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# SYNTHESIS, CHARACTERIZATION AND APPLICATIONS OF MODIFIED NANOCLAY SUSPENSION FROM KAKURI VILLAGE

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**ABSTRACT**

In this study, the preparation of modified nanoclay using different amino acids has been investigated. The modified and unmodified nanoclay sample has been characterized using X- Ray Diffraction (XRD), Brunauer-Emmett Teller (BET), Particle Size and Scanning Electron Microscopy (SEM). The XRD results suggest that the interlayer spacing of modified nanoclay increases with the intercalation of the modifiers. BET showed that nanoclay was successfully synthesized as revealed by the pore width and volume in the range of 2.647-45.23nm and 11.08-862.6cm$^3$/g, with a BET surface area of 262.1m$^2$/g for the control (CTL). Whereas, Arginine, Tyrosine and Aspartic acid modified nanoclay had 1.847-6.503nm, 2.647-45.23nm and 2.647-45.23nm each with a BET SA of 533.9, 325.4 and 356.3m$^2$/g respectively. Study revealed that the clay deposits were composed of a mixture of clay minerals (Quartz, Anorthite, Kaolinite, Montmorillonite, Orthoclase and Muscovite). Particle size shows that unmodified nanoclay had particle diameter in the range of 0.88-68.71nm, Whereas, modified nanoclay sample had particle size value of 0.88-60.52nm for TYS, ASP and ARG respective. SEM images revealed the presence of varying pore sizes distribution across the surface area of both the modified and unmodified nanoclay samples.

**Keywords**: Synthesis, Nanoclay, Modification, Characterization, Antimicrobial

## INTRODUCTION

### Synthesis of nanoclay materials

Nanomedicine has been recently employed for clinical trial of cancer therapy (Sanna *et al.*, 2014). Nanoparticle facilitates the delivery and accumulation of drugs in tumor sites because of their capability to overcome many of the biological transport barriers (Blanco *et al.*,2015) and to achieve better drug targeting by enhanced permeability and retention (Nel *et al.*, 2017) chemical conjunction of anticancer drugs to nanoparticle which is broken by tumor- specific stimulants delivers the chemotherapeutic drugs (Aryal *et al.*, 2009) chemotherapy is a common method for treatment of cancer patient but cons term administration leads to drug resistance. Studies by Rivera *et al*.(2010); Kooh *et al.* (2011) Guo *et al.*(2018); and Alizadeh *et al.*(2020), to overcome drug resistance, designing new nano particulate drug delivery formulation base-targeted moieties has been developed recently. Bio-nanocomposites are biopolymer matrices which have improved mechanical properties (Kaygusuz *et al.*, 2015). In recent years, a series of biopolymer combined with clay minerals layers such as montmorillonite, hectorite, sapiolite and laponite are used in Drug Delivery Services (DDSs) due to their unique structure and properties (Kumar *et al.*, 2017). Laponite and montmorillonite are suitable for DDSs (Ordikhani *et al.*, 2015; Mahkam *et al.*, 2016). However, their hydrophilic surface properties cause them not to be compatible with most polymers. Therefore, it is better to modify their surface and make them more hydrophobic for better surface interactions with hydrophobic polymers (Chen *et al.*, 2015; Feng *et al.*, 2017). Several methods have been used to modify the common properties of clay (surface area and Cation exchange capacity) for enhanced performance and broad application areas. The main effects of these treatments are the collapse of the interlayer, and introduction of structural alterations, diminishing the swelling capacity of the raw clay and modifying the surface charge, respectively. Caitin *et al.* (2013) reported the antibacterial properties of a mixture of natural clay mineral through in vitro antibacterial susceptibility test against a broad-spectrum of bacterial pathogens. These clay mixtures showed remarkable different antibacterial activity against *Escherichia coli* and methicillin resistant *staphylococcus aureus* (MRSA).

## MATERIALS AND METHODS

All reagents used for the preparation of clay and modified nanoclay derivatives were analytical grade supplied by BDH Chemicals Ltd (Poole England) and obtained from a reliable chemical vendor, Nahson, Nigeria Ltd. No further purification was carried out on the chemicals before use. The chemicals include; concentrated HCl, $H_3PO_4$, NaOH, NaCl, $AgNO_3$, $H_2O_2$, $CH_3CH_2OH$, Leucine, arginine, tyrosine, aspartic and glutamic acid, phenylalanine, and alanine, glacial acetic acid, and ammonium hydroxide.

### Sample Collection

Native clay sample was collected from Kakuri village in Paikoro Local Government area (Niger East/Zone B) of Niger State. The sample was placed in polythene bags and transported to the Chemistry Laboratory of the Ibrahim Badamasi Babangida University, Lapai for further analyses.

### Pretreatment of Clay

The native clay sample collected was sun-dried and ground using mortar and pestle, sieved using a mesh size of 80 µm. The fine powdered clay particle was collected and stored in polyethylene bags for further analyses.

### Bleaching of Nanoclay

About 500 mL of the nanoclay suspension was measured into a 1000 mL beaker followed by the addition of 100 mL of hydrochloric acid solution. Afterwards, the mixture was heated for 30 min. After this period of heating, water was added to the reaction mixture to quench the reaction. This mixture was filtered while water was being added continuously until the wash water test neutral to pH paper. The reaction product was sun-dried, crushed and sieved to collect into fine powdered particles and stored in plastic container for further analysis.

**Modification of Nanoclay**

Thirty grams (30 g) of nanoclay was weighed and placed in a 500 mL beaker followed by the addition of 300 mL solution of amino acid and vigorously stirred on a mechanical stirrer equipped with a Teflon-coated magnetic bar for 1 h. The pH of the solution was maintained at pH=2. The resulting product was washed with distilled water until the washed water was free from chlorine ion (no ppt with a test solution of $AgNO_3$). The product was filtered and ovum dry at 105ºC for 1h. The final product ground, and sieved to obtain a fine powdered of the modified nanoclay, which was stored for further analysis. This procedure was repeated all the amino acids used in this work. The level of modification was determined by calculating in terms of weight percentage gain (WPGs) based on weight differences of the treated samples before and after modification according to the equation:

$$\text{Weight percent} = \frac{W2-W1}{W1} \times 100 \quad (1)$$

Where $W_1$ = initial weight before modification, and $W_2$ = final weight after modification

**Microbial Analysis**

***Collection of Samples from General Hospital, Bank and Motor Park***

Samples were collected from three different public places. The General Hospital, Bank and the Motor Park, all in Lapai metropolis, Niger State. Collection was made using a swab stick. The door knob of the general hospital Ward B, Counter of the First Bank and Commercial car handles each was swabbed into a sterile polythene bag, labeled and transported to the Microbiology Laboratory for further analysis.

**RESULTS AND DISCUSSION**

**X-ray Diffraction Analysis of Samples**

The modified or unmodified samples were characterized for the peaks, and phase mineralogy (Table 1). The mineral phases identified in the studied clay and its amino acid-modified derivatives were Quartz, Anorthite, Kaolinite, Montmorillonite, Orthoclase, and Muscovite with the p*hase composition values presented as range.* The d-spacing (Å) is presented in Table 2. The important 2Theta peak indicative of the insertion of the amino acid ammonium ion into the nanoclay layer were 8.978, 9.988, 9.983, 9.999, and 9.998 Å for the CTL, ARG, LEC, TYS, and APS respectively. The observed d-spacing for each sample was calculated by subtracting the 2theta peak, which occurred downfield or leftward due to modification. These values demonstrate the successful modification of the nanoclay interlayer which led to the increase in the d-spacing of the corresponding 2theta peaks.

**Table 1: Phase Analysis and Percent Composition of Modified and Unmodified Nanoclay**

| Mineral Phase | Weight (%) |
|---|---|
| Quartz | 3—18 |
| Anorthite | 3—7 |
| Kaolinite | 7—19 |
| Montmorillonite | 2—5 |
| Orthoclase | 3—8 |
| Muscovite | 2—5 |

**Table 2: 2Theta and D-spacing of CTL and Modified Derivatives**

| CTL | | ARG | | LEC | | TYS | | ASP | |
|---|---|---|---|---|---|---|---|---|---|
| 2θ | Å | 2 θ | Å | 2 θ | Å | 2 θ | Å | 2 θ | Å |
| 8.978 | 9.842 | 9.132 | 9.8 | 8.963 | 8.96 | 8.03 | 11.00 | 8.598 | 10.275 |
| 12.32 | 7.18 | 12.66 | 6.98 | 17.831 | 4.97 | 8.931 | 9.893 | 9.33 | 9.47 |
| 20.5 | 4.32 | 18.07 | 4.906 | 20.88 | 4.251 | 12.40 | 7.130 | 9.464 | 9.33 |
| 26.886 | 3.313 | 25.46 | 3.496 | 24.17 | 3.679 | 17.818 | 4.974 | 12.915 | 6.849 |
| 27.86 | 3.200 | 27.03 | 3.296 | 25.03 | 3.554 | 19.98 | 4.44 | 18.366 | 4.827 |

**BET and Particle Size Analysis.**

The BET analysis (Table 3) of modified and unmodified nanoclay samples was determined using nitrogen adsorption isotherm (Adsorption/Desorption). The result shows that the BET for the control sample denoted as CTL was 262.1m$^2$/g. Modification with the amino acid-ammonium ion, ($TYS^+$, $ASP^+$ and $ARG^+$) increased the surface area. This was similar to the report by Azeh *et al.* (2021) on amino acid-modified nanoclay of Kaffin-Koro and Dogon-Ruwa origin. It was interesting to note that BET values obtained in this study far exceed the values reported for both native and nanoclay samples in other studies. The researchers reported BET values of 11.49 m$^2$/g for modified clays 8.81 m$^2$/g for Kaolinite nanoclay 18.3-47.7 m$^2$/g for raw sample, and 5.1-5.3 m$^2$/g for modified clays by Emeka *et al.* (2013), Illite and montmorillonite values reported were 41 m$^2$/g, and 61 m$^2$/g reported a surface area value of 53.47 m$^2$/g for Kaolinite, Illite, Quartz, and Calcite, which was used for removal of nitrate in water.

The BET values obtained for the CTL sample were 262.1m$^2$/g while those for the modified samples were in the range of 325.4—533.9 m$^2$/g for the modified nanoclay samples. According to Meral *et al.* (2017), clay minerals with values greater than 100m$^2$/g are said to be composed of mixed-clay mineral phases. The increase in the $BET_{SA}$ is probably, due to the insertion of the ammonium ion of the amino acid in the nanoclay interlayer. This implies that the organic molecules were too large to go into the nanoclay pores and so, could not restrict the adsorption of $N_2$ into the pores. This process enhanced the adsorption of $N_2$, which brought about the large surface area recorded for the modified samples.

The BET results agreed with the particle size nanometric diameter for the modified samples. In that, the particle size diameter of the modified nanoclay was in the range of 0.88-60.52 nm while the CTL sample had 0.88-68.71 nm. This indicates that modification further split the nanoclay layers into individual strand/plate and/or there was the absence of agglomerations in the modified samples. This led to the smaller nanometric scale recorded for the modified samples. Research has shown that surface area is a function of particle size. Thus, there is agreement between the BET and the particle size values obtained in this study. A combination of these properties by the modified nanoclay has potential applications in adsorption against bacteria, viruses, and fungi.

**Table 3: BET surface area of modified and unmodified nanoclay samples**

| Sample | BET surface area($m^2/g$) |
|---|---|
| TYS | 325.4 |
| ASP | 356.3 |
| ARG | 533.9 |
| CTL | 262.1 |

Key: CTL = Control, TYS = Tyrosine, ASP = Aspartic acid, ARG = Arginine

The Micropore area (Table 4) of the modified and unmodified products determined using the DR method was in the range of 325.4-533.9 $m^2/g$ for modified products. Whereas, the unmodified CTL sample had a DR value of 262.075 $m^2/g$. This type of pore is significant for application in adsorption of microbes in water or wastewater. The micro pore area values reported in this study far exceeded those reported by Alvarez (2017) on Brazilian clay. Large micro pore volume was recorded for both modified and unmodified nanoclay products than the values recorded for the Brazilian clay by Alvares (2017). This implies that the modified nanoclay can accommodate large quantity of pollutant when used as adsorbent. The pores range from 1.847 – 45.230 nm, which implies that the modified products are predominantly mesopores materials. These types of porous structures could better serve as molecular sieves for the selective adsorption of materials. For example, modified nanoclay structures have been used for the adsorption of $CO_2$ (Wagnera *et al.*, 2017; Chouikhi *et al.,* 2019; Hajjizadeh *et al.,* 2020; Masini and Abate, 2021) and heavy metals (Pires *et al.,* 2018). This type of pore has the potential for the capture of even volatile compounds (Hajjizadeh *et al.,* 2020).

**Table 4: Micropore volume and pore size of samples**

| Sample | Micropore volume ($cm^3/g$) method | | | | Pore size (width) nm method | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | DR | HK | SF | DFT | DR | DA | HK | SF | DFT |
| ARG | 19.05 | 751.3 | 123.9 | 1.370 | 6.503 | 3.00 | 1.847 | 3.479 | 2.647 |
| TYS | 13.62 | 632.8 | 181.9 | 10.99 | 5.749 | 2.800 | 36.75 | 45.23 | 2.647 |
| ASP | 14.54 | 660.0 | 178.6 | 11.47 | 5.839 | 2.840 | 36.75 | 45.23 | 2.647 |
| CTL | 11.08 | 507.4 | 147.3 | 862.6 | 5.878 | 2.820 | 36.75 | 45.23 | 2.647 |

The pore size volume recorded in this study was agreement to that reported by (Azeh *et al.*, 2021).

Results show that all the clay-type investigated had particle size distribution at submicron scale, and there were no primary particles in the range of 1-2µm. Particle size of the samples is presented in (Figure 1-3).

The particle size distribution histogram shows that unmodified nanoclay had particle diameter in the range of 0.88-68.71nm whereas the modified nanoclay samples had particle size values in the range of 0.88-60.52 nm for TYS, ASP, and ARG respectively. The increase in particle size of the modified nanoclay samples was attributed to the surface and interlayer adsorption of the organic modifiers. This confirms the success of the nanoclay synthesis and subsequent intercalation with the organic intercalates. The nanometric scale of the nanoclay could offer robust properties to the materials for the various functional application area.

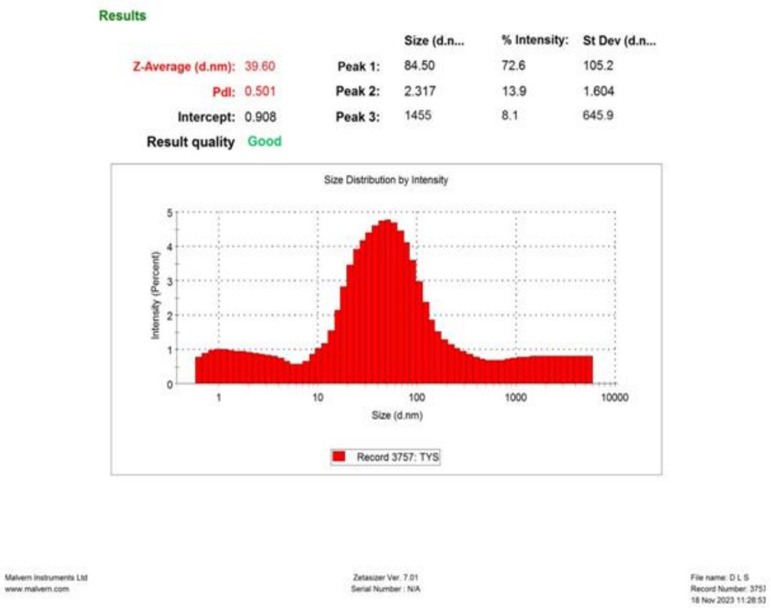


Figure 1: Particle Size Distribution of TYS Modified Sample

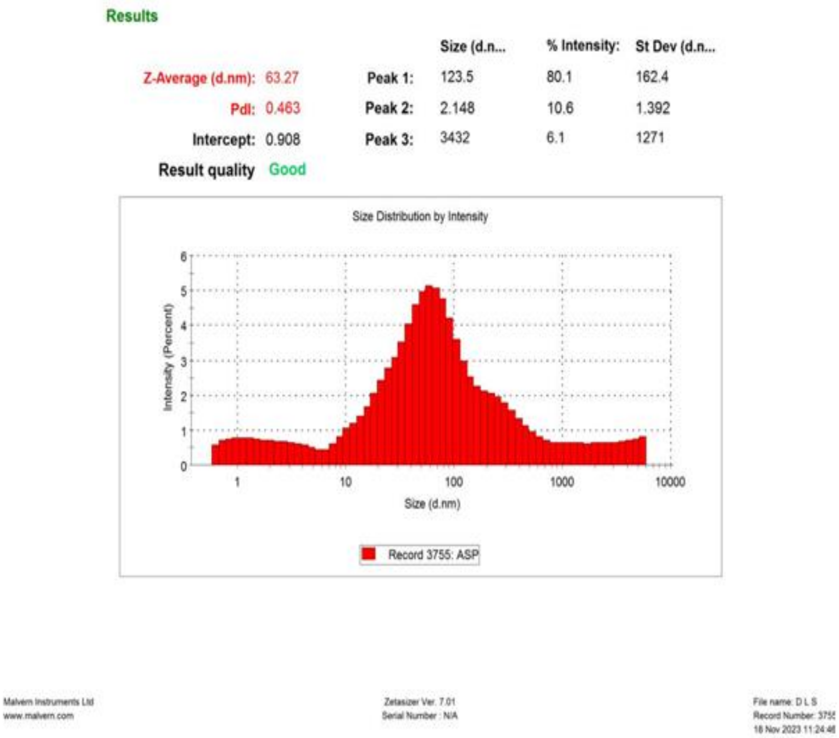


Figure 2: Particle Size Distribution of ASP Modified Sample

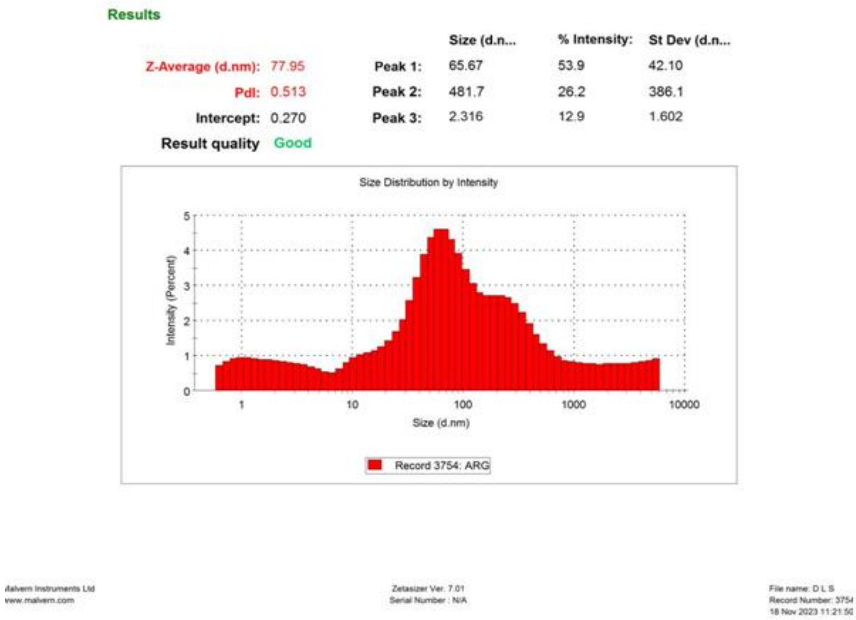


Figure 3: Particle Size Distribution of ARG Modified Sample

**Study of Surface Features of Nanoclay and Modified Derivatives using SEM**

Both the nanoclay and the modified derivatives were further characterized by the SEM technique to explore the surface morphology. Plate 1-3 shows the SEM images of the unmodified nanoclay and modified nanoclay. The SEM images revealed the presence of varying pore sizes distributed across the surface of both the nanoclay (CTL) and its modified derivatives. These pores are due to acid-activation of the nanoclay, and are very important for adsorption of pollutants. The pores were predominantly mesoporous based on the particle size and porosity evaluation (Table 4). The surface texture appears rough and granular, suggesting a high degree of porosity and surface area for adsorption processes. This roughness is attributed to the intricate network of cracks present on the surface, which can enhance the materials adsorption capacity (Lay et al., 2020). The SEM images revealed a heterogeneous of pores, with some regions exhibiting denser porosity compared to others. This non-uniform distribution contributes to the materials ability to selectively adsorb molecules based on their size and chemical properties

Features such as the particle size, bulky, and fluffy massive morphologies attributable to aggregation were observed. Large clay plates were seen, stacked with a compacted morphology, and coupled with different irregular sizes, and shapes, were observed. Stacking of the clay nanoplatelets was visibly clear similar to the findings by Nwankwere *et al.* (2017) on Smectite organ clay. Both the nanoclay and the modified derivatives show the presence of layered edges with some similar features. Nanoclay modified with amino acids show some notable differences in their features such as, the particle size, surfaces and morphologies. Even distribution was observed similar to the findings by Bhattacharya and Aadhar, (2020) on modified sodium-MMT and Islam *et al.* (2017) on modified clay. The modified nanoclay exhibited very highly exfoliated surface and were uniformly distributed, due to the amino acid intercalates (Yusoh *et al.*, 2018; Hajjizadeh *et al.*, 2020). Rough edges, which were seen in raw and nanoclay, disappeared after modification. The appearance of white spots on the SEM micrographs was attributable to the metal crystallites in clay surface, resulting from precipitation.

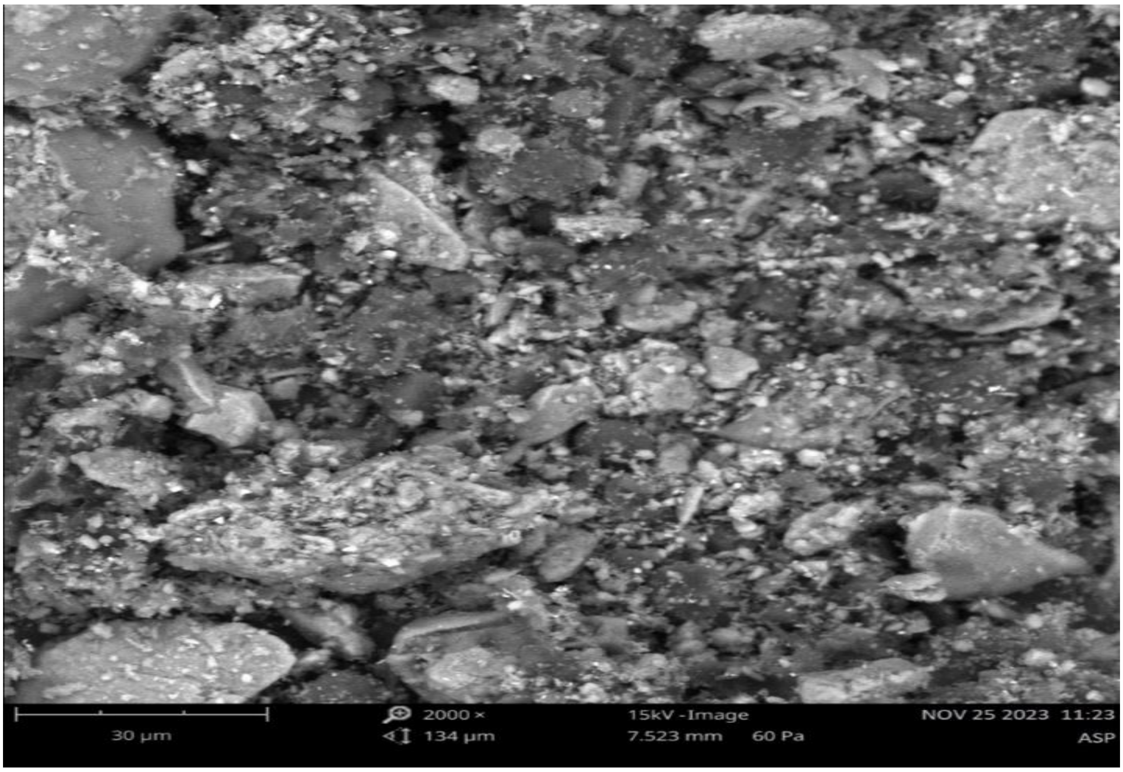


Plate 1: Image of ASP modified nanoclay sample

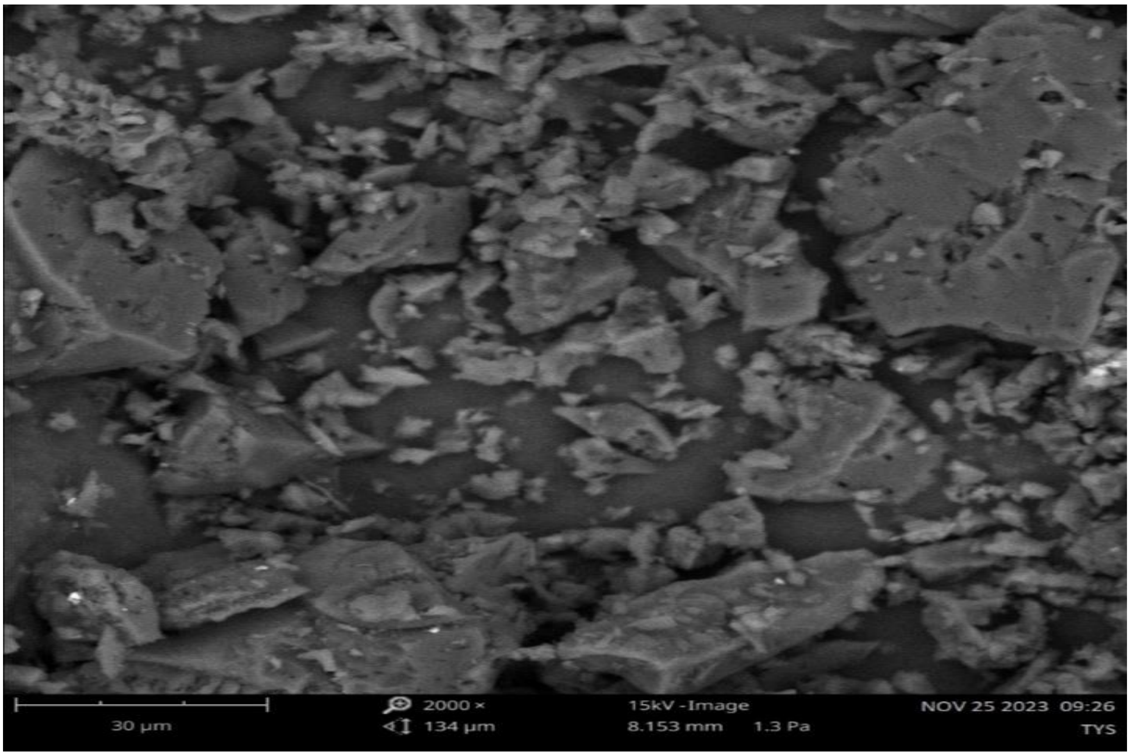


Plate 2: Image of TYS modified nanoclay sample

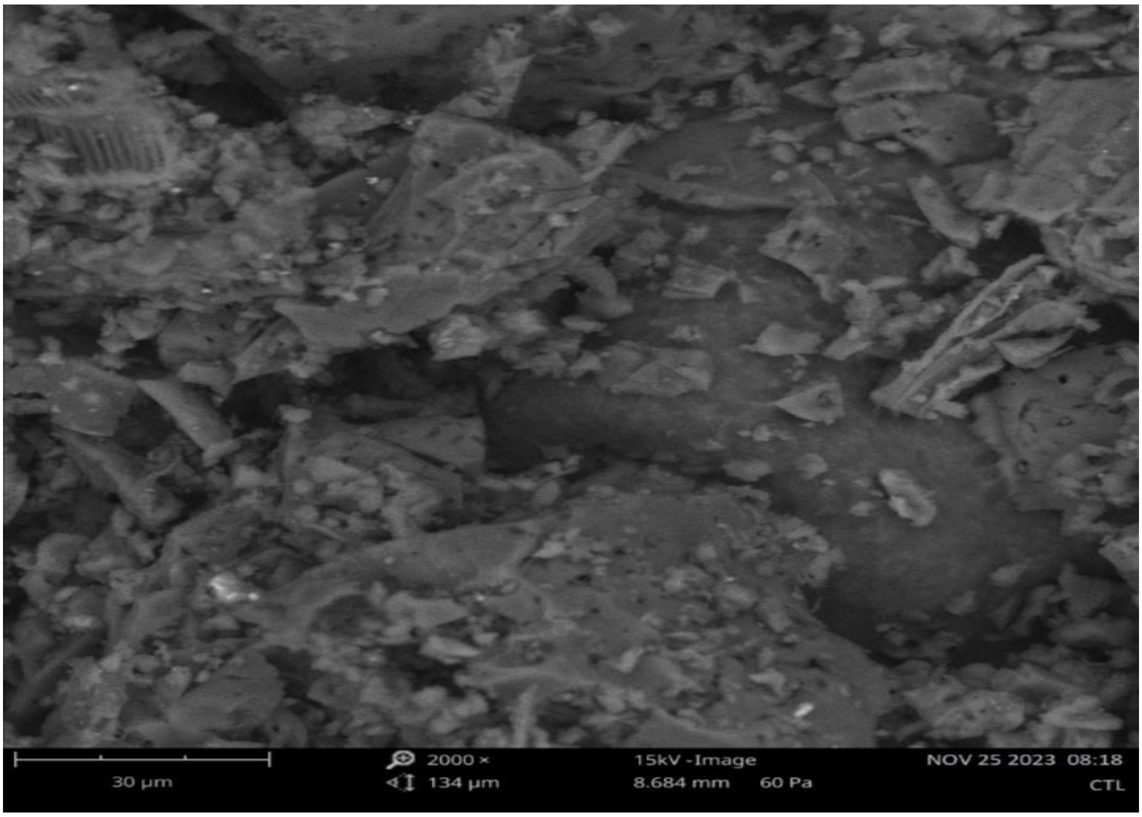


Plate 3: Image of CTL unmodified nanoclay sample

**Microbiological Evaluation of Samples**

***Bacterial Probe of Samples***

Two different species of bacteria were identified in the sample collected in the three public places (GH, FB, and GA) Table 5. These bacteria were *bacillus subtilis* in samples collected from the door knob/handle in General Hospital (GH), and First Bank (FB) both in Lapai, Niger State, Nigeria. While the sample collected at the Garage (GA) shows the presence of *Pseudomonas Sp.* The modified nanoclay derivatives all exhibited varied inhibitory abilities, which ranged from 13-16 mm for *bacillus subtilis* identified in the GH sample while 7-12 mm was recorded for the sample from the FB. The zone of inhibition recorded for the GA sample against *Pseudomonas Sp*., was in the range of 5-12 mm. PHY- and TYS-modified had better activity against *Bacillus subtilis* with a 16 mm zone of inhibition while GLA- and TYS-modified had 12 mm against *Pseudomonas Sp.* Inhibitory activity was also, recorded for the CTL sample (pristine nanoclay), which is due to the intrinsic antibacterial properties of clay. The enhanced activity recorded for the modified samples could be attributed to the increase in the d-spacing, due to the presence of the intercalates molecules in the nanoclay inter-layer. In addition, the high amount of Al, Fe, Cu and Zn may have resulted in the formation of the toxic Fenton reaction. Also, important is the lone-pair on the N-atom, with its propensity to form a hydrogen bond network with the bacterium`s electron-deficient region. This is capable of deactivating, and killing the bacteria Khin *et al.*, 2009; Elele *et al.*, 2020; Azeh *et al.*, 2021). *Bacillus subtilis* and *Pseudomonas Sp.*, may not constitute a serious public health threat in healthy persons. However, it is known to cause significant infection in those with a depressed immune system and hospitalized patients (Emikpe and Oyero, 2007). Most of the bacteria encountered in this study are members of human flora (Prescott *et al.*, 2008).

However, this work offers an economically, and eco-friendly solution for use as surface sterilizing suspension for public use. The MBC and MIC results indicate that 1.43 mg/mL of the nanohybrid suspension is required for the inhibition, and for the total clearance of 99.9 % of the bacteria on any surfaces.

**Table 5: Bacteria Identification in Public Places Sample**

| Sample | G stain | Cat | Coug | SH | Cit | $H_2S$ | IND | MR | VP | CHO | S | L | G | Bacteria |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| GH | +R | + | - | + | + | - | - | - | + | - | + | - | + | *Bacillus subtilis* |
| FB | +R | + | - | + | + | - | - | - | + | - | + | - | + | *Bacillus subtilis* |
| GA | -R | - | - | - | + | - | + | + | - | - | + | - | + | *Pseudomonas spp.* |

Key: G stains= Gram stain, Cat= Catalase test, Coug= Coagulase test, SH= Starch hydrolysis test, Cit= Cittrate Utilization test, $H_2S$= Hydrogen sulphide production test, IND= Indole production test, MR= Methyl red test, VP= Voges prausker test, CHO= Carbohydrate utilization test, S= Sucrose sugar, L= Lactose sugar, G= Glucose sugar

**Table 6: Determination of the Zone of Inhibition (mm) of Sample**

| Sample | ASP | GLA | PHY | LEC | ALN | TYS | ARG | CTL | Organism |
|---|---|---|---|---|---|---|---|---|---|
| GH | 15 | 15 | 16 | 15 | 13 | 16 | 14 | 10 | *Bacillus Subtilis* |
| FB | 8 | 11 | 10 | 12 | 11 | 11 | 10 | 7 | *Bacillus Subtilis* |
| GA | 10 | 12 | 10 | 10 | 10 | 12 | 9 | 5 | *Pseudomonas Sp.* |

KEY: ASP = Aspartic acid, GLA = Glutamic acid, PHY = Phenylamine, LEC = Leucine, ALN = Alanine, TYS = Tyrosine, ARG = Arginine, CTL = Control, GH = General Hospital, FB = First Bank, and GA = Garage

***Minimal Inhibitory Concentration (MIC)***

The MIC and the MBC (Table 3) of the hybrid nanoclay suspensions were determined against the bacteria isolated from surface public places (GH, FB, and GA). The values of the MIC obtained were comparable to those for the MBC for all of the strains tested. The values obtained correspond to the findings by EUCAST (2021). Researchers have shown that it is imperative to determine and establish an effective disinfection protocol for disinfectants against microbes, which can be achieved through MIC and MBC screening against the organisms of interest (O'Neil et al., 2021).

The antibacterial properties of the modified nanoclay suspension were supported by the ability of the clay sample to exchange their metal ions onto the electron-rich region of the organisms, resulting in eventual death. Metal ions such as $Fe^{2+}$, $Zn^{2+}$, $Cu^{2+}$, and the presence of phosphorus have shown high potential for killing or disabling microorganisms (Azeh et al., 2021).

Minimum inhibitory concentrations (MIC) (Table 7) of the nanohybrid suspension were formulated using the ARG-, TYS-modified, and CTL. However, only the ARG-modified sample was active with an MIC value of 0.73-1.43 mg/mL probably due to its high BET surface area (Table 3).The Bacillus subtilis, and Bacillus cereus ,had 0.73 mg/mL and 1.02 mg/mL. This research work implies that the MIC could be used to formulate nanosuspensions from the modified nanoclay for applications as surface sterilizing/disinfecting agents. This can prevent the spread from person to person and during transactions with the naira notes, as well as hand contact with the car knob, door-knob, and hand.

**Table 7: Minimal Inhibitory Concentration of CTL, ARG, and TYS-modified Nanoclay against Bacteria on Surfaces**

| Bacteria/Fungi | CTL | ARG | TYS |
|---|---|---|---|
| | | mg/mL | |
| *Bacillus subtilis* | - | 0.73 | - |
| *Bacillus cereus* | - | 1.02 | - |
| *Pseudomonas aeruginosa* | - | 1.43 | - |

***Minimal Bacteriostatic Concentration (MBC)***

The minimal bacteriostatic concentration (MBC) **(Table 8)** of the modified nanoclay material range from 1.02—1.43 mg/mL. This implies that the minimum concentration required for the elimination of about 99.99 % of the test organism by the nanohybrid clay suspension studied. Research has shown that not all clay deposits have intrinsic antibacterial properties (Lynda et al., 2011; Azeh et al., 2021). This implies that the ARG-modified nanoclay suspension could be used to formulate a cheap and eco-friendly alternative sanitizer against the test organisms in public places. It is designed to be applied as spray on all kinds of surfaces including human hands, and bank counters as a sterilizing agent. The products are smooth, colorless, odorless, harmless, and almost invisible to the eye, and it is eco-friendly.

**Table 8: Minimal Bacteriostatic Concentration on Public Surfaces**

| Bacteria/Fungi | CTL | ARG | TYS |
|---|---|---|---|
| | | mg/mL | |
| *Bacillus subtilis* | - | 1.02 | - |
| *Bacillus cereus* | - | 1.43 | - |
| *Pseudomonas aeruginosa* | - | 1.43 | - |

## CONCLUSION

Nanoclay have been synthesized from native clay samples collected from Kakuri Village in Paikoro local government area. The synthesized nanoclay was successfully functionalizsd by the means of organic cations ion furnished by the acidification of amino acids. X-ray Diffraction characterized the peaks and phase mineralogy. SEM revealed the surface morphology of the modified and unmodified nanoclay samples. BET surface area revealed large exhibition of surface area for both modified and unmodified nanoclay samples. Antimicrobial study revealed the abilities of the various samples synthesized to inhibit /kill microorganisms.

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