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Mineralogical and Elemental Analysis of Clay Sample from Iyinwaogba Umuosode Alike Ikenanzizi Obowo Local Government Area of Imo State

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Abstract

This paper characterizes five clay samples from Iyinwaogba Umuosode Alike Ikenanzizi Obowo, Southeastern Nigeria. The characterization is based on their physicochemical characterization, mineralogy and elemental analysis using Scanning Electron Microscopy (SEM-EDS), Fourier Transform Infra-Red Spectroscopy (FTIR), X-Ray Diffraction (XRD) and Energy Dispersive X-Ray Fluorescence (EDXRF). The pH ranged from 1.91 to 2.89, loss on ignition ranged from 4.75 % - 5.32 %, cation exchange capacity ranged 26.49 meq/100 g to 24.11 meq/100 g, refractive index ranged from 1.45 to 1.68 while the specific gravity ranged from 2.68 to 2.96. The general data revealed that the primary constituents of the clay were kaolinite with high quartz content and average SiO_2 of 58.30±19.32 %. Altogether, the characteristics of the clay from Iyinwaogba 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

1. Introduction

Clays are materials that occur naturally made fundamentally out of fine-grained minerals, which is commonly plastic at fitting water substance and will solidify when dried or terminated [1,2]. Clay deposits or deposit comprise of the primary and secondary stages. The primary clays are framed as a leftover deposit in soil and caught at the site of arrangement while the secondary clays have been moved by water disintegration from their unique area and saved in another sedimentary deposit [3]. Clay deposit can be found in enormous lakes and marine bowls as a result of its amazingly low vitality sedimentary condition. The development of clay takes an extensive stretch of time which is because of what is known as chemical weathering of rocks which happens step by step, typically the silicate-bearing ones, by low centralizations of weakened solvents like carbonic acid [4]. The acidic dissolvable drains the upper endured layers and afterward travel through the enduring stone, and it is in this procedure of aqueous action that some clay minerals are framed. They have differing concoction structure contingent upon both the physical and chemical changes in the earth where clay deposits are found [5,6].

Clay is made chiefly out of silica, alumina and water, much of the time with calculable amounts of iron, alkalies and alkali earth's metals. Two basic units are associated with the atomic cross sections of most clay minerals. One unit comprises of firmly pressed oxygen and hydroxyls in which aluminum, iron and magnesium iotas are installed in an octahedral matrix with the goal that they are equidistant from six oxygen or hydroxyls. The subsequent unit is worked of silica tetrahedrons. The silica tetrahedrons are orchestrated to shape a hexagonal system that is rehashed uncertainly to form a sheet of arrangement, $Si_4O_6(OH)_4$ [7]. The development of clay minerals is reliant on physico-chemical states of the quick enduring condition, nature of the beginning materials and other related outer ecological elements [6,8], along these lines coming about into different types of clay materials. Thusly, the application capability of any clay mineral sort in nature will rely upon its concoction arrangement, structure and other innate properties [9]. The particular clay minerals are recognized by a few strategies including warm differential examination, essential investigation by nuclear retention examination, infrared spectrometry and X-ray diffraction. Substance investigation is a fundamental advance to set up the idea of minerals. On this respect, clay minerals are characterized into various gatherings as follows; Kaolinite, Smectite, Vermiculite Illite and Chlorites [10].

Clay minerals are the most significant mechanical minerals. A large number of tons are used yearly in different applications. These applications remember utilizes for geography, the process industries, agriculture, environmental remediation, development and as impetus in oil industry. The most by and large utilized in the assembling of impetuses are kaolin and montmorillonite [2]. Truth be told, catalysts giving chiefly high octane gas in oil industry have been delivered from clays made out of halloysite, montmorillonite and kaolinites [10], with the goal that the amount of kaolin utilized every year for creation of oil splitting catalysts was assessed at in excess of 200,000 tons [11,12]. The purpose behind usage of certain clay minerals in explicit application is that the physical and compound properties of a specific clay mineral are reliant on its structure and sythesis. The structure and piece of kaolins, smectites, and palygorskite and sepiolite are altogether different despite the fact that they each have octahedral and tetrahedral sheets as their fundamental structure squares. Nonetheless, the arrangement and composition of these octahedral and tetrahedral sheets represent major and minor contrasts in the physical and compound properties of kaolin, smectites and palygorskite [12].

Clays have gotten extensive consideration particularly as expected adsorbents for natural exploration. Numerous analysts around the globe, have shot their pursuit lights on the stage improvements that happened by sintering clay within the sight of certain oxides [13]. The most bountiful, pervasive, and available material on the earth outside layer is clay [14]. It was seen that an incredible accentuation is put on abusing the bountiful strong minerals enrichments in Nigeria with the end goal of enhancing the financial base of the nation, improving Gross Domestic Product (GDP) and mechanical action [12]. One of these enrichments with gigantic potential for financial usage is clay [8,12]. There are a few businesses which can use the promptly accessible and modest clay crude materials so as to help industrial growth and relieve the government off the weight of bringing in such items. The improved modern use of clay minerals in the nation will rely for the most part upon the quality and strength of the material, and for this to be acknowledged, there is requirement for thorough examinations on this asset. As of now, the neighborhood networks in Nigeria are depending on the indigenous information to make some clay items whose quality is difficult to decide and neither does it satisfy the fare guidelines [15]. Notwithstanding the immense possibilities, clay minerals are still horribly underutilized and the couple of pockets of existing clay-based ventures have fundamentally tackled the crude for the creation of fired products and auxiliary items. These clay deposits can possibly be a significant wellspring of unfamiliar pay worker if appropriately saddled. Along these lines, so as to decide the gainfulness of using clay from a specific deposit for any application, it is of central significance to look at the microstructural morphology, decide the mineralogical, basic and utilitarian gathering arrangement in such clay deposits.

In Nigeria, clay raw material deposits are widely distributed across the six geo- political zones of the country [16] which have been widely studied. In Yola Adamawa State, North-East Nigeria, clay samples were collected and studied by James et al. [17] and results showed that the clay sample is a low-grade calcium montmorillonite, which is typical for clay in the region [17-22]. From Lakiri village, southwestern Nigeria, clay samples analyzed by Badmus and Olatinsu [23] showed that the clay were kaolinite, acidic, and contains alkaline metal in high concentrations with mean porosity of 0.46 and bulk density of 1.4 g cm $^{-3}$. The author therefore concluded that the clay may serve as good additives for both industrial and mining purposes. Similarly, kaolinites clays were reported from the Abakaliki Formation in the Niger-Delta part of Nigeria [21]. Clay samples from Ubakala clays in Abia State studied by X-Ray Diffraction showed that it was composed mainly of smectites, kaolin, and albite [24]. Similar observations were made for clay deposits obtained from Okada, Edo State, South-West Nigeria [25] and from Udi in Enugu Sate, South-East Nigeria [26]. Unfortunately, very little attention has been given to clay characterization and mineralogy in Imo state despite the growing demand for clay products and the possibility of creating jobs through cottage industries.

Imo state is one of the major states enriched with clay raw material deposits. These clay materials are yet to be properly characterized. 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 geology of the environment (basin) from which they were obtained. The qualities of clay found determine its application and suitability for ceramic products such as in bricks, ceramic wares, and refractory. In Iyinwaogba Umuosode Alike Ikenanzizi Obowo Local Government Area of Imo State, clay soils in the lower river often serve as a filter for the flowing river and thus help in its purification. 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. This work is aimed at characterization of clays from Iyinwaogba Umuosode Alike Ikenanzizi Obowo Local Government Area of Imo State using X-Ray Diffraction, X-Ray Fluorescence, Scanning Electron Microscopy and Fourier Transform Infrared Spectroscopy.

2. Material and Methods

2.1. Plant material

The examination zone is situated at Iyinwaogba Umuosode Alike Ikenanzizi Obowo Local Government Area of Imo State. The region is arranged in a complex geographical setting. The stratigraphic units watched include: the Benin Formation, The Ogwashi - Asaba Formation, the Bende

- Ameki Formation, Imo Shale Formation, Nsukka Formation and Ajali Formation [27]. The Benin Formation is overlain by lateritic overburden and underlain by the Ogwashi - Asaba Formation which is thus underlain by the Ameki Formation of Eocene to Oligocene age [28]. The Benin Formation comprises of coarse - grained gravelly sandstones with minor intercalations of shales and clay. The sand units which are for the most part coarse grained, pebbly and ineffectively arranged, contain focal points of fine grained sands [29,30]. The particular river were the clay samples were gathered is found topographically between scope 5.5774167 ^{o}N and longitude 7.3279617 ^{o}E with height of 137.30 meters. The waterway is a little one with length of < 100 m and profundity of < 100 cm. The clay soils in the stream fill in as a channel for the river water cleansing (Figure 1).

(a) (b)

Figure 1. Photographs of the study area showing, (a) entire river where the clay was collected; (b) clay soils at the bottom of the river

2.2 Sample collection

Sampling sites was carefully selected based on physiographic zones of the area with samples collected to properly represent the parent materials. The clay soils were retrieved from the area using a shovel and were then plastic wrapped and air tight. Five clay samples were collected randomly around Ikenanzizi Obowo Local Government Area of Imo State, South Eastern Nigeria (Figure 2). Samples were taken at an average depth of < 100 cm below the water surface.

2.3 Sample preparation and analysis

The samples were characterized on the basis of their physicochemical properties, 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.

Figure 2. Photograph of clay samples in the lab for analysis

2.3.1. Physicochemical properties

The physicochemical analysis of the clay soil was conducted following standard and reported methodology [31-34]. Temperature was determined *in situ* using the soil gardeners thermometer while pH using Jenway 3510 pH meter. HANNA HI 8733 EC Meter was used in determining the clay electrical conductivity in µS/cm. Loss on ignition was determined based on weight loss on ignition at 105 ^{o}C. Particle size distribution (% sand, % silt and % clay) was determined using hydrometer.

2.3.2. Morphology, mineralogical and elemental analysis

Every one of the samples was part into equal parts with every half utilized for mineralogical and element investigation. The compositional and mineralogical examinations were evaluated utilizing Scanning Electron Microscopy (SEM-EDS), Fourier Transform Infra-Red Spectroscopy (FTIR), X-Ray Diffraction (XRD) and Energy Dispersive X-Ray Fluorescence (EDXRF) equipment respectively. Morphology and microanalysis of the clay and composite examples were resolved utilizing ultra-high goal field outflow examining electron magnifying lens (UHR-FEGSEM) furnished with vitality dispersive spectroscopy (EDS). The pounded clay samples were already gold covered. The samples were examined utilizing ultra-high goal field emanation filtering electron magnifying instrument (UHR-FEGSEM) furnished with energy dispersive spectroscopy (EDS). Molecule pictures were acquired with an auxiliary electron finder. Infrared (IR) spectroscopy was acted in Attenuated Total Reflectance (ATR) mode with a Fourier Transform Bruker Alpha spectrometer furnished with a precious stone gem in the scope of frequencies from 400 cm^{-1} to 4000 cm^{-1} [35]. The XRD mineralogical investigation was examined utilizing the empyrean PANalytical schimadzu 6000 XRD model machine with CuKα radiation. The activity was set at a voltage of 40 kV with current of 40 mA, a scope of 5-80 deg 2θ and a stage size of 0.017 deg 2θ. A period for every progression of 50.165 s with a uniqueness cut at fixed edge of 0.5°. Glasslike mineral stages were recognized in X'Pert High Score Plus utilizing the PDF-4 Minerals 2013 ICDD database. The amounts of the translucent minerals were resolved utilizing the Rietveld technique. The significant components were dictated by X-beam fluorescence with an ARL® 9800 XP spectrometer. The samples were pummeled utilizing arget pounding machine. The ground samples were guaranteed to pass 150 micro mesh sieves. This was to guarantee homogeneity of the samples. Around 5 g of the pummeled sample was weighed into a container and 1 g of restricting guide (Starch dissolvable) was included. The blend was altogether blended to guarantee homogeneity, which was squeezed constrained to delivered pellets prepared for the evaluation. The pellets were deliberately positioned in the separate estimating positions on an sample transformer of the machine to decide the elemental composition utilizing a current of 14 kV for the significant oxides with a chose channel; "kapton" for the significant oxides. Measurement time for each example was 100 s and the medium utilized was air all through. The machine was then calibrated by the machines gain control, after which the separate samples were estimated by clicking the respective positions of the sample changer.

3.0 Results and discussion

3.1. 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 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 [36]. The ultra-acidity of the clay could be due to the use of fertilizer in the area as ammonium (NH_4^+) composts respond in the soil by the procedure of nitrification to shape nitrate (NO_3^-), and in the process discharge H^+ particles.

Table 1. Physicochemical properties of clay samples

Parameter	**Clay samples**				
	A	**B**	**C**	**D**	**E**
pH	2.02±0.67	2.48±0.22	1.91±1.02	2.89±0.07	2.65±0.62
EC (μS/cm)	735±23.67	833±4.72	2276±100.67	509±19.21	538±22.13
LOI (%)	4.77±0.07	4.99±0.60	4.84±1.02	4.75±0.97	5.32±0.04
CEC (meq/100 g)	25.72±1.46	24.97±2.00	26.49±1.67	24.11±0.29	24.93±0.83
RI	1.45±0.06	1.62±0.07	1.60±0.02	1.68±0.03	1.57±0.03
Density	1.708±0.03	1.736±0.27	1.785±0.01	1.742±0.02	1.725±0.01
SG	2.74±0.02	2.68±0.03	2.96±0.02	2.72±0.01	2.76±0.02
Sand (%)	6.98±0.02	6.61±0.02	4.93±0.02	5.50±0.02	6.69±0.02
Silt (%)	10.12±0.02	7.62±0.02	10.65±0.02	11.74±0.02	5.21±0.02
Clay (%)	82.90±0.02	85.87±0.02	84.42±0.02	82.76±0.02	88.10±0.02
Textural class	Clay	Clay	Clay	Clay	Clay

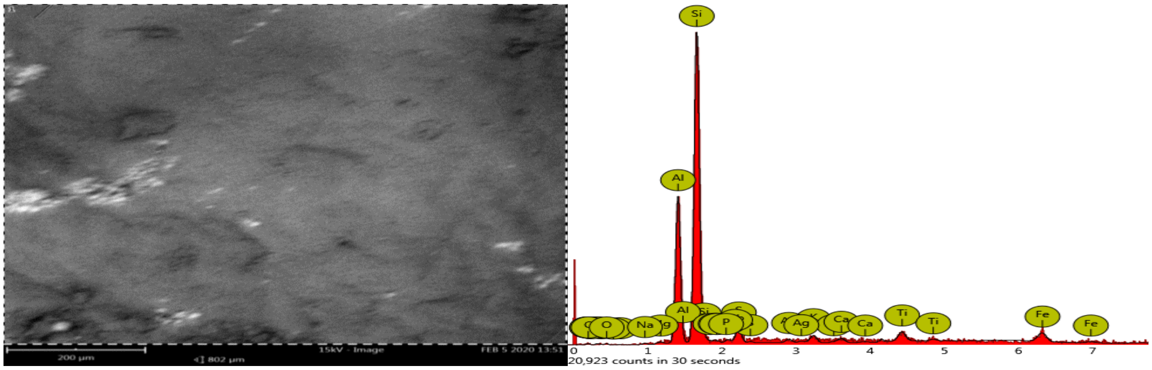
Furthermore, the formation of Kaolinite is favorable at very low pH (~ 3) [41]. Electrical conductivity (EC) is an estimation of the broke down material in a fluid arrangement, which identifies with the capacity of the material to direct electrical flow through it [31]. The higher the dissolved material 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 to 16,000 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. 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 Al_2O_3 and could be more compact. Average quantities of LOI value obtained from clayey minerals ranged from 6.087 to 12.933% in Kenya [15], from 10.27 to 11.66 % for clay samples from Southwestern Nigeria [37] which is higher than the current study while comparable to clay samples in Northern Tunisia reported by [38]. The cation exchange capacity or the CEC level is the proportion of isomorphic replacements that happen with the clay minerals [39]. 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 [40]. 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) [41]. 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 [42]. The recorded refractive index for the clay samples ranged from 1.45 to 1.68, this is typical for clay minerals [43]. For most clay minerals, the specific gravity is within the range from 2 to 3.3 [43]. The current study obtained a specific gravity which ranged from 2.68 to 2.96.

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

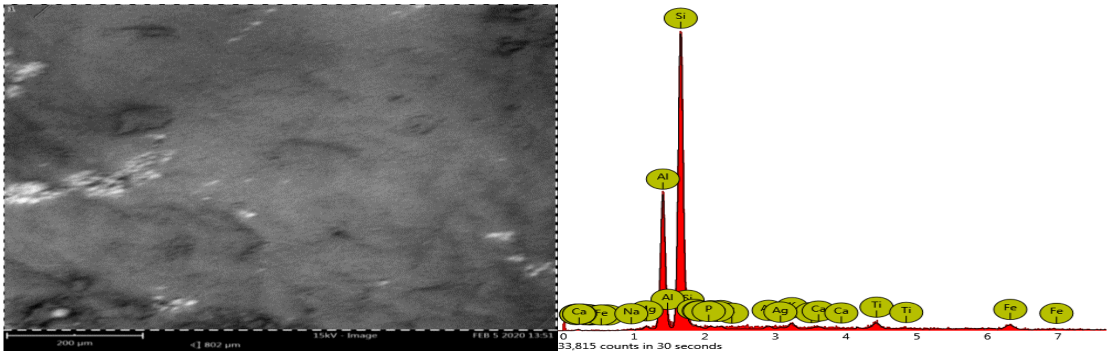
SEM-EDS images of the clay fraction are shown in Figures 3(a)-2(e). This SEM imaging of clay fractions (A to E) depicts a typical structure of conventional quartz and kaolinite. The weakly resolved structures are probably due to the presence of other crystalline structures as impurities in the sample. The pseudo-hexagonal and stratified structures of kaolinite are observed further observed.

3.3 FTIR analysis of clay samples

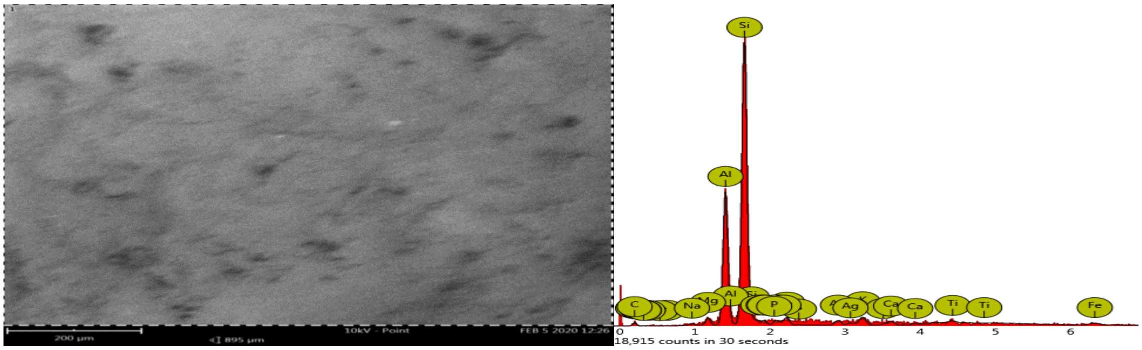
The results for the Fourier transform infrared analysis of the plant extracts are presented in Figures 4(a)-3(e) and summarized in Tables 2.



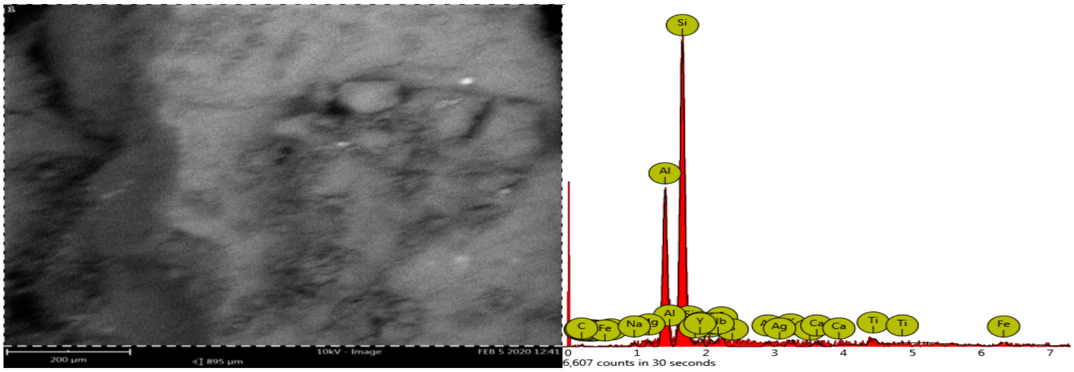
(a) Sample A



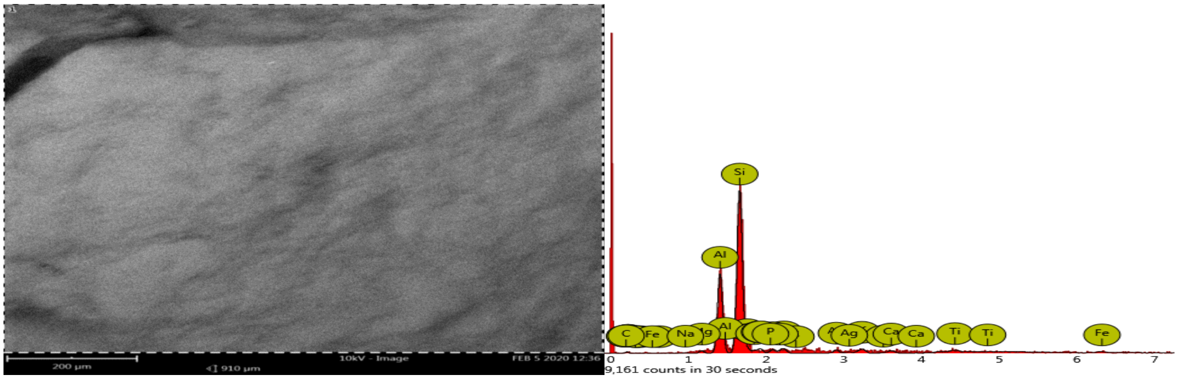
(b) Sample B



(c) Sample C



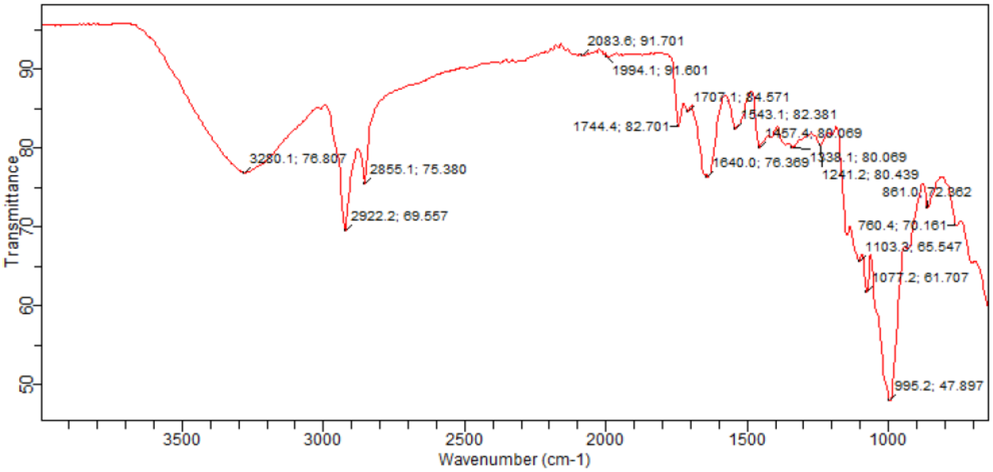
(d) Sample D



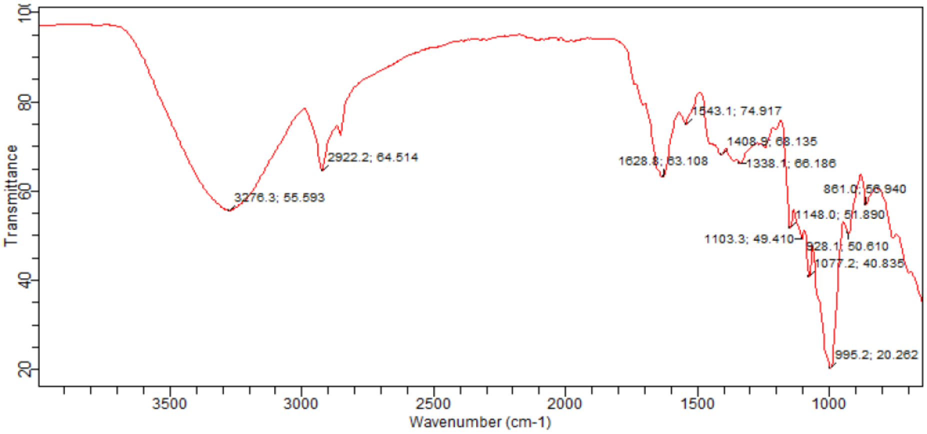
(e) Sample E

Figure 3. SEM-EDS result of clay samples

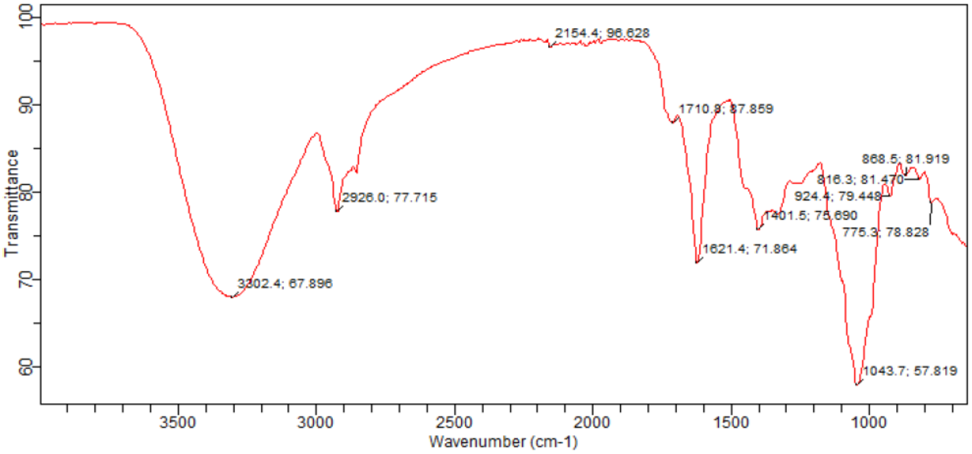
The FT-IR spectrum was used to identify the functional groups and mineralogy of the soil based on the peaks values in the region of Infra-Red radiation either directly or by inference. When the soil samples were passed into the FT-IR, the functional groups of the components was separated based on its 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.



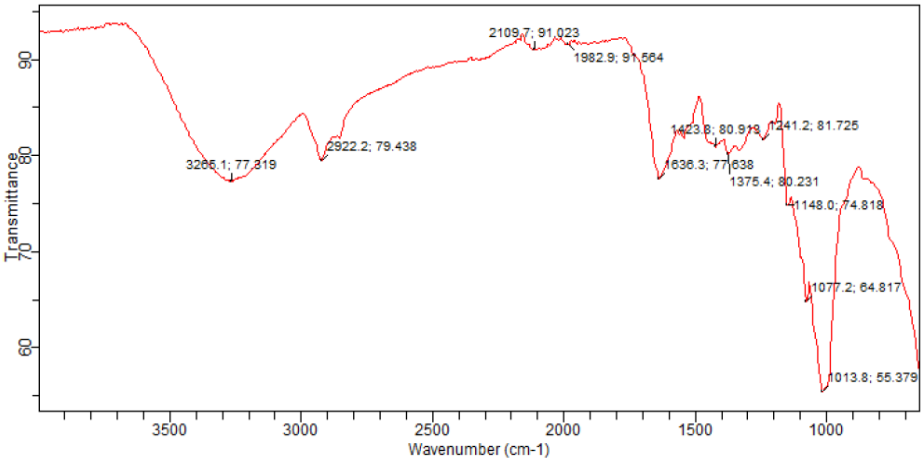
(a) Sample A



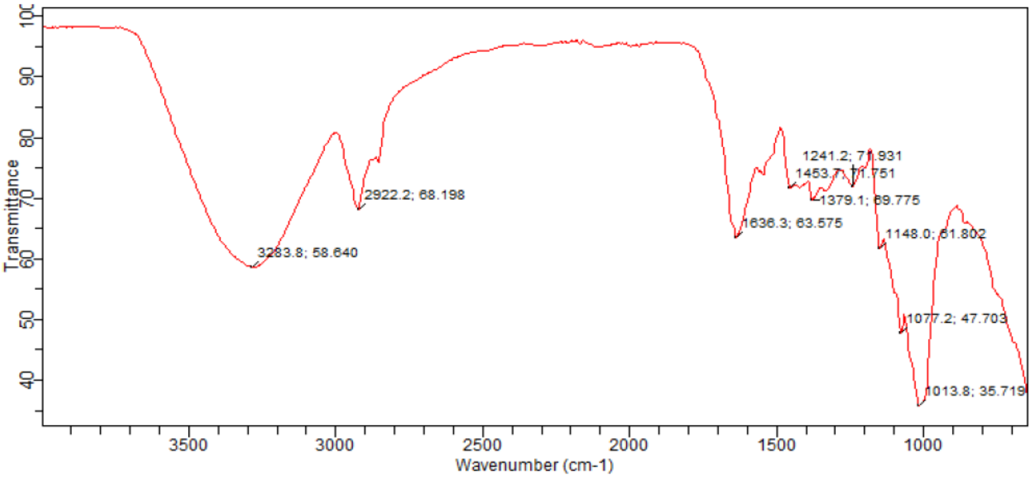
(b) Sample B



(c) Sample C



(d) Sample D



(e) Sample E

Figure 4. FTIR spectra for clay samples

The infrared spectrum of the clay fractions A-E are summarized in Table 2. The clay samples generally showed Kaolinite, C-H Stretching, Si-O Stretching, Al-OH bending vibration and Si-O 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 [44]. Generally, the interatomic bonds Si-O and Al-O which indicate the alumino-silicate nature of sample [35,45,46] correspond with the band between 600 and 1200 cm^{-1}.

Table 2. Infrared band position and assigned mineralogy of clay samples A to E

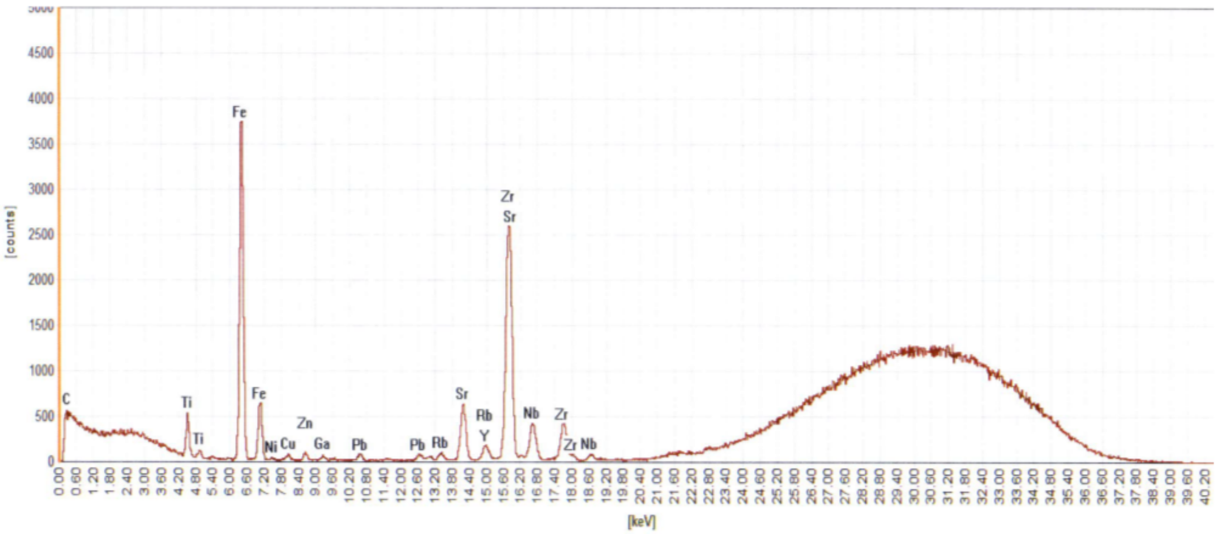
A		**B**		**C**		**D**		**E**	
Peaks (cm^{-1})	Functional group	Peaks (cm^{-1})	Functional group	Peaks (cm^{-1})	Functional group	Peaks (cm^{-1})	Functional group	Peaks (cm^{-1})	Functional group
3280.2	Kaolinite	3276.2	Kaolinite	3302.4	Kaolinite	3265.1	Kaolinite	3283.2	Kaolinite
2922.2	C-H Stretching	2922.2	C-H Stretching	2926.2	C-H Stretching	2922.2	C-H Stretching	2922.2	C-H Stretchi
2855.1	C-H Stretching	1628.8	Kaolinite	2154.4	C-H Stretching	2109.7	C-H Stretching	1636.3	Kaolinite
2083.6	C-H Stretching	1543.1	N-O Stretching	1710.9	Kaolinite	1982.1	C-H Stretching	1453.4	C-H Stretchi
1994.1	C-H Stretching	1408.9	C-H Stretching	1621.8	Kaolinite	1636.3	Kaolinite	1379.1	C-H Stretchi
1744.4	Kaolinite	1338.1	C-H Stretching	1401.5	C-H Stretching	1375.4	C-H Stretching	1241.2	Si-O Stretch
1761.1	Kaolinite	1241.2	Si-O Stretching	1043.3	Si-O Stretching	1148.3	Si-O Stretching	1148.0	Si-O Stretch
1640.0	H-O-H bending of water	1148.0	Si-O Stretching	924.4	Al-OH bending vibration	1077.2	Si-O Stretching	1077.2	Si-O Stretch
1543.1	N-O Stretching	1103.3	Si-O Stretching	868.3	Si-O Quartz	1013.2	Si-O Stretching	1013.8	Si-O Stretch
1457.4	C-H Stretching	1077.2	Si-O Stretching	816.3	Si-O Quartz				
1338.1	C-H Stretching	995.2	Al-OH bending vibration						
1241.2	Si-O Stretching	928.1	Al-OH bending vibration						
1103.3	Si-O Stretching	861.0	Si-O Quartz						
1077.2	Si-O Stretching	760.4	Si-O Quartz						
995.2	Al-OH bending vibration								
861.0	Si-O Quartz								
760.4	Si-O Quartz								

The absorption bands around 861.0 cm^{-1} to 760.4 cm^{-1} are due to Si-O stretching band for quartz[275]. The C-H stretching band in the clay mineral may be due to the intercalation between 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.

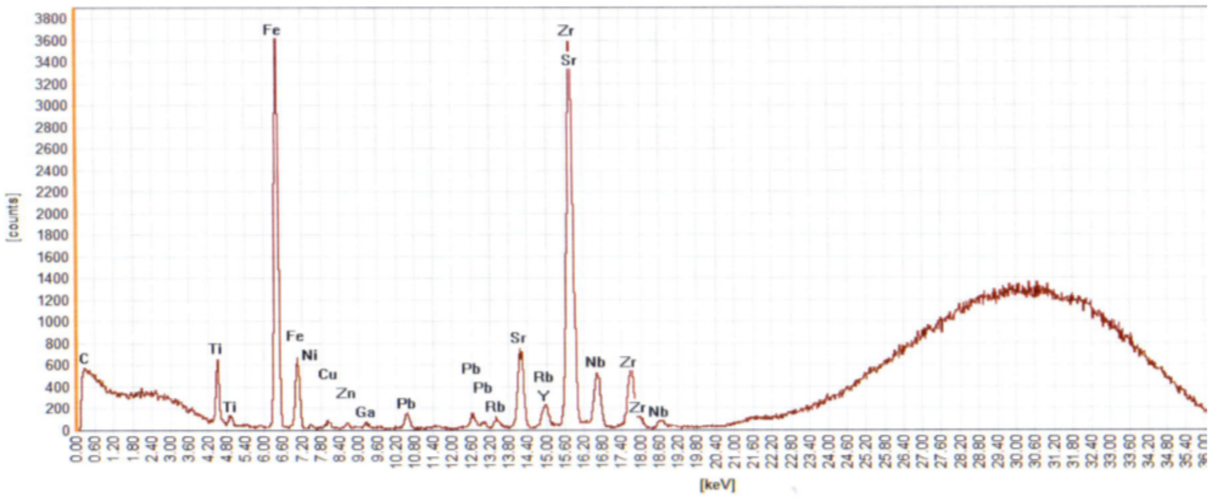
3.4 Chemical composition

3.4.1 Trace elemental composition

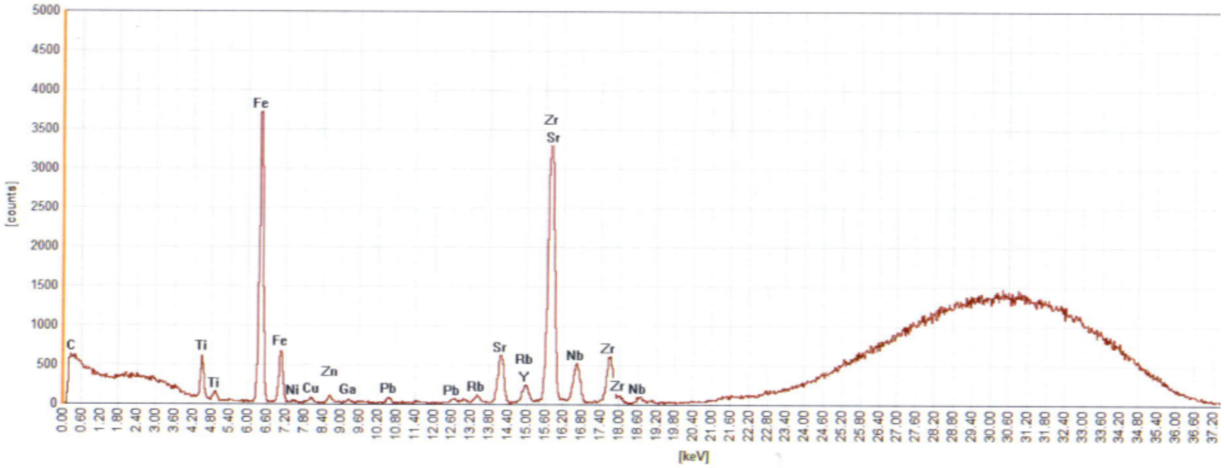
The results of trace elemental analysis of samples A to E conducted with EDXRF are shown in **Figures 5(a)-4(e)**. The spectra were similar for all clay samples. The highest metal in the clay samples was Fe, Zr and Sr, and trace amount of Ni, Pb, Zn, Mn, Ga and Cu. High concentrations of the metal in 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. However, there is no much variation in the trace elements of the samples analysed. Distribution of trace elements in clays and sediments are influenced by weathering processes and nature of the parent rocks.



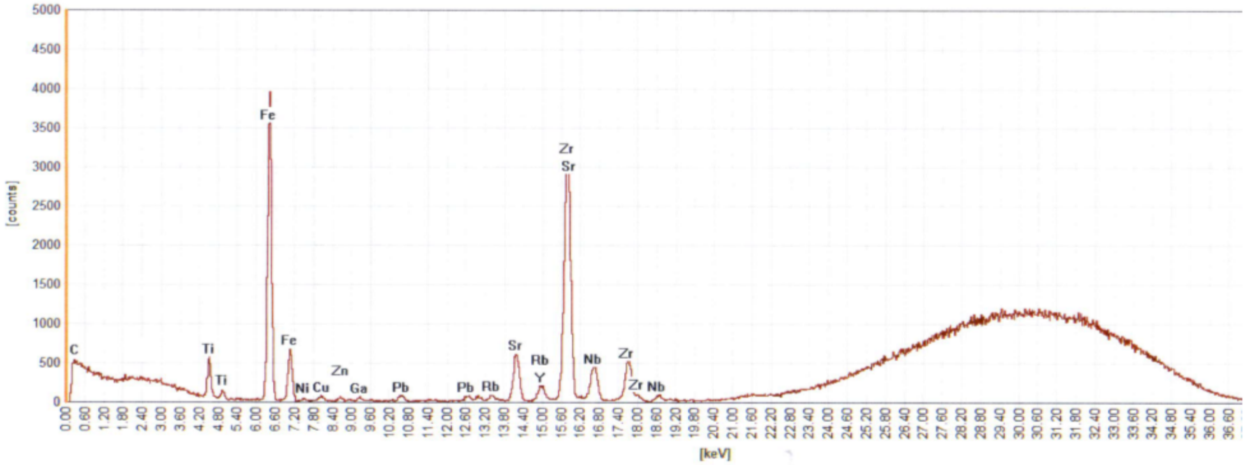
(a) Sample A



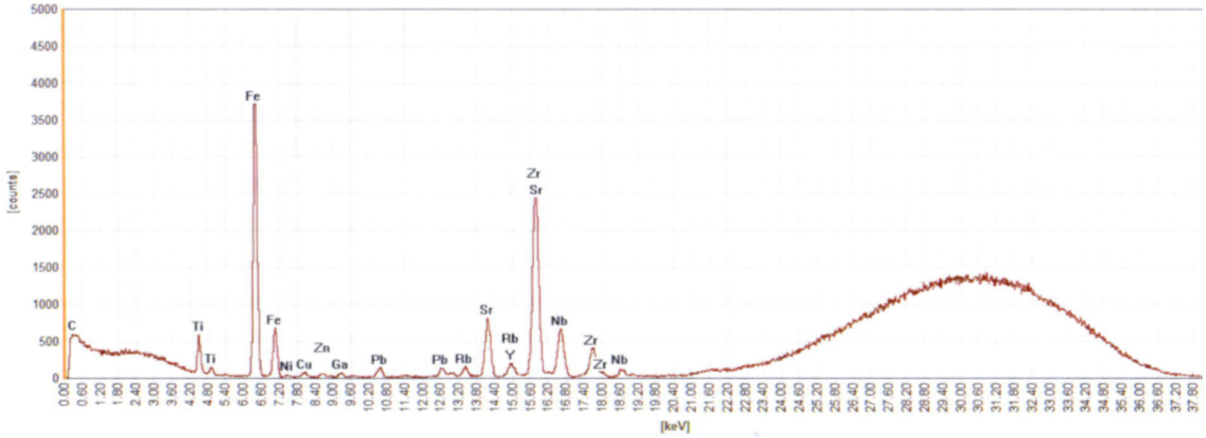
(b) Sample B



(c) Sample C



(d) Sample D



(e) Sample E

Figure 5. EDXRF scans for clay samples

3.4.2 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 3. The elements present in clays have been presented as relative percentages of the elements expressed as oxides in the entire sample.

Table 3. 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
Al_2O_3	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
P_2O_5	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_2O_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
WO_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_2O_3	0	0	0	0	0.00	0.00	0.00
Nb_2O_5	0	0	0	0	0	0.00	0.00

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 the clay may be different [8,35,42]. 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 clay sample D (4.07 %) than all other clay samples (23.53 to 25.13 %). Aramide et al., [37] obtained similar results for clay samples from Southwestern 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 than 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 CaO, MgO, K_2O in the clay samples suggests little or no presence of a talc phase [47] as well as suggesting that the clays are most probably non expandable/swelling and low feldspar content.

3.4.3 Silica to Alumina ratio

In Figure 6, 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 [48] and the presence of free quartz in the samples studied. Similar results were reported by [35] for clay samples collected from Niger. The order for the ratios were E < A < B < C < D.

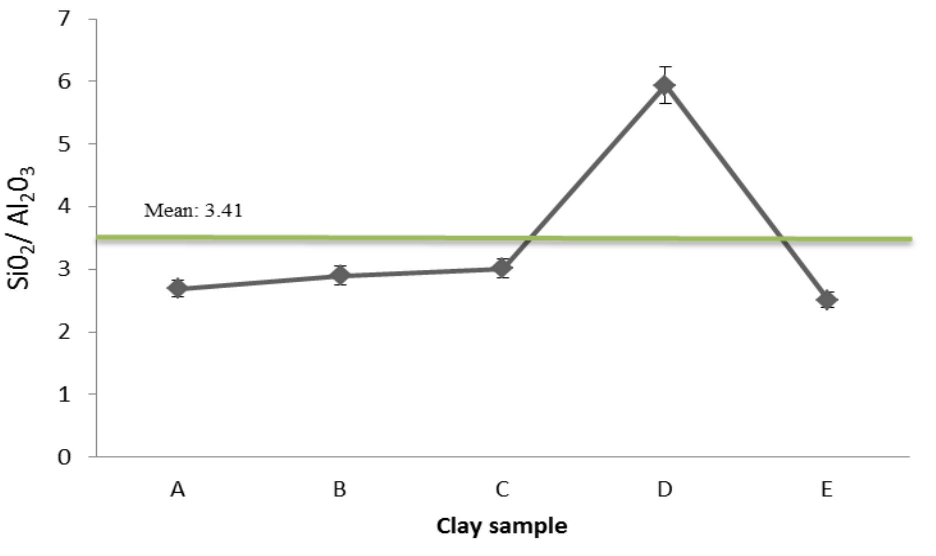
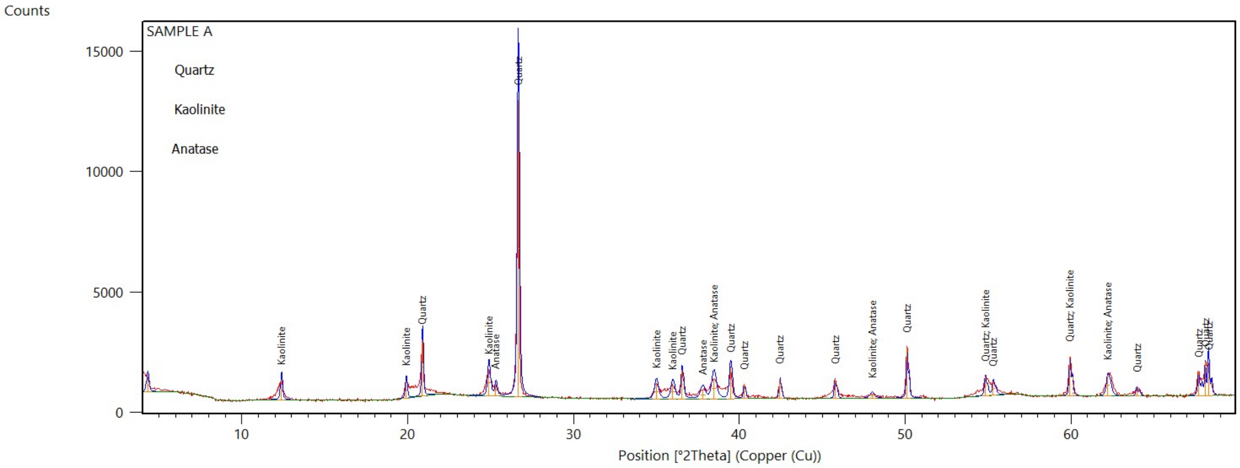


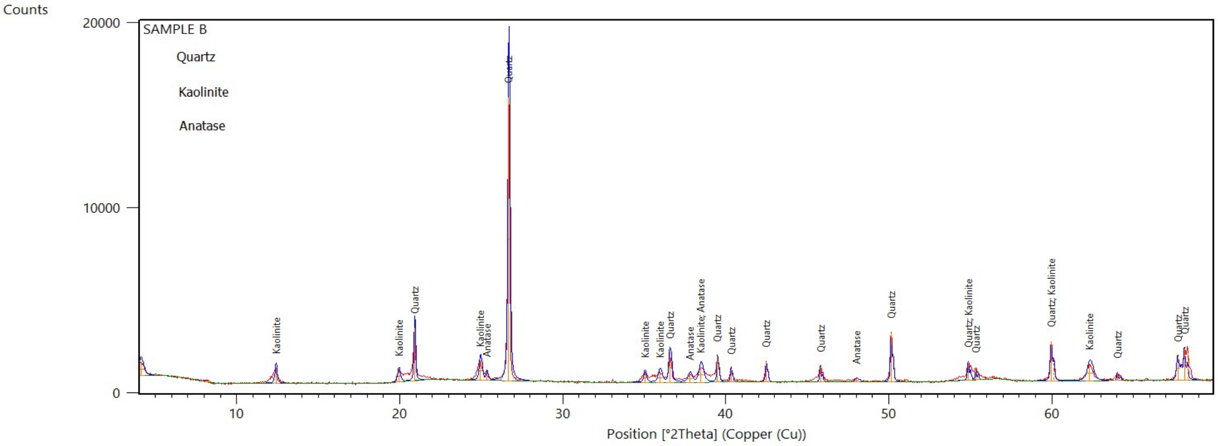
Figure 6. The Silica to Alumina ratio of different samples

3.5. XRD analysis

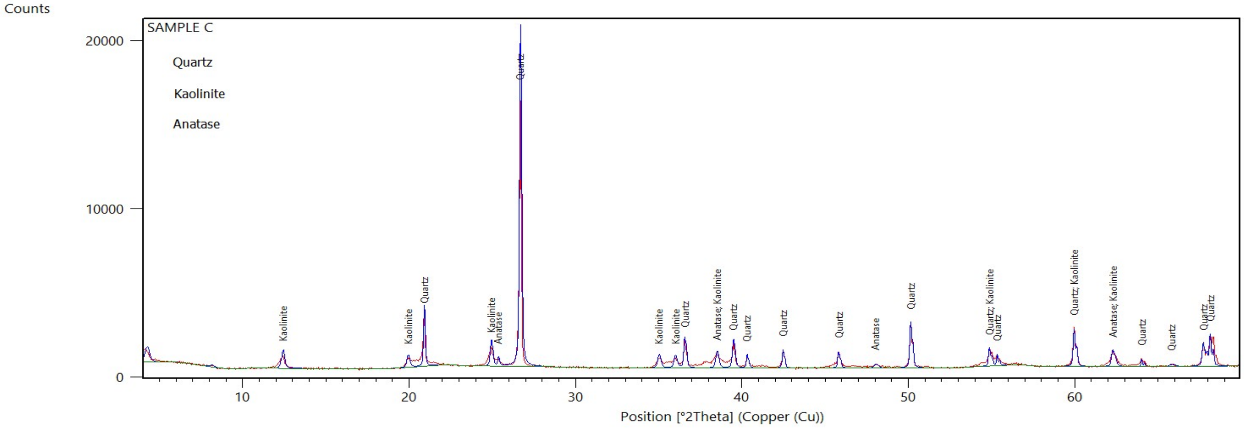
XRD patterns of samples (A-E) are shown in Figures 7(a) to 6(e). The XRD mineralogical data indicates the presence of some mineral phases. The limited number of minerals measured could be as a result of equipment detection limit, which could mean that low concentrations are hard to be picked up by the equipment or could be due to the dominance of these mineral phases in the samples, given that they are clay samples [35,42]. These patterns generally indicated the characteristic peak of quartz, kaolinite, anatase and pyrite in the clay samples.



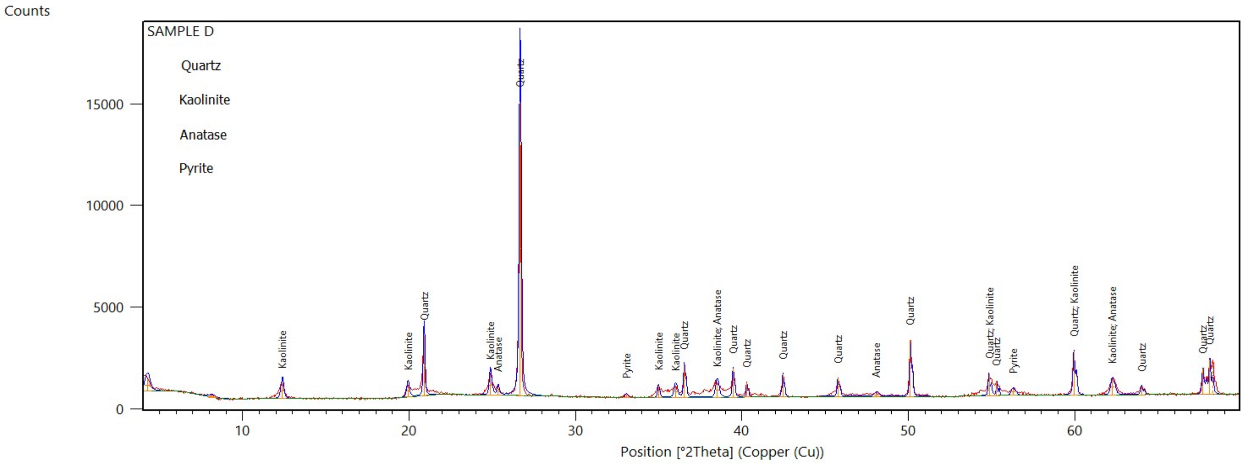
(a) Sample A



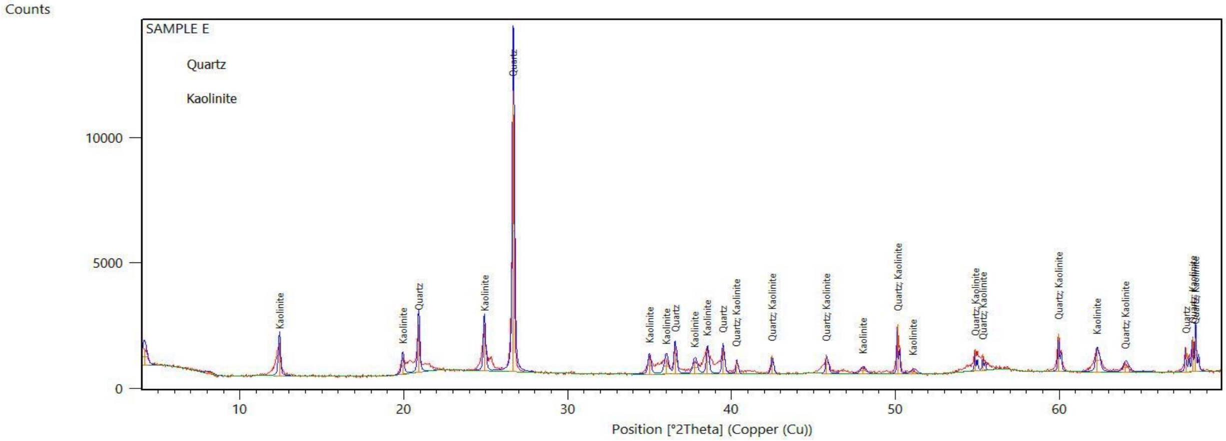
(b) Sample B



(c) Sample C



(d) Sample D



(e) Sample E

Figure 7. X-ray diffraction pattern of clay samples

The distribution summary of different phases present in the clay samples is presented in Table 4.

Table 4. XRD Result of the raw clay samples showing the quantity of different phases present

Samples	Quartz (%)	Kaolinite (%)	Anatase (%)	Pyrite (%)
A	42.42	42.42	15.15	0.00
B	55.00	33.00	15.00	0.00
C	54.00	32.00	14.00	0.00
D	38.00	31.00	14.00	7.00
E	41.00	59.00	0.00	0.00
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 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 for Panyam clays, North - Central Nigeria [49], Mamu and Nsukka formation in Southeastern, Nigeria [41] and Ifon, Ipetumodu and Iseyin clay samples in Southwest Nigeria by [37]. 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 [37].

4.0 Conclusions and recommendation

The study undertaken here has dealt with the mineralogical and morphological characterization of clay from Iyinwaogba 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/Al2O_3 ratios and the loss on ignition values of the clay fraction are within 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 Iyinwaogba 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.

Conflict of interests : The authors declare no conflict of interest

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