



Research article

Characterization of certain Nigerian clay minerals for water purification and other industrial applications

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ABSTRACT

Seven Nigerian clays and clay minerals were characterized by multiple means with respect to their potential application in water purification and other industrial areas. The morphology was determined by means of SEM while chemical/mineral compositions were quantified using EDX, XPS and XRD. FT-IR and UV methods were employed to investigate the functional groups, inter alia the physical and chemical behaviours of adsorbed species. The stability in aqueous solution was determined by zeta potential measurements. The combined results revealed that the clays are mostly kaolin and illite, while clay minerals are predominantly gibbsite and quartz, although other clay-associated minerals and elements were also observed. Two out of the characterized samples will find suitable application in filter media production for water purification due to the possession of exchangeable cations and electrophoresis properties, while the others possess potential industrial applications for refractory linings, ceramics, medical, beauty and cosmetics products. This outcome implies a utilization increase in local content and a value addition to minerals in Nigeria. The results of the study are being used to design and facilitate expanded clay aggregate production to be used for the development of low-cost water filters to address the challenge of poor access to potable water in Africa and other developing continents.

1. Introduction

Clean uncontaminated water is essential for the well-being of both plants and animals. The human body metabolic and catabolic processes need water to optimize their functions. According to the United Nation's 2006 report on power, poverty and the global water crisis, every human has the right to sufficient, safe acceptable, physically accessible and affordable water. Water plays vital roles in socio-economic development, agriculture, domestic life, industry and a sustainable eco-system. Every human being has the right to sufficient, safe acceptable, physically accessible and affordable water (Watkins, 2006; WHO & UNICEF, 2015). Fresh water sources are usually contaminated with chemicals, heavy metals (from wastewater, fertilizers, pesticides, mining activities industrial pollution, and others), pathogens, microbes, and other toxicology contaminants.

The joint report of the World Health Organization (WHO) and United Nations Children's Fund (UNICEF) estimated that 2.1 billion people globally lack access to safe water for household and other utilities, while 4.5 billion people does not have a basic sanitation system (WHO & UNICEF, 2017). Contaminated water together with poor sanitation is estimated to cause approximately 1.8 million deaths and 61.9 million disabilities per year (WHO & UNICEF, 2001). A new born is lost per day globally as a result of infectious diseases caused by a dirty environment and unclean water (WHO & UNICEF, 2015). These unpalatable reports gave rise to goal number six (6) of the Sustainable Development Goals (SDGs), which is clean water and sanitation for all. The relevant agencies, government, non-governmental organizations and researchers have been instrumental to the successes recorded so far. However, the problem is still prevalent in developing countries, especially those in Africa.

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The assessment of water quality using the Water Quality Index (WOI) and every available means are being developed and used by researchers. Lei (2019) and Ismail and Adel (2018) applied the WOI assessment in the evaluation and the validity of an area of a river with one number that checkmated the different parameters for drinking water. The results were able to certify the water safe or not for use according to the specified standards. Drinking water and water for other utilities must be free from these contaminants before it is considered safe for use to promote a healthy lifestyle that is free from the illnesses that are associated with waterborne diseases (WHO & UNICEF, 2001).

One of the ways of removing these contaminants is through filtration, which is a common method used in water purification. It involves the use of a medium in the form of a membrane or aggregates. Filtration utilizes both physical and chemical processes while adsorbing and absorbing contaminants on the medium. Filtration media include but are not limited to ceramic (clay) membranes for point of use filtration, cloth or fibre membranes, compressed granular activated carbon (GAC), polymer membranes, sand, gravel or crushed rock, and clay aggregates. Amongst the other economic benefits of clay such as artefacts, medicines, building materials, electrochemical science, cosmetics, pharmaceuticals, earthen wares and agriculture (Lim et al., 2013; Manukaji, 2013; Iyasara et al., 2016), clay has played a vital role in water purification technology.

Clay ceramic water filters have shown capabilities in removing water contaminants such as microbes (Sengco and Anderson, 2004), chemicals (Nwuzor et al., 2018; Cucarella and Renman, 2009; Zereffa and Bekalo, 2017), and heavy metals (Akapomie et al., 2012; Choudhary, 2018; Zereffa and Bekalo, 2017). Ceramic water filters made from clay and clay minerals are very efficient for water filtration through adsorption/absorption, molecular sieving and ion exchange mechanisms (Wang and Peng, 2010; Margeta et al., 2013; Bergaya et al., 2006). More so, clay is inexpensive, abundant, widespread and readily available. Other considerations are user friendliness, cultural acceptability and a low maintenance cost. The characterization of materials to determine their salient properties for effective utilization and application is the key contributor to many research breakthroughs in the field of science and technology. The mineralogy, chemical composition, mechanical properties (such as plasticity), specific surface area, porosity, functionality and structure, as well as the interactive behaviour of clay and clay minerals, determine their suitability for use in water filtration media and other industrial applications.

Previous studies on the samples of study and most Nigerian clays have focused only on physical, chemical (XRF), mineralogical (AAS and XRD), and SEM (Nsui and Ihitte clay only) (Chukwudi, 2008; Chukwujike and Igwe, 2016) investigations. Multiple characterizations of these samples, especially those that have not been reported, will provide information on these clays, while the already reported ones will be validated or refuted by the current study. Several studies have shown that clay can be used as a refractory lining with improved refractory properties such as shrinkage, abrasion resistance and reduced porosity (Iyasara et al., 2016). Nsui clay has been tested for the adsorption of cadmium(II), heavy metals and chemicals (Nwuzor et al., 2018; Akapomie et al., 2012). The results showed a spontaneous and endothermic adsorption of Cd(II) from aqueous effluents as well as over 60% adsorption of organic and inorganic pollutants from industrial paint effluents.

Characterization reports for Kutigi, Minna and Oboro clay deposits have discussed only their physical analysis and chemical compositions, while there has not been any documented report on Obowo Clay. Nigeria is blessed with clay and clay minerals amongst other abundant natural mineral resources. Unfortunately, value is currently not being added to them except for the ones that are locally mined for art and craft purposes. This paper reports the results of seven Nigerian clay samples investigated for moisture content, morphology, chemical composition, mineralogy, functional groups, zeta potentials and seeks to establish a correlation among them. Multiple techniques were adopted to effectively and efficiently characterize the clay for documentation purposes and to determine their potential suitability in the production of expanded clay

aggregate media for water filtration and other suggested industrial applications.

The structure of this article beyond the introduction is materials and methods, which include the initial preparation of samples after their collection from various locations, visual characterization, microscopic measurements, spectroscopy, diffraction and stability analysis. The results and discussion are then presented and then followed by suggested industrial applications and the conclusions.

2. Materials and methods

2.1. Sample collection and preparation

Samples were collected using geological bedrock maps provided by the Geological Survey Agency of Nigeria for locating mineral deposits across the federation. Three clay samples were collected from Imo State, and their locations are Agbaghara Nsui in Ehime Mbano Local Government Area, Onuiyi River in Obowo Local Government Area and Nkumeato in Ihitte/Uboma Local Government Area. One sample was collected from Isiala Oboro in Abia State. Two samples were collected from Kutigi and Minna in Niger State, while one sample was collected from Afuze in Edo State. The locations covered three out of the six geopolitical zones in Nigeria, namely, South-East, North-Central and South-South indicating tremendous deposits in the country. For ease of identification, the samples were named after their locations as indicated in (Figure 1).

The samples were crushed using a manual jaw crusher (Model: Retsch BB50, made in Germany) set at a gap width of 0.2 mm at a speed of 850 rpm. The crushed samples were soaked in water for 24 h and sieved with (Model: Endecotts Octagon 200 Sieve, made in UK) sets of 150 microns, 106 microns and finally 45 microns. They were dried in an oven (Model: Memmert UN110, made in Germany) at 110 °C for 24 h, similar to the procedure of Cullum and Vo-dinh (2014). The samples were crushed again into powder form before they were packed in zip-lock polymer bags for storage and further experiments.

2.2. Clay sample index and moisture content determination

Visual inspection was performed on the clay to determine their colour and feel when wet.

The knowledge of the moisture content of clay or soil is very essential in its classification. It is generally defined as the mass of water in the soil or clay sample expressed as a percentage of the dry mass after heating at a temperature of 105 ± 5 °C (Eq. 1).

$$\text{Moisture Content, } W = \frac{M_w}{M_D} \times 100\% \quad (1)$$

where

M_w is mass of water
 M_D is mass of dry sample.

The moisture content was determined using a moisture analyser (Model: ADAM PMB 53, made in USA). Clay samples (5 g) were weighed with an accuracy of 0.01 g and introduced into the sample holder. The temperature was set at 110 °C and ran for time intervals of several repeats until stability in the moisture content was achieved.

2.3. Electron microscopy and energy dispersive X-ray (SEM-EDX)

Samples were coated with gold nanoparticles in a mini sputter coater (Model: Quorum SC 7620, made in UK) to prevent the samples from charging and reflection. Scanning electron microscope (SEM) coupled with energy dispersive X-ray (EDX) images were captured with a Carl Zeiss SEM (Model: evo10LS-EDAX, made in Germany) at a very high

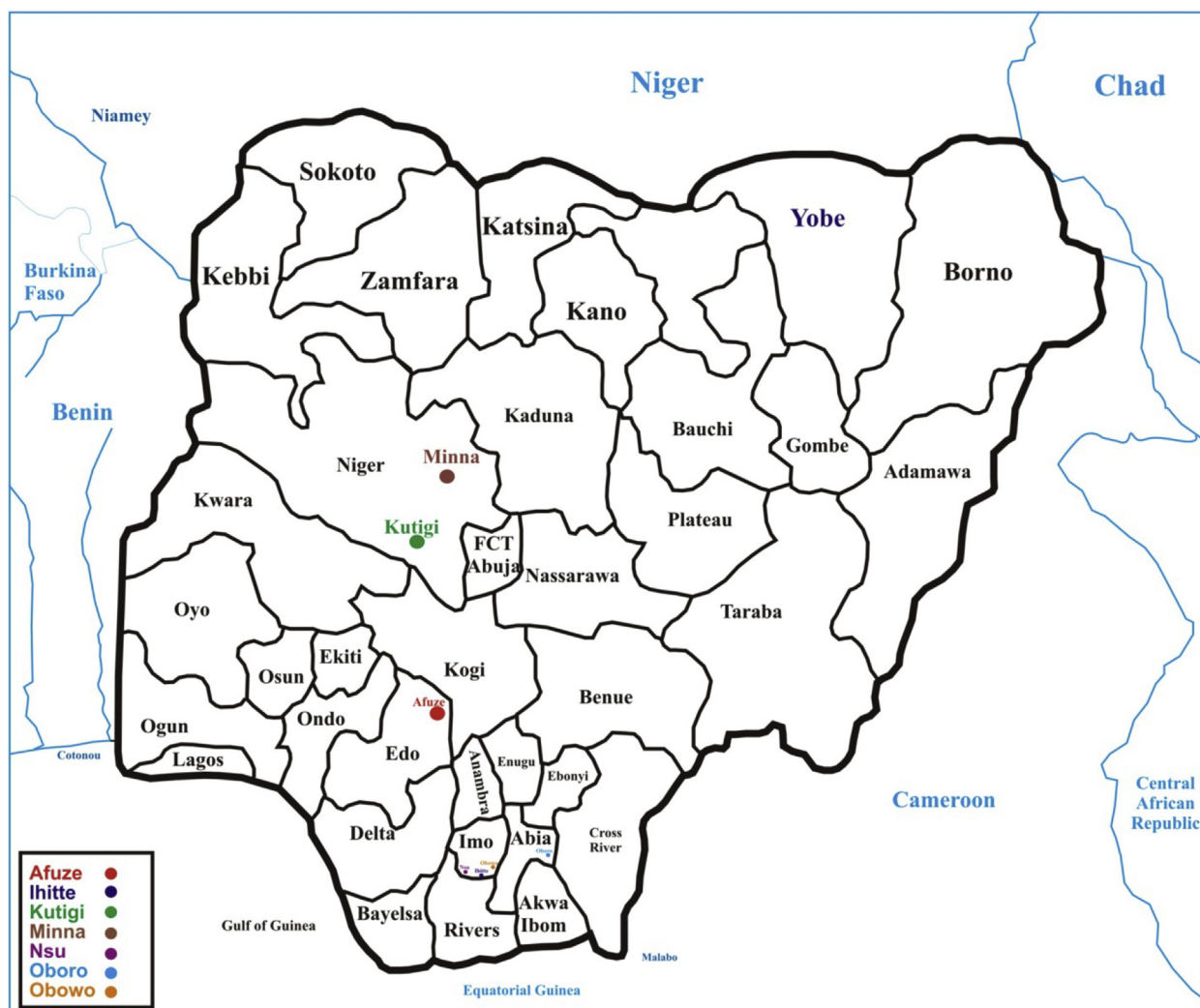


Figure 1. Map of Nigeria showing the location of sample sites.

count per second. SEM was carried out to determine the morphology of the samples. The obtained micrographs were mapped by EDX spectroscopy to determine the elemental compositions of the samples.

2.4. X-ray photoelectron spectroscopy (XPS)

The XPS analysis was carried out to determine the surface chemical composition of the clays. First, 20 mg of each clay sample was measured using a Sartorius microbalance with a precision of 0.001 mg (Model: MC5, made in Germany). The weighed samples were transferred into 20 ml glass bottles containing 5 ml of deionized water to form a dispersion, which was homogenized for 20 s with a homogenizer (Model: CV334, made in Germany). Then, 1 cm² silicon wafers were used as substrates. Sonication for 5 min was carried out in a sonicator (Model: RK-52, made in Germany) using acetone, for 10 min in isopropyl alcohol, and then dried with air and nitrogen to ensure appropriate cleaning (Moulder et al., 1979). Next, 10 µl of the dispersion was taken from each sample and separately drop-cast onto the substrate. These were air dried for an hour and then placed in a desiccator under vacuum for approximately 48 h.

XPS measurements were done following the steps already described by Schampera et al. (2015) and Todea et al. (2013) using electron spectroscopy (Model: Omicron Full lab System, made in Germany). The C 1s peak binding energy of adventitious carbon was used for the charge referencing correction to 285 eV. The survey spectra were quantified in

terms of atomic % for the elements identified with the CasaXPS software (UK) package and a Shirley-type background removal using the element library casaxps_KratosAxisC1s.

2.5. X-ray diffraction (XRD)

The X-ray diffraction measurements were carried out using a Rigaku SmartLab 9kW unit with a rotating anode at 45 Kv and 150 mA to obtain the mineralogy present in the samples. Patterns were recorded at 2θ degrees with a scan speed of 0.03° per second and a 1.54 Å wavelength. Mineralogical interpretations were carried out using the PDXL Ver.1.8.1 Integrated X-ray powder diffraction software and the Whole Powder Pattern Fitting (WPPF) empirical peak shape function.

2.6. Fourier-transform infrared spectroscopy (FTIR)

Analytical grade KBr obtained from Guangzhou Jinjuda Chemical Reagent Company Limited was mixed with each of the clay samples in the ratio of 10:1 and pressed into pellets using a 10-t press. Optimal spectra in the region of 4000-400 Cm⁻¹ were obtained at high resolution, and several scans were recorded with Fourier-transform infrared Thermo Scientific Equipment (Model: Nicolet IS5, made in USA). This was done to obtain the functional groups present in the samples.

2.7. UV-vis spectroscopy

Clay dispersions were prepared by mixing the clay powder with distilled water in cuvette cells and were referenced to a blank. The UV-vis spectra of structural elements and functional groups of samples were recorded in the wavelength range of 195–800 nm using a UV-vis (Model: 6850 UV/Vis-Spectrometer, ANALTIKJENA Germany).

2.8. Zeta potential measurements

Electrostatic interactions exist at the effective boundary between the particle and its surrounding. The zeta potential is the key indicator of the stability of colloidal dispersions. The potential differences in the surfaces of the clay samples, inter alia, solution stabilities, exchangeable cations/adsorption, electrophoresis and electrokinetics, when dispersed in water have been very relevant in the study of colloidal processes and properties (Celik, 2004; McFadyen and Fairhurst, 1993; Gungor and Dilmac, 1996). A NanoBrook Zetaplus (Model: 220001, made in USA) was used in the measurement. Samples were prepared by dissolving 0.101 g of KNO₃ in 1000 ml of distilled water, followed by the dissolution of 1.0 g of each clay sample in 20 ml of 1 mM KNO₃. The mixture was sonicated with an ultrasonic cleaner, (Model: SB-4200, made in China) at a working frequency of 40 KHZ, a settling temperature of 25 °C and measuring temperature of 21 °C for 5 min. The supernatant and residue separation was achieved by using an Eppendorf centrifuge (Model: 5804 R, made in Germany) at 3500 rpm and a temperature of 21 °C for 2 min.

3. Results and discussion

3.1. Physical examination, morphology and elemental composition

The results (Table 1) determined by the visual examination, feel when wet and the moisture meter analyser indicate the sample from Obowo has the highest moisture content of 57%, while that of Afuze has the lowest moisture content of 26.8%, which is indicative of the fact that the higher the moisture content is, the more plastic and more mouldable the clay. The colour (Figure 2) variations may have resulted from the formation due to weathering (redox reaction), humid climate, excess leaching, presence of impurities, organic matter, moisture content, and the elemental and mineral compositions of the samples (Spielvogel et al., 2004; Leger et al., 1979). This is discussed later in detail with the other results.

The SEM micrographs (Figure 3) display the silicate flakes of kaolinite and quartz for the Afuze clay mineral, while the EDX spectrum of the mapped area (not displayed) indicates the presence of silica and aluminium in high quantities and traces of potassium, iron and oxygen. The pinkish Ihitte clay mineral shows a spongy-porous tubular surface with an elemental composition from the EDX spectrum revealing a high content of silica and aluminium with trace elements of oxygen and iron. Well-formed stacks of kaolinite layers are observed for the Kutigi sample with silica and aluminium as the major constituents and oxygen and titanium are the minor constituents. The Minna clay mineral show

hexagonal flakes surface, while EDX also reveals high contents of aluminium and silica with trace elements of iron, potassium and oxygen.

The morphology of Nsu clay shows pseudo-hexagonal sharp edge platelets in a face-to-face arrangement corroborating the work of Chukwudi (2008). The samples from Oboro and Obowo show a honeycomb spherical surface and sheet-like flakes, respectively. Their major elemental constituents are silica and aluminium with minor constituents of iron, potassium, titanium and oxygen for Nsu and iron, magnesium, gold, titanium, krypton, osmium and oxygen for Oboro, while oxygen is the only trace element for Obowo.

3.2. Mineralogy and chemical composition

The XPS results of all the clay samples (Figure 4a) are typical of spectra of clay and clay minerals. The individual samples with their elemental atomic percentages are presented in Figure 4b–h. The presence of carbon in varying relatively high concentrations is a result of weathering during formation and surface-atmosphere interactions or residual precursors (Todea et al., 2013), while that of oxygen is due to the elemental oxygen, oxides, oxygen in water and metal oxides associated with the elements. To evaluate the changes in chemical bonding, the Al 2p and O 1s peaks were deconvoluted into four components to determine the chemical environment of oxygen in silicates, while the Si 2p was deconvoluted into five components for all the samples based on the geometry of the bands, and the interpretation is based on these three energy levels.

The Al 2p shows bonding agreement with the O 1s in the deconvoluted components except those for Oboro. The observed line widths might have resulted from variations in the chemical environment of oxygen since they originate from the coordination of oxygen with the cation(s) (Al³⁺, Fe²⁺, K⁺, and Ca²⁺) present in the samples. The shift in binding energy for the O 1s photoelectrons can be explained by a slight increase in the electron density around the oxygen atoms by surface changes, while the broadening of the full width at half maximum points out a larger distribution of the oxygen sites (Shaikhutdinov and Freund, 2013).

The O 1s high-resolution spectra of the samples are well fitted with four components conforming to the different coordinations of the cations with oxygen. The presence of the components at 532.17–532.21 eV are closely related to the oxygen in Si–O–Si and in Si–O–Al which overlap with the silicone/siloxane bonds between 101.57–102.85 eV except for those for Oboro and that of the silicate bond (oxides) between 101.41–103.67 eV. The O 1s high-resolution spectra of the samples apparently consist of relatively symmetric peaks conforming with established binding energies in the literature (Tissot et al., 2016; Schampera et al., 2015; Boscoboinik et al., 2013; Moulder et al., 1979; Zschornack, 2007). The component at ~534 eV is due to the presence of surface C bonded to O, which indicated an organic contaminant or the mineral formation route.

The binding energy peak at approximately 533 is attributed to the Si–O–Si bridging oxygen and to adsorbed water resulting from Al–OH groups. Additionally, the peak at 531.75 eV can be correlated with great

Table 1. Sample index of clays with % moisture content.

Location	State	M.C	Description
Afuzé	Edo	26.8	Non-plastic orange-brown powder
Ihitte	Imo	44.8	Plastic pink powder
Kutigi	Niger	27.2	Non-plastic white powder
Minna	Niger	53.2	Moderately plastic orange-yellow powder
Nsu	Imo	43.6	Plastic light-brown powder.
Oboro	Abia	52.4	Plastic grey-white powder
Obowo	Imo	57.0	Very plastic yellow-brown powder.

The plasticity was determined by touch after wetting with water.



Figure 2. Clay samples showing colour variations: (a) Afuze (orange-brown), (b) Ihitte (pink), (c) Kutigi (white), (d) Minna (orange-yellow), (e) Nsu (light brown), (f) Oboro (grey-white) and (g) Obowo (yellow- brown).

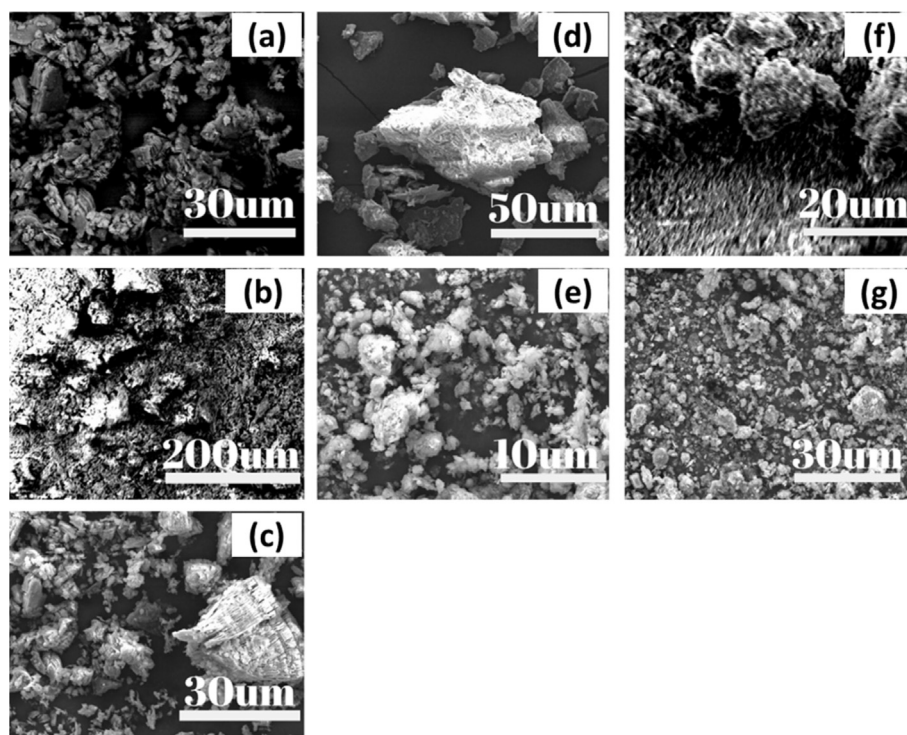


Figure 3. SEM images of clay minerals showing their morphological variations. (a) Afuze showing sheets of kaolinite and quartz flakes, (b) Ihitte clay showing a spongy-porous fibrous surface, (c) kutigi- stacked or thick kaolinite platelets, (d) Minna- hexagonal flakes, (e) Nsu- pseudo-hexagonal kaolinite in a face-to-face arrangement, (f) Oboro- honeycomb with porous spherical grains, and (g) obowo- sheet-like flakes.

amount of octahedral Al 2p at 74.83 eV, as reported by Tissot et al. (2016). Aluminium in transition alumina can either be present in octahedral sheets (hexacoordinated aluminium) or tetrahedral sheets (tetra-coordinated aluminium) (Malki et al., 2014). The binding energies of gibbsite ($\text{Al}(\text{OH})_3$) for all the clay samples range from 73.16 eV to 75.53 eV indicating coordination of the octahedral sites of Al to the surface OH groups (531.75–532.24), while the binding energies of tetrahedral sites of Al 2p and Si 2p are influenced by the negative charge on the silicate framework.

Lower binding energies, 71.16 eV–72.96 eV, recorded for Al metal are in agreement with that already reported (Crist, 2007; Moulder et al., 1979) and the database of elements, <https://xpsimplified/element/aluminum.php>. Aluminium hydroxides present in all samples (except for Oboro) between the range of 74.34 eV–75.77 eV are typical of binding energies common to kaolinites, which result from the Al–OH translation of gibbsite. The peaks for aluminium oxides are recorded at the binding energies of 74.00, 74.36, 74.33, 72.96, 74.86, and 74.09 for Afuze, Ihitte, Kutigi, Minna, Nsu and Obowo samples, respectively, typical of those

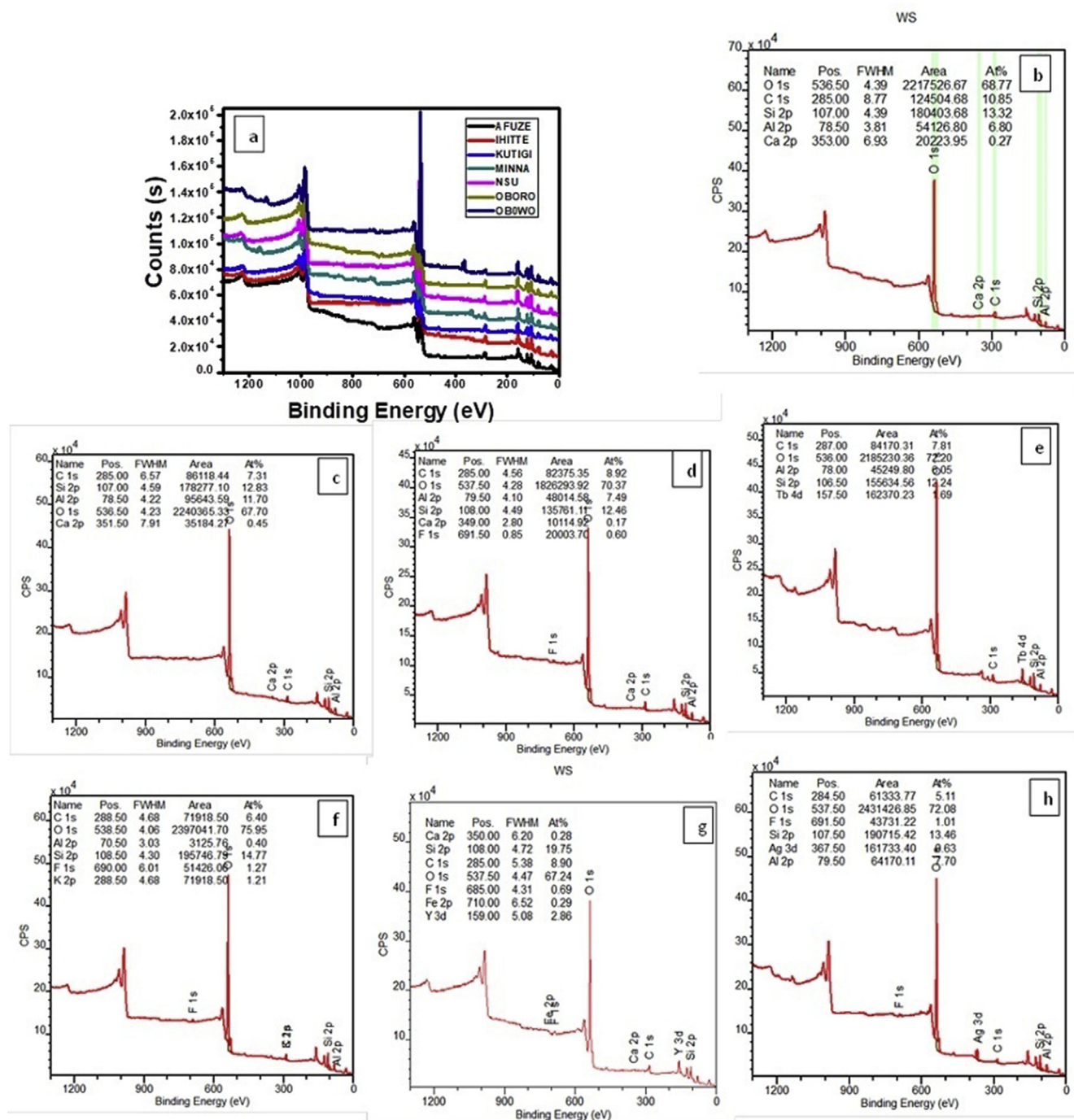


Figure 4. (a) XPS Spectroscopy of all the clay samples, (b) spectra of Afuze, (c) spectra of Ihitte, (d) spectra of Kutigi, (e) spectra of Minna, (f) spectra of Nsu, (g) spectra of Oboro, and (h) spectra of Obowo. All elemental compositions are in atomic weight %.

recorded by the previous XPS analyses of similar clay and clay minerals (Todea et al., 2013; <https://xpssimplified/element/aluminum.php>; Elmi et al., 2016; Tissot et al., 2016).

Afuzo showed a prominent peak of SiO_2 at a binding energy of 103.67. This value is similar to that mentioned by Elmi et al. (2016)'s review on tetrahedral layer silicates and quartz. The observed chemical shift in the photoelectron binding energies for Si 2p between 99.05 eV to 99.64 are attributed to metal silicates and silicon, while the lower binding energies observed for Oboro could not be explained. Apparently, lower binding energies suggests sputtering damage to the air-cleaved surface by a systematic error due to lower energy positively charged Ar ion bombardment (Elmi et al., 2016) or other random error, although

there is no known category that addresses changes in BE numbers (Crist, 2007).

The mineralogical results from XRD patterns (Figure 5) reveal that Afuzo is predominantly kaolin clay (kaolinite, nacrite and dickite) and quartz mineral. The result conforms with the Si_2O_5 sheets bonded to aluminium oxide/hydroxide layers ($\gamma\text{-Al}(\text{OH})_3$, called gibbsite layers, as shown by the Al 2p XPS (Figure 4) and EDX, which recorded no traces of other elements other than Al, Si and oxygen. High-angle XRD reflections are observed for sudoite-chlorite in the Ihitte clay sample (Figure 5). The high content of magnesium-rich dioctahedral chlorites is usually pinkish to white, which is in conformity with the pink colour observed for the sample in Figure 2.

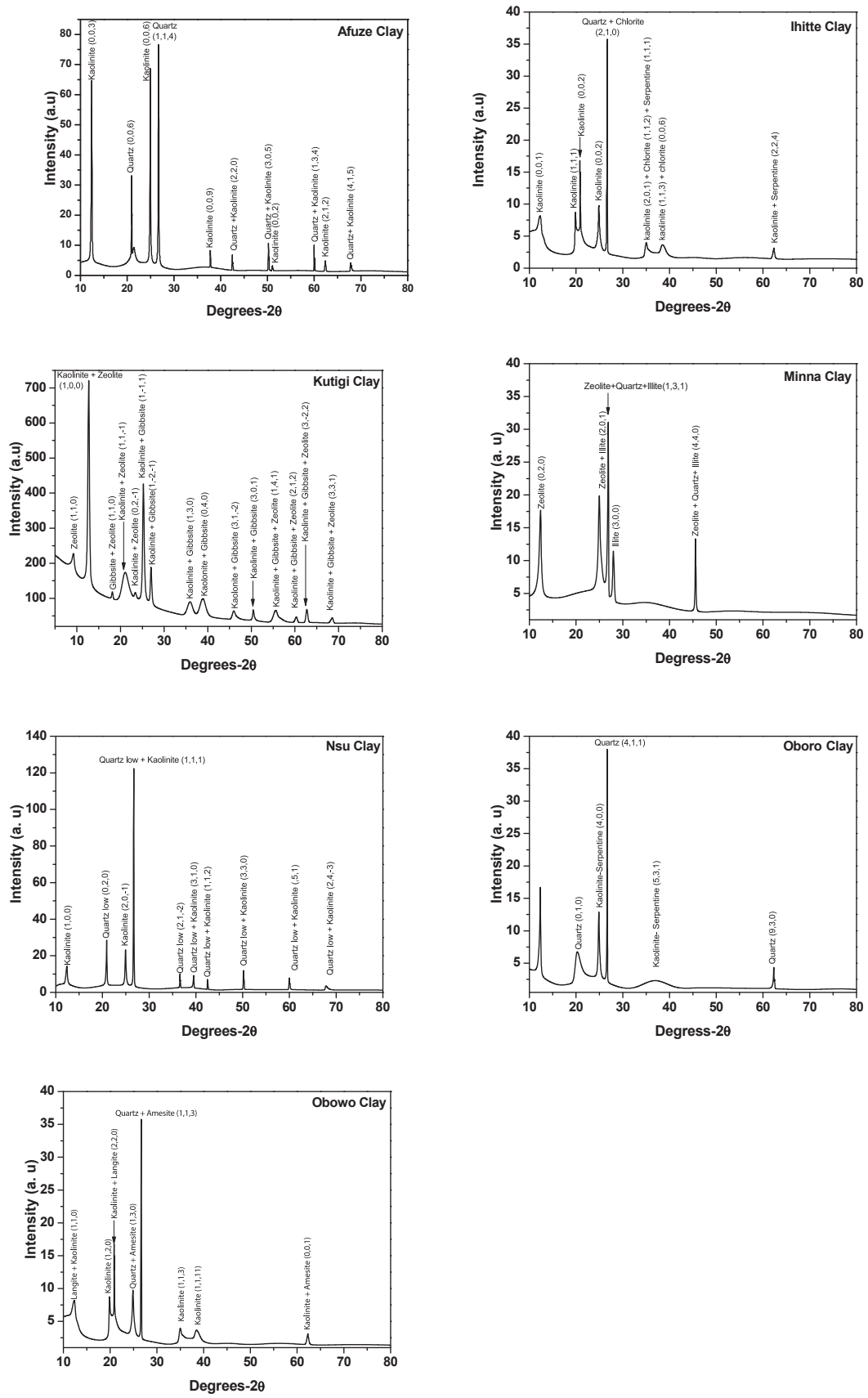


Figure 5. XRD patterns of Afuze, Ihitte, Kutigi, Minna, Nsu, Oboro and Obowo clay and clay minerals.

The trace elements calcium and iron observed in XPS and EDX, respectively, can be linked to the 20.84% of the transition metal fluoro compound, CaFeF_5 with an octahedral cis-chain structure capable of halogen exchange with or fluorination of organic compounds. The Kutigi clay sample revealed both strong and broad reflections for kaolinite and calcium tecto-dialuminotetrasilicate hydrate (Figure 5). Kaolinites possess a dioctahedral structure and are known for their 1:1 silicate layers sandwiching a gibbsite layer. The two characterizations of XPS and XRD confirm this conclusion for this sample, although XPS reveals stronger peaks for aluminium oxides than gibbsite. The 3% Ti recorded for the mapped area in EDX might result from impurities that are associated with dickite during formation due to the weathering of feldspar, whereas the trace of calcium captured by XPS results from hydrated aluminosilicate. Hydrated calcium aluminosilicate mineral, laumontites, and the hydrated phyllosilicate mineral of aluminium and potassium, muscovites, are the major constituents of Minna clay (Table 2).

The XRD quantification conforms with the result of EDX of 6% Fe, K_2O -rich contents due to the interlayer K in illite/muscovite, and traces of terbium, which has a resemblance to calcium, as captured by XPS. The impurities of terbium may be a result of secondary mineralization, and iron coloured it brown-yellow (Figure 2). Kaolinite and quartz are observed for Nsu clay. The presence of Ti, Fe and K captured by EDX, XPS

and XRD indicates a 1:1 layer structure, but trioctahedral sheets filled with Mg^{2+} antigorite confirms the previous publications by Chukwujike and Igwe (2016); Nwuzor et al. (2018); and Iyasara et al. (2016) in their elemental composition of oxides. Quartz and berline minerals dominate Oboro, as seen in the XRD pattern (Figure 5). The white-grey colour of the sample might come from potassium tectosilicate and kaolinite. Calcium tecto-dialuminotetrasilicate hydrate is the major component of Obowo with reflections of quartz and the uncommon amesite minerals.

3.3. Spectroscopy analysis

The combined spectra for the seven samples are presented in Figure 6 but are outlined in Table 3 for clarity. The O–H stretching bands from medium to strong intensities are between 3700–3300 for most kaolinite and illite clays (Fadil-Djenabou et al., 2015; Nayak and Singh, 2007; Bantignies et al., 1997; Frost and Vassallo, 1996; Larkin, 2011). Bands for Si–O stretching occur between 1095–1009 cm^{-1} in clay minerals, and the Si–O–Si of quartz (Nayak and Singh, 2007; Bishop et al., 2017) and Al–O bending falls within the range of 1200–700 cm^{-1} . For SiO_2 , a strong band is at approximately 1100 cm^{-1} , bending bands between 600–150 cm^{-1} , and medium bands of SiO_2 at approximately 470 cm^{-1} . Metal O–H bands are seen in the bending mode between 950 and 600 cm^{-1}

Table 2. Quantification of clay minerals as revealed by XRD.

Name	Chemical Formula	% Mass Composition	Group
Afuze			
Quartz	SiO_2	37.44	Silica
Kaolinite	$\text{Al}_2\text{SiO}_5(\text{OH})_4$	44.40	Kaolin
Nacrite	$\text{Al}_2\text{SiO}_5(\text{OH})_4$	3.69	Kaolin
Dickite	$\text{Al}_2\text{SiO}_5(\text{OH})_4$	14.47	Kaolin
		100.00	
Ihite			
Sudoite	$\text{Mg}_2(\text{Al,Fe}^{3+})_3\text{Si}_3\text{AlO}_{10}(\text{OH})_8$	45.93	Chlorite
Alpha-Magnesium Sulphate	$\alpha\text{-MgSO}_4 \cdot 4.2\text{K}$	14.81	Sulphate
Calcium Iron Fluoride	CaFeF_5	20.84	Fluoro Compound
Guidottiite	$\text{MnFe}^{3+}\text{SiFe}^{3+}\text{OH}_4$	18.37	Serpentine
Lizardite	$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$	0.01	Kaolin-Serpentine
	$\text{Al}_2\text{CaH}_{15-68}\text{O}_{11-84}$	0.04	Kaolin-Serpentine
		100.00	
Kutigi			
Kaolinite	$\text{Al}_2\text{SiO}_5(\text{OH})_4$	18.71	Kaolin
Dickite	$\text{Al}_2\text{SiO}_5(\text{OH})_4$	44.26	Kaolin
Lizardite-2H2	$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$	22.63	Kaolin-Serpentine
Nacrite	$\text{Al}_2\text{SiO}_5(\text{OH})_4$	14.40	Kaolin
		100.00	
Minna			
Laumontite	$\text{Ca}(\text{AlSi}_2\text{O}_6)_2 \cdot 4\text{H}_2\text{O}$	69.85	Zeolite
Muscovite	$(\text{KF})_2\text{Al}_2\text{O}_3 \cdot 3(\text{SiO}_2) \cdot 6(\text{H}_2\text{O})$	30.15	Illite/Mica
		100.00	
Nsu			
Quartz Low	SiO_2	80.14	Quartz-Tectosilicate
Dickite	$\text{Al}_2\text{SiO}_5(\text{OH})_4$	19.86	Kaolin
		100.00	
Oboro			
Quartz	SiO_2	49.72	Tectosilicate
Berlinite	$\text{Al}(\text{PO}_4)$	44.46	Phosphate
Leucite	$\text{K}(\text{AlSi}_2\text{O}_6)$	5.82	Tectosilicate
		100.00	
Obowo			
Calcium tecto-dialumotetrasilicate	$\text{Ca Al}_2 \text{ Si}_4 \text{ O}_{12} (\text{H}_2\text{O})_3 \cdot 0.2$	92.08	Tectosilicate-Zeolit
Amesite	$(\text{Fe, Mg})_4\text{Al}_4\text{Si}_2\text{O}_{10}(\text{OH})_8$	7.92	Serpentine
		100.00	

Table 4. Zeta potential results for clay minerals in aqueous solution.

Sample	Zeta Potential (mv)	Mobility (μs)/(v/cm)	Conductance (μs)
Afuze	-33.64	-2.63	309
Ihitte	-26.64	-2.08	330
Kutigi	-28.42	-2.22	336
Minna	-27.10	-2.12	396
Nsu	-28.50	-2.23	323
Oboro	-26.91	-2.10	313
Obowo	-24.06	-1.88	319

Mean values of 5 tests for each sample.

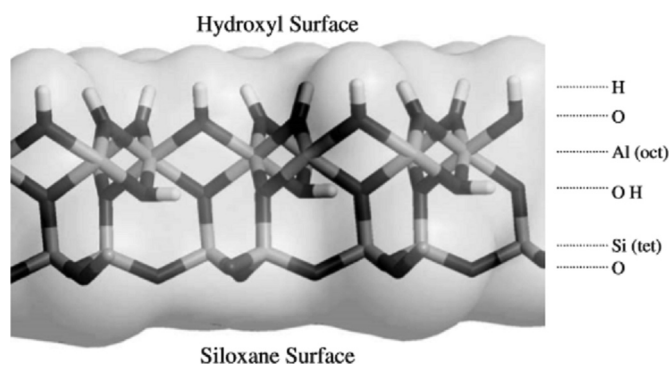


Figure 7. Hydroxyl and siloxane surface of kaolinite “Reprinted from *Handbook of Clay Science. Surface and Interface Chemistry of Clay Minerals* written by R. A. Schoonhedydt and C. T. Johnston. Development in Clay Science vol. 1, *Handbook of Clay Science* (2006) with permission from Elsevier”.

Kutigi and Minna clay minerals are suitable for the production of ceramic water filters because of their mineral compositions and special properties. Rich in zeolite content and the kaolinite nature of both samples indicate the capability of isomorphous substitution, cation exchange (Bergaya et al., 2006), water softening, removal of odour and molecular sieving through their 3D cage-like framework structure. Heavy metals such as Zn, Cu, and lead are strongly attracted to the negatively charged sites on the 1:1 layer minerals. These are caused by the dissociation of the surface hydroxyls of these minerals.

Furthermore, zeolites are resistant to high temperatures, high pressures, acid and other inorganic solvent attacks, and they do not dissolve in water or oxidize in air. Their flexible porosity can be engineered to suit purpose-driven applications. It is expected that during the production of expanded clay aggregates, the Fe^{2+} content of Minna clay will convert to Fe^{3+} , which is more stable because of its diamagnetic properties due to the half-filled $3d^5$ electron configuration. This is also validated by the zeta potential results for the two clays.

Kaolinite Nsu clay was reported by Akapomie et al. (2012) to have successfully adsorbed cadmium(II) and iron from effluents. Such clay can also be used as an extender in aqueous-based paints and fillers in polymers. Non-plastic kaolinite, such as Afuze and Kutigi, can be used as refractories, ceramics products, paints, fillers for plastics and catalyst (Lopez-Galindo & Viseras, 2004; Bergaya et al., 2006; Douglas, 1993) composites due to their earlier mentioned properties. Apart from Kutigi and Minna clays, Afuze, Nsu and Obowo have great potential for the production water filters, while multi-mineral Ihitte and Oboro are suitable for applications, such as ceramic wares, porcelain, paints, plastic fillers, etc. However, such clays can be modified to suit petrochemical, filtration and catalysis applications.

In addition to using these clays for water filters, refractories, ceramics, etc., they can also be used to synthesize composites with other raw materials, such as agricultural residues and natural fibres. These

composites can find suitable application in the construction industry as materials for roads, blocks, and roof and floor tiles. These and other minerals in various locations in Nigeria, with good planning, can provide the raw material base for clusters of small and medium enterprises (SMEs), which can be established in each of the 774 local government areas of Nigeria.

5. Conclusions

A scientific procedure for using the chemical composition, morphology, mineral content, functional groups and stability in determining the industrial application of selected clay minerals was established in this study. Valuable information is extracted from the multiple means of characterization of the Nigerian clays and clay minerals. Based on the above, out of the seven studied clay minerals, two (Kaolin from Kutigi and Fe-rich Minna clay) are found to be more suitable for the production water filter media due to their potential ability to soak up ions and scavenge for heavy metals and chemical contaminants within their structural framework, amongst other special properties. Although the minerals have potential industrial applications, unfortunately they are not contributing much to national development as value is not being added to them at present. All the examined methods of characterization are in tandem with one another except for a slight disparity in Oboro clay (EDX and XPS). Kaolin and Illite are the major clay components, while quartz, gibbsite, antigorite, berillinite, sudoite, amesite, chlorite, lizardite and leucite are the associated minerals. The results of this study are currently being used to select the suitable type of clay to produce expanded clay aggregates to be used to design and fabricate low-cost water filters. The implication of the study is that these clays can be used for various applications based on their characteristics, thereby increasing local content usage of and value added to minerals in Nigeria. Future work will look at characterizing the plastic behaviour of the clays, their mineral oxides and the thermal analysis of the minerals. The expected result will serve as a guide together with the present study to select appropriately the best materials for the filter media. Consequently, the expanded clay aggregate will be produced and tested for efficiencies in various contaminant removals.

Declarations

Author contribution statement

Gina O. Ihekwebe: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Josiah N. Shondo: Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

Kingsley I. Orisekeh, Godwin M. Kalu-Uka: Performed the experiments; Contributed reagents, materials, analysis tools or data.

Iheoma C. Nwuzor: Analyzed and interpreted the data; Wrote the paper.

Peter A. Onwualu: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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