mineral deposit at lyinwaogba Umuosode Alike Ikenazizi Obowo L.G.A of Imo State South-Eastern Nigeria.
- Determination of profitability of utilizing the mineral clay from this particular deposit for any possible application(s).

1.3 AIM AND OBJECTIVES OF THE STUDY

This work is aimed at characterization of clays from lyinwaogba Umuosode Alike Ikenanzizi Obowo of Imo State using X-Ray Diffraction, X-Ray Fluorescence, Scanning Electron Microscopy and Fourier Transform Infrared Spectroscopy

The specific objectives set to achieve the aim are as follows;

- To determine the elemental composition of the clay samples
- To determine the functional chemicals in the clay samples
- To classify the clay sample using the results obtained i.e Mineralogical classification.

1.4 Justification and Significance of the Study

Imo State is one of the major states in Nigeria enriched with clay raw material deposits. These clay materials are yet to be properly characterized. The qualities of clay founddetermine its application and suitability for various applications such as in bricks, ceramic wares, and refractory. In lyinwaogba Umuosode Alike Ikenanzizi Obowo Local Government Area of

Imo State, clav soils in the lower stream often serve as a filter for the flowing stream and thus help in itspurification. There are no studies/reports regarding the composition of raw clay deposits in this area. This study therefore sets to fill this knowledge gap. Furthermore, the findings of the study will also provide documentation of relevant information on clay reserves, mineral locations, and the economic significance of the minerals.

1.5 SCOPE OF THE STUDY

The study covered the mineralogical and elemental analyses of clay samples using XRD, XRF, SEM and FTIR and comparing obtained results with standards andother literature.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1. Characterization of Clay Minerals

The characterization of clay mineral is necessary for the identification of engineering and physico-chemical behavior of fine-grained soils. In addition,, design of stabilizers also requires a specific determination of clay mineral. Previous works done in the area of characterization of clay deposits was based on a regional study of the locations containing them. Moreover, such studies in Nigeria have indicated that the clays are mostly low-grade and would require beneficiation using sodium salt as part of methods to improve its quality.

The pioneering characterization study of clay deposits in Nigeria can be traced to the work of Oyawoye and Hirst (1964). They carried out a mineralogical study using X-Ray Diffraction (XRD) and thermal analysis of clay samples obtained from Ropp in the Plateau Province of the old Northern Nigeria. The number of locations sampled in their study was just one. The clay sample was a calcium montmorillonite with the dominating oxides being siliconoxide (47.38%). aluminum oxide (21.27%) and ferric oxide (10.66%).Other oxides present in the clay samples were <1%.

Marine shale units that are vastly supplemented in montmorillonite occur in all known sedimentary basins in Nigeria. These inarine shale units include the Agwu shale unit in Eastern Nigeria, Fika shale unit in North-East Nigeria, Imo shale unit (this forms a belt across the southern part of Nigeria), and the shale units of the Dukamaje and Kalambaina formations in North-West Nigeria. These formations are known to contain over 80% montmorillonite enriched in calcium with little or no section with sodium. Inspite of this, it cannot be said conclusively that the impact of the geology of the environment affects formation, due to the fact that more needs to be done as not all locations with substantially proven deposits of bentonite clays have been studied.

James et al. (2008) carried out a beneficiation and characterization study of bentonite clay sample obtained from Yola in Adamawa State, North-East Nigeria. Compositional study of this Yolabentonite clay revealed that the clay sample is a low-grade calcium montmorillonite and this is typical of other samples from regions that have been investigated (James et al., 2008; Obaje, 2013; Nwekeet al., 2015).

James et al. (2008) compared the wet and dry beneficiation methods in treating raw bentonite clay samples obtained from Yola in Adamawa State, North-East Nigeria and observed through material characterization that wet beneficiated Yola clay samples showed improved values in pH, swelling power, cation exchange capacity. apparent viscosity and yield when compared to the dry beneficiated Yola clay samples. However, in terms of bulk density the dry beneficiated Yola clay samples showed higher values than the wet beneficiated Yola clays. This may be attributed to the inefficiency of the dry method in properly removing impurities present in the sample (Ajugwe et al., 2012a,b). Some wet beneficiation procedure may also prove ineffective if the bentonite clay is not allowed to properly hydrate and homogenize with the chemicals used for the beneficiation study (Ajugwe et al., 2012a,b).

Chemical analysis carried out on samples of kaolin clay collected from Lakiri village, southwestern Nigeria by Badmus and Olatinsu (2009) showed that the kaolin clay is acidic and contains high concentration of alkaline metals. The physical analyses revealed the kaolin clay to have an average porosity of 0.46 and bulk density of 1.4 g cm^{-3}. They concluded that the properties of the clay make it good as additive for both industrial and mining purposes.

Ahmed et al. (2012a,b) carried out mineralogical studies on clays obtained from the Pindiga formation in Gombe State, North-East Nigeria. Experimental findings indicate that the clay samples contain montmorillonite, which is predominantly rich in calcium, and this is more stable when compared to Magnesium, Potassium and Sodium based montmorillonite. Compositional analysis of the clay samples showed that it contains oxides of Aluminum, Silicon, Calcium and Iron.

Obaje (2013) investigated clays in Borno State, North-East Nigeria anc previous works done on clays in that region discovered that it was rich in montmorillonite containing predominantly calcium and requires beneficiation to improve the quality of the clay.

Dewu et al. (2011 a,b) carried out mineralogical characterization of clay samples obtained from the Fika formation in North-East Nigeria. The mineralogy of the clay samples were mainly calcium-based montmorillonite and would require beneficiation with sodium carbonate to convert it to sodium based montmorillonite via ion exchange. The mineralogical and elemental study of Nigerian bentonite clay deposits carried out by researchers in the 80s, 90s and early 2000s has revealed that beneficiation of these bentonite clays is a necessary step if recourse must be made to it for application in the oil and gas industry. This is important, as most of the clay deposits studied so far do not meet the requirementsof the .American Petroleum Institute (API) in terms of rheological properties.

Nweke et al. (2015) carried out mineralogical characterization of clay samples from the Abakaliki Formation in the Niger-Delta part of Nigeria. The minerals present are mainly montmorillonite and illite with traces of kaolinite. Elemental analysis indicates high calcium and potassium oxides. Olugbenga et al. (2013) also characterized bentonite clay samples from the Niger Delta region of Nigeria. Their mineralogical study using X-Ray Diffraction (XRD) on the clay sample indicated that it was a montmorillonite rich in calcium and chemically stable. In addition, beneficiation of the clay samples with sodium carbonate improved the rheological properties of the clay, which gives a promising sign for drilling mud application as per American Petroleum Institute (API) and Oil Companies Material Association (OCMA) recommendation.

Apugo-Nwosu et al. (2011) carried out a suitability study of the Ubakala clays in Abia State. Mineralogical analysis of these clays using X-Ray Diffraction showed that it was composed mainly of smectites, kaolin, and albite. Chemical analyses results showed that in the Ubakala clay, theAl_2O_3/SiO2 ratio was about 1/4.35. The presence of alkalis and magnesia in the samples suggests significant presence of montmorillonite.

Osadebe et al. (2011) also carried out chemical and mineralogical analysis of clay deposits obtained from Okada, Edo State, South-West Nigeria. The analysis was mainly done using X-Ray Diffraction and the results showed that silicon dioxide was more in abundant in the clays followed by aluminum oxide. This was comparable with the works carried out by Ademibawa (1999a,b), James et al. (2008), Abdullahi et al. (201 la,b) and Obaje (2013).

Nwosu et al. (2013) characterized clays samples obtained from Udiin Enugu Sate, South-East Nigeria using X-Ray Diffraction and Fourier Transform Infrared

Spectroscopy. The findings from the compositional analysis indicated that silicon oxide (53.2%) was the dominant oxide in the clays samples followed by aluminum oxide (5.906%) other oxides like Fe_2O_3, MgO, CaO, Na_2O, K_2O etc. were bl%. Joel and Nwokoye (2010) also carried out a study on clay samples obtained from the Niger-Delta region. Silicon dioxide and aluminum oxide were both in substantial quantities while other metal oxides were less than a percent.

Olugbenga et al. (2013) also investigated the mineralogy and elemental composition of clays obtained in the Niger Delta region using X-Ray Fluorescence (XRF) and X-Ray Diffraction (XRD). Analysis of the clay samples revealed the presence of amontmorillonite, which was calcium based and would require beneficiation with a sodium salt in order to improve its properties for drilling mud application. In addition, silicondioxide was in large quantity (47.4%) followed by aluminum oxide (20.97%) and ferric oxide (5.73%) respectively. Tables 2.3 and 2.4 give a summary of researchers work on Nigerian clays from different parts of the country.

Ojoet. al., (2015)studied the chemical and mineralogical compositions of the clay deposits at Akerebiata area in Ilorin (north-central Nigeria), southwestern basement complex, Nigeria. X-Ray Diffraction (XRD) method was employed for the mineralogical analysis while X-Ray Fluorescence (XRF) and Inductively Coupled Plasma-Mass Spectrophotometer (ICPMS) methods were used to for thedetermination of the bulk elemental composition. XRD analysis revealed kaolinite as the predominant clay mineral (54.2 to 90.9 wt. %) indicating intensive chemical weathering of aluminium-rich source rocks and exhaustive leaching under a warm, humid condition. Other non-clay minerals in the assemblages are quartz, rutile, anatase, microcline and plagioclase. Results of geochemical analysis from their study showed the predominance of SiO? (47.14 to 64. 92 wt. %) and $A1_2O_3$ (19.47 to 29.39 wt. %) which support the kaolinitic nature of the clay and classify the clay as aluminosilicates. The relatively high mean values of the Chemical Index of Alteration (CIA) and Chemical Index of Weathering (CIW) (87.15 and 90.09) also suggest an intensive chemical weathering in the source area. Other relevant geochemical indices; plot of TiO_2, ratios of Th/Co, Th/Cr, Cr/Th and relative proportion of Ni and Cr reveal felsic igneous parent rock. The clays were characterized by light colour, fmeness, low-moderate LOI, mineral assemblage and chemical composition that make them favorably compared with standards for refactory, ceramics, pottery and paints.

Oyedoh et al. (2016) carried an experimental investigation into the use of clays obtained from Afuze in Edo State for drilling mud formulation. The mineralogical analysis showed that the clays are mainly calcium montmorillonite and would require beneficiation with sodium salt into order to convert to sodium montmorillonite.

Table 2.1. Mineralogical Analysis of some Clay Deposits in Nigeria

Location	Mineralogical composition	References
Ropp	Montmorillonite, Biotite, Quartz and Beidillite	Oyawoye and Hirst (1964)
Igbokoda	Montmorillonite, Kaolinite and Illite	Loto and Omotosho (1990)
Pindiga	Montmorillonite, Kaolinite. Quartz, Calcite, Biotite,	Falode et al. (2008)
Ibere	Montmorillonite, Kaolinite, Quartz, Feldspar, Illite,	Mark and Onyeamaobi
Uzuakoli	Montmorillonite, Kaolinite, Quartz, Feldspar, Illite	(2009)
Ohiya	Montmorillonite, Kaolinite. Quartz, Calcite	
Oboro	Montmorillonite, Kaolinite, Quartz, Calcite	
Odukpani	Kaolinite, Quartz, Feldspar and Illite	Osabor et al. (2009)
Benue Trough •	Montmorillonite, Kaolinite, Dolomite, Ankerite.	Abdullahi et al. (201 la,b)
Kutigi	Kaolinite, Quartz, Feldspar and Illite	Akhirevbulu et al. (2010a,b)
Ubakala	Montmorillonite, Kaolinite, Quartz, Biotite, Calcite and Feldspar	Apugo-Nwosu et al. (2011)
Maiduwa	Montmorillonite, Kaolinite, Quartz and Illite	Dewu et al. (201 la,b)
Pindiga	Montmorillonite, Quartz and Graphite	Ahmed et al. (2012a,b)
Kaduna &Sokoto	Calcium-Smectites. Illite, Chlorite, Kaolinite,	Omole et al. (2013)
llorin	Kaolinite, Quartz, Rutile. Anatase, Microcline and	Ojo et. al., (2014)
Abbi	Montmorillonite, Kaolinite, Illite and Chlorite	Akinade and Afolabi (2015a,b)
Abakaliki	Montmorillonite, Kaolinite, Quartz, Calcite,	Nweke et al. (2015)

Table 2.2. Elemental analysis of some clay deposits in Nigeria.

References	Location	SiO_2	AI_2O_3	Fe_2O_3	MgO	CaO	K_2O	Na_2O	TiO_2	P_2O_S	LOI
Oyawoyeand 11 irstf 1 9 64)	Ropp	47.38	21.27	10.66	0.42	0.78	0.08	0.12	—	—	9.60
Ademibawa(1999a,b)	Pindiga	53.06	12.09	2.71	1.10	1.30	1.25	6.40	1.53	—	20.19
Jamcsctal.(2008)	Yola	61.35	14.09	7.14	0.87	0.12	1.05	1.15	1.453	0.06	12.23
Osaborctal.(2009)	Odukpani	47.52	24.01	2.38	0.188	0.038	—	1.78	—	—	12.00
Akhirevbulnetal.(201 Oa.b)	Kutigi	66.00	26.87	0.99	—	—	—	—	1.45	—	—
LawalandAbdullahi(2 010)	Lokoja	27.18	13.76	5.82	—	1.17	2.68	—	0.71	—	—
Mark(2010)	Ibere	52.06	27.87	3.25	1.43	0.34	2.92	0.38		—	9.2
	Oboro	60.21	19.05	3.78	1.50	0.30	2.16	0.42			-10.2
Olokodeetal.(2010)	Ajebo	46.40	34.00	2.49	0.04	0.02	0.08	0.03		0.04	17.70
Abdullahietal.(201 la, b)	Fika	35.17	13.05	7.35	6.17	10.36	1.69	0.06	0.64	0.31	15.73
Dewuetal.(2011 a,b)	Pindiga	53.00	18.00	4.68	2.60	0.67	2.28	0.6 1	0.90		15.12
	Futuk	46.76	18.40	8.17	2.34	0.57	2.59	0.45	0.70		14.82
	Arawa	52.80	20.80	7.53	2.95	0.77	2.61	0.28	0.67		1 5.63
Dewuetal.(2012)	Ngalda	—	7.32	—	2.71	2.68	—	1.25	0.45	—	9.73
	Maiduwal	—	4.64	—	3.56	5.59	—	2.43	0.28	—	8.77

	Maiduwa2	—	6.5 I	—	4.19	5.07	—	2.04	0.28	—	9.24
Osadebeetal.(201 1)	Okada	55.77	20.60	0.70	0.20	0.30	0.30	2.0	1.15	0.012	16.80
Apugo-	Ubakala	69.60	16.00	2.99	0.156	0.22	0.59	0.06	2.64	—	—
Ahmedetal.(2012a,b)	Pindiga	46.90	15.00	24.15	—	2.46	3.71	3.52	2.15	—	6.63
Obaje(2013)	New Marte	24.21	60.05	0.03	3.02	0.60	1.01	1.98	—	—	9.10
	Dikwa	26.30	58.40	0.01	3.22	0.45	0.98	2.01	—	—	7.71
Olugbengaetal.(2013)	Niger-Delta	47.40	20.97	5.73	9.48	4.23	0.98	—	1.18		—
Nwosuetal.(2013)	Udi	53.20	5.91	0.44	—	0.01	0.12	1.42	—	—	4.00
Aramideetal.(2014)	I fon	56.77	27.46	1.32	1.96	0.18	0.04	1.62	—		10.27
	Ipetumodu	54.82	25.90	1.44	2.08	0.12	0.20	1.57	—	—	11.64
	Iseyin	59.42	35.88	2.42	1.40	0.17	0.04	0.09	—	—	1 1.66
Nwekeetal.(201 5)	Abakaliki	58.96	25.08	4.67	2.02	5.42	1.40	1.98	2.10	—	—

The mineralogical and chemical analysis done by most researchers on Nigerian clays has largely been on the determination of the oxide components of the montmorillonite that make up the clay deposits and quantifying it. Silicon dioxide. SiO_2 and Aluminum Oxide, $A1_2O_3$ are the major oxide of the clay deposit and the $A1_2O_3$ to SiO_2 ratio ranges from 0.23 to 2.48 which compares favorably with standard Wyoming clay ratio of 0.38.

Some clay samples obtained from deposits in Nigeria has been observed to contain impurities in its raw form hence the need for beneficiation(James et al., 2008; Obaje, 2013). Beneficiation is simply a procedure for removing impurities or associated minerals that are not needed thereby improving the quality of the bentonite clay (Olugbenga et al., 2013). Beneficiation can be done using sodium salt such as sodium carbonate (Na_2CO_3) or sodium hydrogen carbonate($NaHCO_3$)which allows for the conversion of the mainly calcium montmorillonite clays to sodium montmorillonite via an ion exchange mechanism. Furthermore, the beneficiation method used in treating the raw clay does play an important role in enhancing the quality of the resulting clays.

It cannot be said precisely if regional distribution of clays in Nigeria play an important role in the mineralogy, elemental composition and performance of these clays since not all deposits of clay have been studied. The mineralogy of these clay deposits could be tied to the geolog}' of the environment (basin) from which they were obtained. A broad characterization of Nigerian clay deposits is still required as well as the partitioning of the compositional elements and spatial distribution of the elements. This is necessary for subsequent treatment and processing.

CHAPTER THREE

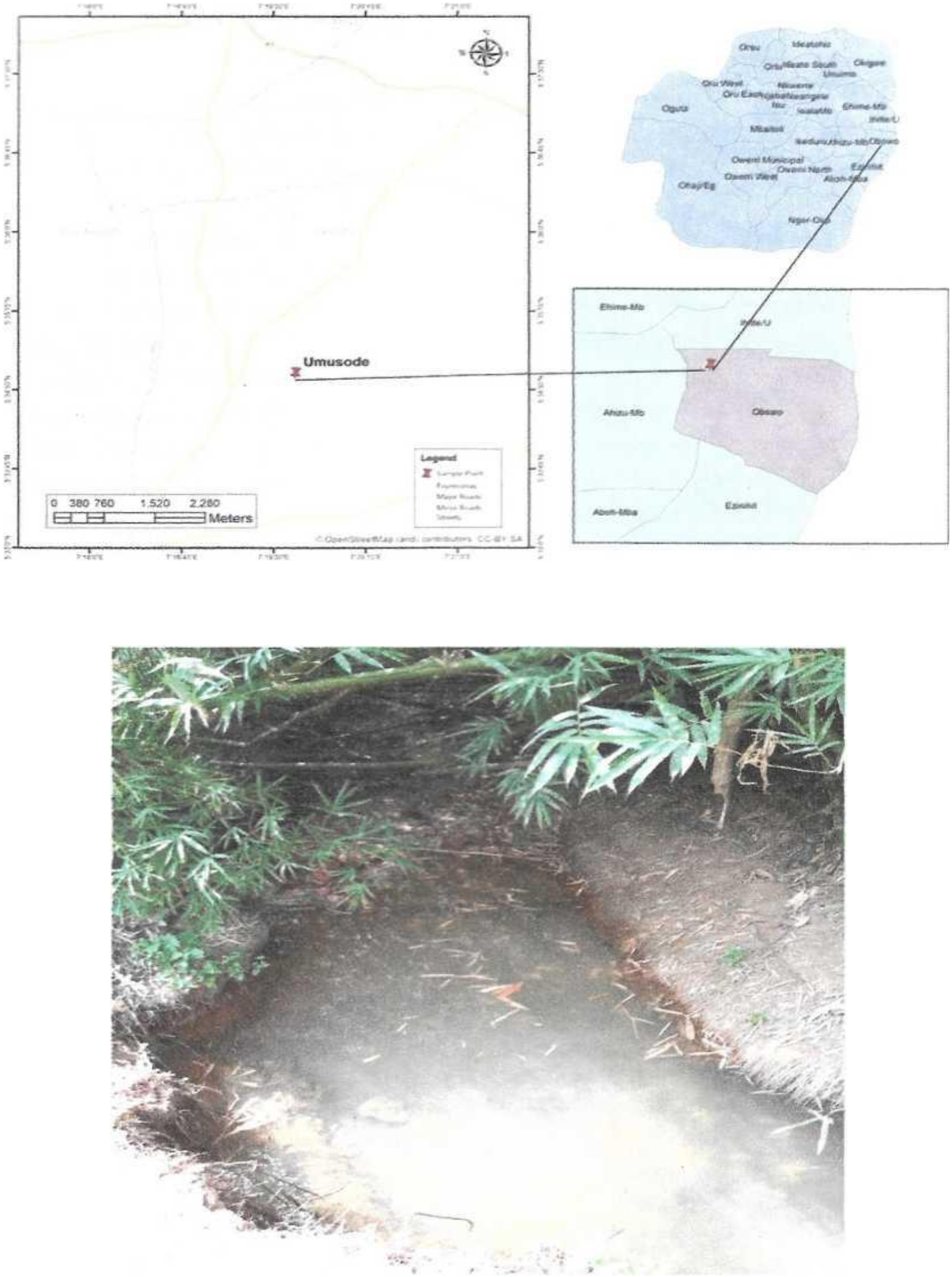
3.0 MATERIALS AND METHODS

3.1 Materials

3.2 Study area

The study area is located at lyinwaogba Umuosode Alike Ikenanzizi Obowo Local Government Area of Imo State. The area is situated in a complex geological setting. The stratigraphic units observed include: the Benin Formation, The Ogwashi - Asaba Formation, the Bende - Ameki Formation, Imo Shale Formation, Nsukka Formation and Ajali Formation. (Akaolisa & Selemo, 2009). The Benin Formation is overlain by lateritic overburden and underlain by the Ogwashi - Asaba Formation which is in turn underlain by the Ameki Formation of Eocene to Oligocene age (Mbonu et al., 1990). The Benin Formation consists of coarse - grained gravelly sandstones with minor intercalations of shales and clay. The sand units which are mostly coarse grained, pebbly and poorly sorted, contain lenses of fine grained sands (Onyeaguocha, 1980; Short & Stauble, 1967).

The specific stream where the clay samples were collected is located geographically between latitude 5.5774167 °N and longitude 7.3279617 °E with altitude of 137.30 meters. The stream is a small one with length of < 100 m and depth of < 100 cm (Figure 3a). The clay soils in the stream serve as a filter for the stream water purification (Figure 3b).



(a)


Clay

(b)

Figure 3.0. Photographs of the study area showing, (a) entire stream where the clay was collected; (b) clay soils at the bottom of the stream

3.3 Sample collection

Sampling sites were carefully selected based on physiographic zones of the area with samples collected to properly represent the parent materials. Sampling design involves the selection of the most efficient method for choosing the samples used to estimate the properties of the population. Probability sampling was adopted that selects sampling points along the water course. The clay soils were retrieved from the area using a shovel and were then plastic wrapped and air tight.

Fiveclay samples were collected randomly around Ikenanzizi Obowo Local Government Area of Imo State, South Eastern Nigeria (Figure 3.1). Samples were taken at an average depth of 90cm below the water surface.

Figure 3.1. Photograph of clay samples in the lab for analysis

3.4 Sample preparation and analysis

The samples were characterized on the basis of their mineralogical and elemental (trace and oxides) composition. Each of the samples was split into two halves with each half used for mineralogical and elemental analysis. The compositional and mineralogical analyses were done using X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF) equipment respectively.

3.5 Qualitative and quantitative XRD

The samples were prepared for XRD analysis using a back loading preparation method (Abdoulaye et. al., 2019). They were analysed using a PANalytical

X'Pert Pro powder diffractometer with' X'Celerator detector and variable divergence- and receiving slits with Fe. filtered Co-Ka radiation. The phases were identified using X'Pert Highscore plus software. The receiving slit was placed at 0.040^{s}. The counting area was from 5 to 70° on a 29 scale. The count time was 1.5 s. The temperature-scanned XRD data were obtained using an Anton Paar HTK 16 heating chamber with Pt heating strip.

The relative phase amounts (weight %) was estimated using the Rietveld method (Autoquan Program). Amorphous phases, if present were not taken into consideration in the quantification.

3.6 Scanning electron microscopy

Morphology and microanalysis of the clay and composite samples were determined using ultra-high resolution field emission scanning electron microscope (UHR-FEGSEM) equipped with energy[7] dispersive spectroscopy (EDS). The pulverized clay samples were previously gold coated. The samples were studied using ultra-high resolution field emission scanning electron microscope (UHR-FEGSEM) equipped with energy dispersive spectroscopy (EDS). Particle images were obtained with a secondary electron detector.

3.7 Chemical analysis

3.8 X-Ray Fluorescence (XRF)

The major elements were determined by X-ray fluorescence with an ARL® 9800 XP spectrometer. The pulverized clay samples were mixed with lithium tetraborate for chemical analysis. The ignition loss was measured by calcinations at 1000 °C.

3.9 Fourier Transform Infra-Red Spectroscopy (FTIR)

Infrared (IR) spectroscopy was performed in Attenuated Total Reflectance(ATR) mode with a Fourier Transform Bruker Alpha spectrometer equipped with a diamond crystal in the range of wavelengths from 400 $cm^{'1}$ to 4000 cm^{-1} (Abdoulaye et. al., 2019).

3.10 Data Analysis

The obtained., were analyzed for mean and standard deviation. One factor analysis of variance (ANOVA) was used to determine significant differences at $p < 0.05$. All data analysis were conducted using Microsoft Excel 2013.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Physicochemical characteristics of clay samples

Clay mineral characterization is important to identify the engineering and physico-chemical behavior. The physicochemical properties of clay samples are presented in Table 4.1. The pH measures the acidity and alkalinity of the clay samples and relies upon the mineral arrangement of the parent material, and the enduring responses experienced by that parent material. The pH ranged from 1.91 in sample C to 2.89 in sample D, indicating that the clay samples are ultra-acidic (USDA, 1993). The ultra-acidity of the clay could be due to the use of fertilizer in the area as ammonium (NHty) composts respond in the soil by the procedure of nitrification to shape nitrate (NOs'). and in the process discharge FT particles. Furthermore, the formation of Kaolinite is favorable at very low pH (~ 3) (Uzoegbu and Agbo, 2019).

Electrical conductivity (EC) is an estimation of the broke down material in a fluid arrangement, which identifies with the capacity of the material to direct electrical flow through it (Enyoh & Isiuku, 2020). The higher the dissolved material in a water or soil sample, the higher the EC will be in that material.

According to the United States Department of Agriculture (USDA), electrical conductivity (EC) of soils is classified as: non-saline (0 µS/cm to 2000 µS/cm);slightly saline (2100 to 4000 µS/cm), moderately saline (4100 µS/cm to 8000 µS/cm), strongly saline (8100 µS/cm to16,000 µS/cm); and very saline (>16,000 µS/cm). The obtained EC ranged from 735 to 2276 μS/cm, indicating non-saline to slightly saline at sample D.

Table 4.1. Physicochemical properties of clay samples

	A	B	C	D	E
PH	2.02^{a}	2.48 ^{a}	1.91^{C}	2.89^{d}	2.65^{d}
EC (pS/cm)	735 ^{a}	833^{b}	2276^{C}	509 ^{d}	538 ^{d}
LOI (%)	4.77 ^{a}	4.99 ^{a}	4.84 ^{a}	4.75 ^{a}	5.32 ^{b}
CEC (meq/100 g)	25.72^{a}	24.97 ^{b}	26.49°	24.1 1^{b}	24.93 ^{b}
RI	1.45 ^{a}	1.62 ^{b}	1.60 ^{b}	1.68 ^{b}	1.57b
Density	1.708 ^{a}	1.736 ^{a}	1.785 ^{b}	1.742°	1.725 ^{a}
SG	2.74 ^{a}	2.68 ^{a}	2.96 ^{b}	2.72 ^{a}	2.76 ^{a}
Sand (%)	6.98 ^{a}	6.61 ^{b}	4.93°	5.50 ^{d}	6.69 ^{b}
Silt (%)	10.12 ^{a}	7.62 ^{b}	10.65^{a}	11.74°	5.21^{d}
Clay (%)	82.90 ^{a}	85.87^{b}	84.42 ^{b}	82.76 ^{a}	88.10 ^{b}
Textural class	Clay	Clay	Clay	Clay	Clay

The values with the same alphabet in rows are not significantly different while values with different alphabet are significantly different ($p > 0.05$).

The loss on ignition of the selected clays used in this study lie in the range of 4.75 % - 5.32 %, an indication that heating clays to 105°C results in loss of structural water from the clay. The reactions occurring in the clay materials include dehydration and dehydroxylation of soil used, therefore the obtained LOI of clay samples might imply that, they possess finer grains, high content of $A1_2O_3$ and could be more compact. Average quantities of LOI value obtained from clayed minerals ranged from 6.087 to 12.933% in Kenya (Ombaka, 2016), from 10.27 to 11.66 % for clay samples from Southwestern Nigeria (Aramide et al., 2014) which are higher than the current study while comparable to clay samples in Northern Tunisia reported by Sghaier et al., (2014).

The cation exchange capacity or the CEC level is the proportion of isomorphic replacements that happen with the clay minerals (Mitchell, 2005). The isomorphic replacements are expected to tetrahedral and octahedral sheets containing cations rather than a glorify structure (for example aluminum in the spots of silicon, magnesium rather than aluminum, and so on.). At the point when the isomorphic replacement happens, various cations are supplanted with different cations of different valances inside the structure to keep up harmony inside the clay structure (Firoozi et al., 2016). The CEC value is a manual for gauge the overwhelming clay mineral. Also, the CEC shows how stable the clay mineral is to isomorphic replacement. When the quantifiable CEC increases the isomorphic replacement inside the clay mineral also increase. The highest and lowest CEC were recorded in clay sample C (26.49 meq/100 g) and D (24.11 meq/100 g) which falls within the standard range for Kaolinite (10-150 meq/100 g) (Uzoegbu & Agbo, 2019).

The complex refractive index of soil particles is central to the appreciation of light associations with soil and the estimation of amounts, for example, reflectance and albedo (Ishida et al., 1991). The recorded refractive index for the clay samples ranged from 1.45 to 1.68, this is typical for clay minerals (Mukherjee, 2013). For most clay minerals, the specific gravity is within the range from 2 to 3.3 (Mukherjee, 2013). The current study obtained a specific gravity which ranged from 2.68 to 2.96.

4.2 Scanning Electron Microscopy and Energy Dispersive Analysis (SEM-EDS)

SEM-EDS images of the clay fraction are shown in Figures 4.1-4.5. This SEM imaging of clay fractions (A to E) depicts a typical structure of conventional quartz and kaolinite. The weakly resolved structures are probably due to the presence of other crystalline structures as impurities in the sample. The pseudo- hexagonal and stratified structures of kaolinite are further observed.

Figure 4.1.SEM-ED Sresult of clay sample A

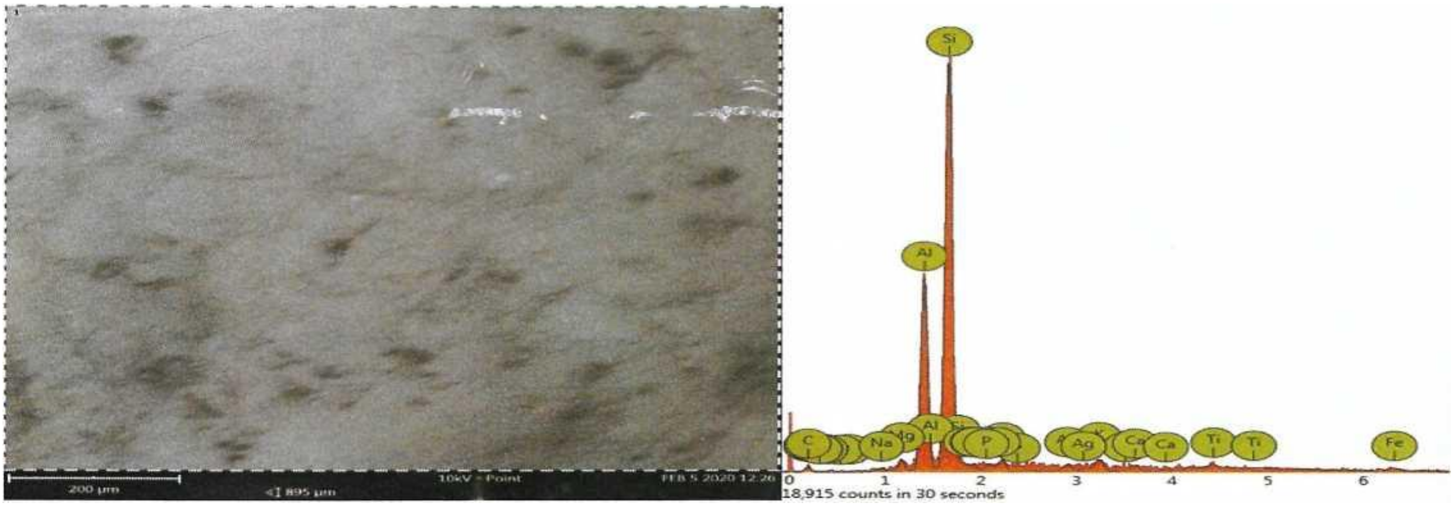


Figure 4.3.SEM-EDS result of clay sample C

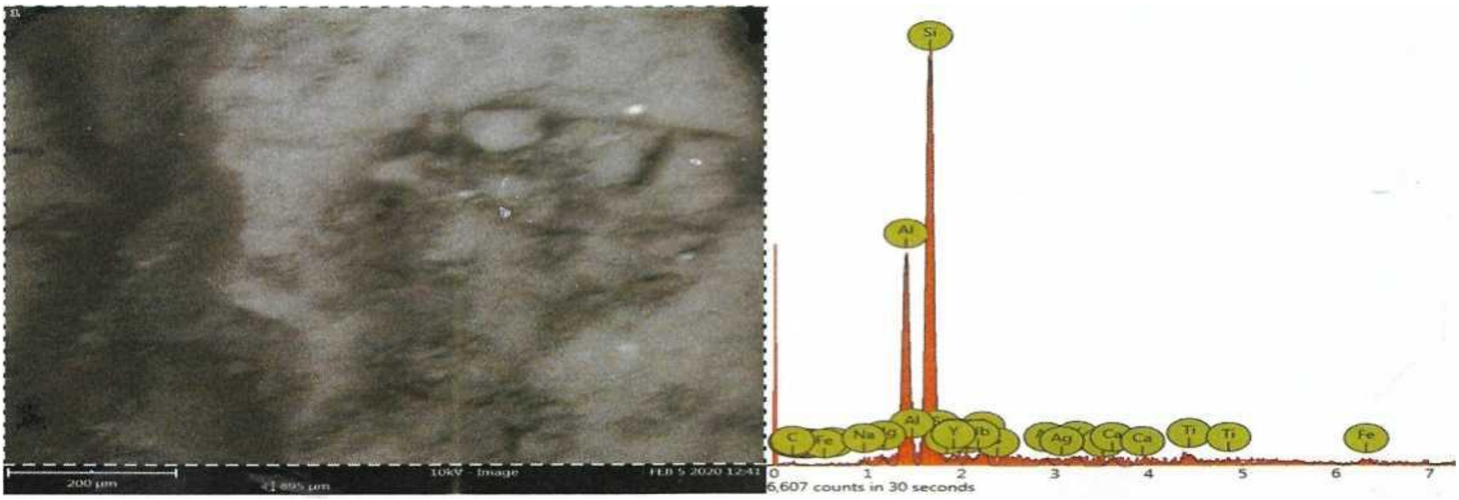


Figure 4.4.SEM-EDS result of clay sample D

4.3 FTIR analysis of clay samples

The results for the Fourier transform infrared analysis of the plant extracts are presented in Figures 4.6- 3.10,and summarized in Tables 4.2-4.6. The FT-IR spectrum was used to identify the functional groups and mineralogy of the soil based on the peaks values in the region of Infra-Red radiation either directly or by inference. When the soil samples were passed into the FT-IR, the functional groups of the components was separated based on its peaks ratio. The associated changes in the spatial arrangement of the groups involved are reflected in the infrared spectrum as additional bands and added complexity.

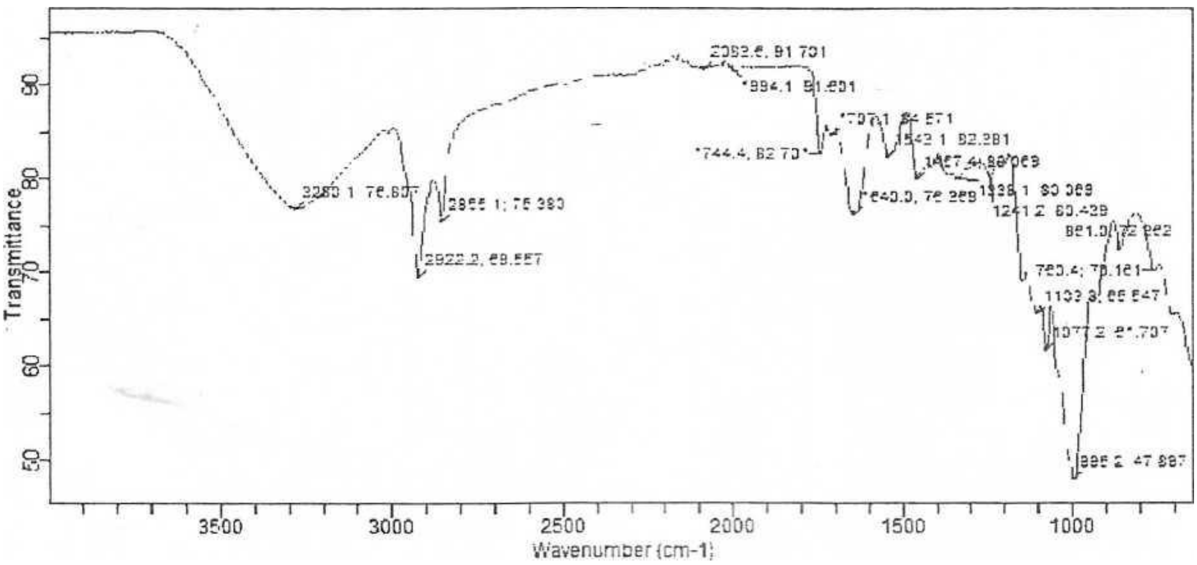


Figure 4.6. FTIR spectra for sample A

Table 4.2. Infrared band position and assigned mineralogy of clay sampleA

Peaks (cm^1)	Functional group
3280.2	Kaolinite
2922.2	C-H Stretching
2855.1	C-H Stretching
2083.6	C-H Stretching
1994.1	C-H Stretching
1744.4	Kaolinite
1761.1	Kaolinite
1640.0	H-O-H bending of water
1543.1	N-0 Stretching
1457.4	C-H Stretching
1338.1	C-H Stretching
1241.2	Si-O Stretching
1103.3	Si-O Stretching
1077.2	Si-0 Stretching
995.2	Al-OH bending vibration
861.0	Si-0 Quartz
760.4	Si-0 Quartz

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Table 4.3. Infrared band position and assigned mineralogy of clay sample B

Peaks (cm^4)	Functional group
3276.2	Kaolinite
2922.2	C-H Stretching
1628.8	Kaolinite
1543.1	N-0 Stretching
1408.9	C-H Stretching
1338.1	C-H Stretching
1241.2	Si-0 Stretching
1148.0	Si-0 Stretching
1103.3	Si-0 Stretching
1077.2	Si-O Stretching
995.2	Al-OH bending vibration
928.1	Al-OH bending vibration
861.0	Si-O Quartz
760.4	Si-0 Quartz

Table 4.4. Infrared band position and assigned mineralogy of clay sample C

Peaks (cm^1)	Functional group
3302.4	Kaolinite
2926.2	C-H Stretching
2154.4	C-H Stretching
1710.9	Kaolinite
1621.8	Kaolinite
1401.5	C-H Stretching
1043.3	Si-0 Stretching
924.4	Al-OH bending vibration
868.3	Si-0 Quartz
816.3	Si-0 Quartz

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Table 4.5. Infrared band position and assigned mineralogy of clay sample D

Peaks (cm^1)	Functional group
3265.1	Kaolinite
2922.2	C-H Stretching
2109.7	C-H Stretching
1982.1	C-H Stretching
1636.3	Kaolinite
13*75.4	e-H Stretching
1148.3	Si-0 Stretching
1077.2	Si-0 Stretching
1013.2	Si-0 Stretching

Table 4.6. Infrared band position and assigned mineralogy of clay sample E

Peaks (cm[1])	**Functional group**
3283.2	Kaolinite
2922.2	C-H Stretching
1636.3	Kaolinite
1453.4	C-H Stretching
1379.1	C-H Stretching
1241.2	Si-0 Stretching
1148.0	Si-0 Stretching
1077.2	Si-O Stretching
1013.8	Si-0 Stretching

The infrared spectrum of the clay fractions A-E are summarized in Table 4.2 tc 4.6. The clay samples generally showed Kaolinite, C-H Stretching, Si-0 Stretching. A1-0H bending vibration and Si-0 Quartz. The stretching band at 3283.2 cm^{-1} to 3302.4 cm”^{1} and around 1638.9 cm^{-1} to 1710 cm^{-1}indicate the presence of kaolinite (El Kasmi et al., 2016).Generally, the interatomic bonds Si-0 and Al-0 which indicate the alumino-silicate nature of sample (Farmer. 1974; Murray, 2006; Abdoulaye et al., 2019) correspond with the band between 600 and 1200 cm'^{1}. The absorption bands around 861.0 cm'^{1} to 760.4 cnf’are due to Si-0 stretching band for quartz[275](Tables 4.5 to 4.10). The C-H stretching band in the clay mineral may be due to the intercalationbetween the clay with soil organic material containing aliphatic CH group. In this process of intercalation the reactive guest molecules enter the interlamellar space and break up the hydrogen bonds and new bonds are formed.

4.4 Chemical composition

4.5 Trace elemental composition

The results of trace elemental analysis of samples A to E conducted with EDXRF are shown in Figures 4.11-4.15. The spectra were similar for all clay samples. The highest metal in the clay samples was Fe, Zrand Sr, and trace amount of Ni, Pb, Zn, Mn, Ga and Cu. High concentrations of the metal in the natural kaolin negatively affect catalyst performance. Thus, the chemical composition of the clayey fraction makes it an excellent raw material for

producing zeolite for catalysis after further purification to improve its catalytic properties.

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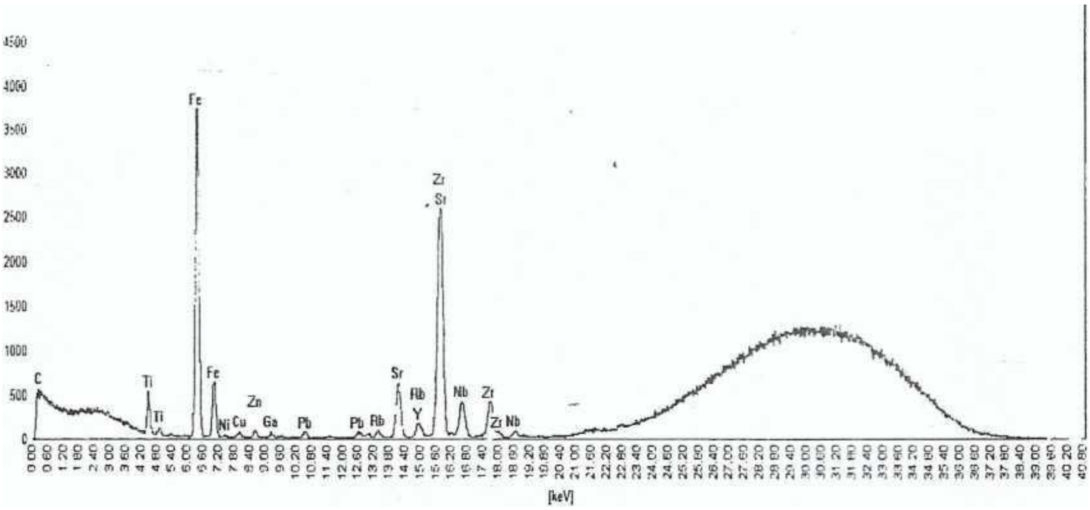

Figure 4.11. EDXRF scans for clay sample A

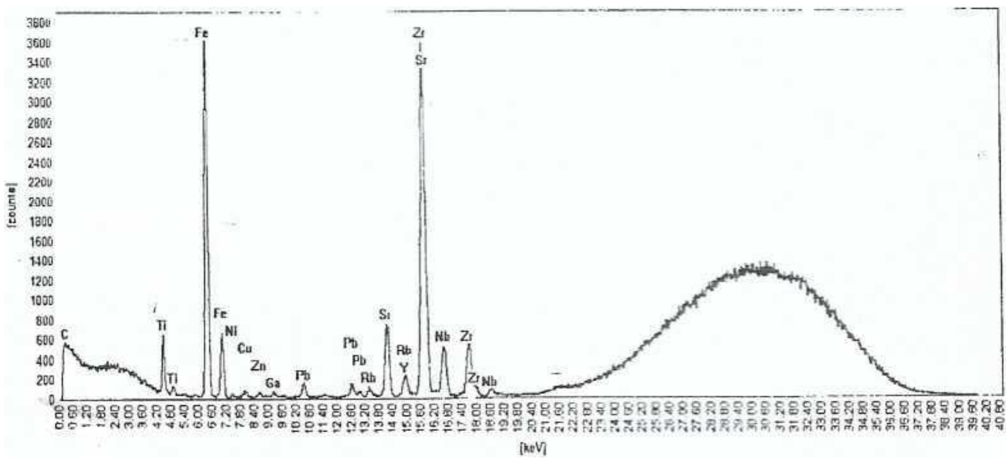

Figure 4.12. EDXRF scans for clay sample B

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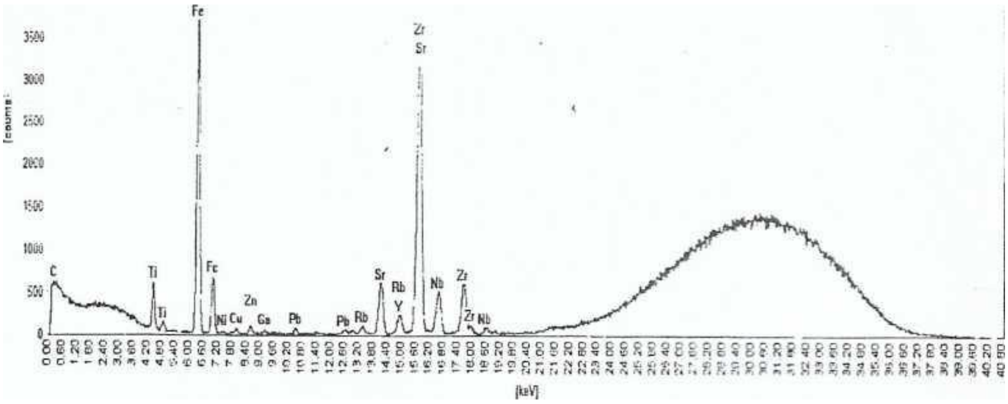


Figure 4.13. EDXRF scans for clay sample C

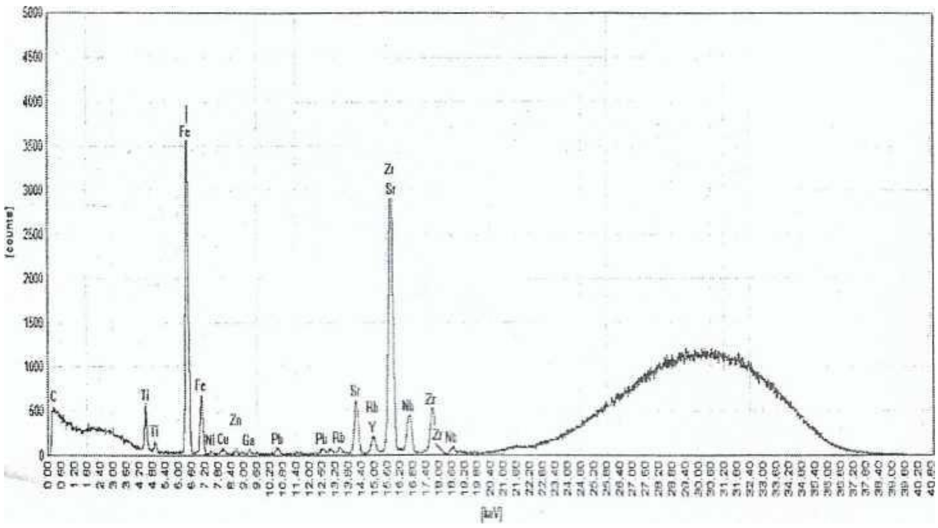


Figure 4.14. EDXRF scans for clay sample D

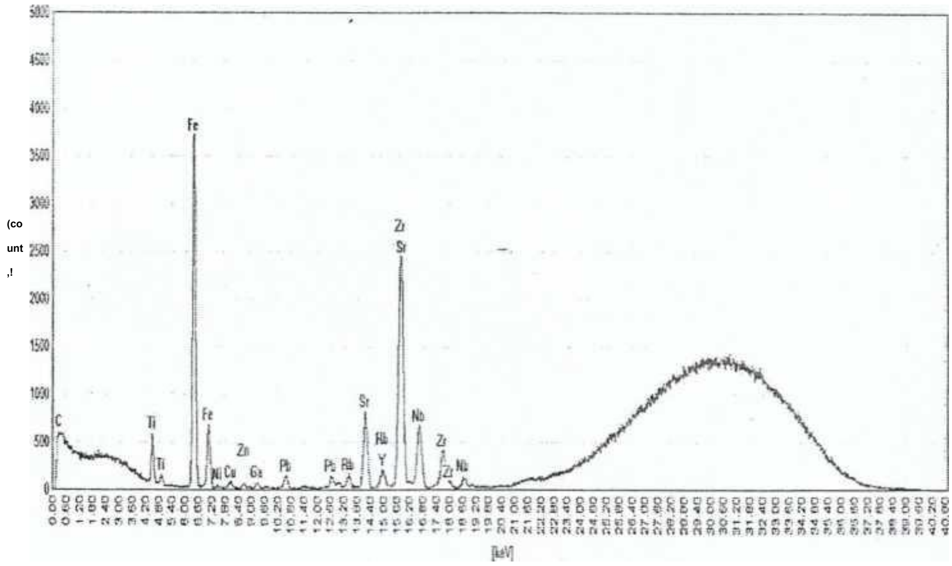


Figure 4.15. EDXRF scans for clay sample E

4.6 Major Elemental composition

Elemental analyses of clays have always revealed the class of alumino-silicates to which the analyzed material belongs. For example, smectites commonly give different elemental compositions from kaolinites. In a study involving clays, it is important to establish the elemental constitution of the solid because surface and bleaching properties of clays and clay material depend on the elements present. The averaged data obtained in the elemental analyses of selected clays are in Table 4.7. The elements present in clays have been presented as relative percentages of the elements expressed as oxides in the entire sample.

The clay samples had more than 50% silicon dioxide except for clay sample D. This is in correlation with the pH as sample D had the least acidity and diagenetic paths for theclay may be different. High silica/quartz content gives higher chances of exposing hydroxyl groups and adsorption of water on silica which causes the clays to be acidic. The small differences in silica content indicated that the parent rocks in these sets of deposits are very similar because of similarity in the parent rock which weathered to give the clays. Similarly aluminum oxides were lowest in claysample D (4.07 %) than all other claysamples (23.53 to 25.13 %). Aramideet. al., (2014) obtained similar results for

clay samples from South western Nigeria.

All clay samples had low iron oxide concentrations except for sample D (67.22 %). The presence of higher concentrations of iron oxides in sample D deposit and all other deposits sampled and may indicate higher surface acidities and bleaching capacities when acid-leached than other clays studied. All other elements were in low concentrations for all samples. The low values of alkaline oxides (K_2O) in clay mineral samples implied presence of low percentage of flux minerals. The very low presence of Magnesium oxide in the clay samples suggests little or no presence of a talc phase (Marcos and Rodriguez, 2010).

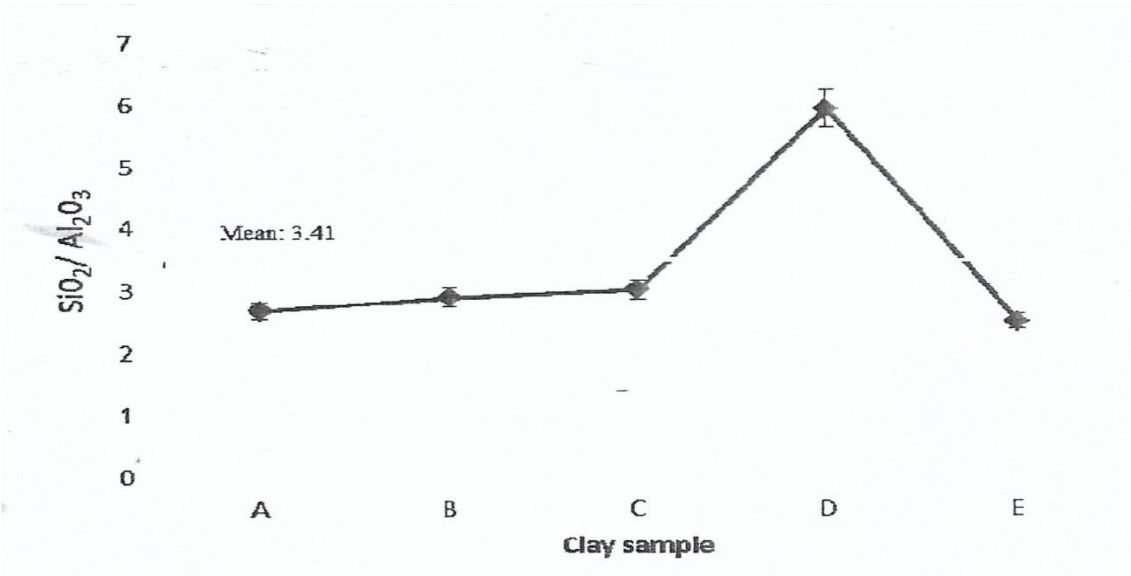
Table 4.7.Major elemental composition of clay samples

Element	Elemental composition (%) •						
	A	B	C	D	**E**	Mean	SDV
Fe_2O_3	2.73	2.30	2.47	67.224	2.53	15.45	28.94
SiO_2	65.17	68.29	70.9	24.16	62.97	58.30	19.32
AI7O3	24.15	23.54	23.53	4.07	25.13	20.08	8.98
MgO	3.36	2.4	4.02	0.202	2.07	2.41	1.46
P2O5	0.17	0.19	0.2	0.8	0.20	0.31	0.27
SO_3	0.54	0.56	0.6	1.81	0.18	0.74	0.62
TiO_2	1.58	1.82	1.87	0.02	1.67	1.39	0.78
MnO	0.01	0.02	0.02	0.04	0.01	0.02	0.01
CaO	0.04	0.03	0.05	0.19	0.08	0.08	0.07
K_2O	0.24	0.19	0.21	0	0.34	0.20	0.12
CuO	0	0	0	0.01	0	0.00	0.00
ZnO	0.02	0.01	0.02	0.01	0.01	0.01	0.01
Cr_2O_3	0.02	0.01	0.01	0.03	0.01	0.02	0.01
V_20_5	0.04	0.03	0.03	0	0.04	0.03	0.02
As_2O_3	0	0	0	0.02	0	0.00	0.01
PbO	0.02	0.03	0.01	0.02	0.03	0.02	0.01
Rb_2O	0	0	0	0 00	0.00	0.00	0.00
Ga_2O_3	0.01	0.01	0	0	0.01	0.01	0.01
NiO	0	0	0	0.00	0.00	0.00	0.00
Cl	0.06	0	0.09	0.07	0.04	0.05	0.03
ZrO_2	0.19	0.22	0.24	0.21	0.01	0.17	0.09
Bao	0	0.01	0	0	0.01	0.00	0.01
Ta_2O_5	0.01	0.01	0.01	0.02	0.02	0.01	0.01
$W0_3$	0.07	0.05	0.07	0.05	0.04	0.06	0.01
Br	0	0	0	0	0	0.00	0.00
SrO	0.44	0.45	0.41	0.41	0.49	0.44	0.03
CeO_2	0.02	0.02	0.02	0.02	0.02	0.02	0.00
ThO_2	0	0	0	0	0.00	0.00	0.00
Y_20_3	0	0	0	0	0.00	0.00	0.00
Nb_2O_5	0	0	0	0	0	0.00	0.00

4.7 Silica to Alumina ratio

In Figure 4.16, the results for the Silica to Alumina ratio (SiO_2/Al_2O_3) of different samples were presented. The result showed that SiO_2/Al_2O_3 ratios ranged from 2.51 to 5.94 with mean of 3.41. These ratios are higher than those of standard kaolinite reported to be in the range of 1.73 and 1.8. These SiO_2/Al_2O_3 ratios values are probably due to an abundant quartz contents and interbedded mineral pyrite/anatase (Zaki et al., 2008) and the presence of free quartz in the samples studied. Similar results were reported by Abdoulaye et al., (2019) for clay samples collected from Niger. The order for the ratios were E < I

A<B<C<D.



4.8 XRD analysis

XRD patterns of samples (A-E) are shown in Figures 4.16 to 4.20. The XRD mineralogical data indicates the presence of some mineral phases. The limited number of minerals measured could be as a result of equipment detection limit, which could mean that low concentrations are hard to be picked up by the equipment or could be due to the dominance of these mineral phases in the samples, given that they are clay samples (Moore & Reynolds, 1997).These patterns generally indicated the characteristic peak of quartz, kaolinite, anatase and pyrite in the clay samples.

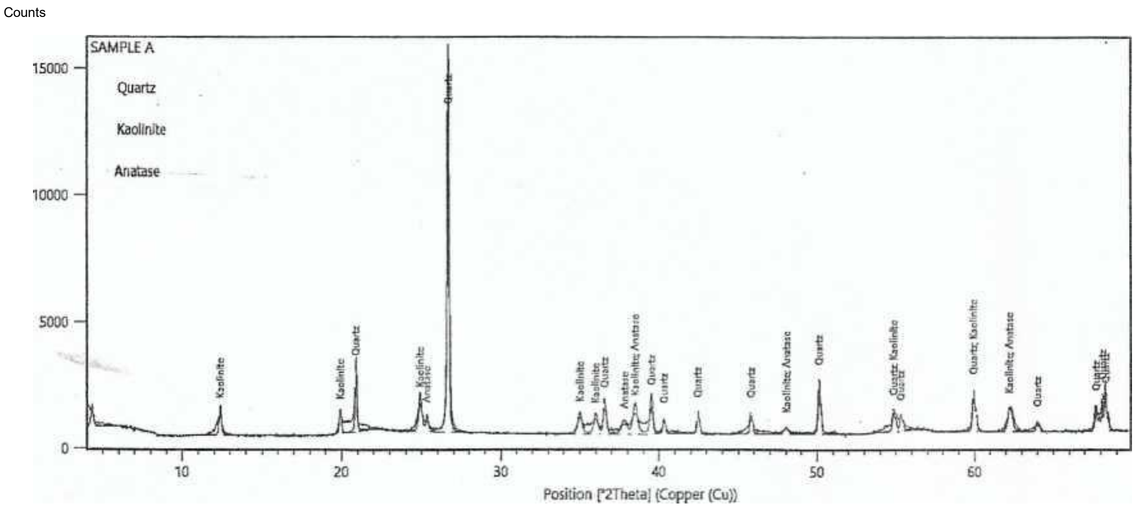


Figure 4.17: X-Ray diffraction pattern of Sample A clay material.

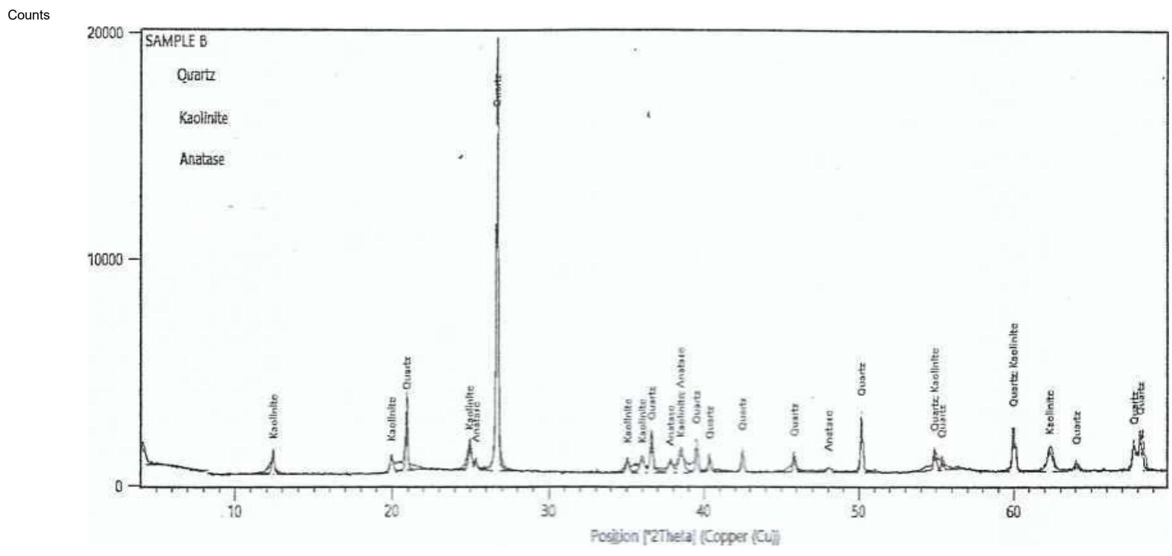


Figure 4.18: X-ray diffraction pattern of Sample B clay material.

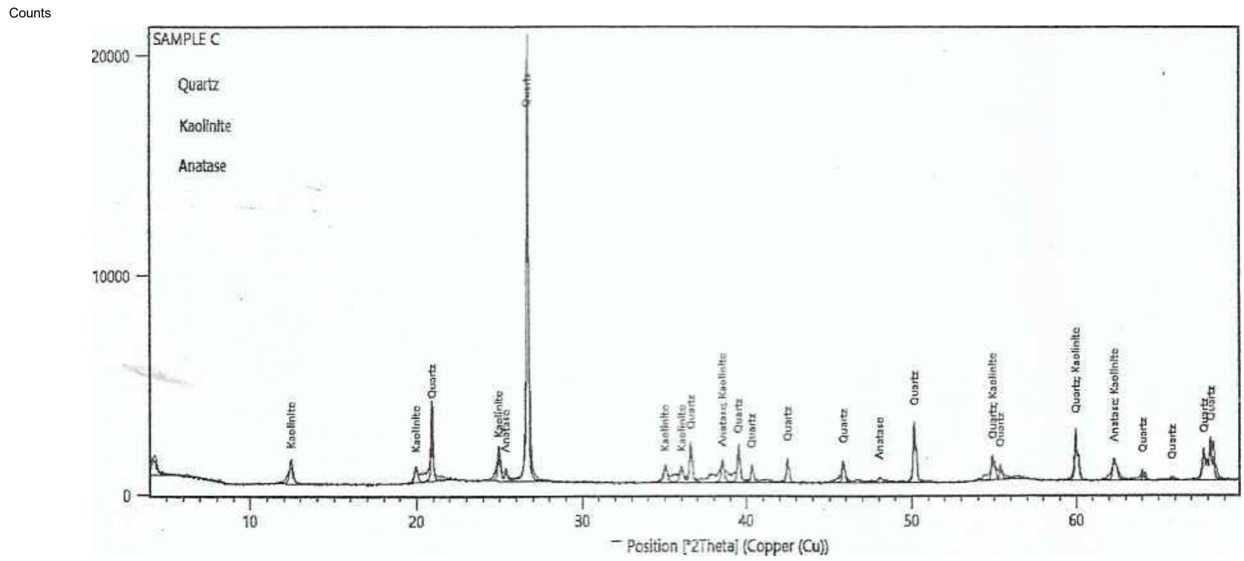


Figure 4.19: X-ray diffraction pattern of Sample C clay material.

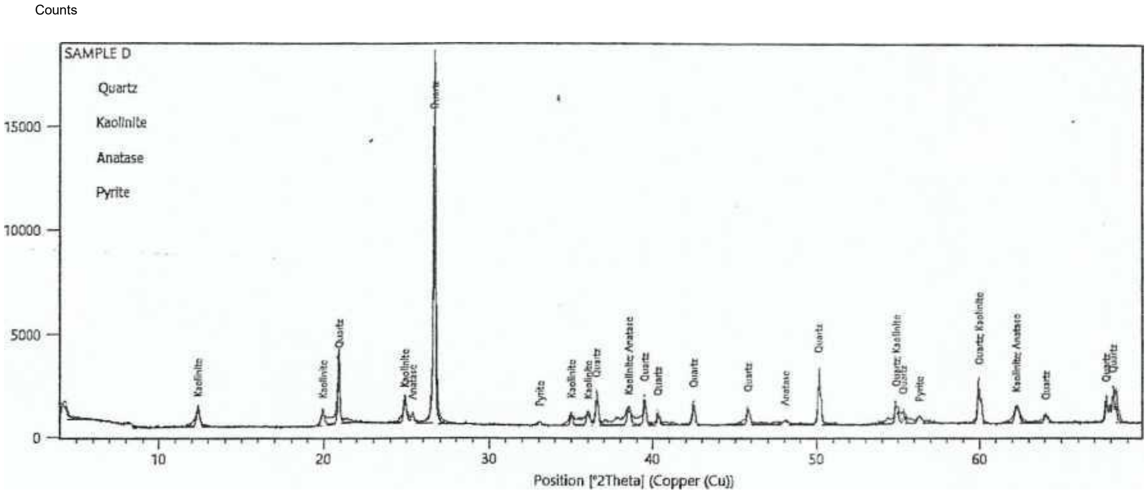


Figure 4.20: X-ray diffraction pattern of Sample D clay material.

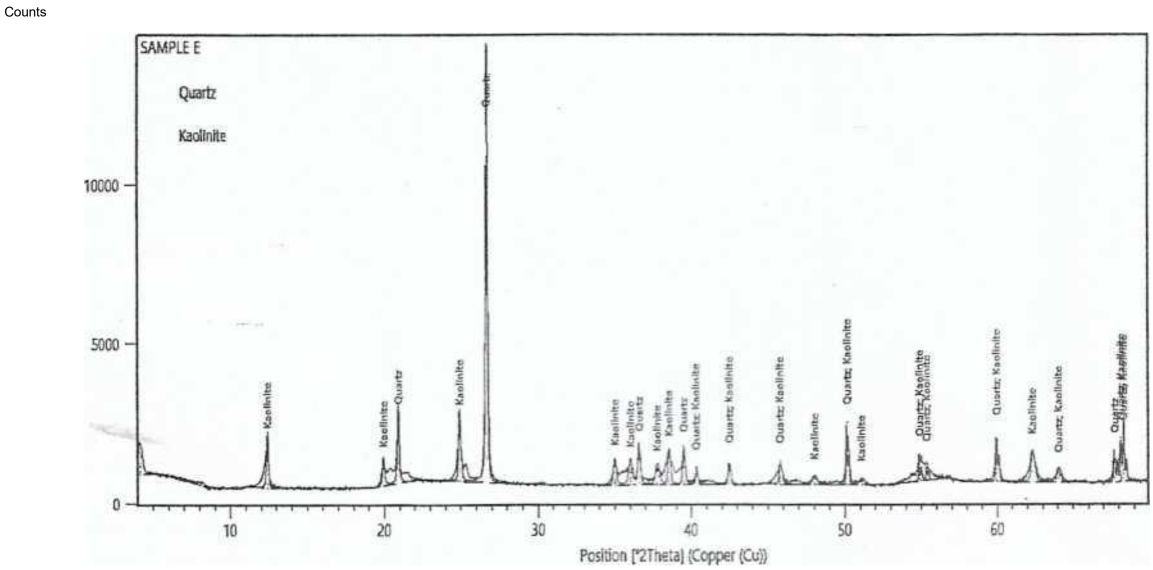


Figure 4.21: X-ray diffraction pattern of Sample E clay material.

The distribution summary of different phases present in the clay samples is presented in Table 4.8.

Table 4.8.XRD Result of the raw clay samples showing the quantity of different phases present

Samples	Quartz (%)	Kaolinite (%)	Anatase (%)	Pyrite (%)
A	42.42[a]	42.42[a]	15.15[a]	o.oo[a]
B	55.00[b]	33.00[b]	15.00[a]	o.oo[a]
C	54.00[b]	32.00[b]	14.00[b]	o.oo[a]
D	38.00[c]	31.00[b]	14.00[b]	7.00[b]
E	41.00[a]	59.00°	o.oo[c]	o.oo[a]
Mean	46.08	39.48	11.63	1.4
Standard Deviation	7.85	11.83	6.52	3.13
%CV	17.04	29.96	56.06	223.57

The values with the same alphabet in columns are not significantly , different while those in different alphabet are significantly different (p > 0.05).

The distributions were; in sample A: quartz (42.42 %) / kaolinite (42.42 %) > anatase (15.15 %), in sample B: quartz (55 %) > kaolinite (33 %) > anatase (15 %), in sample C: quartz (54 %) > kaolinite (32 %) > anatase (14 %), in sample D: quartz (55 %) > kaolinite (33 %) > anatase (15 %), in sample D: quartz (38 %) > kaolinite (31 %) > anatase (14 %) > pyrite (7 %) while in sample E: quartz (41 %) > kaolinite (59 %). These showed that quartz and kaolinite were the most distributed phase in the clay samples while the anatase and pyrite could be impurities. Similarly, high weight %for quartz and kaolinite was reported by Umbugadu and Igwe (2019) for Panyam clays, North - Central Nigeria, for Mamu and Nsukka formation in Southeastern, Nigeria (Uzoegbu & Agbo,

2019) and Ifon, Ipetumodu and Iseyin clay samples in Southwest Nigeria by < Aramide et al., (2014). Although these studies also found other phases not found in the current study such as Microcline, Muscovite/Illite, Plagioclase/Albite. Hence, the clay from the study area is a candidate for the production of mullite fibber reinforced ceramic composite (Aramide et al., 2014).

CHAPTER FIVE

5.0 CONCLUSIONS AND RECOMMENDATION

A

5.1 CONCLUSION

The study undertaken here has dealt with the mineralogical and morphological characterization of clay from lyinwaogba Umuosode Alike Ikenanzizi Obowo Local Government Area of Imo State. This clay is mainly composed of kaolinite with a high quartz proportion of about. The kaolin character of the sample studied is confirmed by the X-Ray Diffraction and Infrared spectroscopy. The CEC, $SiO_2/A12O_3$ ratios and the loss on ignition values of the clay fraction is closed to the standard values despites the presence of free quartz as impurity. The pseudo-hexagonal and stratified structure of kaolinite was also observed by. Scanning Electron Microscopy. Altogether, the characteristics of the clay from lyinwaogba Umuosode Alike Ikenanzizi Obowo Local Government Area of Imo State are a good candidate as a support in the manufacture of industrial catalysts for a petroleum catalytic cracking operation and can be used also to produce good refractory materials for high temperature applications because of their high content of kaolinite.

5.2 RECOMMENDATIONS

- It is recommended that further research on economic beneficiation of the clean samples at lyinwaogba Alike Ikenazizi Obowo L.GA. of Imo State be carried out.
- Investigation on applications of the clay samples obtained from lyinwaogba Alike Ikenazizi Obowo L.G.A. be carried out.
- The Imo State government should as a matter of urgency look into the economic viability of the clay samples at lyinwaogba Alike Ikenazizi Obowo L.G.A. to ascertain a possible economic earning.
- Efforts should be made by Imo State Government to gazette the occurrence of the clay at lyinwaogba Alike Ikenazizi Obowo L.G.A with the Nigeria Mining Corporation and The Raw Material Research Development Council and Federal Ministry of Mining Steel and Power in order to put to record the existence of such natural deposit.

5.3 CONTRIBUTION TO KNOWLEDGE

- The existence of mineral clay deposit at lyinwaogba Umuosode Alike Ikenazizi Obowo Imo State has been investigated and basic information established.
- The economic values of the clay deposit have been exposed as to make revenue return to the government.

- The characterizations of the clay mineral deposit for economic beneficiation have equally been carried out.
- The possibility on further research of the mineral clay deposit at lyinwaogba Alike Ikenazizi Obowo of Imo State has been laid out.

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