Traektoriâ Nauki = Path of Science. 2020. Vol. 6, No 6 ISSN 2413-9009

Instrumental Characterization of Unmodified and HDTMA-Br Modified Kaolinite Clay: SEM-EDX, Quantachrome and TGA-DTA

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DOI: 10.22178/pos.59-1

LCC Subject Category: QD1-65

Received 14.04.2020
Accepted 28.05.2020

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Abstract. Kaolinite clay from Alkaleri Northeast Nigeria was pre-treated and beneficiated using physical process. The treated clay of cation exchange capacity (CEC) 9.5 meq/100 g was modified with cationic surfactant hexadecyltrimethylammonium bromide (HDTMA-Br) with amount equivalent to and doubled the CEC. The unmodified kaolinite clay (UKC) and the resultant organo-kaolinite clays: monolayer modified clay (MMC) and bilayer modified clay (BMC) were characterized using the following instruments: Energy Dispersive X-ray spectrometer (EDX), Scanning Electron Microscopy (SEM), Quantachrome and Thermogravimetric-Differential Thermal Analysis (TG-DTA). EDX profile analysis shows 22.41 % C, 56.17 % O & 10.56 % Al in UKC; 21.06 % C, 55.49 % O & 11.66 % Al in MMC and 18.98 % C, 54.59 % O & 12.14 % Al in BMC respectively; with Fe and K found in MMC. The SEM morphology shows UKC has high porosity and large particles, while MMC and BMC showed fine particles and darker than UKC with textural non-uniformity. TGA curve shows that UKC attains equilibrium decomposition at 997.20°C with 15.32 % weight loss, MMC 997.30 °C with 32.67 % weight loss and BMC 998.90 °C with 37.23 % weight loss. The revealed weight loss indicates water of hydration and dehydroxylation. The DTA curves shows endothermic at 510 °C, 250 °C and 520 °C for UKC, MMC and BMC respectively. The single point surface area were 11.9754 m^2/g, 3.0132 m^2/g and 3.8225 m^2/g for UKC, MMC and BMC with corresponding adsorption average pore width 355.0050 Å, 478.6275 Å and 752.8364 Å respectively. Clay materials being promising minerals when modified can achieve desired surface properties for best performance in adsorption applications.

Keywords: Alkaleri-Northeast Nigeria; Characterization; Hexadecyltrimethylammonium bromide; Kaolinite clay; Quantachrome; Scanning electron microscopy / Energy dispersive X-ray spectrometry; Thermogravimetric / Differential Thermal Analysis.

INTRODUCTION

Kaolinite clay mineral in which silicon occupies all the tetrahedral sites and Aluminum two thirds of the octahedral sites (the remaining third of the sites being vacant), the composition is $Si_4^{iv}Al_4^{vi}O_{10}(OH)_8$, where *‘iv’* is used to indicate tetrahedrally coordinated ions and *‘vi’* those octahedrally coordinated [1, 5]. Kaolin clay is soft, earthy and usually white mineral produced by chemical weathering of aluminum silicate minerals like feldspar. Usually, it is colored pink-orange-red by iron oxide giving it a distinct appearance [7, 11], thus the resultant structural formula for one layer unit of Kaolinite clay from Alkaleri, North-Eastern Nigeria is $Na0.263K0.043Ca0.012Si4.054ivAl3.552Ti0.14Fe0.0733+Ni0.0007Zn0.0003Cr0.0015Mn0.054viO10OH8$ where the Na, K and Ca are ‘exchangeable’, with the chemical composition SiO_2=53.8 %, Al_2O_3=40.0 %, TiO_2=2.44 %, Fe_2O_3=1.29 %, NiO=0.011 %, ZnO=0.006 % Cr_2O_3=0.024 %, MnO=0.008 %, CaO=0.15 %, Na_2O=1.821 % and K_2O=0.45 % [1].

Kaolinite clay mineral has a low-cation exchange capacity (CEC) ranges from 3–15 meq/100 g, the low values probably representative of pure kaolinite and the increase could depend on impurities and particle sizes [4, 8]. The CEC of Kaolinite clay from Alkaleri as determined by ammonium acetate method is 9.5 meq/100 g [1].

Kaolin as a result of its well-packed structure, are not easily broken down and its layers are not easily separated. Most sorption activity occurs along the edges and surfaces of the structure [12]. The silicates nature that makes kaolinite effective in removal (or treatment) of contaminants has to undergo purifications. The render layered silicates miscible with polymer matrices, normally hydrophilic silicate surface has to be converted to an organophilic surface to make intercalation of polymeric chain between the silicate layers, this is done by ion-exchange reaction with cationic surfactants [15].

Organoclay refers to the natural clay minerals which have their surface modified to improve their adsorption ability, capacity and affinity for oxyanion contaminants by the replacement of the natural inorganic cations with surfactants cations such as quaternary ammonium compounds (QACs) [3, 17]. The possible application of generated organoclay is the better intercalation of polymer chains between the stack of clays, which when modified will be useful in sustaining ecosystem friendly with improved properties. This method is done by modifying the clay surface in traditional ion-exchange, and organoclay which must be treated before it can be used to make a nanocomposite. Making a composite out of untreated clay would not be very effective because most of the clay would be unable to interact with the matrix [15].

Cation exchange such as Na^+, Ca^{2+} and Mg^{2+} may occur between the silicates layers associated with water molecules. These elements are exchangeable and their exchange reaction is very important in most of the clay application. Na^+ or Ca^{2+} or Mg^{2+} by quaternary ammonium cations of the forms $[(CH_3)_3NR]^+$ or $[(CH_3)_2NRR']^+$ at the exchangeable site of natural clays results in organoclay derivatives with organophilic properties that can act as a sorbent contaminant hydrocarbons [2, 9]. The R and R' is the alkyl or aromatic hydrocarbons.

The degree of surfactant ($HDTMA^+$) addition is limited to the CEC of the clay being modified, where $HDTMA^+$ replaces the charge balancing cations on the surfaces [2]. The net negative charge of the natural clay minerals is balanced by alkali metal and alkali earth metals cations such as Na^+, Ca^{2+} and Mg^{2+} [9]. The substitution of cations is presented in Equation (1) [2], while the anions are halides such as; Cl^-, Br^-, I^- and $clay^-$ which is exchanged with the cations at surfaces.

$$M.clay + HDTMA^+ \rightarrow clayHDTMA + M^+ \quad \ldots (1)$$

where M^+ is the metal cation such as Na^+, Ca^{2+} and Mg^{2+}.

Some common examples of monatomic/inorganic cations (metals) are alkali metal, alkaline earth metals, and transition metals while anions (halides) are chloride, bromide and iodide. Polyatomic/organic cations (metals) are ammonium, pyridinium and triethanolamine (TEA) while anions are tosyls, trifluoromethanesulfurnates and methyl sulfate. Equation (2) presents the surface action of the quaternary compounds and the clay, where clay minerals with negative charge will exchange with $HDTMA^+$ at the surface to form organoclay.

$$M.clay + HDTMA.X \rightarrow clayHDTMA + M.X \quad \ldots (2)$$

where halides (X) are chloride (Cl^-) or bromide (Br^-) or iodide (I^-).

Adsorbents are usually irregular granules extruded pellets and formed spheres. The size reflects the need to pack as much surface area as possible into given volume of bed and also minimize pressure drop for flow through the bed [6]. Good adsorbents should have these qualities: large internal surface area, accessible through pores large enough to admit molecules to be adsorbed, while small pores will exclude molecules that are not desired to be adsorbed, it should not age rapidly such that it does not lose its adsorption capacity through continuous recycling and it should be mechanically strong enough to with stand bulk handling and vibration from industrial.

This research work is to instrumentally characterize unmodified and organically modified kaolinite clay from Alkaleri Local Government Area of Bauchi State, North-Eastern, Nigeria.

MATERIALS AND METHODS

The procedure used for this research work are; pretreatment and beneficiation of the raw kaolinite clay, modification of purified kaolinite clay with equivalent ratios of cationic surfactant to form organically modified kaolinite clay.

Pretreatment and beneficiation of kaolinite clay. Kaolinite clay was obtained directly from the mining site at Alkaleri Local Government Area, Bauchi State, North-Eastern Nigeria. The clay lump was broken into particles, soaked in excess de-ionized water in a pretreated plastic container for effective dissolution and homogeneity for 48 hours. The slurry was blunged and allowed to settle for 48 hours before decantation of the excess de-ionized water and the clay residue was sun dried. This was followed by oven drying at 105 °C for 3 hours to ensure moisture free adsorbent. The dried clay, was grinded using pestle & mortar and passed through mesh sieve of 100 μm to obtain unmodified Alkaleri kaolinite clay (raw kaolinite clay), which was characterized and stored safe in a desiccator for further usage.

Preparation of organically modified kaolinite clay. The characterized kaolinite clay from Alkaleri Local Government of Bauchi State, North-eastern Nigeria with 9.5 meq/100 g CEC [2] was modified with organic surfactant (HDTMA-Br), 99 % purity and 364.45 g/mol molecular weight, without any further treatment. The modification of kaolinite clay was carried out in two categories: the monolayer (CEC equivalent) and bilayer (twice CEC equivalent) modifications.

The synthesis of organo-kaolinite clays was carried out by weighing equivalent CEC amount of surfactant (HDTMA-Br) to produce monolayer and twice CEC to produce bilayer, dissolved in 250 mL of de-ionized water and stirred efficiently to ensure proper dissolution of surfactant; this was then followed by addition of known amount of unmodified kaolinite clay (UKC) with cation exchange capacity 9.5 meq/100 g clay to the already dissolved surfactant. The mixtures were stirred perfectly followed by addition of de-ionized water to make it up to 500 mL. The mixture was then charged into a batch reactor and run at 740 rpm for 24 hours at 25 °C and 1 atmospheric pressure to achieve homogeneity [3]. After 24 hours of agitation in a batch reactor, the slurry was transferred into 800 mL beaker and allowed to settle for 24 hours, the supernatant was decanted and washed every 24 hours for four times with de-ionized water to reduce the bromide content. This was followed by drying at 25 °C for 48 hours and oven drying for 3 hours at 104 °C, which was then ground using pestle & mortar and passed through mesh sieve of 100 μm size to produce monolayer modified organo-kaolinite clay (MMC) and bilayer modified organo-kaolinite clay (BMC) respectively.

Characterization of unmodified and modified kaolinite clays. The unmodified and modified kaolinite clays prepared were characterized using, scanning electron microscopy (SEM), energy dispersive X-ray spectrometer (EDX) to determine their morphologies, porosity, textural uniformity, fissures and mineralogical compositions [14]. Quantachrome analysis was carried out to determine the surface area, pore size and pore volume of the clays [2]. Thermogravimetric analyzer/differential thermal analyzer (TGA/DTA) was carried out to examine the weight loss arising from degradation of organic substances [2, 4].

Scanning electron microscopy/ Energy dispersive X-ray spectrometry. Scanning Electron Microscopy (SEM) is an electron that describes the sample by scanning a beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample surface topography, composition and properties - properties such as electrical conductivity. Scanning electron microscopy with energy-dispersed X-ray analysis (SEM/EDX) is commonly used for single particle study. It provides useful information on the morphology, elemental composition and particle density and also gives us a better insight about the origin of particles [11, 13]. The EDX/SEM analysis was carried out using spectroscope on window SATW spectrum model. The spectrum detector was set at its maximum (X-max) to detect all elements present in the clay mineral at an elevation temperature, accelerating voltage, magnification and processing time. The adsorbent was deposited on a brass hold, followed by sputting with a thin coat of gold in a vacuum to study their morphology and surface structure. While the EDX beam were set focused into the adsorbent under study [14]. This same process was carried out for all the adsorbents to determine their mineralogical compositions and morphologies respectively.

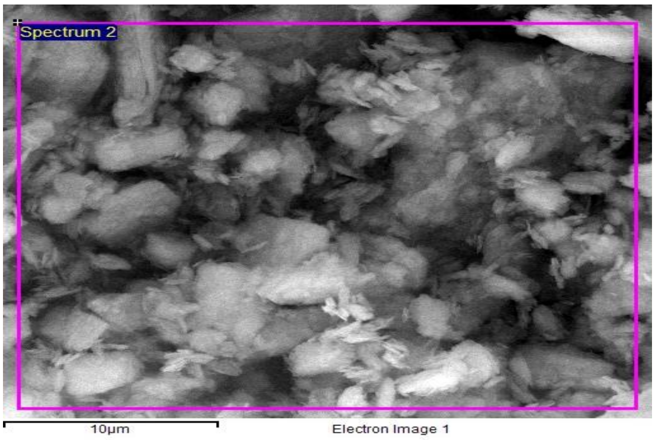
Quantachrome analysis. Quantachrome instrument Autosorb Automated Gas Sorption System; ASAP 2020 V4.02 (V4.02 H) operating with Nitrogen as degas analyzer for adsorption analysis was used [2]. The system operated at the following conditions; thermal correction was set, warm free space was measured as well as cold free space, pressure dose and mass of adsorbent (sample). The surface area-pore, volume-pore size of sample clay and pore size the adsorption was measured by setting the width. These operating conditions include bath temperature, outgassing temperature, processing time, P/Po tolerance zero, equilibrium interval time and analysis time. This same process was carried out on each adsorbent.

Thermogravimetric analysis / Differential thermal analysis. Changes in chemical or physical properties of materials as a function of temperature in a controlled atmosphere may be determined by thermal analysis [4]. This includes changes in energy, weight of materials and enablement to determine their heating patterns. The weight loss arising from the degradation of adsorbate was examined using Netsch DTA/TGA instrument thermocouple [2]. It was carried out by preconditioning the adsorbent gas flow at room temperature for 20 minutes; which was followed by heating up to 1000 °C. The TGA/DTA trace was used to determine the weight percent at interval of 20 °C /minute until equilibrium value. This same process was carried out on all adsorbent to determine the temperature at which the organic content of the adsorbent degraded.

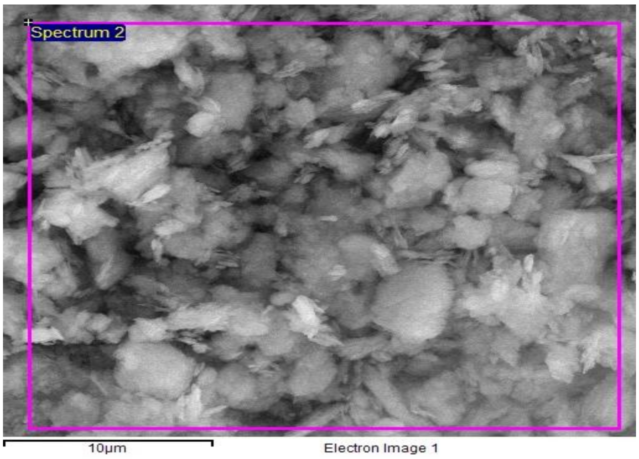
RESULTS AND DISCUSSION

Characterization of unmodified and modified kaolinite clays was carried out using SEM/EDX, Quantachrome and TGA/DTA. The results of findings are thus presented below:

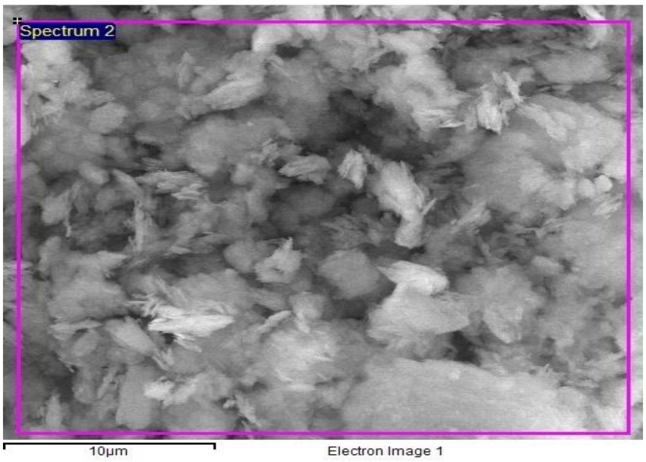
Scan electron microscopy of unmodified and modified kaolinite clays. The SEM of unmodified and modified kaolinite clays was carried out for their morphologies, porosity and textural formation as shown on plate I. The SEM electrons were selected to run at 10 μm × 10000 magnification to produce the images. It is always better to investigate morphologies of sorption studies of adsorbent under high magnification as it plays vital role in knowing the pressure that can allow adsorption to take place in a substance [14]. The SEM micrograph shows that UKC is highly porous, with large particle and pore sizes compared to MMC and BMC. The fissures and channels are major in UKC compared to MMC and BMC, while BMC has finer particles compared to MMC and UKC. The BMC consists of many layers and textural non-uniformity due to adequate intercalation of surface modified clay. The SEM images of unmodified kaolinite clay (UKC), monolayer modified kaolinite clay (MMC) and bilayer modified kaolinite clay (BMC) are shown in Plate I (a), (b), and (c) respectively.



(a) Unmodified clay



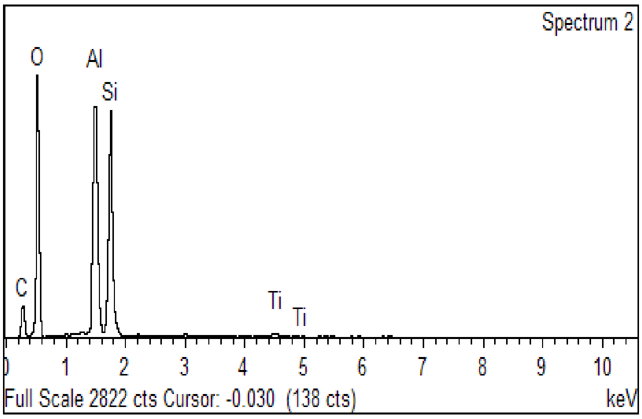
(b) Monolayer modified clay



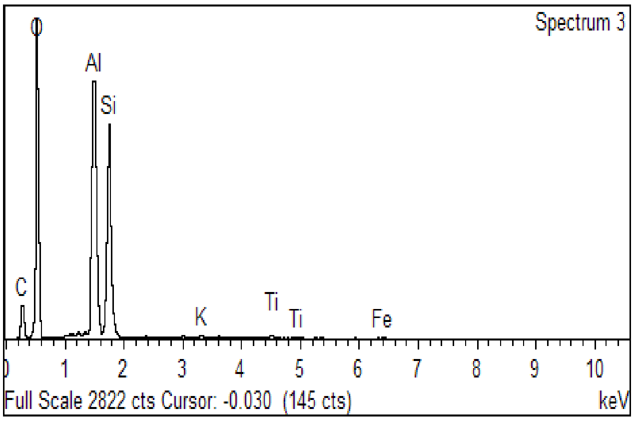
(c) Bilayer modified clay

Plate I – SEM of (a) unmodified clay, (b) monolayer modified and (c) bilayer modified clay

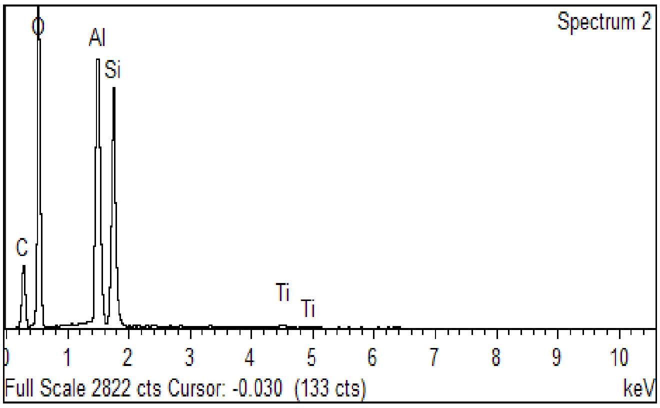
Energy dispersive X-ray spectrometry of unmodified and modified kaolinite clays. The energy dispersive X-ray spectrometry was carried out on the adsorbents to determine their profiles (Figure 1) and elemental composition (Table 1).



(a) Unmodified clay



(b) Monolayer modified clay



(c) Bilayer modified clay

Figure 1 – EDX profile of (a) unmodified, (b) monolayer modified and (c) bilayer modified clay

Table 1 – EDX elemental composition of unmodified and modified kaolinite clays

Element	UKC		MMC		BMC	
	Weight %	Atomic %	Weight %	Atomic %	Weight %	Atomic %
C K	22.41	30.34	21.06	28.92	18.98	26.58
O K	56.17	57.09	55.49	57.21	54.59	57.39
Al K	10.56	6.36	11.66	7.13	12.14	7.57
Si K	10.54	6.10	11.01	6.47	13.89	8.32
K K	0	0	0.20	0.080	0	0
Ti K	0.32	0.11	0.28	0.10	0.40	0.14
Fe K	0	0	0.30	0.090	0	0
Total	100	100	100	100	100	100

The corresponding percentage compositions are as follows: UKC 22.41 % C, 56.17 % O, 10.56 % Al, 10.54 % Si, 0.32 % Ti; MMC 21.06 % C, 55.49 % O, 11.66 % Al, 11.01 % Si, 0.20 % K, 0.28 % Ti, 0.30 % Fe and BMC 18.98 % C, 54.59 % O, 12.14 % Al, 13.89 % Si, 0.40 % Ti. Table 1 presents the overall view of EDX analysis elemental composition for unmodified and modified kaolinite clays. Before modification, the weight of C was 22.41 % which reduces to 21.06 % in MMC and 18.98 % in BMC, while Al and Si weight % increased with K and Fe found in MMC.

Quantachrome analysis of unmodified and modified kaolinite clays. Quantachrome of both unmodified and modified clays was carried out to ascertain their surface area, pore volume and pore size by surface area analyzer using Brunauer-Emmet-Teller (BET) isotherm, Barrett-Joyner-Halenda (BJH) isotherm, Langmuir isotherm, t-plots, which was performed under these conditions; ground low temperature, nitrogen adsorption-desorption isotherms using an autosorb1 quantachrome instrument.

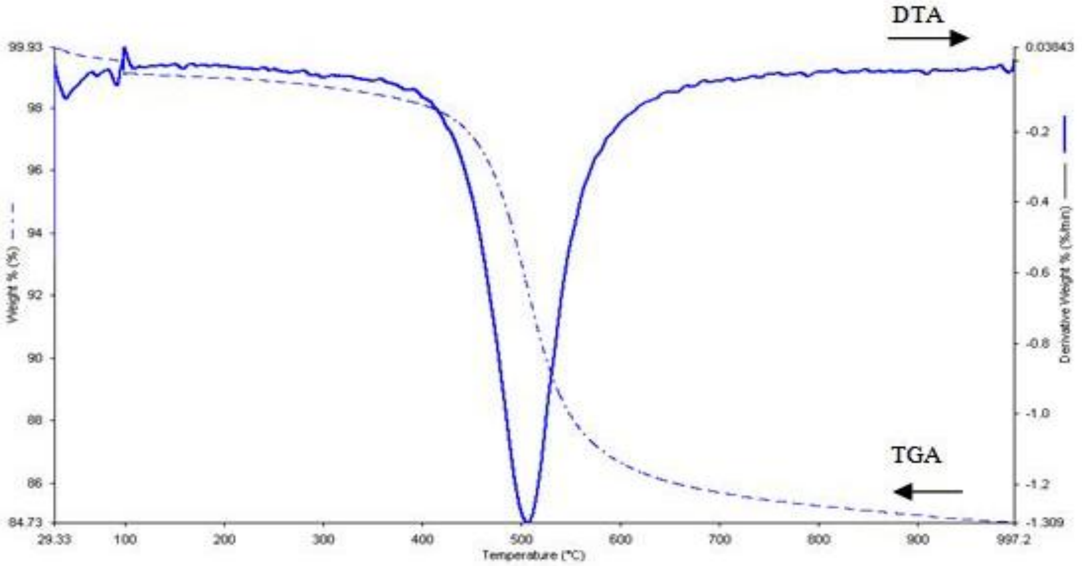
The clay surface area widely used as starting material for adsorbent varies from 10–700 m^2/g [17]. The BET surface areas for UKC, MMC and BMC are 11.9754 m^2/g, 3.0132 and 3.8225 m^2/g respectively while the BJH adsorption cumulative surface areas for UKC, MMC and BMC are 11.403 m^2/g, 3.879 m^2/g and 7.906 m^2/g respectively. The Langmuir surface areas for UKC, MMC and BMC are 15.6659 m^2/g, 5.6691 m^2/g and 7.5577 m^2/g respectively. All surface areas for UKC was found within the range of 10–700 m^2/g, while MMC and BMC less than 10 m^2/g indicating effect of surface modifications. Total pore volume was calculated from the amount of nitrogen adsorbed at a relative pressure of p/p_0 and while average pore size was calculated based on (4V/A by BET) Å and (4V/A) Å as presented in Table 2. The micro pore area, micro pore volume and external surface area were obtained from t-plot method [10, 16].

Table 2 – Quantachrome analysis for unmodified and modified kaolinite clay

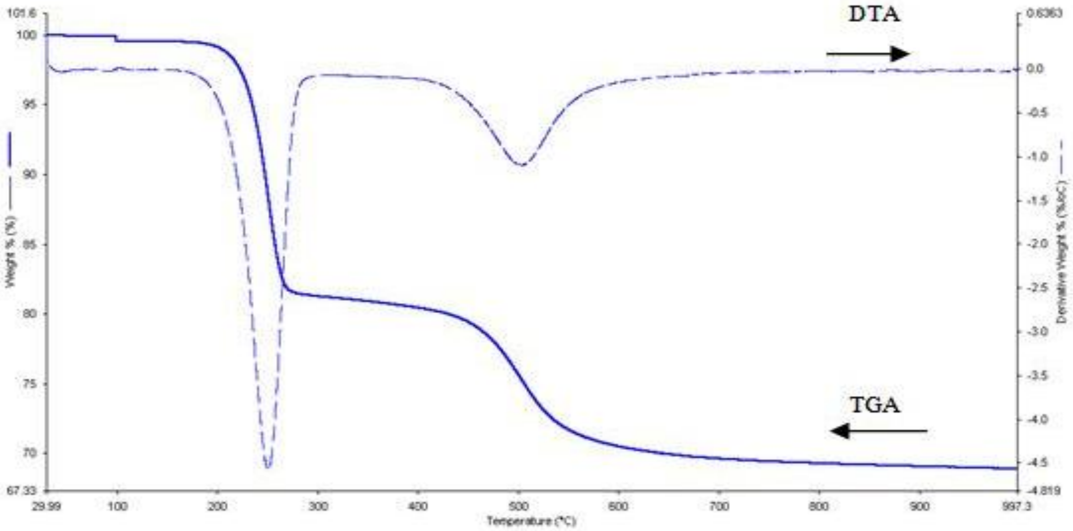
Conditions	UKC	MMC	BMC
Adsorptive analysis	N_2	N_2	N_2
Analysis Bath temperature (°C)	-195.672	-195.718	-195.634
Thermal condition	No	No	No
Warm free space (cm^3)	27.6944	28.0750	28.1473
Sample mass (g)	0.2051	0.2170	0.3350
Cold free space(cm^3)	84.2454	87.2358	84.1281
Equilibrium intervals (s)	10	10	10
Ambient temperature (°C)	22.00	22.00	22.00
Low pressure dose (cm^3/g STP)	5.000	5.000	5.000
Automatic degas	Yes	Yes	yes
Surface areas (m^2/g)			
Single point surface area	11.9754	3.0132	3.8225
BET surface area	11.7037	3.6862	4.7882
Langmuir surface area	15.6659	5.6691	7.5577
t-plot micro pore area	7.0766	0	0
t-plot external surface area	4.6271	4.7748	6.5820
BJH adsorption cumulative surface area	11.403	3.879	7.906
BJH desorption cumulative surface area	14.5855	5.0126	9.4495
Pore volumes (cm^3/g)			
Single point adsorption total pore volume	0.103872	0.044108	0.090119
Single point desorption total pore volume	0.098565	0.055458	0.134071
t-plot micropore volume	0.003324	-0.000734	-0.001178
BJH adsorption cumulative volume	0.125009	0.067801	0.153947
BJH desorption cumulative volume	0.124918	0.067588	0.153844
Pore sizes Å			
Adsorption average pore width	355.0050	478.6275	752.8364
Desorption average pore width	336.8698	601.7882	1120.0029
BJH adsorption average pore width	438.513	699.134	778.933
BJH desorption average pore width	342.583	539.342	651.223

Thermogravimetric / Differential thermal analysis of unmodified and modified kaolinite clay. Figure 2(a), (b) and (c) presents TGA/DTA of UKC, MMC and BMC respectively which were heated between 0 to 1000 °C. The TGA curve for UKC decomposition began at 29.34 °C with a corresponding weight of 99.93092 %, TGA curve shows gradual decomposition at different temperatures. At 480 °C UKC exhibits decomposition of 1.97 % weight loss, as heating progressed at 540 °C about 12.93 % weight loss was attained and calcination continued until when the curve showed peak at 997.20 °C with 15.32 % weight loss indicating equilibrium decomposition was attained. The DTA curve began at 29.34 °C with corresponding derivative weight of -0.19 %, at 100 °C the corresponding derivative weight is -0.03843 %, between 450 °C and 700 °C the curves showed a sharp endothermic at 500 °C with -1.309 % weight derivative. This showed normal process of surface water loss and dehydroxylation of clay material [2, 4].

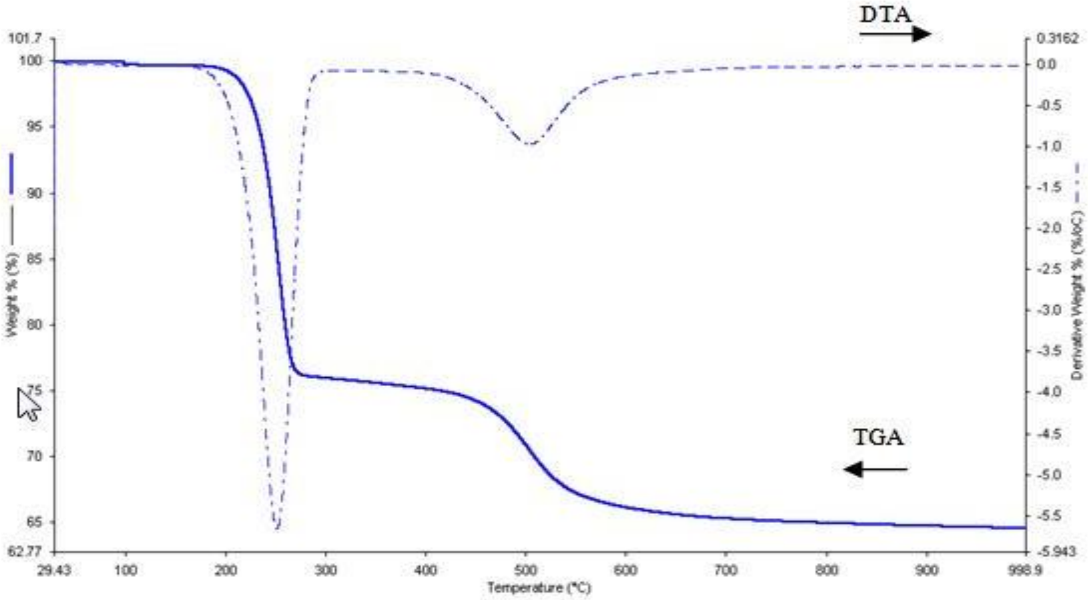
The TGA curve for MMC decomposition began at 29.99 °C exhibiting 1.6 % weight loss. The curve was peaked at 240 °C with 3.6 % weight loss, at 270 °C the curve shows 19.6 % weight loss while at 480 °C the weight loss was 21.6 %. Also, at 570 °C the weight loss was 29.6 % until equilibrium decomposition at 997.30 °C with the corresponding weight loss of 32.67 % was attained.



(a) Unmodified clay



(b) Monolayer modified clay



(c) Bilayer modified clay

Figure 2 – TGA/DTA of (a) unmodified clay, (b) monolayer modified clay and (c) bilayer modified clay

DTA curve showed two endothermic decompositions, between 200 and 300 °C the curve is peaked at 250 °C with a corresponding derivative weight -4.5 % and between 480 and 600 °C the curve is peaked at 520 °C with a corresponding derivative weight of -0.9 %. The loss is associated with surface water loss and dehydroxylation of clay materials [2, 4].

The TGA curve for BMC decomposition began at 29.43 °C exhibiting 1.7 % weight loss, the curve shows 26.7 % weight loss at 250 °C and on further calcination the curve shows 32.50 % decomposition at 570 °C until equilibrium of 998.90 °C and 37.23 % weight loss was attained. The loss is associated with surface water loss and hydration of clay materials [2, 4]. The DTA curve shows two endothermic peaks between 200 and 300 °C is peaked at 250 °C with corresponding derivative weight -5.8 % and between 400 and 600 °C the curve is peaked at 520 °C with corresponding derivative weight -1.0 %.

CONCLUSION

The SEM micrograph showed UKC with more porosity, has large particle sizes compared to MMC and BMC due to surface modification which resulted into formation of layers and textural non-uniformity. EDX show reduction in C, O and Ti in UKC and increased in their percentages in both MMC and BMC. The quantachrome analysis reveal that UKC single point surface area (11.9754 m^2/g) falls within the range of clay surface area of 10–700 m^2/g while MMC (3.0132 m^2/g) and BMC (3.8225 m^2/g) were less. The corresponding adsorption average pore width for UKC, MMC and BMC were 355.0050 Å, 478.6275 Å and 752.8364 Å respectively as evidently shown by SEM micrograph for clay surface modification. The TGA of UKC, MMC and BMC were degraded at 1000 °C resulting in weight losses of 15.32 %, 32.67 % and 37.23 % respectively, while the DTA had endothermic processes for UKC, MMC and BMC at 500 °C, 250 °C and 520 °C respectively.

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