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Preparation and Characterization of Amino Acid-Modified Nanoclay

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Abstract

Clays are low-cost, naturally occurring nanoparticles of inorganic origin, which could be isolated through careful experimental techniques. Functional intercalation of nano clay particles is aimed at attaching new functionalities for a broader application. Nanoclay was isolated and subsequently, activated using H_3PO_4 *to increase the surface porosity and then, modified using phenylalanine/aspartic acid. The modified product was characterized using Fourier transform infrared spectroscopy (FT-IR), Scanning electron microscopy (SEM), X-ray fluorescence (XRF), and thermogravimetry analysis (TGA/DTG). The SEM results show that the nanolayers were partially eroded, due to the acid activation. Other features observed were plate stacking, cracks, plate-like layers, and particle clustering, which was due to agglomerations. The smooth surface observed was due to the hydrophobic groups of the intercalates. TGA/DTG revealed that the modified product was thermally stable, due to the presence of nanolayers, which protected the amine group and thus, enhanced their thermal stability up to 250* ^oC*. The maximum decomposition temperature reached was around 420-480* ^oC*. In conclusion, nanoclay particles have been synthesized and subsequently, intercalated using essential and non-essential amino acids. The thermal stability of the new functional moieties was enhanced. The implication is that such materials could find useful applications as novel adsorbents for water treatment, as well as for the formulation of high-temperature polymers for automobile and other applications.*

Keywords: Amino acid, characterization, modification, Nanoclay

INTRODUCTION

Man has been familiar with clay since pre-historic times (Rocha *et al.*, 2014; Azeh *et al.*, 2021). The wide range of applications includes the production of many consumer goods as well as potentially viable therapeutic systems (Elele *et al.*, 2020; Azeh *et al.*, 2021) often, after purification and/or chemical surface modification. They also contain associated minerals such as carbonates, feldspar, quartz, and hydroxides of iron and aluminium (Elele *et al.*, 2020). Organic matter and associated phases may be present (Acevedo *et al.*, 2017). The presence of silica, alumina, magnesia, or both, and water, Iron, alkalis, and alkaline-earth metals have been found in substantial concentrations (Acevedo *et al.*, 2017). Clays are heterogeneous or

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mixed minerals whose characteristics depend on their geological formation as well as the mining location. In addition, clay materials can be functionalized through chemical/physical treatment to achieve new surface properties for industrial, domestic, and pharmaceutical uses. Research has shown that organic modification enhances the adsorptive potentials of native clays for the uptake of organic (dyes, fungi, viruses, bacteria) and inorganic (metals) pollutants (Elele *et al.,* 2020; Azeh *et al.,* 2021; Sarkar *et al.,* 2010). Nanomaterials are new materials with highly robust properties for domestic and industrial functional uses. Nanoclay is not an exception, with its large surface area coupled with other properties that are normally found with nanoscale matter, it shows enhanced capacity for adsorption of fungi, bacteria, or viruses on different surfaces, including the lining of the human stomach. More importantly, modification using the organo-cation of the amino acids further enhances its adsorptive performance and interactions with the organisms' cell contents by bonding via –NH, ─COOH, ─NH_2, ─CO, ─N─R_3, ─N─CO─, and $^+NR_4$ and so, disable them. It is expected that the insertion of the amino group into the amino acid sequence may alter the configuration of the helix chain sequence, leading to the eventual death of the bacteria/viruses/fungi. Clay is a fine-grained, earthy material that becomes plastic when wet. However, based on the layered structure, they are categorized as 1:1 or 2:1 type, fundamentally built of one tetrahedral silicate (Si-O) sheet and one octahedral metal oxide/hydroxide (M-O- or M-OH) sheet (Elele *et al.,* 2020; Azeh *et al.,* 2021). Chemically, they are hydrous aluminium phyllosilicate minerals with variable amounts of Iron (Fe), Magnesium (Mg), Alkali metals, and other cations found on or near some planetary surface. Properties include plasticity, shrinkage under firing and air drying, fineness of grain, colour after firing, hardness, cohesion, antibacterial properties, and capacity of the surface to take decoration. They are rich in different minerals, which gives them different abilities such as wide spectrum anti-fungal and antibacterial activity (Elele *et al.,* 2020; Azeh *et al.,* 2021).

The concept of nanotechnology was introduced by Richard Feynman in 1959 (Khanemhosseini and Langer, 2006), and involves utilizing particles within the range of 1-100 nm in at least one dimension (Faheem and Uddin, 2008). Nanomaterials like nanoclay, consisting of plate-like, layered minerals with a thickness in the nano-dimension, can be modified significantly to exhibit new properties and performance. Clays are usually hydrophilic due to the hydration of exchangeable inorganic cations and the nature of the Si-O group. However, their surface can be modified to become organophilic by using positively charged organic modifiers. The modification involves attaching cationic surfactants to the clay, resulting in increased miscibility and reactivity with other molecules. This process enhances the clay's anti-fungal/antibacterial properties through hydrophobic interactions and hydrogen bonding with functionalities on the fungi/bacteria's carbon skeleton. Hajjizadeh et al. (2020) modified montmorillonite (MMT) using L-glutamic acid to use it as an adsorbent to remove landfill leachate. Peris et al. (2018) intercalated MMT with Glycine, Arginine, and L-histidine for the sorption of CO_2. Arginine and lysine-modified MMT have been studied to remove arsenate in wastewater (Shokri et al., 2017). Reyes (2018) reported the modification of Na-montmorillonite (Na-MMT). In a bid to find cheap alternatives antibiotic to antibacterial resistance species, Elele et al. (2020) and Azeh et al. (2021) both demonstrated the efficacy of amino acid-functionalized nanoclay against certain bacterial species. Modification of nanoclay using amino acids is a relatively, new area of research aimed at finding novel materials with potentially new application areas such, as in the formulation of composites, controlled release matrix for agrochemicals/pharmaceuticals, and adsorbents for wastewater treatment, cleanup of mycotoxins in agricultural produce and animal feeds. This study aimed to modify local clay with the organic cations of amino acids differing in chemical structure and determine the physicochemical properties of the local clay before and after modification in an aqueous medium. This was to gather information on the local clay's mineral composition and the modified derivatives' thermal properties for potential applications. This work advances the basic understanding of the local clay collected at different sites and its modification with amino acids.

MATERIALS AND METHODS

Collection of Samples

Native clay was collected from two local mining sites, Kaffin-Koro and Dogon-Ruwa, in Paikoro and Bosso Local Government Areas, respectively in Niger State, Nigeria.

Preparation of clay sample

The method reported by Azeh *et al.* (2021) was used. In brief, 2000 g of oven-dry native clay was weighed and placed in a mortar and ground into fine powder using a pestle. The fine powdered clay was sieved using a 30 µm mesh size sieve.

Synthesis of Nanoclay

Nanoclay was synthesized according to the method described by Elele *et al.,* (2020); Azeh *et al.,* (2021). In brief, fine particles of crushed layered mixed clay minerals with particle size less than 30 µm, sieved through a 30 mm mesh sieve were mixed with 1:30 times by weight of water. The mixture was stirred and allowed to stand still for 24 h for the layered clay mineral and water to undergo hydration. The suspension was decanted, stirred, and allowed to stand for 48 h to sediment followed by decantation. Into this was added 1.0 mold^{-3} of a saturated solution of sodium acetate followed by treatment with 90 % solution of hydrogen peroxide and 3.5 % solution of hypochlorite system at pH of 8.2 to eliminate organic matter that may be present and was allowed sediment and then, saturated with NaCl. Afterwards, the mixed clay slurry and the suspension were centrifuged and washed with deionized water (2-3 times) and dried at 100-110 ^{o}C. The dried nano clay cake was crushed using a mortar and pestle into a fine powder, sieved, and collected as nano clay. The prepared nano clay was extensively characterized using different Spectro-analytical techniques like FT-IR, XRD, SEM, TGA, and Particle size analytical techniques (Elele *et al.,* 2020; Azeh *et al.,* 2021).

Modification of Nanoclay

Ten grams (10 g) of nano clay was dispersed into 250 mL deionized water followed by the addition of an excess amount of different molar equivalents of the organo-cations generated from amino acids at a pH range of 1-2. The resulting mixture of organocation and nano clay suspension was stirred on a mechanical stirrer at room temperature (^{o}C) for 3 h until precipitation occurred. The reaction product (Precipitate) was filtered, washed, dried, and ground into fine powder and kept in plastic sample bottles for further analyses (Elele et al., 2020; Azeh et al., 2021). Characterization of the modified nano clay derivatives was carried out using FT-IR, XRD, SEM, TGA, BET, and XRF Spectro-analytical techniques. The equation below shows the modification reaction of clay with an organo-cation under acidic conditions (Azeh *et al.,* 2016).

$$\mathrm{HOOCRNH_2 + Na^{+}\;{}^{-}Clay\text{-}nano + HCl \longrightarrow HOOCRH_3N^{+}\;{}^{-}Clay\text{-}nano + NaCl}$$

Eq. 1: General representation of the reaction of nano clay with amino acid in an acidic medium

Fourier Transform Infrared Spectroscopy (FT-IR)

The FT-IR spectra of phenylalanine-modified nanoclay were determined using an FT-IR-84000S Fourier Transform Infrared Spectrometer in the spectra range of 4000-400 cm^{-1}. Phenylalanine-modified nano clay samples were run as (KBr) pellets.

Thermogravimetric Analysis (TGA)

The thermal stability of the phenylalanine-modified nano clay sample was determined using a thermogravimetric analyzer model (PerkinElmer thermal analysis) from 30 °C to 950 °C with a heating range of 10 °C / min, nitrogen atmosphere, and at a flow of 20 mL/min

X-ray Diffraction (XRD)

X-rays are directed at the nano clay sample, and the resulting diffraction pattern provides information about its crystalline structure. The peak positions and intensities are analyzed to determine the crystalline phases.

X-ray Fluorescence

The EDXRay Fluorescence was used. The used EDXRF system in this work is the installed central Laboratory of the Kaduna State Polytechnic. The X-ray tube of this system is equipped with a 50 W, high-power X-ray tube, max. voltage 50 kV, with polarizing HighSense™ beam path, equipped with a HighSense™ ULS Silicon Drift Detector.

Scanning Electron Microscopy (SEM)

The samples were coated with gold under a vacuum using TESCAN sputtering before imaging to increase the image resolution. All SEM images were taken at an acceleration voltage of 5.0 keV.

RESULTS AND DISCUSSION

FT-IR Study

The FT-IR of the modified sample is depicted in **Table 1 and Figure 1.** The FT-IR result shows a strong sharp peak at around 3604-3642 cm^{-1} corresponding to –OH bond stretching vibration (Azeh et al., 2019; Azeh et al., 2023). The spectra of all the modified samples gave new absorption bands at 2399 cm^{-1}, owing to ─N─H stretching vibrations. This absorption band confirms the successful insertion of ─NH^+ ion into the nano clay interlayer and surface modification (Katti *et al.*, 2006; Katti *et al.*, 2008).

The aromatic overtones for the C=C were found around 2102 cm^{-1}, indicating the presence of a phenyl ring structure in the modified nanoclay. This confirmed the success of intercalation with the phenyl-NH_3^+. This band was missing in the aspartic acid-modified derivative. The band around 1738-1797 cm^{-1} was due to C=O vibrations, resulting from an amide bond in the intercalated nanoclay (Karbownik et al., 2019; Azeh et al., 2023). The bands seen at 1612, 1643 cm^{-1}, and 1947 cm^{-1} indicate the presence of the intercalate molecules in nano clay. These bands are due to the –N-H bend, non-bonded/free carbonyl (─C=O) stretching band of the carboxylic group of amino acids. The strong and sharp absorption at 1413 cm^{-1}, corresponds to the C-O stretching vibration of the ester bond. The bending vibration of -CH was recorded at 1402 cm^{-1}. The peaks at 1059 and 712 cm^{-1} belong to the stretching and bending vibrations of Si-O and M-O of the nano clay layers. The shift to lower frequency was due to the attraction between Si-O or M-O groups and carboxylate ions. Thus, FT-IR provided evidence for the structural changes of the clay from hydrophilic to hydrophobic character.

Table 1: Band Assignment for Phenylalanine-modified Nanoclay

Sample	Wavenumber (cm^{-1})	Band Assignment (Functional group)	References
Modified Nanoclay	3642	O-H	Azeh *et al*., 2021
	2102	C=C aromatic	Karbownik *et al*., 2019
	1797	C=O amide	Karbownik *et al*., 2019
	1413	C-O	Chandra *et al*., 2002
	1059	Si-O	Sadek *et al* 2014
	712	Si-O-Si	Sadek et al., 2014
	872	M-O	Sadek *et al*., 2014

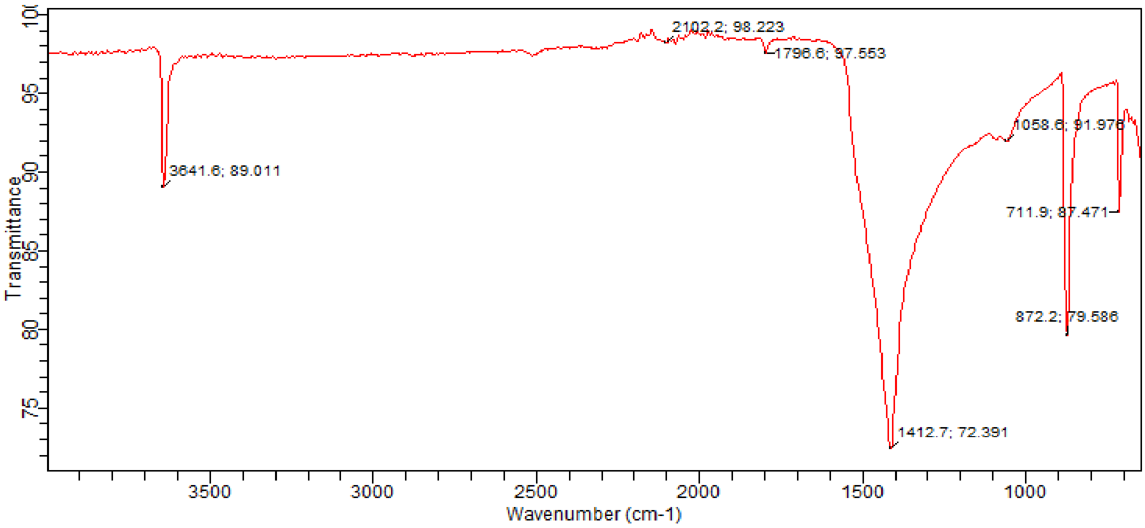


Fig. 1: FT-IR Spectra of PDRC

Table 2: FT-IR Spectra of Aspartic acid-Nanoclay

Sample	Wavenumber (cm^{-1})	Band Assignment	References
Modified Nanoclay	982	Al–OH stretching	Azeh *et al*., 2016
	1287	–NH anime stretching	Yao *et al*., 2019
	1402	C–H stretch	Saliu *et al*., 2018
	1612	N–H	Azeh et al., 2023
	1738	C=O	Coman, 2018; Azeh et al., 2023
	1947	Carboxyl (COO-) stretch	Asep *et al*., 2019
	2042	C=C	Tufan *et al*., 2017
	2166	C=C stretch	Asep *et al*., 2019
	2252	CH_3 in-plane bend	Katti et, al., 2008
	2399	$N{-}H^+$	Asep *et al*., 2019
	2545	C–C skeletal vibration	Azeh et al., 2023
	3500	N–H	Socrates, 2001
	3602	O–H	Socrates, 2001; Azeh et al., 2023

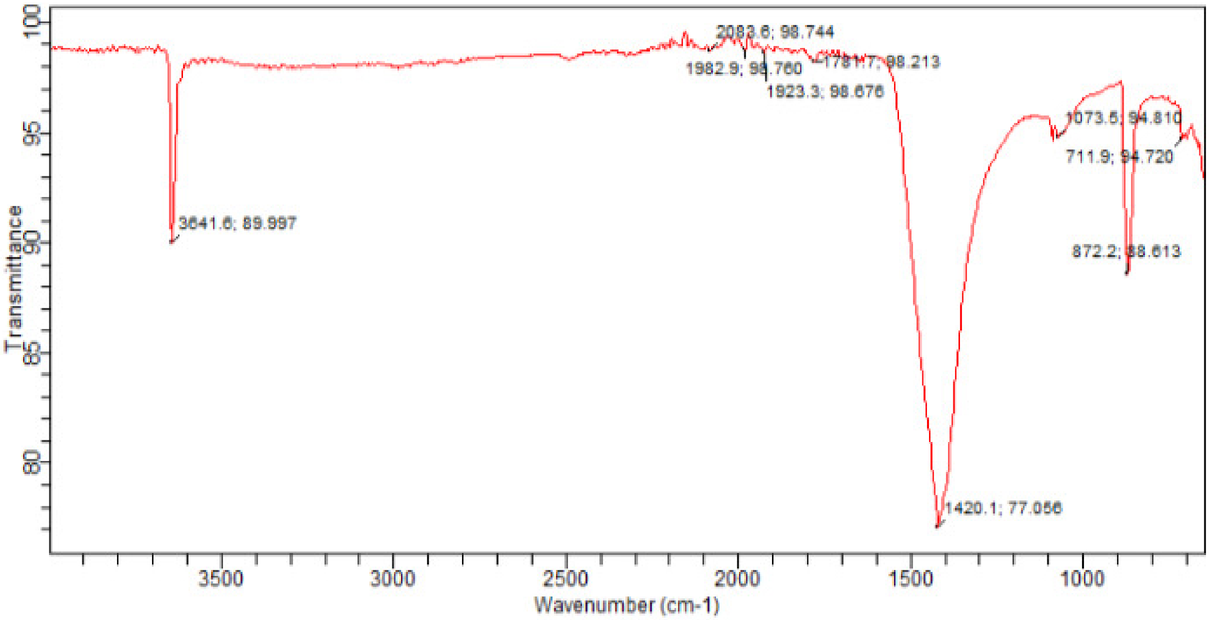


Fig. 2: **FT-IR Spectra of the Prepared ADRC Sample**

Thermogravimetry Analysis

Figure 2 above shows the TGA result of a Phenylalanine-modified nano clay. The degradation of the modified nano clay was considered at T_{95} and T_{90} for 5 and 10 wt% mass loss respectively. Degradation of the modified nano clay at T_{95} and T_{90} (5 and 10 wt% mass loss) occurred around 284 ^{o}C attributable to the loss of absorbed/adsorbed water. The degradation temperature recorded around 312 ^{o}C has been attributed to the loss of the intercalate molecules in between the nanoclay layers and the amino acid ammonium ion that are electrostatically adsorbed on the nanoclay surface. This observation is attributable to the protective influence of the silicate nanolayers and its remarkable heat resistance properties similar to findings by Al-Juhani, (2015) and Azeh et al. (2021). The observed second-step decomposition at 383 ^{o}C may be due to the production of phenylalanine phenolic analogue during pyrolysis (Azeh et al., 2021). At 479-664 ^{o}C the elimination of hydroxylated (OHs) species as inner water from the nano clay layer occurred. The Aspartic acid-modified nanoclay exhibited a one-step degradation pattern observed at 126 ^{o}C and 215 ^{o}C for the decompositions at T_{95} and T_{90} respectively. These depict an extended degradation of the surface and bound water molecules caused by the presence of nano clay stacked silicate layers (Boumediene et al., 2016; Azeh et al., 2021). The thermal decomposition of the phenylalanine-modified nanoclay was closely related to the work documented by Boumediene *et al*. (2016) on the thermal degradation of ionic liquid-modified bentonite. The sample coded as ADRC had T_{95} and T_{90} as 333 and 359 ^{o}C for the 5 and 10 wt% mass loss of the sample. These decomposition temperatures are responsible for the elimination of the amino acid intercalate molecules. The extended pyrolytic temperatures could be due to the shield from the nano clay silicate layers. The absence decomposition peak was an indication that the ADRC sample was essentially, hydrophobic. The DTG showed different decomposition steps for each sample **(Figure 2)**. Sample ADRC, show a one-step decomposition pattern at 299 ^{o}C while sample PDRC shows three decomposition peaks at 270, 358, and 427 ^{o}C. Mass loss due to degradation at 270, 299, 358, and 427 ^{o}C, corresponds to the elimination of the surface-bound and loaded intercalate molecules, similar to the report by Azeh et al. (2021).

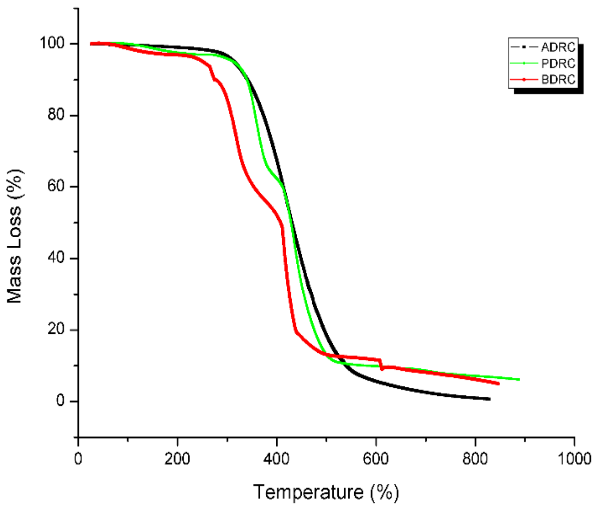


Fig. 2: TGA of Modified and Bleached Nanoclay

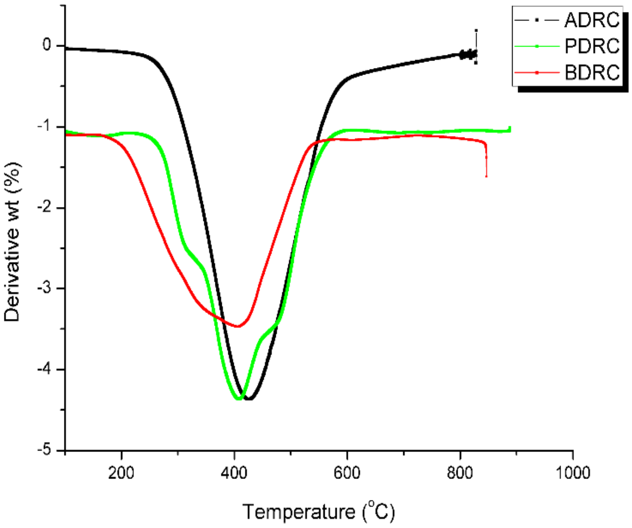
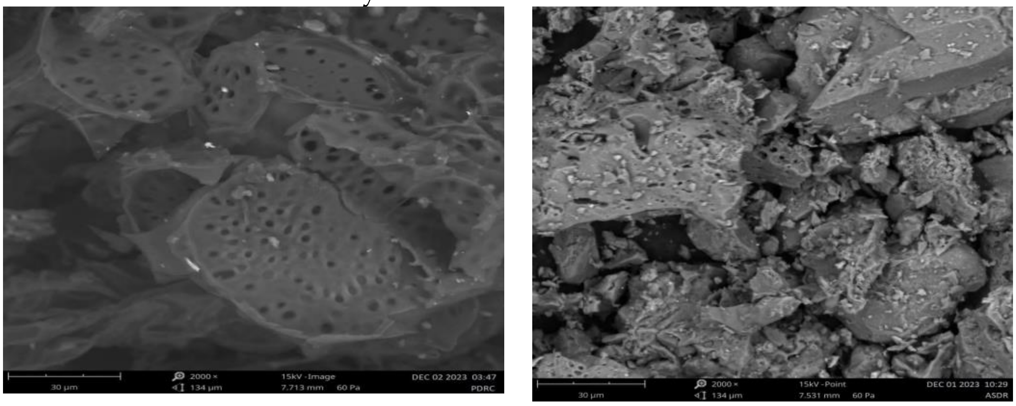


Fig. 3: DTG of Modified and Bleached Nanoclay

SEM Study of Morphological Property of Phenylalanine-modified Nanoclay

Plate I show the image of phenylalanine-modified nano clay^{a} and aspartic acid-modified nano clay^{b} with different morphological surface features, ranging from porous, block-like/ platelets particles, similar to the report by Perera *et al.* (2014); Samzadeh *et al.* (2016) and Azeh *et al.* (2023) on PANI/Arg-Modified-Nanoclay/CMC/EG nanocomposites. The nano clay derivative exhibited quite a good number of pores on the surface. This was attributed to the exfoliation of the nano clay surface by H_3PO_4, heat, and bleaching time during the activation of the nano clay plates. The interconnected porous network was visibly clear. These features can be very useful for applications as adsorbent materials for oil, organic, and/or inorganic pollutants. Surface smoothness, due to the hydrophobicity of the modified nano clay derivative was observed. This was similar to the findings by Fernando *et al.* (2012). A few observed white spots were due to the leaching of metals out of the nano clay plates. A similar observation was reported by Almansoori *et al.* (2019) on nano clay/polymer composite powders for laser sintering applications. The SEM image revealed an exfoliated type of composite material. The surface of the nano clay plates was composed of hallows and valleys, which can enhance thermal stability.



a

B

Plate I: SEM image of Phenylalanine-modified Nanoclay (a) and Aspartic acid-modified Nanoclay

X-ray Fluorescence Analysis

The X-ray fluorescence results revealed the per cent composition of the various metal oxides in the clay. According to ASTM-C 618-98, 70 % is set as the minimum value for the sum of SiO_2, Iron oxide, and alumina of the total compounds found in clay. In the present study, we recorded 81 % for the sum of SiO_2, Iron oxide, and alumina. A value slightly above the ASTM-C 618-98 (Nnaji et al., 2016).

Table 3: Percentage Composition of Metal oxide in Dogon-Ruwa clay

Component (Oxide)	Mass (%)
Na_2O	0.0640
MgO	0.3840
Al_2O_3	19.2884
SiO_2	55.6615
P_2O_5	0.0205
SO_3	0.2033
Cl	0.0251
K_2O	2.7216
CaO	0.5010
TiO_2	1.7156
Cr_2O_3	0.0472
MnO	0.1968
Fe_2O_3	6.1783
NiO	0.0200
ZnO	0.0112
Ga_2O_3	0.0072
Rb_2O	0.0190
SrO	0.0124
ZrO_2	0.0711

CONCLUSION

In conclusion, nano clay particles have been synthesized and subsequently, functionalized by intercalation of the clay layers with phenylalanine (essential) and aspartic acid (non-essential) amino acids. The thermal stability of the new functional moieties was enhanced. The implication is that such materials could find useful applications as novel adsorbents for water treatment, as well as for the formulation of high-temperature polymers for automobile applications. The sum of aluminium, silica, and iron oxides in the clay was 81 %.

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