Physicochemical Properties of Organophilic Clay Developed Using Hexadecyltrimethylammonium Chloride (HDTMAC) Modifier

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Authors' contributions

This work was carried out in collaboration among all authors. Authors OC and I-EMU designed the study. Author AII performed the experiment, managed the literature searches, wrote the protocol, and wrote the first draft of the manuscript. Authors OC and I-EMU vetted the manuscript. Author OC managed the correspondence. All authors read and approved the final manuscript.

Original Research Article

ABSTRACT

Aims: Ogwuta clay from Unwana in the South Eastern part of Nigeria was modified by ion exchange reaction using hexadecyltrimethylammonium chloride (HDTMAC).
Study Design: This study was analyzed experimentally and instrumentally.
Place and Duration of Study: This study was carried out at the Department of Pure and Industrial Chemistry, Faculty of Science, University of Port Harcourt, Nigeria. The sample collection, literature search, experiment, results and analysis lasted for one and half years.
Methodology: Physicochemical and thermal properties of the clay were determined after modification using classical and spectroscopic techniques. A combination of the wet and dry method (X-ray Fluorescence) was used to determine the metal oxide composition. Other techniques included; Fourier Transform Infrared (FTIR), X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), and Thermogravimetry (TG). The Cation Exchange Capacity (CEC) was determined using the methylene blue method with a value of 16.4 meq/100g after modification.

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Results: The product was slightly acidic with pH 4.3. Silica (SiO_2), alumina (Al_2O_3), Na^+, and K^+ were found to be 47.58 %, 18.99%, 2.27, and 0.23% respectively. The clay was limited in mineral impurities with 0.0% T^{4+}, 0.41% Mg^{2+}, and 0.11% Ca^{2+} but high in carbonaceous matter with loss on ignition (LOI) of 13.17%. A C-H asymmetric stretching was visible around the 2931.9 cm^{-1} region as revealed by the Fourier Transform Infra-Red analysis. The X-Ray Diffraction analysis of the modified clay showed a basal spacing of 8.121 Å. Also, the X-Ray Diffractogram revealed kaolinite as the major clay mineral with the presence of quartz and polygorskite.

Conclusion: This study posits that the modified clay can be potentially suitable for the adsorptive removal of organic contaminants in aqueous and real life media.

1. INTRODUCTION

Clay minerals are naturally occurring materials composed of fine-grained phyllosilicates (minerals which 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, they are composed of silica, alumina, magnesia and water. Iron substitute for aluminum and magnesium to varying degrees and appreciable quantity of potassium, sodium and calcium are frequently present [3]. Structurally, clay minerals like all phylosilicates are characterized by two dimensional sheets of 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 particle size less than 2μm and are distinguished from other fine-grained particles such as silt by their plasticity 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 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.
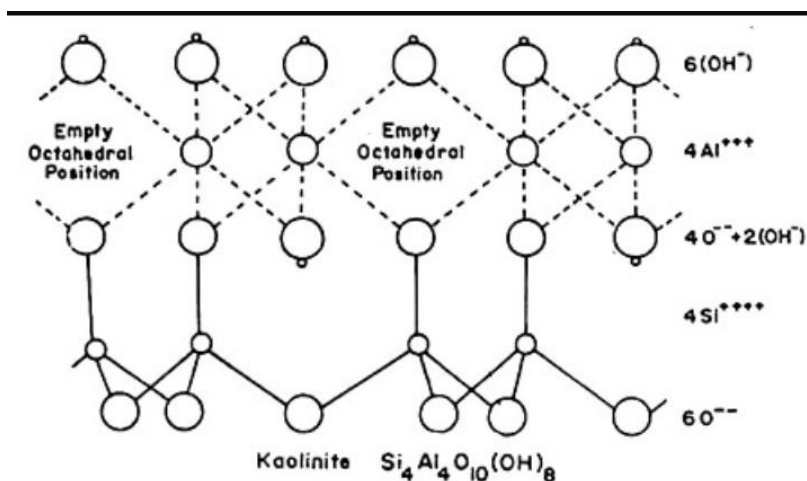

Fig. 1. Structure of a 2:1 clay [5]

These properties make clay minerals find wide applications. Smectites are useful as an annular seal or plug for water wells and as protective liner for landfills. Other uses include as an anti-caking agent in animal feed. Approximately 40% of kaolin produced worldwide is used in the filling and coating of paper. Cellulose fibers are mixed with kaolin to give it body and enhance its printability and opacity [8]. Also, due to high fusion temperature and white burning characteristics of kaolin, it is very suitable for making white wares. 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 concrete mix, accelerates the hydration of Portland cement [9]. Bhattacharyya and Gupta [10] 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 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 substituents, R and R^1 are alkyl or aromatic hydrocarbons. The presence of this compound increases the interlaminar distance or basal spacing of d_{100} plane and modifies the surface properties of the clay by changing from hydrophilic to organophilic [11]. This change enhances the application of organoclays as an effective material for removing hydrocarbon contaminants in wastewater treatment.

There are several identified and unidentified clay deposits in Nigeria ranging from the Northern to the Eastern parts of the country [12,13]. It is therefore imperative that these clay minerals be x-rayed in physical, chemical, thermal, refractory properties and documented for immediate and future use.

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), and Thermogravimetric analysis (TGA). Other physical parameters such as pH, surface area, pore volume, and cation exchange capacity were investigated.
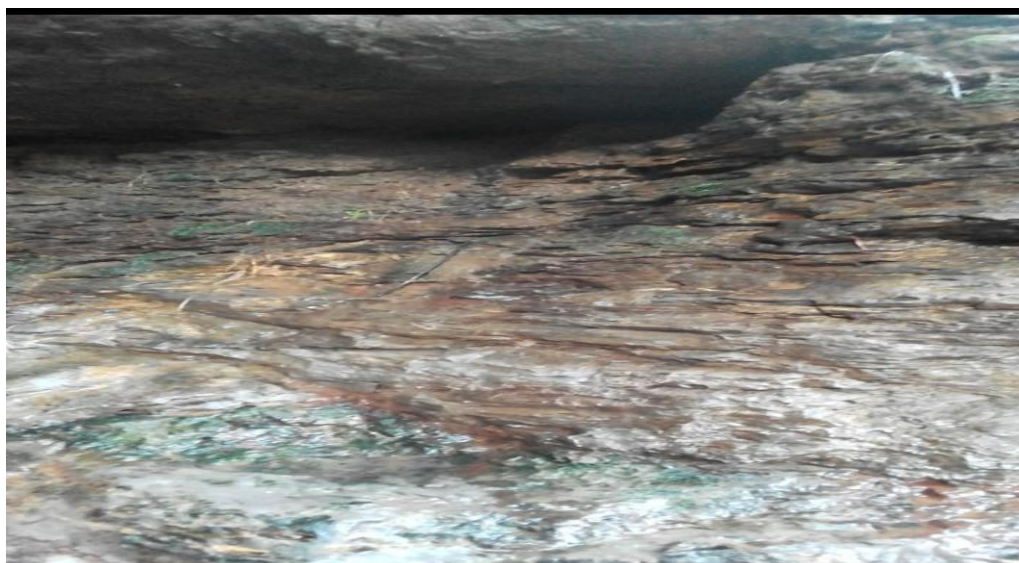

Plate 1. Ogwuta clay deposit

2. MATERIAL AND METHODS

2.1 Materials

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

Hexadecyltrimethylammonium chloride (HDTMAC) surfactant was obtained from Sigma-Aldrich and used without further purification. All other chemicals were of analytical grade.

2.2 Organophillization of Source Clay

According to Ltifi et al. [14], a 20 g of clay was dispersed in a 2 L capacity beaker containing 1000 ml of water for 90 min at a rotation of 250 rotations per min (rpm) and at 80°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 after which the solid was filtered using a vacuum filtration apparatus. The modified clay was oven-dried for 24 hrs at 80°C, ground into powder using mortar and pestle, labelled and then stored in a desiccator.

2.3 Characterization of Modified Clay

2.3.1 pH determination

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

2.3.2 Surface area determination

The surface area of the clay sample was determined according to the method of Alvarez et al. [15]. A 1.5 g of clay sample was agitated in 100 ml of dilute HCl, that had been diluted to pH of 3.0. Then, 30 g of 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 equation:

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

2.3.3 Specific gravity determination

This was determined using the Archimedes principle described by Dada et al. [16]. Briefly, 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) measured. The clay sample (10 g each) was added to an empty dry specific bottle and the weight (w_3) recorded. Finally, the bottle containing the sample was then filled with water and all air bubbles expelled before the weight (w_4) was measured. The specific gravity ($s.g$) of the clay was calculated as below:

$$s.g = \frac{\text{weight of sample}}{\text{weight of equal volume of water}}$$
$$s.g = \frac{w_3 - w_1}{(w_2 - w_1) - (w_4 - w_3)} \qquad (2)$$

2.3.4 Determination of total pore volume

The total pore volume of the clay sample 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 increase in weight divided by the density of the water (1 g/cm^3).

2.3.5 Cation exchange capacity determination

The cation exchange capacity of the clay was determined according to the standard test method for methylene blue index for clay designated by C837-09. A 2.0 g of previously dried clay was placed in 1L beaker containing 300 ml of water. The mixture was stirred until uniform dispersion was achieved. The pH of the slurry was determined and sufficient sulphuric acid 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 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 observed. This continued until the endpoint marked by the appearance of a light blue halo around the drop. The Methylene Blue Index (MBI) was calculated thus:

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

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

2.3.6 Metal oxide composition determination

This was done using a combination of the wet and the dry methods. Oxides of K, Al, Mg, Fe, Ca and Na were analyzed using XRF Analyzer (DCC-6000 Mineral mode).

Silicon dioxide (SiO_2) was analyzed according to the method of Costanzo [17]. 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 $AgNO_3$ 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 platinum crucible. The oxide was determined using Atomic Absorption Spectrophotometer. The loss on ignition (LOI) was determined by burning 1.0 g of sample at 1000^oC in a muffle furnace.

2.3.7 Fourier Transform Infra-Red (FTIR) scan

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 pestle to homogenize the mixture. A little amount of the mixture was placed in a miniature press and compressed to form a disc or pellet of about 1mm thickness. This was placed in the appropriate sample holder, the holder, with 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 printed out.

2.3.8 Scanning Electron Microscopic (SEM) scan

SEM scan on modified clay sample was done according to the method reported by Rajkumar et al. [18].

2.3.9 Thermogravimetric analysis

The thermal analysis of sample was done 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^oC at a heating rate of 10^oC/min under air purge gas drawn at 20 ml/min and pressure of 2.5 bar. Traces were recorded as percentage weight loss versus temperature.

3. RESULTS AND DISCUSSION

From Table 1, the pH of the HDTMAC-modified clay sample at 30^oC was 4.3 indicating slight acidity. 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 [19], that is, clay samples from areas with lots of rainfall have pH values less than 3.5. The result agrees with the observation by Suedina and Carla, [20] 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. Therefore, this higher than expected pH value may have arisen from the reduced capacity of the modified clay to hold hydrogen ion which is a consequence of reduced cation exchange capacity [10].

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

Parameter	modified clay
pH	4.3
Surface Area	129.2 m^2g^{-1}
Specific Gravity	2.11 gcm^{-3}
Pore Volume	0.53 m^3g^{-1}
CEC	16.4 meq/100g

3.1 Specific Surface Area

The specific surface area of the HDTMAC-modified clay was found to be 129.2 m^2g^{-1}. This value agrees with that made by Uzochukwu [21] 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 [22].

3.2. Specific Gravity

The observed specific gravity of 2.11g/cm^3 for the HDTMAC-clay falls within the range of a

minimum of 1.8 to a maximum of 2.6 for clays [23]. This however is expected to be less than the unmodified source clay due to the intercalation of surfactant molecules.

3.3. Cation Exchange Capacity

The cation exchange capacity of the HDTMAC-clay at pH 6 was found to be 16.4 meq/100g. This property of clay arose from isomorphous substitution, a crystal lattice defect in which a given ionic series may be replaced by another in a crystal lattice [24]. According to Neeraj and Chandra [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 Composition

The results of the metal oxide composition of the modified clay as presented 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 [25]. The loss on ignition value of 13.17 % revealed that the modified clay *was high in carbonaceous matter (Pushpaletha* et al. [26]. Also, the recorded percentage composition of Mg, Ca, Na and K are 0.41, 0.11, 2.28, and 0.23 respectively. Substantial amount, 1.12 % of Cl⁻, which could be as a result of possible interaction of the non-substituted cations with the anion was recorded. 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 [27]. However, with zero Ti content and less than 2% Mg and Ca content, the clay showed limited mineral impurities [28].

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

Parameter	Modified Clay
Al	18.99
Si	47.58
Mg	0.41
Ca	0.11
Na	2.28
K	0.23
Fe	6.87
Ti	0.00
Cl⁻	1.12
LOI	13.17
Moisture	0.43

3.4 Scanning Electron Micrograph (SEM)

The Scanning Electron Micrograph of the HDTMAC-modified clay as presented in Fig. 2 revealed apparently smaller in sized, disordered, thin sheet particle aggregates. This observation could be due to the fact that organophilization enhanced the formation of a disordered and less cohesive aggregates arising from the reduction of edge-to-edge and face-to-face interactions [19].
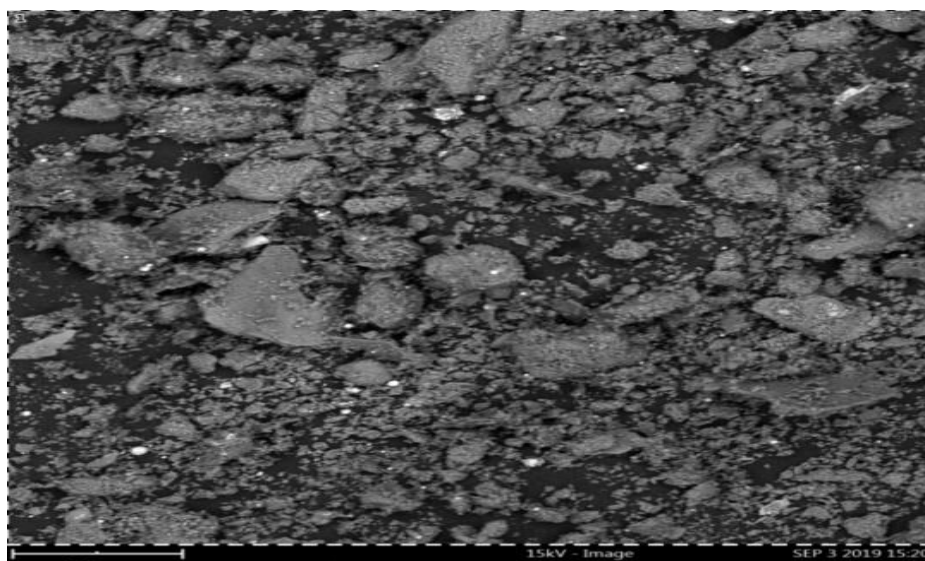

Fig. 2. SEM image of HDTMAC-Clay

3.5 Thermal Analysis

The thermal behavior of the modified ogwuta clay as presented in Fig. 3 showed thermal behavior similar to most kaolinitic clay samples in literature [29,30]. The clay showed initial exothermic weight gain that peaked at $39.84^{o}C$. This might be attributed to hygroscopic behavior of the samples enhanced by not using very dried air [31]. However, all gained weight was lost completely at $45.51^{o}C$. The sample exhibited characteristic exothermic weight loss (2%) around $100-150^{o}C$, which could be associated with the physically adsorbed water [32]. 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 sample was observed between $388-450^{o}C$, 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. [30] was due to the dehydroxylation of the hydroxyl group of the clay sample.

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 (XRD) was employed. The Ogwuta HDTMAC-modified clay was subjected to this method. The d_{001} peak displacements of modified clay as shown in Figs. 4-6 showed a value of 12.398^{0} at the 2θ angle. This led to a corresponding increase in the d_{001} 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 clay interstice did not collapse after modification [33].
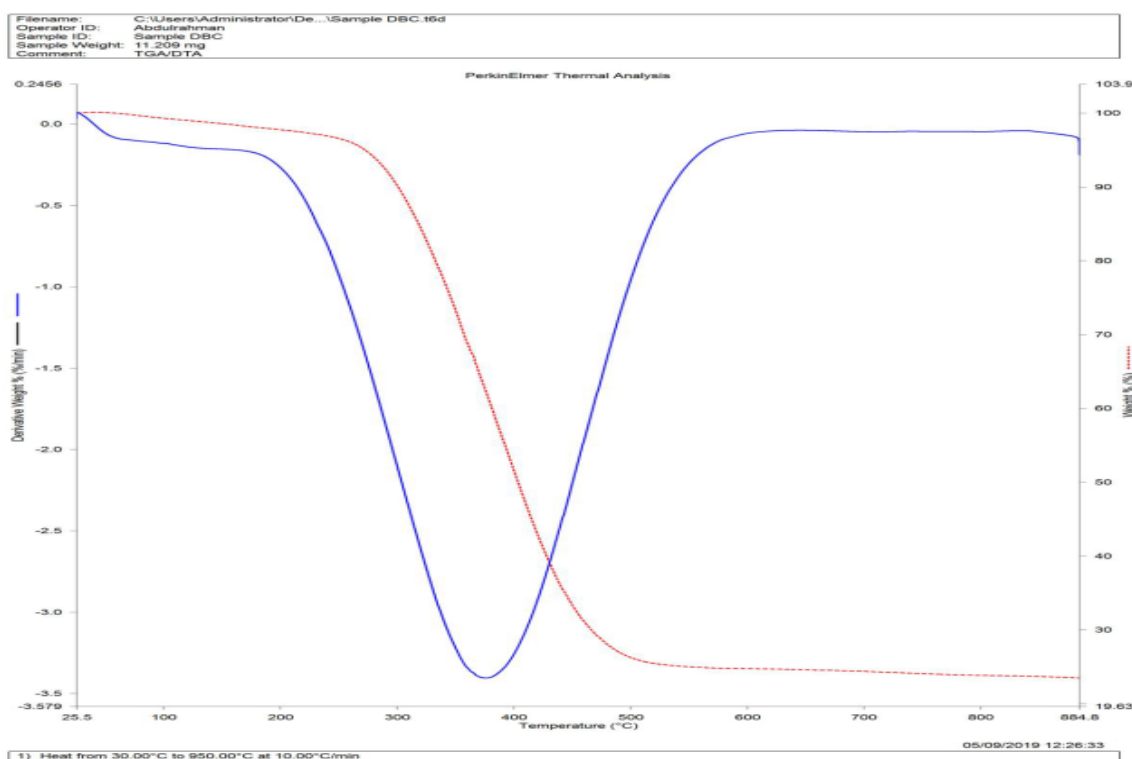

Fig. 3. TGA/DTA of HDTMAC-Clay

Table 3. Interlayer spacing of HDTMAC-modified clay

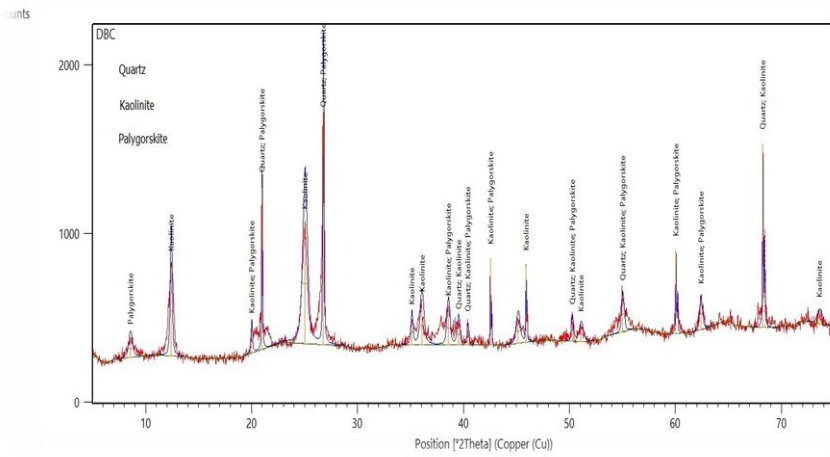| Sample	d(Å)	$2\theta(^{0})$
HDTMAC-Clay	8.121	12.398

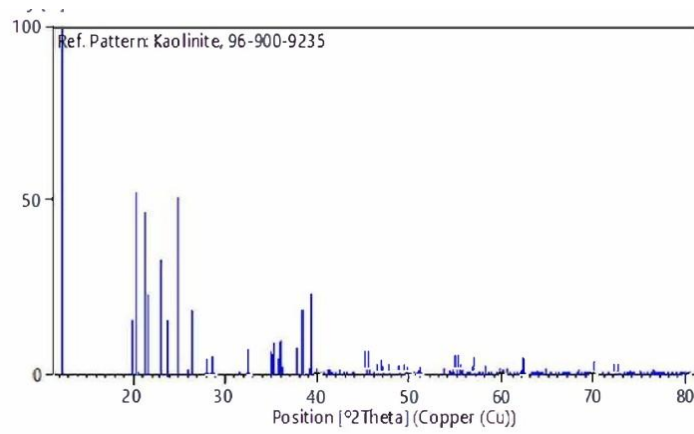**Fig. 4. XRD spectrum of HDTMAC-clay**

Fig. 5. XRD stick pattern for HDTMAC-modified clay
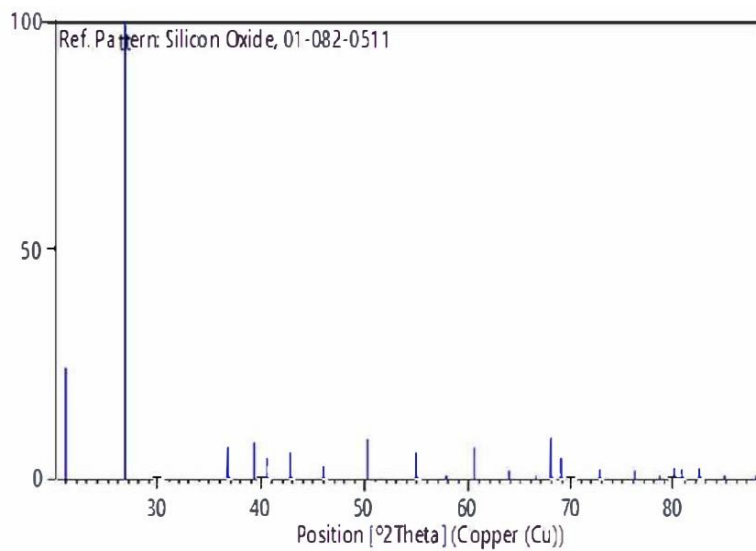
Fig. 6. Stick Pattern showing Silicon Oxide

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Table 4. Vibrational bands for the HDTMAC-modified clay

S/N	Band (cm^{-1})	Assignment
1	671.25	Al-O-Si stretching
2	771.55	Al-OH-Fe bending in quartz
3	918.15	Al-OH-Al bending (deformation of inner surface hydroxyl group
4	1010.75	Si-O stretching in Kaolinite
5	1651.12	H_2O bending
6	2931.9	C-H asymmetric stretching
7	3371.68	H_2O bending from Inner octahedral Al-OH
8	3618.58	OH stretching in Kaolinite
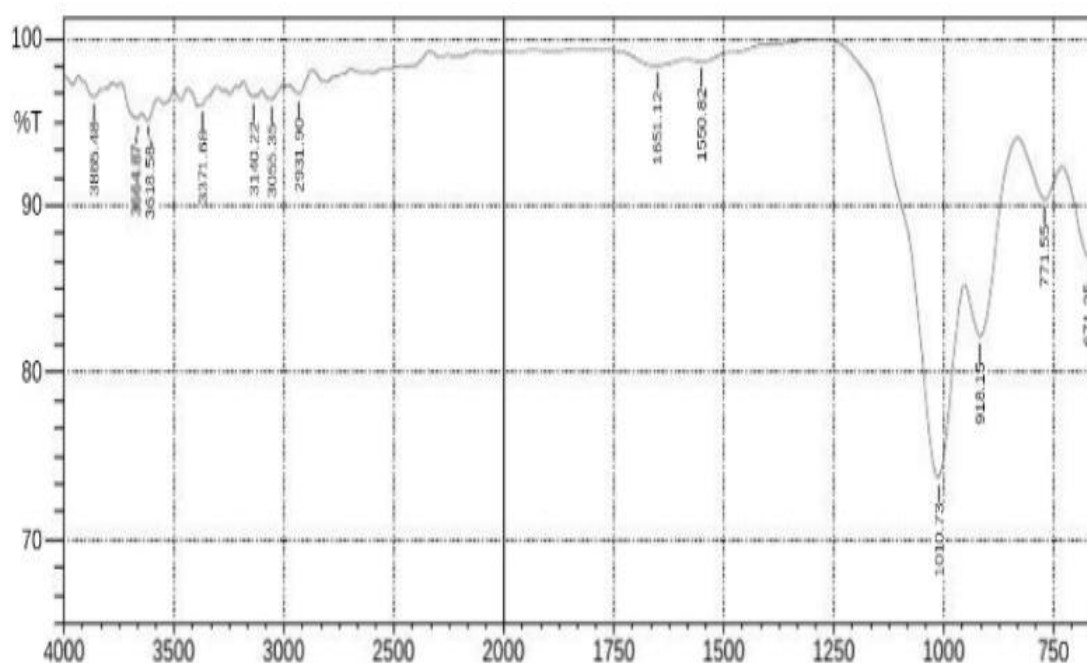
Fig. 7. FTIR spectrum of HDTMAC-clay

3.7 FTIR Spectrum

The Fourier Transform Infra-Red spectrum and the vibrational band assignment for the HDTMAC-modified Ogwuta clay sample as presented in Fig. 7 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 [34]. 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 was observed at1651.12 cm^{-1}, while water molecule stretching characteristic of montmorillonite was observed at 3371.68 cm^{-1} [35]. One distinctive band was observed at 2931.9 cm^{-1} showing the C-H asymmetric stretching [36]. This band may have been the product of activation of the source clay.

4. CONCLUSION

Ogwuta clay was sourced from its natural deposit and modified by ion exchange using hexadecyltrimethylammonium chloride. Some physical properties of the product showed that it was slightly acidic with a pH of 4.3 and a total surface area of 129.2 m^{2}g^{-1}. Spectroscopic techniques such as FTIR, XRD, SEM, and XRF were employed for further characterization of the organophilic product. The Fourier Transform infra-red micrograph showed a C-H asymmetric stretching at 2931.9 cm^{-1} in the sample usually absent in most natural clays from the Eastern part of Nigeria. XRD results, in addition to showing an increase in the basal spacing to 8.121Å, which was indicative of intercalation of organic surfactant, matched a kaolinitic clay with reference code 96-9-9235. 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 mineral. This evaluation of source clay makes it a veritable tool for diverse industrial application.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Ivana S, Stanisa S, Ivan S, Dragoljub G. Industrial application of clay and clay Minerals. Earth Sciences in the 21st Century, Nova Science Publishers Inc. New York, 2014.

2. Barton CD, Karathanasis AD. Clay Minerals, In: Lal, R. Ed/, Encyclopaedia of soil science, Mansreal Dekker, New York, USA. 2002;187-192.

3. Moore D, Reynolds RC. X-Ray diffraction and the identification and analysis of clay minerals. 2nd edtion. New York, Oxford University Press; 1997.

4. Neeraj K, Chandra M. Basics of clay minerals and their characteristic clay and clay minerals; 2021. DOI: 10.5772/intechopen.97672.

5. Sarkar B, Singh MM, Mandal S, Churchmen G, Bolan S. Organic matter interaction in relation to carbon stabilization in soil: The future of soil carbon. Clay Miner. 2018;71-86.

6. Walter IP. Economic Geology: Principles and Practce, 5th Ed. Warshington, John Wiley & Sons;2011.

7. Claudiane O, Rod J, Abir A. Comparison between grannlar pillared organobentonites for hydrocarbon and metal ion adsorption. Appl. Sci. 2012;67:91-98.

8. Haydn HM. Developments in Clay Science 2, 2006. DOI:10.1016/s1572-4352(06)02005-8

9. Levista T, Gehor S, Eijarvi E, Sarpola A,;Tanskanen J. Characteristics and potential applications of coarse clay fractions from puolance, Finland. Cent. Euro. J. Eng. 2012;2(2):239-247.

10. Bhattacharyya GK, Gupta SS. Influence of acid activation of kaolinite and montmorillonite on adsorptive removal of Cd(II) Ion from Water. Ind. Eng. Chem. Res. 2008;46(11):3734-3742.

11. Pankil S, Rajeev M, Siddh NP. Clay modification by the use of organic cations. Green Sustain. Chem. 2012;2:21-25.

12. Agbo SC, Nnaneme EO, Onuegbu TU., Okwute EC. The characterization of local clay from anambra state nigeria for its potential application in the production of ceramics white wares. Asian J. Chem. Sci. 2020;8(2):73-86.

13. Ituma CG, Etukudoh AS, Mark A, Obioha IC. Utilization of nkpuma-akpatakpa clay in ceramics: Characterization and microstructural studies. J. Appl. Sci. Environ. Manage. 2018;22(1):47-52.

14. Ltifi I, Ayari F, Chehimi DBH, Ayadi MT. Physicochemical characteristics of organophilic clays prepared using two organo-modifiers: alkylammonium cation arrangement models. Appl. Water Sci. 2018;8(91):
https://doi.org/10.1007/s13201-018-0732-8.

15. Alverez AN, Rocha MC, Bertolino LC. Mineralogical characterizatioin of natural clay from brazillian southeast region for industrial application. Ceramica. 2017;63(2017):253-262.

16. Dada AO, Olalekan PA, Olatunya A. Langmuir, freundlich temkin and dubinin-radushkevich isotherm studies of equilibrium sorption of Zn^{2+} unto phosphoric acid modified rice husk. J. Appl. Chem. 2012;3(1):38-45.

17. Costanzo PM. Data and industrial minerals, including clay and clay mineral deposits. J. Clay Clay Mater. 2001;59(5):372-373.

18. Rajkumar U, Haunshi S, Paswan C, Raju MVLN, Rama RSV, Chatterjee RN. Characterization of indigenous Aseel chicken breed for morphological, growth, production and meat composition traits from India. Poult. Sci. J. 2017;96:2120-2126.

19. Denis LG, Rubia RV, Claudio A. Adsorption of thorium (iv) on chemically modified amazon clay. J. Braz. Chem. Soc. 2009;20(6):1164-1174.

20. Suedina ML, Carla RC. Application of infrared spectroscopy to chitosan/clay nano composites. Infra-red Spectroscopy-Material Science, Engineering and Technology. Theophanides Theophile (Ed). Shanghai. Intech Publishing;2012.

21. Uzochukwu CU. Measurement of Surface Area of Modified Clays by Ethylene Glycol

Monoethyl Ether Method. Asian J. Chem. 2017;29(9):1891-1896.

22. Ahmet RM., Angel FC. Baseline studies of the clay mineral society, chemical analysis of major elements. Clays Clay Miner. 2010;51(5):381-386.

23. Dominique R, Francoise E. Characterization of soil clay minerals. Clays Clay Miner. 1996;44(6): 791-800.

24. Bergraya F, Vayer M. CEC of clays: Measurement by adsorption of a copper ethylenediamine complex. Appl. Clay Sci. 2009;12: 275-280.

25. Nweke ES, Ugwu EI. Analysis and Characterization of Clay Soil in Abakaliki, Nigeria. The Pacific J. Sci. Technol. 2007;8(2): 190-193.

26. Pushpaletha P, Rugmini S, Latithambika M. Correlation between Surface Properties and Catalytic Activity of Clay Catalysts. Appl. Clay Sci. 2005;30(1): 141-153.

27. Nnuka EE., Enejo C. Characterization of Nahuta Clay for Industrial and Commercial Application. NJEM, 2001;2(3): 9 -13.

28. Umbugadu A, Igwe O. Mineralogical and Major Oxide Characterization of Panyam Clays, North Central Nigeria. Inter. J. Phys. Sci. 2019;14(11): 108-115.

29. Hassan UJ, Abdu SG. Structural Analysis and Surface Morphology of Kaolin. Science World Journal, 2014;9(3): 33-37

30. Conconi MS, Morosi M, Maggi J, Zaiba P, Cravero F, Rendtoff N. Thermal Behaviour (TG-DTA-TMA) Sintering and proportion of Kaolinitic Clay from Buenos Aires. Ceramica, 2019;(65): 374-379.

31. Tadele AS., Fikiru T. Synthesis and Characterization of Ethiopian Kaolin for the Removal of Basic Yellow (BY-28) dye from Aqueous Solution. Helyon;2020;6.

32. Wang H, Li C, Peng Z, Zhang S. Characterization and Thermal Behaviour of Kaolin. J. Therm. Anal. Calori. 2011;(105):157-160.

33. Okoye IP, Obi C. Synthesis and Characterization of Al-pillard Bentonite clay minerals. Res. J. Appl. Sci. 20011;6 (7-12):447-450.

34. Alemayelu K, Gholap A, Giovanni E. Fourier Transform Infrared Spectroscopic Characterization of Clay Minerals from Rocks of Lalibela Churches, Ethiopia. Inter. J. Phys. Sci. 2013;8(3):109-119.

35. George-Ivo EE. Fourier transform infrared spectrophotometry as a complementary technique in characterizing clay size fractions of kaolin. J. Appl. Sci. Environ. Manage. 2005;9(2):43-48.

36. Bhattacharya S, Mandot A. Studies on preparation and analysis of organoclay nanoparticles. Res. J. Eng. Sci. 2014;3(3): 10-16.

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