



Chemical and Mineralogical Characterization of Locally Sourced Nigerian Clay

*Sumanu, O. M¹, Dim, P. E². & Okafor, J. O³.

¹ Engineering Department, Federal University of Technology, PMB 65, Minna, Niger State, Nigeria

² Department of Chemical Engineering, Federal University of Technology, PMB 65 Minna, Niger State, Nigeria

³ Department of Chemical Engineering, Federal University of Technology, PMB 65, Minna, Niger State, Nigeria

*Corresponding author email: olorunyomisumanu@gmail.com, +2348036781858

ABSTRACT

The application of various clay minerals is related to their structural, physical, and chemical characterization. The utilization of clay in any form is been dictated by the physical and chemical properties of the clay minerals. This study investigates the chemical and mineralogical composition of clay sample collected from Umunze, Nigeria. Some quantitative and qualitative analytical methods were employed for the purpose of chemical and mineralogical characterization. The methods include Brunauer, Emmett and Teller (BET) Analysis, Cation exchange capacity (CEC), X-ray diffraction (XRD) Scanning electron microscope (SEM) and Fourier Transform infrared spectroscopy (FTIR). The results obtained suggests that the clay is of kaolinite with traces of montmorillonite.

Keywords: Clay, Characterization, Kaolinite, Mineralogy, XRD.

INTRODUCTION

The study of clay and its minerals is generating new interest all over the world with an aim of providing solutions to problems of pollution eradication. The readily availability of clay in abundance which interestingly constitute a larger percentage of water in nature, justifies the need for the study. Oxygen and Silicon alone account for 75% of the mass of the earth crust and Oxygen for 90% of the total volume (Schulze, 2015). Clay, a small particle, found naturally on the surface of the earth composed mainly of silica, alumina, water and weathered rock (Uddin, 2017). Clay minerals play an important role in physico-chemical properties determination. The corresponding bulk of physico-chemical properties of certain clay distinguish clay minerals based on their different crystal structure. Kaolinite is a major mineral constituent of clay that is rich in kaolinite called Kaolin. Kaolinite is a clay mineral with chemical composition $Al_2Si_2O_5(OH)_4$ with a single silica tetrahedral layer linked through Oxygen atoms to a single alumina octahedral layer (Olaremu, 2015). Kaolinite structure possesses great advantages in many processes, due to its high chemical stability, cation capacity and low expansion co-efficient (Uddin, 2017) Characterization of clay play an important role in determining the properties. The method employed to characterize the clay sample include chemical analysis, X-ray diffraction (XRD), X-ray fluorescence (XRF), Fourier Transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM), surface area and pore size measurement. Normally a combination of several methods are needed

for sufficient characterization of the material obtained (Khalifa *et al.*, 2016). The objectives of this study is to characterize a new locally sourced clay, to determine its physical, chemical and mineral properties.

METHODOLOGY

Clay sample collected from Umunze, Nigeria was used as raw material. It was treated by hand picking to remove the dirt and other foreign bodies and after which it was sieved with a 125 μ m mesh sieve. The collected particles were sun dried.

BET surface analysis and porosity: Nitrogen adsorption/desorption isotherms in relative pressure ranging from 10⁻⁶ to 0.999 were measured at 77 K on an automatic adsorption instrument (Quantachrome Instruments, Model Nova1000e series, USA). Prior to the measurement, the given sample was crushed to powdery form to shorten the time required for reaching equilibrium in the isotherm study and degassed at 250°C under nitrogen flow for 16 hours.

The infrared spectra were obtained using a Perkin-Elmer 1720 spectrometer (the sample was diluted with potassium bromide:50mg of sample mixed with 350mg of potassium bromide). The FTIR spectra of the samples were recorded between 4000 and 450 cm^{-1} .

SEM analysis: The clay sample morphology was observed using Zeiss Auriga HRSEM. XRD analysis: The mineralogical phase characterization and estimation of the average crystallite size of the various synthesized materials were performed on a Bruker AXS D8 X-ray diffractometer system coupled with Cu-K α radiation of 40 kV and a current of 40 mA. The λ for

$K\alpha$ was 0.1541 nm, scanning rate was 1.5°/min, while a step width of 0.05° was used over the 2 θ range. The powder samples were placed and clipped into the rectangular aluminium sample holder. The diffractograms were recorded in the 2 θ range of 200 - 900 and the phase identification was done. The chemical analysis of the raw clay was carried out using XRF.

Cation exchange Capacity (CEC) was determined by Gillman and Sumpter method of Compulsive exchange.

RESULTS AND DISCUSSION

BET analysis

According to Babaki *et al.*, (2008) texture characteristics such as pore volume, or pore size and surface area played an extensively important role in clay mineral applications such as adsorption. The results presented in Table 1, are for pore size, pore volume and surface area of raw clay sample using BET analysis. The surface area of the raw clay from the Table is 84.233 m²/g. The result is in agreement with the findings of other work (Valenzuela Díaz and de Souza Santos, 2001), who suggested that Smectite has BET surface area varying from 16 - 97 m²/g, without any chemical treatment.

Cation exchange Capacity

Cation exchange Capacity (CEC) CEC can be described as the quantity of positively charged ions held by the negatively charged surface of clay minerals. It was determined by Gillman and Sumpter method of Compulsive exchange. The caption exchange capacity (CEC) of pure kaolinite minerals range from 3-15 Cmol/100g (Olaremu, 2015). The value as shown in Table 1 represents the determined CEC of clay sample. The CEC value of raw clay sample calculated for this work is 22.298 cmol/100g higher than the literature value for kaolinite, this is probably due to impurities and pore size (Olaremu, 2015).

Table 1: Properties of raw clay sample

Property	Pore size (nm)	Pore Volume (cc/g)	Specific Surface Area (m ² /g)	Cation Exchange capacity (CEC) cmol/100g
Value	2.115	5.266 x 10 ⁻²	84.223	22.29

XRF analysis

Table 2 shows the results of chemical analysis and loss on ignition of raw clay sample. The chemical composition of

the clay sample is in (%). The high loss of ignition (see Table 2) is associated with the dihydroxylation of the clay minerals and the oxidation of organic matter (Savazzini-Reis *et al.*, 2017).

The chemical analysis of raw clay shows that the major elements are SiO₂ and Al₂O₃ while traces of Magnesium, Chromium, Manganese, Calcium, Titanium and Zinc oxides are found in form of impurities. ZnO has the lowest percentage composition in the clay sample which may be attributed to the environmental and geographical contribution of the earth crust of an area where the Umunze clay sample was collected. Silicon (IV) oxide has been reported to constitute the highest percentage composition of kaolinite sample (Lin and Wen, 2002). The second highest constituent identified to be aluminium oxide. The ratio of alumina silica was estimated to be 1:5.4.

Table 2: Chemical analysis (wt %) and loss in ignition of raw clay sample.

Components	Percent
SiO ₂	49.752
Al ₂ O ₃	9.203
Fe ₂ O ₃	6.943
CaO	0.357
TiO	1.024
MgO	1.395
Cr ₂ O ₃	0.023
ZnO	0.009
MnO	0.105
LI	31.189

XRD analysis

The mineralogical composition of the sample was determined by the use of x-ray diffractometer studies. The sample composed majorly of Quartz (which is the non-clay mineral in clay) it is characterized by strong d-lines, Kaolinite and Montmorillonite. From Figure 1, Montmorillonite is represented by M, Kaolinite by K and quartz with Q. Kaolinite and Montmorillonite showed good absorbance for removal of toxic heavy metals as (Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, and Zn (Talaat *et al.*, 2011). Kaolinite is clay that is rarely found in a pure state, it is a

major part of the kaolin clay and is a very good type, consisting of aluminosilicate minerals (Al_2O_3 SiO_2 H_2O) (Naswir *et al.*, 2013).

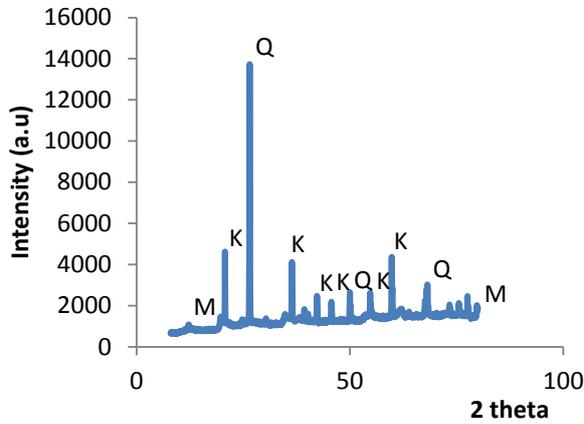


Figure 1.: Diffractogram (XRD) of raw Umunze clay.

FTIR analysis

The FT-IR spectra of the raw clay samples were carried out in the range from $400\text{-}4000\text{cm}^{-1}$ to study the effect of leaching of the clay minerals from the raw or natural sample shown in Figure 2, the inner surface OH stretching vibrations are represented at 3696 and 3623cm^{-1} , while the absorption band at 3457cm^{-1} represents the outer surface OH stretching vibration. These OH groups function as the active sites for the binding of positively charged cations. The absorption bands at 469.66 and 1030cm^{-1} represented the Si-O-Si stretching vibration (Li *et al.*, 2014; Juan Yin *et al.*, 2018). The absorption band at 916cm^{-1} represents the Al-OH bending vibration while those at 798 and 694cm^{-1} represent the Si-O stretching vibration (Olgun and Atar, 2012). The (Si-O) bands are strongly evident in the infrared spectrum by adsorption band in the 1030cm^{-1} . While those at 798.94cm^{-1} and 694.46cm^{-1} represent the stretching vibration (Dawodu *et al.*, 2014). The characteristic bands at 3686cm^{-1} , 3657cm^{-1} and 916cm^{-1} indicated the presence of kaolinite. The presence of adsorption bands at 3623cm^{-1} support the presence of montmorillonite. According to Spence and Kelleher, 2012 and Long *et al.*, 2013, Kaolinite has wave numbers peak of hydroxyl (OH) group of 3696 , 3671 and 3650cm^{-1} and Montmorillonite with wave numbers peak of 3624cm^{-1} (Al-OH), and 3422cm^{-1} (water).

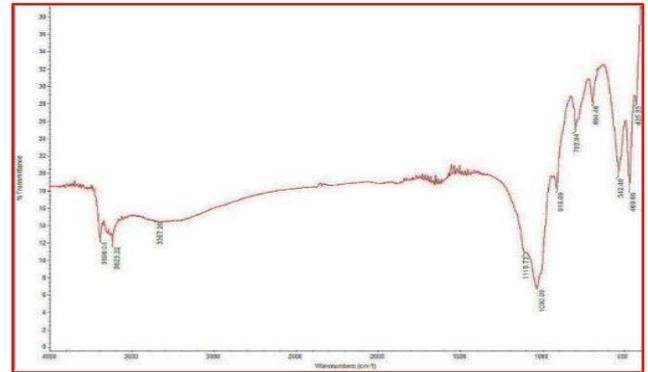


Figure 2: Infrared spectra (IR) of Umunze clay.

SEM analysis

The Scanning electron microscopy (SEM) of raw clay was carried out to assess the surface morphology of the clay. The micrograph of the natural adsorbent can be clearly observed from Figure.3 which shows the aggregate mass size made up of aggregated mass of irregularly shaped particles that appeared to have been formed by several flaky particles stacked together in form of agglomerates.

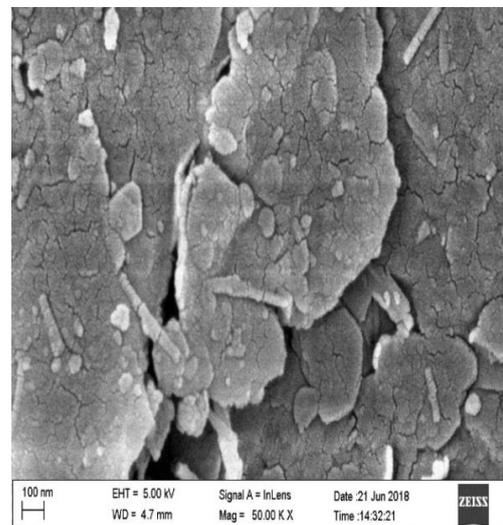


Figure 3: Scanning electron microscope of raw Umunze clay.

CONCLUSION

The study investigated the chemical and mineralogical analysis of raw clay sample. The surface area, chemical and mineralogical composition, morphological properties were studied using various techniques. It was found that raw clay has a BET surface area of $84.223\text{ m}^2/\text{g}$. The chemical analysis of the clay consists of high impurities of chemical oxides such as Fe_2O_3 , TiO_2 , MnO , MgO , Cr_2O_3 , and ZnO . Generally, quartz and iron were the major impurities present in the raw sample. The XRD results indicated that



the clay mineral is of kaolinite type with traces of montmorillonite and present of quartz, which was confirmed by the XRF results. The finding shows that clay minerals can be exploited for the removal of wastewater using low cost and environmental friendly techniques through acid activation to reduce the levels of iron, quartz and other impurities to acceptable levels.

ACKNOWLEDGEMENTS

The author acknowledges support from the Federal University of Technology, Minna for the use of departmental library and other facilities. The author would like to express utmost thanks to Dr. Tijani Oladejo, and Mr. Pius Ikokoh of SHESTCO, Sheda-Abuja for helping to conduct some of the experiments.

REFERENCE

- Babaki, H., Salem, A., and Jafarizad. (2008). "Kinetic model for the isothermal activation of Bentonite by Sulfuric acid." *J. Mat. Chem. Phy.* 108: 263-268.
- Dawodu, F.A. and Akpomie, K.G. (2014). Simultaneous adsorption of Ni(II) and Mn(II) ions from aqueous solution onto a Nigerian kaolinite. *J. Mater. Res. Technol.* 3, 129-141.
- Khalfa, L., Bagane, M., Cervera, M. L., and Najjar, S. (2016). Competitive adsorption of heavy metals onto natural and Activated clay: Equilibrium, Kinetics, and Modelling. *International Scholarly and Scientific Research & Innovation*, 10(5), 583-589.
- Lin, C. P. and Wen, S. B. (2002). *J. A. Am. Ceram. Soc.* 25, 129.
- Long, H., Wu, P., and Zhu, N. (2013). "Evaluation of Cs⁺ removal from aqueous solution by adsorption on Ethylamine-Modified Montmorillonite". *Chemical Engineering Journal* 225: 237-244.
<http://doi.org/10.1016/j.vibspec.2012.02.019>
- Naswir, M., Arita, S., Marsi, and Salmi. (2013). Characterization of Bentonite by XRD and SEM-EDS and Use to Increase PH and Colour Removal, Fe, and Organic Substances in Peat water, *Journal of Clean Energy Technologies*. 1(4), 313-317.
- Olaremu, A. G., (2015). Physico-Chemical Characterization of Akoko mined Kaolin clay. *Journal of Minerals and Material Characterization and Engineering*. 3, 353-361.
- Olgun, A., and Atar N. (2012). "Equilibrium, thermodynamic and kinetic studies for the adsorption of lead (II) and nickel (II) onto clay mixture containing boron impurity". *J Indust Eng Chem.* 18(5):1751-1757.
- Savazzini-Reis, A., Sagrillo, V. P. D., de Oliveira, J. N., Teixeira, P. G., and Valenzuela-Diaz, F.R. (2017). "Characterization and evaluation of Ceramic properties with spherical and prismatic samples of clay used in red ceramics". *Research material*. 20(2):543-548. DOI:<http://dx.doi.org/10.1590/1980-5373-MR-2016-0915>.
- Schulze, C. D. (2015). Clay Minerals in: Hillel D.(ed) *Encyclopedia of the soils in the environment, Elsevier*, 246-252.
- Spence. A., and Kelleher, B. P. (2012). " FT-IR Spectroscopic Analysis of Kaolinite-microbial interactions". *Vibrational spectroscopy*. 61, 151-155.
- Talaat, H. A., El Defrawy, N.M., Abulnour, A. G., and Hani, H. A. (2011). "Evaluation of Heavy metal removals using Egyptian clays". *2nd International Conference on Environmental Science and Technology, IPCBEE*. 6:37-42.
- Uddin, M. K. (2017). A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade. *Chemical Engineering Journal* 308, 438-462
- Valenzuela Diaz, F. R., and de Souza Santos, P. (2001). "Studies on the acid activation of Brazilian Smectite clay". *Quim. Nova*. 24 (3):345-353.