Original Research Article

Physicochemical Characteristics of Organophilic Clay Developed using ~~hexa~~Hexadecyl-trimethyl ~~ammonium~~Ammonium ~~chloride~~ Chloride (HDTMAC) Modifier

ABSTRACT

Ogwuta ~~source~~ clay from Unwana in the South Eastern part of Nigeria was modified by ~~ion~~ ion-exchange reaction using hexadecyl-trimethyl ammonium chloride (HDTMAC) synthesized from ~~hexa~~Hexa-decyl-chloride ~~intermediate~~ and tri-methylamine. Physicochemical and thermal ~~properties~~ characteristics of the clay were ~~determined~~ evaluated before and after modification and compared using Fourier Transform Infrared (FTIR), X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), and Thermogravimetry (TG). The metal oxide composition was analyzed using X-ray Fluorescence (XRF) analyzer, while the Cation Exchange Capacity (CEC) was determined using the methylene blue method. The results revealed that cation exchange capacity was ~~results~~ decreased from 18.8 meq/100g ~~in the source clay~~ to 16.4 meq/100g, as well ~~after modification.~~ Na^+ and K^+ ~~also~~ decreased from 4.67% to 2.28% and 1.05% to 0.23% respectively after modification. The C-H asymmetric stretching ~~absent~~ absence in ~~the unmodified~~ clay was visible around the 2931.9 cm^{-1} regions in the modified clay as revealed by the Fourier Transformed Infra-red analysis. X-~~Ray~~ ray diffraction (XRD) analysis showed the enhancement of basal spacing, increasing from 7.134 to 8.121Å. The ~~results revealed the~~ predominant mineral in the clay was kaolinite and desired organophilization was achieved. This study posits that the produced modified clay could be a veritable catalyst for pollution and other industrial processes.

Keywords: Modification, organophilization, characterization, kaolinite, natural clay

1. INTRODUCTION

Clay minerals are naturally occurring materials composed of fine-grained phyllosilicates (minerals ~~which~~ that show plasticity through a variable range of water content, trapped in the mineral structure by polar attractions) [1]. They could also be referred to as any group of hydrous aluminum silicates with a layer structure and very small particle size (< 2μm) [2].

Essentially, clay minerals are composed of silica, alumina, magnesia, and water. Iron substitutes for aluminum and magnesium to varying degrees and appreciable ~~quantity~~ quantities of potassium, sodium, and calcium are frequently present [3]. Structurally, clay minerals like all phyllosilicates are characterized by ~~two~~ two-dimensional sheets of ~~corner~~ corner-sharing SiO_4 tetrahedra and /or AlO_4 Octahedra. The sheet units have the chemical composition $(AlSi)_3O_4$. Different clays have different ways these layers of sheets are packed or arranged. Consequently, clays are categorized depending on the tetrahedral-octahedral sheet sequence. If there is only one tetrahedral and one octahedral in each layer,

the clay is known as a 1:1 (T-O) clay. The other composition known as 2:1 (T-O-T) clay, has two tetrahedral sheets with the unshared vertex of each sheet pointing toward each other and forming each side of the octahedral sheet.

Based on their structures and chemical compositions, the clay minerals can be divided into four main classes of kaolinite, smectites, illites, and micas [4]. However, Sarkar *et al.* [5] and Walter [6] refer to two or three classes of clays since illites are sometimes referred to as a 2:1 layer and not a 2:1:1. Also, illites/micas are sometimes grouped with smectites. Clays have a particle size of less than 2µm and are distinguished from other fine-grained particles such as silt by their plastic~~ity~~ properties. Most clay particles are characterized by high swelling capacity, large specific surface area, and high cation exchange capacity [7]. Kaolinites on the other hand have a low shrink-swell capacity and a low cation exchange capacity (1-15 meq/100g) with a triclinic crystal system and specific gravity of 2.16-2.68.

These properties make clay minerals find wide applications. Smectites are useful as ~~an~~ annular seals or plugs for water wells and as protective liners for landfills. Other uses include as an ~~anti-~~anti-caking agent in animal feed, in paper-making, to minimize deposit formation, and as a retention and drainage aid component. In the oil and gas industry, montmorillonite is a major component of the drilling mud which helps in keeping the drill bit cool and removing drilled solids. The endothermic dehydration of kaolinites produces disordered metakaolin which is a complex amorphous compound that when added to the concrete mix, accelerates the hydration of Portland cement [8]. Bhattacharyya and Gupta [9] added that they are effective as an adsorbent for the removal of heavy metals. This is possible because clay minerals have a net negative charge due to the isomorphous substitution of silicon ion by aluminum ion in the tetrahedral layers or likely substitution of aluminum ion by magnesium ion. Thus, cations such as sodium, potassium, and calcium may be attracted to the mineral surface to neutralize the layer charge. This property reduces the application of clay in an organic medium. To enhance its application, it becomes imperative to modify it with the organophilic molecule to increase its organophilic property.

Organoclays are prepared by either impregnation, ion exchange, intercalation, or grafting quaternary ammonium salts of the form $[(CH_3)_3\ NR]^+$ or $[(CH_3)_2\ NRR^1]^+$ unto clay minerals. The substituent, R and R^1 are alkyls or aromatic hydrocarbons. The presence of this compound increases the interlaminar distance or basal spacing of the d_{100} plane and modifies the surface properties of the clay by changing from hydrophilic to organophilic [10]. This change enhances the application of organoclays as an effective material for removing hydrocarbon contaminants in wastewater treatment.

There are several clay deposits in Nigeria ranging from the Northern parts to the Eastern parts of the country (both identified and unidentified) in commercial and small scale quantities. It is therefore imperative that these clay minerals should be x-rayed in physical, chemical, thermal, refractory properties, etc and documented for immediate and future use.

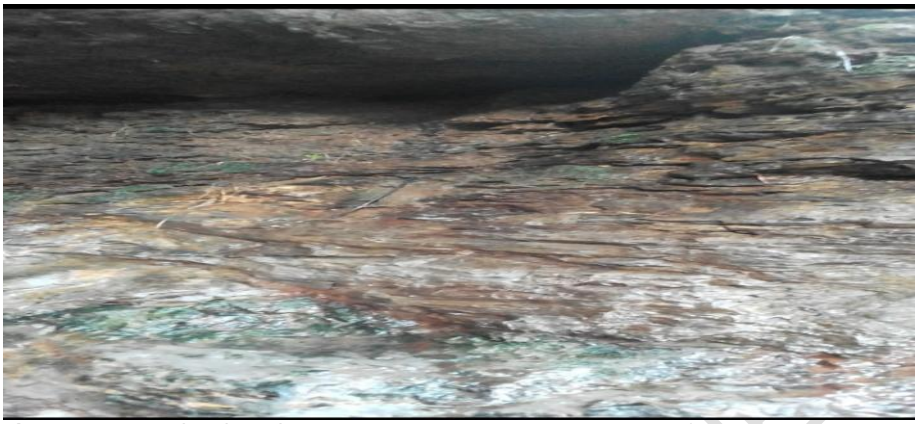

Plate 1: Ogwuta clay deposit

In this study, source clay from Unwana, Afikpo was modified with hexadecyltrimethylammonium chloride salt. The organoclay product was characterized by X-ray Fluorescence (XRF), Fourier Transform Infra-red (FTIR), X-ray diffraction (XRD), thermo-gravimetric analysis (TGA), and the results obtained were compared with that of the source clay.

2. MATERIAL AND METHODS

2.1 Materials

The clay samples ~~was~~ were collected from its natural deposit at 12 cm below earth surface in Unwana, Afikpo North Local Government Area of Ebonyi State, South-Eastern Nigeria. The samples ~~was~~ were sun-dried for 2-3 days. The impurities found on the clay samples were removed by hand. The samples ~~was~~ were further oven-~~-~~dried at 105^{o}C for 2 h~~rs~~ using BTOV 1423 oven~~,~~ and crushed with an iron roller to fine particle sizes. These clay particles were sieved into 63 µm size and stored in a glass bottle.

Hexadecanol, thionyl chloride, and trimethylamine for intermediate and surfactant syntheses were obtained from Sigma-Aldrich and were used without further purification. All other chemicals such as acetone~~,~~ and methanol ~~etc,~~ were of analytical grade.

2.2 Methods

2.2.1 Synthesis of ~~hexa~~Hexa-decyl-trimethyl ammonium chloride (HDTMAC) Surfactant

The synthesis was ~~done~~ carried out in line with ~~the method described by~~ Asdani *et al.* [11]. The process involved the preparation of ~~hexa~~Hexa-decyl-chloride intermediate from ~~hexadecanol~~ Hexa-decanol and thionyl chloride, as well as ~~and subsequently~~ used in the synthesis of ~~hexadecyltrimethylammonium~~ Hexa-decyl trimethyl ammonium chloride. A 1.0 M ~~hexadecanol~~ Hexadecanol was prepared by dissolving 23.5 g in 1000 cm^3 ether and 1.0 M ~~sulphurous~~ sulfurous dichloride was prepared by making up 7.3 cm^3 to 1.0 dm^3 using ether. Up to 500 ml each were mixed in a flask and refluxed for 24 h~~rs~~ at 60^{o}C. The condenser was removed and shaken for another 2 h~~rs~~ before being allowed to cool at 10^{o}C for 24 hrs. About 11.2 cm^3 of tri-methylamine was ~~further~~ added and refluxed for another 24 h~~rs~~ at 60^{o}C. The ~~slightly~~ light yellow liquid mix~~ture~~ was cooled overnight and stored in a bottle.

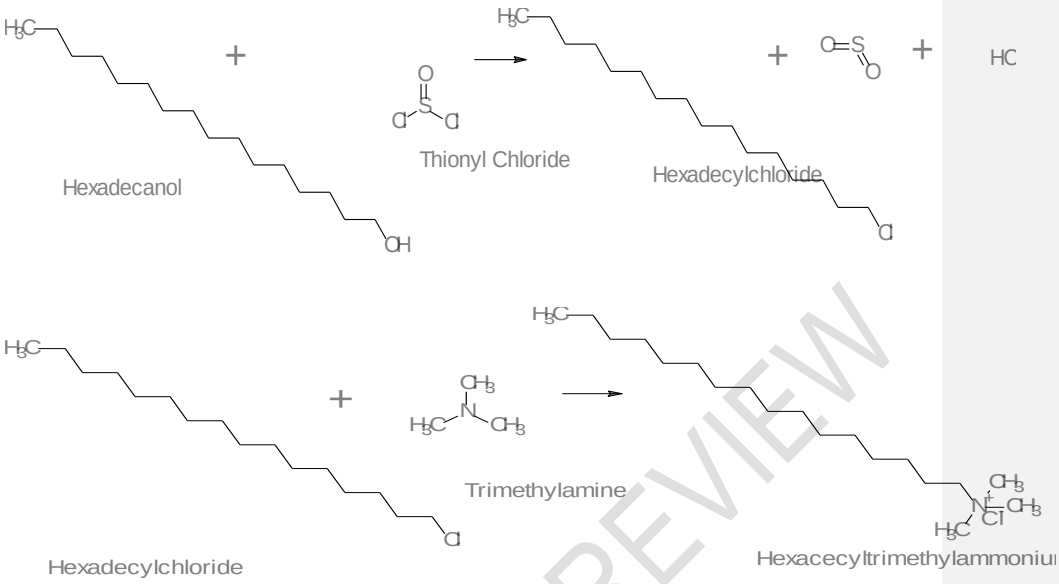

Figure 1. Reaction equations for the synthesis

2.3. Organophillization of ~~Source~~ Clay

The organophillization of clay was carried after~~According to~~ Shirin *et al.,* [12].~~,~~ ~~a~~ A 20 g of clay was dispersed in a 2 L capacity beaker containing ~~1000 ml~~1 liter of water for 90 min at a rotation of 250 ~~rotations per min (~~rpm~~)~~ and ~~at~~ 80^{o}C. A solution containing 10 g of HDTMAC with 4.2 ml concentrated HCl in 500 ml hot distilled water was subsequently added and allowed to mix for another 90 min at the same rotation rate after which the solid was filtered using a vacuum filtration ~~apparatus~~device. The modified clay was oven-dried for 24 h~~rs~~ at 80^{o}C, ground into powder using mortar and pestle, labeled, and then stored in a desiccator.

2.4 Characterization of a~~A~~dsorbent (modified and unmodified)

2.4.1 pH Determination

A 50 ml of deionized water was added to 10 g of the modified and the unmodified clay sample~~s~~ in a 250 ml beaker in the ratio of 1:5 of clay to water. The mixtures were stirred with a glass rod and allowed to stand for 30 min and the pH taken.

2.4.2 Determination of the ~~Surface~~ surface ~~Area~~ area ~~Determination of the Sample~~

The surface area of the two clay samples was determined ~~according to the method of~~following Alvarez *et al*. [13]. A 1.5 g of each clay sample was agitated in 100 ml of dilute HCl, which had been diluted to a pH of 3.0. Then, 30 g of sodium chloride (NaCl) was added while stirring the suspension. The volume was made up to 150 ml with deionized water, resulting in the change of pH to 4.0. A 0.1M NaOH was used to raise the pH from 4.0 to 9.0 and the volume (V) of NaOH used was recorded. The surface area *s,* was calculated using the following equation:

$$S = 32V - 25 \quad (1)$$

2.4.3 Determination of the ~~Specific~~ specific ~~Gravity~~ gravity ~~Determination of Clay Sample~~

~~This was d~~Determined using the Archimedes principle ~~described by~~following Dada *et al.* [14]. ~~Briefly, t~~The weight of an empty 50 ml specific bottle (w_1) was measured on a weighing balance. Then the bottle was filled with water and the weight (w_2) was measured. The clay sample (10 g each) was added to an empty dry specific bottle and the weight (w_3) was recorded. Finally, the bottle containing the sample was then filled with water and all air bubbles were expelled before the weight (w_4) was re-measured. The specific gravity ($s.g$) of the clay was calculated as ~~below~~follows:

$$s.g = \frac{\text{Weight of sample}}{\text{Weight of equal volume of water}}$$

$$s.g = \frac{w_3 - w_1}{(w_2 - w_1) - (w_4 - w_3)} \quad (2)$$

2.4.4 Determination of ~~t~~Total ~~Pore~~ pore ~~Volume~~ volume

The total pore volume of the clay samples was determined by boiling 20 g of the sample immersed in water. After the air in the sample had been displaced, the sample was superficially dried and weighed. The total pore volume was calculated as an increase in the weight divided by the density of the water (1 g/cm^3).

2.4.5 Determination of c~~C~~ation ~~Exchange~~ exchange ~~Capacity~~ capacity~~Determination of Clay Sample~~

The cation exchange capacity of the clay was determined according to the ~~the standard test method for~~ methylene blue index for clay designated by C837-09 (2014). A 2.0 g of previously dried clay was placed in a ~~1~~one-~~L~~ liter beaker containing 300 ml of water. The mixture was stirred until a uniform dispersion was achieved. The pH of the slurry was determined and sufficient sulphuric acid was added to bring the range to within 2.5-3.8. With the slurry still under the mixer, 5 ml of 0.01N methylene blue solution ~~was~~ were added and stirred for 1-2 min. With the help of a dropping pipette, a drop of the slurry was made on the edge of a filter paper and the appearance of the drop was observed. This continued until the endpoint was marked by the appearance of a light blue halo around the drop. The Methylene Blue Index (MBI) was calculated ~~thus~~as follows:

$$MBI = \frac{0.01 \times V}{2} \times 100 \quad (3)$$

Where, V represents the volume, in milliliters of the methylene blue solution required for the titration

2.4.6 determination of m~~M~~etal oxide ~~Composition~~ composition~~Determination~~

This was ~~done~~ carried out using a combination of the wet and the dry methods. Oxides of K, Al, Mg, Fe, Ca, and Na ions were analyzed using XRF Analyzer (DCC-6000 Mineral mode). Silicon dioxide (SiO_2) was analyzed according to ~~the method of~~ Park et al. [15]. Briefly, 1.0 g of the sample was washed three times with a homo-ionic solution of 1M NH_4Cl and then with a 50% (v/v) mixture of ethanol and distilled water until the supernatant solution is free of Cl^- by the silver nitrate ($AgNO_3$) method. The sample was oven-dried overnight at 105ºC. The elemental composition of the sample was determined following digestion with analytical grade aqua regia and boric acid in an oven using a platinum crucible. The oxide was determined using Atomic Absorption Spectrophotometer. The loss on ignition (LOI) was determined by burning 1.0 g of samples at 1000^{o}C in a muffle furnace.

2.4.7 Fourier ~~Transform~~ transform ~~Infra~~infra-~~Red~~ red (FTIR) ~~Scan~~ scan of ~~Clay~~ clay ~~Sample~~

A 1.0 mg ~~of the~~ sample was mixed with a little quantity of KBr in the ratio of 1:10 (1 mg: 10 mg) and finely pulverized in an agate mortar with a pestle to homogenize the mixture. A little amount of the mixture was placed in a miniature press and compressed to form a disc

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or pellet of about 1mm thickness. This was placed in the appropriate sample holder, the holder, with the sample, was mounted on the sample compartment of the FTIR Spectrometer. The system was set to make 16 scans within 4000 cm^{-1} to 400 cm^{-1} and on completion of the scan, the spectrum was displayed on the 'view' window automatically. The individual peaks on the spectrum were labeled with their corresponding wavelengths and the spectrum was printed out.

2.4.8 Scanning Electron electron Microscopic microscopic (SEM) Scanscan

SEM scans on both the modified and the unmodified clay samples were done carried out according to the method reported by Obi and Apemiye [16].

2.4.9 Thermo-gravimetric Analysis analysis of Samplessamples

The thermal analysis of samples was done carried out using a simultaneous TGA-DTA (Pekin Elmer TGA 4000) analyzer. Approximately 11.209 mg of powder sample was loaded into the platinum sample pan and heated from ambient temperature to 950^{o}C at a heating rate of 10^{o}C/min under air purge gas drawn at 20 ml/min and pressure of 2.5 bars. Traces were recorded as percentage weight loss versus temperature

3. RESULTS AND DISCUSSION

From Table 1, tThe pH of the clay samples at 30^{o}C was 2.8 for the unmodified and 4.3 for the HDTMAC-modified (Table-1), indicating a 53.6% increase. This increase arose from the reduced capacity of the modified clay to hold hydrogen ions which is are a consequence of reduced cation exchange capacity [9]. Generally, the acidic value of clay can largely be accounted for by the composition of the parent rock- material from which it was formed and partly by environmental factors such as rainfall [17], that is, clay samples from areas with lots of rainfall have pH values less than 3.5. The result agrees with the observation bythose of Suedina and Carla, [18] that clays have 0.67 units of negative charge per unit cell resulting from the isomorphic substitution of Al^{3+} by Mg^{2+} and Si^{4+} by Al^{3+}. Consequently, they behave as weak acids with pH values less than 4. The acid level, more often than not is related to the cation exchange capacity (CEC) of the clay sample.

Table 1: Some physical properties of clay used in this work

Parameter	Unmodified Clay	Modified Clay
pH	2.8	4.3
Surface Area	133.4 m^2g^{-1}	129.2 m^2g^{-1}
Specific Gravity	2.16 gcm^{-3}	2.11 gcm^{-3}
Pore Volume	0.45 m^3g^{-1}	0.53 m^3g^{-1}
CEC	18.8 meq/100g	16.4 meq/100g

3.1. Specific Surface surface Areaarea

The specific surface area revealed a decreased from 133.4 m^2g^{-1} in the unmodified clay to 129.2 m^2g^{-1} in the HDTMAC-modified clay. This decrease in the specific surface area of the modified clay was due attributed to the incorporation of the organic cations into the clay interlayer [19]. This observation agrees with that made byThe results were compatible with Uzochukwu [20] who revealed that after measuring the surface area of modified clays using Ethylene Glycol Monoethyl Ether method. Finer particles of a given sample pose values that are higher than coarser particles. Specific surface area values range from 50 m^2/g to as high as 736 m^2/g in silica-bonded montmorillonite [21].

3.2. Specific Gravitygravity

The specific gravity of the HDTMAC-clay ~~was found to be~~recorded about 2.11 g/cm^3~~,~~ which is lower compared to ~~a decrease from~~ 2.16 g/cm^3 of the unmodified clay. The decrease was expected following the intercalation of surfactant causing an increase in volume per unit mass. This value falls within the range of a minimum of 1.8 to a maximum of 2.6 for clays [22]. The value was comparable to the clay from Ihitte Oboma with a value of 2.14 [23] and those from the Abakaliki area with values of 2.23 and 2.28 [24].

3.3. Cation ~~Exchange~~ exchange ~~Capacity~~ capacity

The cation exchange capacity of the clay was ~~was determined to be~~recorded up to 18.8 meq/100g for the unmodified and 16.4 meq/100g for the HDTMAC-clay at pH 6. This property of clay arises from isomorphous substitution, a crystal lattice defect in which a given ionic series may be replaced by another in a crystal lattice [25]. The decrease in the values of CEC is due to the reduction in the electrostatically charged surfaces, arising from the substitution of cations by surfactant ions, which ultimately reduced the tendency of the clay to attract and hold ions. According to Neeraj and Chandraa [4], values of CEC range from 3-15 in kaolinites through 15-40 in chlorites and illites, 70-100 in montmorillonite, and 100-150 in vermiculite.

3.4. Metal ~~Oxide~~ oxide ~~Composition~~composition

The results of the metal oxide composition of both the modified and unmodified clays ~~as presented~~revealed in Table ~~–~~2 ~~showed~~ that the alumina and silica oxide was in major quantity. ~~———~~The high iron oxide content of over 6% was consistent with other local clays such as Oboro and Abakaliki [24, 26]. The loss on ignition value of 11.29% revealed that the unmodified clay was high in the carbonaceous matter [27]. This value expectedly increased to 13.17% after modification. Also, the percentage composition of Mg, Ca, Na, and K decreased from 1.62, 0.34, 4.67, and 1.05 in the unmodified clay to 0.41, 0.11, 2.28, and 0.23 in the HDTMAC-clay respectively. This could ~~possibly~~ be ~~due~~ attributed to the substitution of these cations by the surfactant ions. The Cl^- content was observed to also increase from 0.51 to 1.12 which was as a result of possible interaction of the non-substituted cations with the anion. Also noted was the considerable amount of iron suggesting the presence of impurities, which was commonly seen in clays formed from soils under tropical conditions [28]. However, with zero Ti content and less than 2% Mg and Ca content, the clay showed limited mineral impurities [29].

Table 2. Metal oxide compositions (%) of the clay used in this study

Element	Unmodified Clay	Modified Clay
Al	19.08	18.99
Si	48.62	47.58
Mg	1.62	0.41
Ca	0.34	0.11
Na	4.67	2.28
K	1.05	0.23
Fe	6.99	6.87
Ti	0.00	0.00
Cl^-	0.57	1.12
LOI	11.29	13.17
Moisture	0.55	0.43
Others	5.25	8.83

3.4. Scanning ~~Electron~~ electron ~~Micrograph~~ micrograph (SEM)

The Scanning ~~Electron~~ electron ~~Micrographs~~ micrographs of the unmodified and the HDTMAC-modified clay as presented in Figures 2a and 2b respectively revealed particles

formed by large agglomerates of irregular sizes and shapes. From the modified micrograph, the particles were observed to be ~~apparently~~ smaller in size and composed of disordered, thin sheet particle aggregates. This observation could be ~~due to the fact that~~because organophilization enhanced the formation of ~~a~~ disordered and less cohesive aggregates arising from the reduction of edge-to-edge and face-to-face interactions [17].

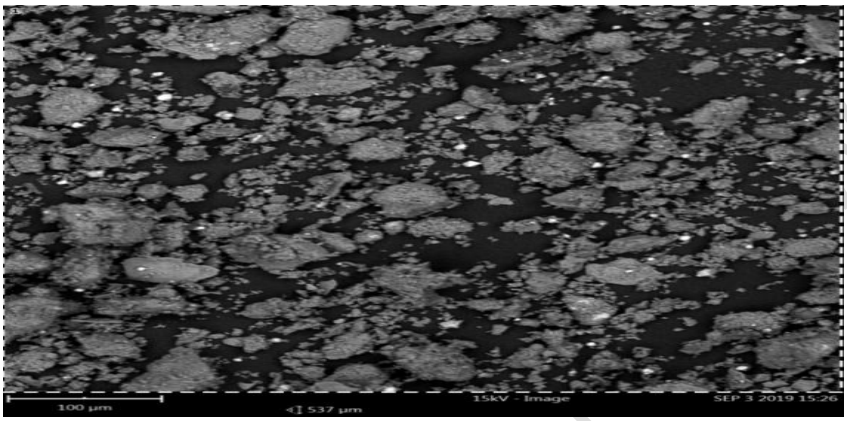

Figure 2a: SEM Image of Unmodified Clay

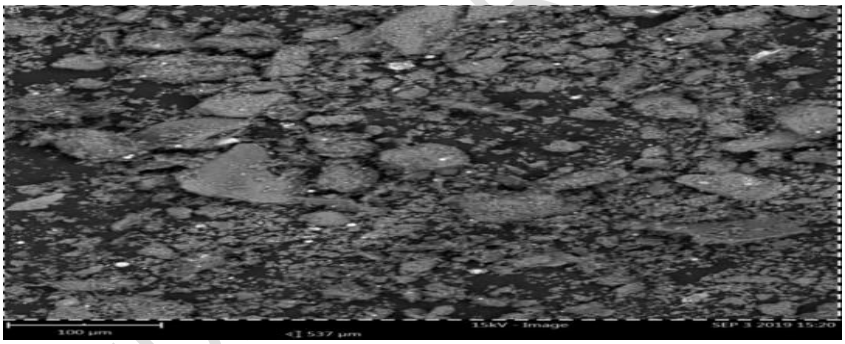

Figure 2b: SEM image of HDTMAC-Clay

3.5. Thermal ~~a~~Analysis

The thermal behavior of the modified and unmodified Ogwuta clay is ~~as presented~~revealed in Figures 3a and 3b with ~~showed~~ thermal behavior similar to most kaolinitic clay samples ~~in literature~~ [30, 31]. Both the unmodified and the HDTMAC-modified clay showed initial exothermic weight gain that peaked at 39.84^{o}C. This might be attributed to the hygroscopic behavior of the samples enhanced by not using very dried air [32]. However, all gained weight was lost completely at 45.51^{o}C and 57.81^{o}C for the unmodified and modified clay respectively. Also, both samples exhibited characteristic exothermic weight loss (2%) around 100-150^{o}C. This could be associated with the physically adsorbed water [33]. From 153-325^{o}C, the observed weight percent loss was due to the removal of water of crystallization of the interlayer cations. Drastic loss of weight, characteristic of the modified clay was observed between 388-450^{o}C. This was assumed to be due to the degradation of ammonium chloride surfactant. The last step of weight loss was observed between 532^{o}C and 776^{o}C which,

according to Conconi *et al.* [31] was due to the dehydroxylation of the hydroxyl group of the clay samples.

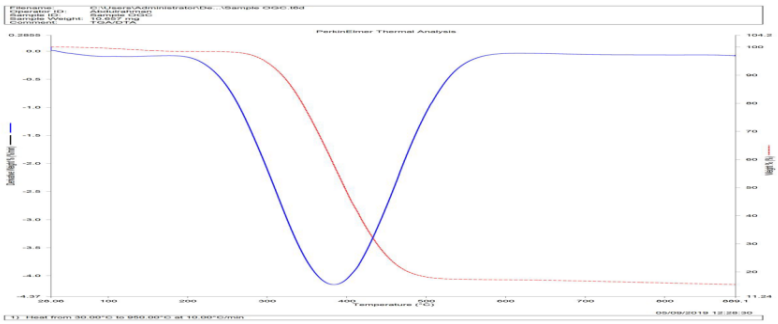

Figure 3a: TGA/DTA of UM-clay

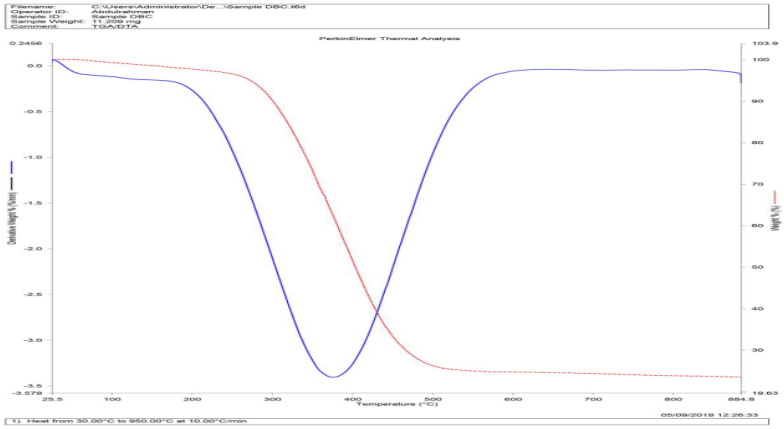

Figure 3b: TGA/DTA of HDTMAC-clay

3.6. X-Ray Diffractogram

Clay materials are made of layers of silicates. To study the interlayer distance and displacements after organophilization, ~~the~~ X-ray ~~defractometry~~ diffractometry (XRD) was employed. The ordinary Ogwuta and HDTMAC-modified clays were subjected to this method. The d_{001} peak displacements ~~as shown~~ in Figures 4a-4e showed a slight decrease of the 2θ angle from 14.115^{o} in the unmodified clay to 12.398^{o} in the HDTMAC-modified clay. This led to a corresponding increase in the d_{001} from 7.134 Å to 8.11 Å. Consequently, this change in the 2θ and the interlayer spacing of the organoclay confirms the intercalation of the organic HDTMAC surfactant into the interlayer spacing of the clay. This also shows that the clay interstice did not collapse after modification [34].

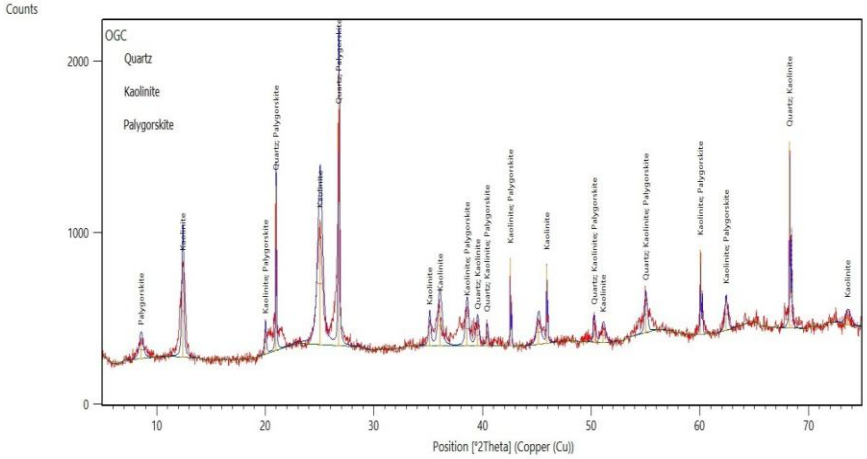

Figure 4a: XRD spectrum of UM-clay

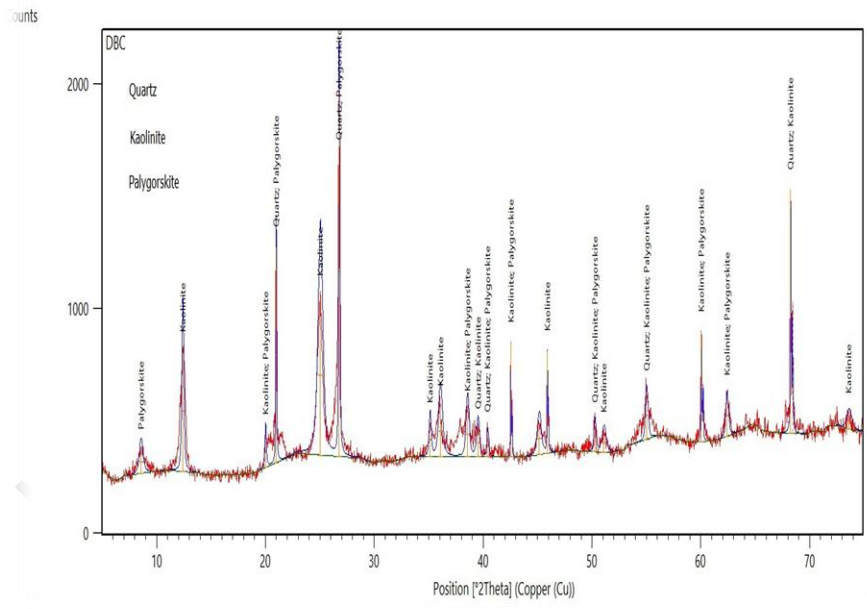

Figure 4b: XRD spectrum of HDTMAC-clay

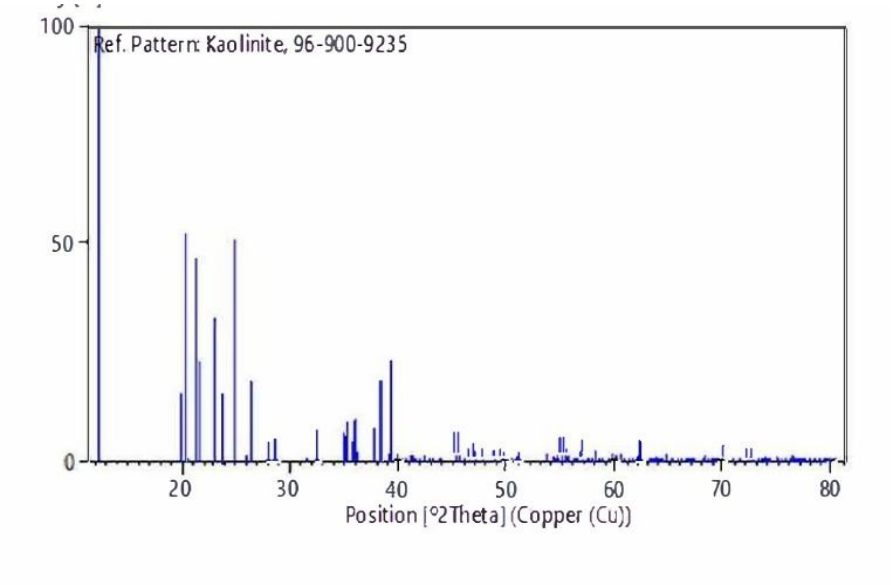

Figure 4c: XRD stick pattern for unmodified kaolinite clay

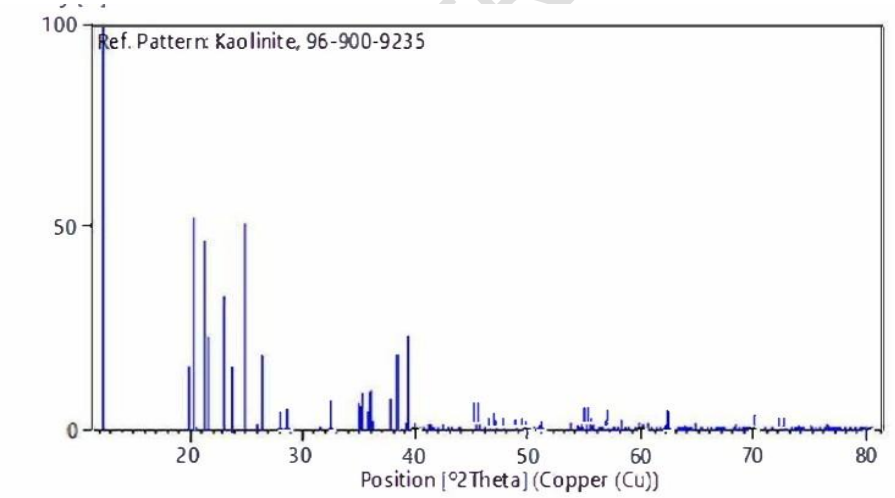

Figure 4d: XRD stick pattern for HDTMAC-modified kaolinite clay

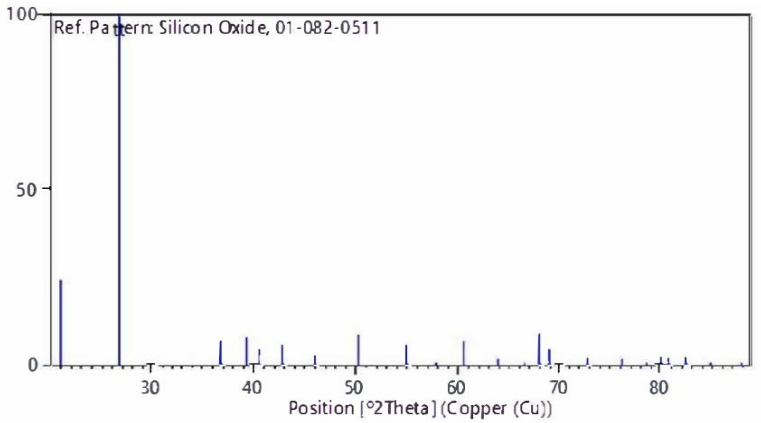

Figure 4e: Stick Pattern showing silicon oxide

Table 3: Interlayer spacing of modified and unmodified clays

Sample	d(Å)	2θ(^{0})
Unmodified Clay	7.134	14.115
HDTMAC-Clay	8.121	12.398

3.7 FTIR ~~Spectrum~~spectrum

The Fourier Transform ~~Infra~~ Infra-Red spectra and the vibrational band assignment for the unmodified and the HDTMAC-modified Ogwuta clay samples ~~as presented~~ in Figures 5a and 5b and ~~in~~ Table 4 revealed that the Peak at 671.25 cm^{-1} was due to Al-O-Si stretching while that at 771.55 cm^{-1} belongs to the Al-O-Fe bending in quartz [35]. The inner surface hydroxyl group (Al-OH-Al) deformation band was observed at 918.15 cm^{-1} and the bands associated with Si-O stretching, characteristic of kaolinite was 1010.75 cm^{-1}. Kaolinite H_2O bending bands for both samples were observed at1651.12 cm^{-1} for the HDTMAC-modified clay and 1635.69 cm^{-1} for the unmodified clay, while water molecule stretching characteristic of montmorillonite was observed at 3371.68 cm^{-1} and 3356.25 cm^{-1} respectively for the modified and the unmodified [36]. One distinctive band on the modified sample was observed at 2931.9cm^{-1} showing the C-H asymmetric stretching [37]. This band may have been the product of activation of the source clay. A close look at Figures 5a and 5b showed that this additional band did not cause any major distortion of clay structure, making the process of activation and sandwiching of the organic material in between the clay layers a huge success [34].

Table 4: Vibrational bands for the HDTMAC-modified and the unmodified clay used

S/N	HDTMAC-CLAY (cm^{-1})	UM-CLAY cm^{-1}	ASSIGNMENT
1	671.25	671.25	Al-O-Si stretching
2	771.55	771.55	Al-OH-Fe bending in quartz
3	918.15	918.15	Al-OH-Al bending (deformation of the inner surface hydroxyl group
4	1010.75	1010.75	Si-O stretching in kaolinite
5	1651.12	1635.69	H_2O bending
6	2931.9	-	CH asymmetric stretching
7	3371.68	3356.25	H_2O bending from Inner octahedral Al-OH
8	3618.58	3626.29	OH stretching in kaolinite

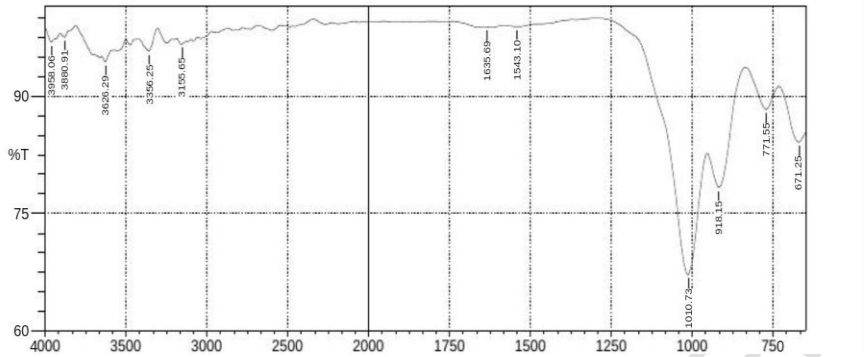

Figure 5a: FTIR spectrum of UM-clay

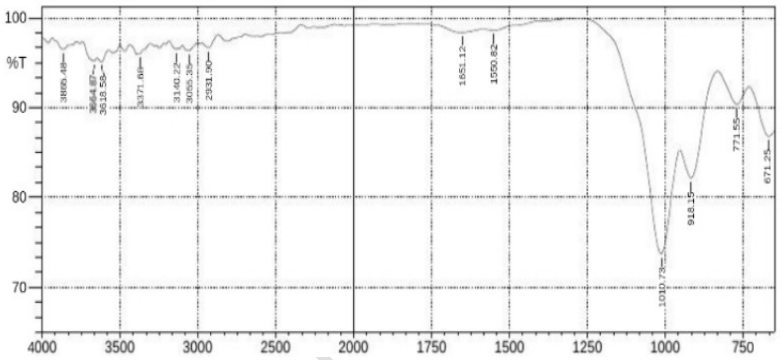

Figure 5b: FTIR spectrum of HDTMAC-clay

4. CONCLUSION

Ogwuta clay was sourced from its natural deposit and modified by ~~ion~~ ion-exchange using hexadecyltrimethylammonium chloride, a product of the reaction between H~~h~~exa-decyl chloride intermediate (prepared using hexadecanol and thionyl chloride) and tri-methylamine. Simultaneous characterization was performed on both samples. The Fourier Transform infrared micrograph showed a C-H asymmetric stretching in the modified sample and XRD results showed an increase in the basal spacing to 8.121Å, indicative of intercalation of organic surfactant. The number of steps from the TG results, in addition to the CEC value of not more than 19 meq/100g fits values of clays that are composed of predominantly kaolinite minerals. This evaluation of source clay makes it a veritable tool for copious industrial applications.

COMPETING INTERESTS DISCLAIMER:

Authors have declared that no competing interests exist. The products used for this research are commonly and predominantly used products in our area of research and country. There is ~~absolutely~~ no conflict of interest between the authors and producers of the products

because we do not intend to use these products as an avenue for any litigation but ~~for~~ the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by the personal efforts of the authors.

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Comment [es3]: MUST BE UPDATED as 27% (10 out of 37) of the listed references were published in the past five years. This percent has to be raised to 35-40% at least.

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