

Characterization of Clay Modified with Alkali Extracted from Plantain Peels

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Authors' contributions

This work was carried out in collaboration among all the authors. Authors OOO, EOD and TOS jointly designed the study. Author AOA wrote the protocol while author EOD wrote the first draft of the manuscript. Author IAA managed the literature searches. All authors managed the analyses carried out in the study. All authors read and approved the final manuscript.

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ABSTRACT

Modification of clays and clay minerals by using chemical reagents is receiving research attention due to the use of clay in various industrial applications where it may be utilized as adsorbent and catalyst carriers among others. The employed synthetic chemicals, however, unavoidably result in high costs and generate negative impact within the environment. The option to replace the synthetic compounds with non-synthetic materials to cut down cost and to reduce environmental impact has not been properly explored. In this study, the effect of KOH extracted from plantain peel obtained locally on clay modification was investigated. A varying concentration of the extracted KOH was used to treat the clay obtained at Asa River valley in Kwara State in Nigeria. Characterization of the modified clay samples was carried out using Scanning Electron Microscope (SEM), X-ray Florescence (XRF) and Fourier Transform Infrared Spectroscopy (FTIR). The micro

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structural images of the modified clays clearly showed the effect of KOH concentrations on porosity enhancement in the selected samples. X-ray fluorescence analysis of the Kaolin showed a high silica and aluminum content while an appreciable increase in K_2O was also observed in the modified clay compared to the raw Kaolin. The FTIR spectra of the modified clay showed the formation of some functional groups (O-H, C-H, C=C, C-O, Al-O-Si,) within the band range of 500 to 4000 cm^{-1} . It can be concluded that the clay treated with alkali obtained from green source can effectively replace those produced via conventional methods which involve the use of synthetic materials.

Keywords: Modified clay; instrumental characterization; alkali; plantain peels.

1. INTRODUCTION

Kaolin are rocks rich in Kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) [1]. Kaolin, a soft, earthy, and usually white mineral (dioctahedral phyllosilicate clay), is chemically inert (does not react with other elements) over a varied range of pH values and temperatures and often exists in nature as a free element. Impurities such as iron minerals often change the colour of white Kaolin. These minerals occur as hydroxides, oxides, sulphides and carbonates along with iron-stained quartz/anatase and mica in Kaolin [2]. Kaolin serves as raw material for catalyst and adsorbent production [3-5]. It is also useful in the treatment of nuclear wastes, as well as in the manufacture of paper, earthen-wares and fillers [6-8]. It is usually produced by the chemical weathering of Aluminium silicate minerals such as feldspar. However, its colour may vary when it occurs in combination with other elements. For instance, it appears pink-orange in combination with iron oxide; yellow or light orange when in combination with Aluminium silicate (feldspar) and brown when mixed with sand. Hence, its initial colour and the agents involved in the modification process determine its final appearance.

Modifications of clays and clay minerals by using different chemical reagents have been receiving increased attention in recent years [9,10]. The employed synthetic chemicals, however, unavoidably result in high costs and thus, generate negative impact within the environment. One option is to replace the synthetic compounds with non-synthetic materials to cut down cost and reduce the environmental impact. The research in this area, however, has not been properly explored.

Nigeria is ranked amongst the largest plantain producing countries in the world [11]. Despite this claim, the country rarely exports plantain because the bulk of the plantain produced is consumed locally. The demand for less time-

demanding and convenient foods made from locally produced plantain, and the rise in the number of small scale industries that use plantain for snacks (plantain chips) in the urban area of the country has continued to increase its rate of consumption [12]. Consequently, huge amount of plantain peels often regarded as waste materials are discarded and sometimes used for animal feeds. About 17,397,000 metric tons of plantain peels in African countries could be put into use for the extraction of alkali, ethanol and other medicinal products [13]. Research on the metallic analyses of ash derived alkalis from banana and plantain peels (*Musa spp.*) have been conducted [12].

In this study, the effect of KOH extracted from locally produced plantain peels on clay modification was investigated. A varying concentration of the extracted KOH was used to treat the clay obtained at Asa River valley in Kwara State in Nigeria. Characterization of the modified clay samples was carried out using Scanning Electron Microscope (SEM), X-ray Florescence (XRF), and Fourier Transform Infrared Spectroscopy (FTIR).

2. MATERIALS AND METHODS

2.1 Preparation of Samples

The Kaolin was obtained from Asa river valley, Ilorin, Kwara State (Latitude $8^{\circ} 33' N$, and Longitude $4^{\circ} 34' 46 E$). Caustic potash (KOH) was extracted from plantain peels and characterized using chemical assay. The obtained clay sample was grinded and wet beneficiated to remove impurities. The purified clay was dried and calcined at $750^{\circ}C$ for 2 hours in a muffle furnace (NYC-12 model) and was converted into metaKaolin [14]. Twelve experimental Runs were designed using the Central Composite Design (CCD) of the design expert software for the impregnation of KOH into metaKaolin (grinded fine particles) at varying

quantities and mixing times. The impregnation was conducted in a mechanical shaker operated at 60°C. KOH and metaKaolin was simultaneously introduced into sample bottles and a small quantity of water was added to the mixture to induce plasticity. The sample bottles were later transferred into the mechanical shaker to enhance thorough mixing. After impregnation, the slurry was dried in an oven operated at 110°C for 4 hours to remove moisture and the dried modified clay was calcined in a muffle furnace (NYC-12 model) operated at a temperature of 400°C for 5 hours [15]. Prepared solids were weighed and their weights were recorded.

2.2 Analytical Techniques

2.2.1 Scanning Electron Microscopy (SEM)

Morphology and microanalysis of the Kaolin and modified clay samples were determined using ultrahigh resolution field emission scanning electron microscope (HV-SEM). The scanning electron microscopy (SEM) is a technique used for producing images of interaction between the electrons and materials present in a sample surface. SEM principle is based on the fact that electron beam bombards the surface of the sample to be analyzed. This leads to the emission of certain particles analyzed by various detectors which gives a three-dimensional image of the surface captured. In a typical run, a very small amount of the sample (less than 1.0 mg) was picked and placed on the sample stab. The stab containing the sample was placed in the sputter coater for surface polishing with graphite film. After the sample preparation and sputtering, the sample stab was placed in the analysis chamber of the SEM equipment and the vacuum was put on. Scanning of the sample commenced when the vacuum reached about 9.6×10^{-5} torr. The magnification and voltage were set and the focus of the microscope was manipulated until a sharp clear image was obtained and picture captured. SEM micrographs of the virgin and modified clay were taken in different resolutions with a view of comparing the level of modification in the modified sample.

2.2.2 Energy Dispersive X-ray Fluorescence (EDXRF) analysis

The elemental analysis of raw and modified Kaolin was determined using Energy Dispersive X-ray fluorescence (EDXRF) spectrometer of model "Minipal 4". The samples (raw and

modified Kaolin) were pulverized using an arget pulverizing machine (planetary micro mill pulverisette 7). The ground samples were sieved with 150 micro meshes. 5 g of the pulverized sample was transferred into a beaker and mixed with 1 g of binding aid (Starch soluble). The mixture was pressed under high pressure (6 MPa) to produce pellets. The pellets were labeled and packaged for the analysis. The pellets were carefully placed in the respective measuring positions on a sample changer of the machine. Maximum voltage of 20 kV was applied to produce the X-rays that excite the sample for a preset time (100 sec for each sample). Loss on ignition (LOI) was determined gravimetrically by heating 1g of the powdered sample in a cleaned weighed crucible at 1000°C after which the crucible and the content was weighed to get the weight loss before and after heating.

$$LOI = \frac{a-b}{a} \times 100\% \quad (1)$$

where, LOI is the loss on ignition of the sample(s) and a and b are the sample weights before and after heating respectively.

2.2.3 Fourier Transformed Infrared (FTIR) analysis

Fourier Transformed Infrared (FTIR) spectroscopic analysis was used to study the level of functionalization of the Kaolin and modified clay across a range of 400 to 5000 cm^{-1} in the samples using FTIR (FTIR-2000, Pelkin Elmer). Prior to the sample analysis, background spectrum of air at ambient condition was run. During analysis, 0.07 g wafers from each of the samples (raw Kaolin and modified clay) consisting of 1% of the sample and 99% KBr window was used. The mixture of each sample was pressed under pressure of about 12 MPa to produce a thin film wafer. The wafers for each sample were inserted into the sample holder of the FTIR equipment in succession, then, FTIR spectra of the samples were recorded. The spectra gave information about the characteristics of the functional groups on the surface of the raw and modified Kaolin clays.

3. RESULTS AND DISCUSSION

3.1 Clay Modification Results

Table 1 shows the results of modified clays at varying conditions. It can be deduced from the table that the quantities of KOH and MetaKaolin determine the yield of modified clays. Hence,

Run 1, 5, and 12 had the highest yield of 8.1, 8.1, and 8.9 g respectively. Run 12 with the highest yield could be attributed to the higher quantity of MetaKaolin when compared with Runs 1 and 5. This agreed with the trend reported in previous study [16]. Mixing time is not really a significant factor as can be seen from the table that a higher mixing time did not constitute a higher yield. This is equally justified in Run 7.

3.2 Characterization of Modified and Raw Kaolin

3.2.1 SEM micrographs of kaolin and modified clay

The surface morphologies of raw and the modified Kaolin are shown in Figs. 1 and 2

respectively. From Fig. 1, it can be inferred that the surface structure of raw Kaolin was not well developed. Hence, the micrograph revealed the formation of agglomerated particles with irregular shapes. However, a more regular shape was observed in the micrograph of the modified clay (Fig. 2). This is as a result of clay modification using KOH. During the modification process, K-KOH reaction rate increases. This increase therefore helps in developing large pores on the modified clay samples. Also, due to the loss of volatile components during K-KOH reaction, new pores were formed and the porosity of the modified clay also increases [17]. 50µm resolution was used as the basis for the above comparison. Therefore, the physiochemical treatment of the clay increases its surface area by producing porous structure of the modified clay.

Table 1. Clay modification results

RUNS	KOH (g)	MetaKaolin (g)	Time for mixing (Min)	Modified Clay (g)
1	2.5	6.0	15	8.1
2	0.5	6.0	30	6.2
3	2.5	1.0	30	2.6
4	1.5	3.5	22.5	4.8
5	2.5	6.0	30	8.1
6	1.5	3.5	22.5	4.9
7	0.5	1.0	30	1.2
8	1.5	3.5	9.89	4.8
9	1.5	3.5	22.5	4.9
10	3.18	3.5	22.5	5.1
11	1.0	3.5	22.5	2.5
12	1.5	7.7	22.5	8.9

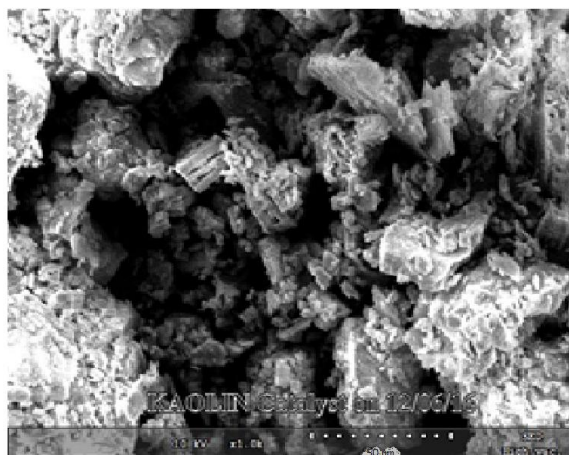


Fig. 1. SEM of raw Kaolin

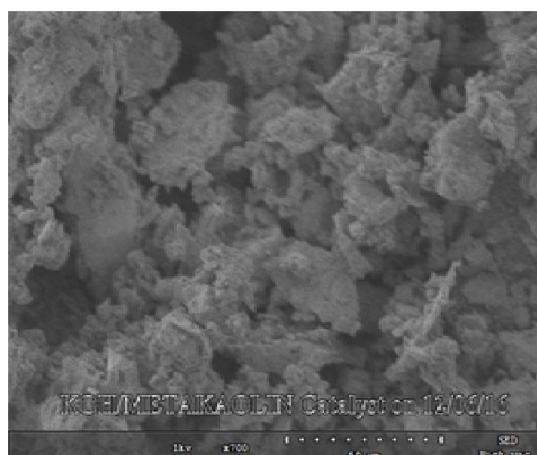


Fig. 2. SEM of the modified Kaolin

3.3 X-ray Fluorescence Measurements

Table 2 presents the chemical analysis of the raw and modified Kaolin. The major oxides present in the clay samples were SiO₂, Al₂O₃, K₂O, Na₂O, CaO, TiO₂, V₂O₅, Cr₂O₃, MnO, Fe₂O₃, CuO, and ZnO. The result showed that some interlayer cations were removed after clay activation with green potassium hydroxide (KOH). This shows that more active sites are generated on the clay surface. The prevalent oxides in the raw and modified Kaolin samples are oxides of silica, alumina, and potassium. Comparing the modified Kaolin with raw sample, the percentage composition of silica and alumina oxides decreased from 49.59% to 32.40% and 32.20% to 19.10% respectively after activation. This variation explains the extent of isomorphic substitution in the modified Kaolin when alkaline is used. The lower percentage composition of silica oxide in the KOH modified clay showed that isomorphic substitution of Al³⁺ for Si⁴⁺ is high. This implied that more negative charge will be produced in the crystal of modified Kaolin. Hence, the modified Kaolin will exhibit a higher adsorption property. Part of Fe³⁺ and Ca²⁺ present in the raw Kaolin were removed after activation. These cations may be said to have been replaced by monovalent hydrogen ion during the beneficiation process. An appreciable increase of K₂O was observed in the modified clay. This increase is likely due to the fact that green KOH was impregnated into metaKaolin during activation. MnO was not detected in the raw Kaolin but was discovered in trace after modification with green potassium hydroxide. Meanwhile, more negative charge was produced due to the substitution of ions on the surface of the clay. These negative charges attract any positive charges in order to balance up and hence, the adsorption efficiency of the modified Kaolin is improved. Also, the compositions of Na₂O and CuO in modified clay increased compared with raw Kaolin. This could also be as a result of the presence of some percentage of Na and Cu in the caustic potash extract [18]. CaO was observed to have reduced by 6.1% in the modified clay. The reduction likely occurred as a result of washing off of soluble salts of calcium during the beneficiation process. The loss on ignition (LOI) of raw Kaolin was 13.06 wt%, it decreased by 1.68% in the modified clay. The decrease in LOI after clay modification could be attributed to dehydroxylation of the clay during calcination; resulting into driving off of the chemically combined water in the modified clay [18]. TiO₂ appearance0 in the raw and

modified Kaolin is as a result of the presence of impurities such as rutile in the clay sample.

3.4 Fourier Transform Infrared Spectroscopy Results

The Fourier Transform Infrared spectroscopy helps to reveal the presence of several functional groups in the raw and modified Kaolin. The spectra of Kaolin before and after modification are shown in Figs. 3 and 4 respectively. The spectra characteristics of raw and modified Kaolinite is given in Table 3. In Table 3 (raw Kaolin), the band at 3458 cm⁻¹ is assigned to O–H stretching of alcohol or carboxylic group, and that at 2371 cm⁻¹ is assigned to C–H stretching of an alkanes. The absorption at 1634 cm⁻¹ is assigned to C=C stretching of aromatics and a broad absorption at 1009 cm⁻¹ is assigned to C–O stretching vibration of ether. The fundamental band of kaolin (Al–O–Si) was revealed at 469 cm⁻¹ [19].

By comparing Fig. 3 with Fig. 4, it can be clearly seen that some functional groups in the clay modification spectrum have shifted to lower wave number (O–H stretching of alcohol, C–H stretching of alkane and C=C stretching of aromatic) or higher wave number (C–H bending of alkane and C–O stretching vibration of ether). This is as a result of high temperature in activation process that broke some intermolecular bonds, i.e. forces holding molecules together [20]. The changes in spectra confirm the effect of the KOH modification resulting in a reduction, broadening, disappearance or appearance of new peaks after modification. Meanwhile, the broader peak around 3431 cm⁻¹ is attributed to the external hydroxyl group from absorbed water [21]. During a previous study that investigated scavenging rhodamine B dye using moringa oleifera seed pod it had been observed that there were shifts in the FTIR bands [22].

3.5 Comparison between the Use of Synthetic and Green KOH in Kaolin Modification

Characterization and optimization of alkaline activated clays has been reported [23]. Meanwhile, synthetic alkaline was used for the activation of the clay samples. The result of the chemical analysis of raw and activated Kaolin (activation was carried out by impregnating synthetic KOH into beneficiated Kaolin) are presented in Table 4.

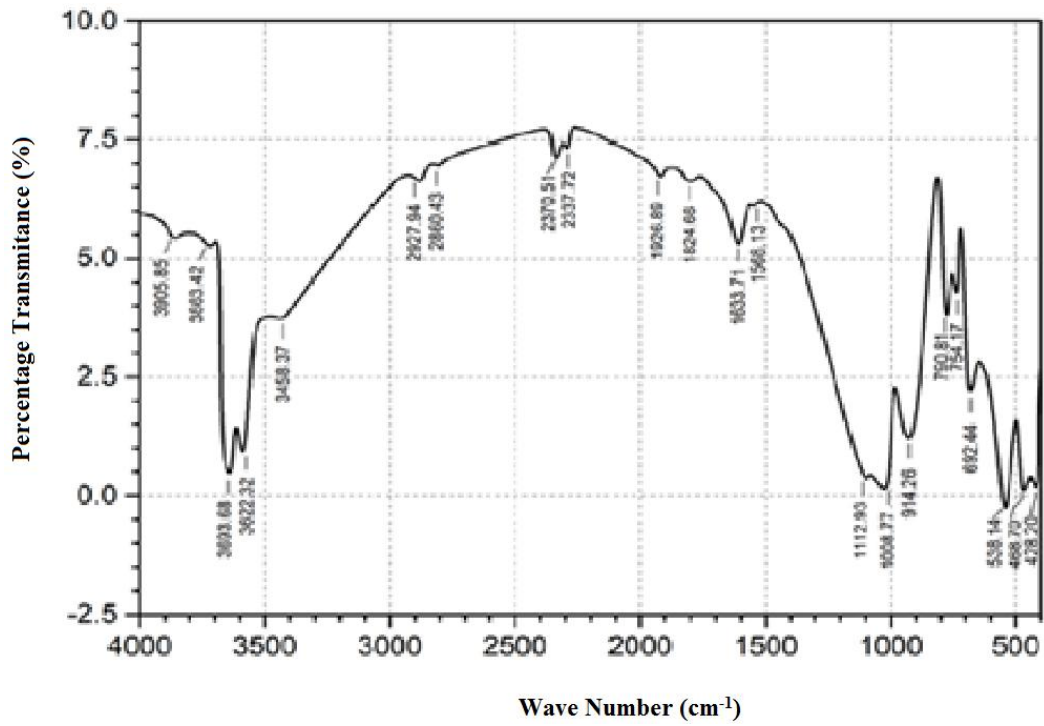


Fig. 3. FTIR spectra for raw Kaolin clay

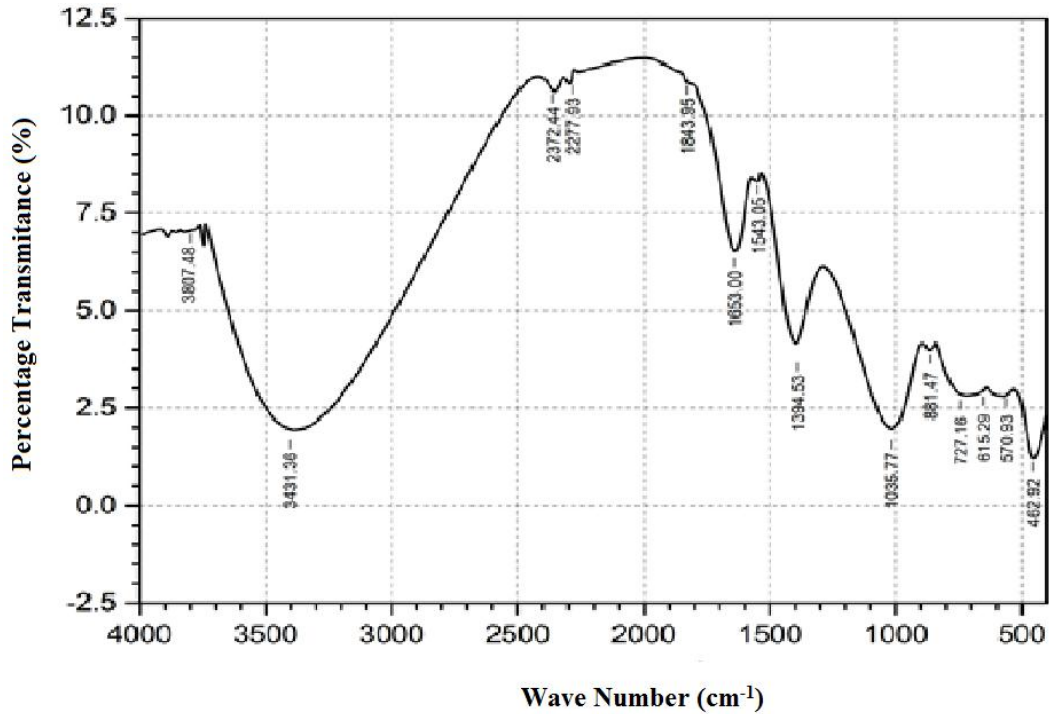


Fig. 4. FTIR spectra for modified Kaolin clay

Table 2. XRF Results of Kaolin impregnated with Green KOH

Composition (%)	Raw Kaolin	Modified Kaolin
SiO ₂	49.59	32.40
Al ₂ O ₃	32.20	19.10
K ₂ O	1.00	31.19
Na ₂ O	0.11	0.21
CaO	0.98	0.92
MgO	Nd	Nd
TiO ₂	0.63	0.75
V ₂ O ₅	0.025	0.020
Cr ₂ O ₃	0.029	Nd
MnO	Nd	0.004
Fe ₂ O ₃	2.30	2.04
CuO	0.032	0.30
ZnO	0.042	0.014
L.O.I.	13.06	12.84

Nd: Not detected

Table 3. FTIR Spectra characteristics of raw and modified Kaolin

I.R Peaks	Wave numbers (cm ⁻¹)			Band assignments
	Raw Kaolin	Modified Kaolin	Differences	
1	3458.37	3431.36	-27.01	O-H Stretching, H-bonding of alcoholic phenols
2	2370.51	2372.44	1.93	C-H Stretching of alkanes
3	1633.71	1653.00	19.29	C=C Stretching of aromatics
4	1008.77	1035.77	27.00	C-O Stretching vibration of ether
5	468.70	462.92	-5.78	Al-O-Si of Kaolin

Comparing the results obtained in Tables 2 and 4, irrespective of the nature of KOH used the percentage compositions of silica and alumina oxides in the activated clays decreased after activation. An appreciable increase of K₂O was also observed in the modified clays. This increase is likely due to the fact that KOH was impregnated into metaKaolin during modification. CaO was observed to have reduced by 6.1% when green KOH was used while CaO present in the clay samples activated using synthetic KOH were completely dissolved after clay

modification. The reduction and total dissolution of CaO likely occurred as a result of washing off of soluble salts of calcium during the activation process.

It can be inferred that the impregnation of green KOH into Kaolin helps to improve its adsorption efficiency as does when synthetic KOH is used. This implies that the clay treated with alkali from green source can effectively replace the conventional method by synthetic materials.

Table 4. XRF Results of Kaolin impregnated with synthetic KOH [23]

Major Oxides	Raw Kaolin (%)	Activated Kaolin (Using synthetic KOH)(%)
SiO ₂	52.4	43.9
Al ₂ O ₃	34.2	29.2
Na ₂ O	0.32	3.13
K ₂ O	8.10	18.36
MgO	0.14	ND
CaO	0.21	ND
TiO ₂	1.073	1.075
MnO	0.019	0.026
Fe ₂ O ₃	0.09	0.16
P ₂ O ₅	ND	0.011
L.O.I	3.04	3.98

4. CONCLUSION

The effect of alkaline treatment on the structural and chemical properties of Kaolin has been studied in this paper. The XRF and SEM study clearly indicated the disintegration of the clay sheet after being treated with KOH. The research results prove that the impregnation of alkaline solution (KOH extracted from plantain peels) into Kaolin can be regarded as an alternative to conventional consolidation treatment of clays. The XRF results of raw Kaolin showed the presence of high alumina (Al_2O_3) and silica (SiO_2) contents while there was an appreciable increment of K_2O contents in the modified clay as a result of the introduction of KOH. The existence of silica and alumina in Kaolin and the modified clay was further confirmed by using FTIR techniques. The peak intensity is found to have shifted in the modified clay as a result of KOH impregnation and high temperature applied during clay activation. SEM analysis of raw Kaolin show that it's made up of irregular shape while that of the modified clay was more regular as a result of modification using KOH. The physiochemical treatment of the clay increases its surface area by producing porous structure of the modified clay. The characterization methods used in this study viz FTIR XRF and SEM were sufficient to characterize the modified Kaolin clay as shown from the results discussed above

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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