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Comparative Analysis of 15% and 20% NaOH Modified Kaolinite Clay Samples

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ABSTRACT

This study investigated the effects of 15% and 20% NaOH treatment on clay samples with the aim of improving the surface characteristics and adsorption capacity for wastewater treatment. The morphological, chemical composition and molecular properties of the raw and modified clay samples were analyzed using scanning electron microscopy coupled energy dispersive Xray spectroscopy (SEM-EDS) and Fourier-transform infrared spectroscopy (FTIR). The results obtained showed that the 15% and 20% NaOH treatment improved the surface properties of the clay samples. Additionally, the absence of peak at 3059 cm^{-1} in the raw clay spectrum was notable in the FTIR spectra, as it corresponds to O-H bending due to adsorbed water. Also, a similar outcome was observed for 15% and 20% modified clay samples, the peaks observed between 3200-2500 cm^{-1} indicated O-H stretching vibration, while those between 2160-2120 cm^{-1} signify -N stretching vibration. Thus, we believe the modification of surface properties of the modified clay samples will improve the adsorption capacity of different contaminants present in wastewater.

Keywords: Adsorption, Clay, Kaolinite, SEM-EDS, Wastewater

INTRODUCTION

Globally, effluents that are discharged from wastewater treatment systems represent one of the largest sources of pollution. The negative impacts of these effluents to aquatic ecosystems and to humans have been documented both at national and international levels (Edokpayi *et al.*, 2017). Some of these impacts include death of aquatic life, habitats destruction and long term toxicity from chemical contamination in the food chain (Mustafa and Hayder, 2020). Furthermore, industrial wastewater from industries such as metal plating facilities, mining operations, fertilizer industries, tanneries, batteries, paper industries and pesticides contains heavy metals that are directly or indirectly discharged into the public sewage system and environment (Iloms *et al.,* 2020). These heavy metals are also often persistent in wastewater treatment systems due to their non-biodegradable and recalcitrant character (Whitehead *et al*., 2018).

In other words, high concentration of heavy metals such as zinc, copper, nickel, mercury, cadmium, lead and chromium are of concern in treatment of industrial effluent (Kanwal *et al.,* 2017). Heavy metal removal from inorganic effluent can be achieved by conventional treatment processes such as chemical precipitation, ion exchange, and electrochemical removal. These processes have significant disadvantages, which are, for instance, high cost, incomplete removal of the metals, high-energy requirements, and production of toxic sludge (Iloms *et al.*, 2020). Therefore, numerous approaches have been studied for the development of cheaper and more effective technologies, both to decrease the amount of wastewater produced and to improve the quality of the modified effluent. Adsorption using clay, zeolites, agricultural wastes, biomass, and polymeric materials has been used due to their easy availability, high surface area, good adsorption properties and eco-friendliness (Soltani *et al.*, 2021). Additionally, clay is one of the potential alternatives to activated carbon as well. Their sorption capabilities come from their high surface area, high cation exchange capacities, low permeability, swelling ability, chemical and mechanical stability, and layered structure (Nadziakiewicza *et al.*, 2019). The negative charge on the structure of clay minerals gives clay the capability to attract metal ions (Na, 2019).

Clay minerals can be classified into four main groups: kaolinite group, illite group, smectite group, and vermiculite. The kaolinite group includes kaolinite, dickite, nacrite, and halloysite, which are formed by the decomposition of orthoclase feldspar (Akisanmi, 2022). Additionally, clays and their modified forms have received wide attention recently for use as adsorbents of metal ions from aqueous medium because of their easy availability and comparatively low cost. The adsorption of heavy metals from aqueous solution using clay minerals are influenced by several factors such as pH, temperature, the presence of other compounds, and initial concentration. Moreover, the pH of the solution is a crucial factor in the adsorption of heavy metals onto clay minerals, the surface layer charge of the clay minerals varies with the pH and the exchange capacity is a function of pH. Thus, the pH value significantly influences the solution chemistry of heavy metals (precipitation, hydrolysis, complexation, redox reaction, etc.) (Mnasri-ghnimi & Frini-srasra, 2019).

Furthermore, the removal of heavy metals by natural clays and their modified forms, kaolinite and montmorillonite in particular, has been reviewed by a number of studies such as Yahaya *et al.* (2017), who investigated the morphology and elemental composition of acid modified kaolin clay. The outcome showed that acid treatment increases the silicon content and decreases aluminium content as revealed by EDX analysis. The leaching of Al^{3+} ions increase with gradual increase in concentration of the acid. Therefore, kaolin reflux with acid at lower strength (2 M and 4 M) were more dispersed and more industrially useful than that which is modified at higher acid strength. Additionally, Lawal *et al.* (2020) conducted adsorption study for the removal of Zn, Fe, Pb and Cr metal ions from wastewater using raw and modified kaolinite clay. The clay samples were characterized using Xray diffractometry (XRD), Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and Brunanuer-Emmett-Teller (BET) method. The thermodynamic analysis of the adsorption findings showed that the metal ions adsorption was spontaneous, endothermic and accompanied by positive entropy change. Therefore, this study aimed to modify kaolinite clay using 15% and 20% NaOH to improve the adhesion properties (surface characteristics) and adsorption capacity in industrial wastewater treatment.

MATERIALS AND METHOD

Collection of the Clay

The clay sample was collected within Kaduna South Metropolis, along River Kaduna water bank. The clay sample was sieved with 0.06 mm mesh and washed with distilled water to remove solid impurities before subjecting it to the NaOH treatment.

Preparation of 15% and 20% NaOH Solution

For 15% NaOH: 150g of sodium hydroxide pellets were accurately weighed into a 250 cm^3 beaker and dissolved with a sufficient amount of distilled water. The resultant solution was transferred into a cleaned 1000cm^3 volumetric flask and then diluted to the mark with distilled water. Whereas for 20% NaOH; 200g of sodium hydroxide pellets were accurately weighed into a 250 cm^3 beaker and dissolved with a sufficient amount of distilled water. The resultant solution was transferred into a cleaned 1000 cm^3 volumetric flask and then diluted to the mark with distilled water.

Surface Treatment of the Clay Samples

100 grams each of the clay sample was weighed and separately soaked in 15 and 20% NaOH solution at a temperature of 65 ºC under constant stirring for 4 hours. The clay puree was stirred to enable the NaOH solution to penetrates and react with the surface of the clay (Akinwande *et al.*, 2014). A final rinse in distilled water until the clay samples were neutral to litmus paper and then dried in open air for 72 hours. Equation 1 present the reaction process.

$$Clay - OH + NaOH \rightarrow Clay - O - Na + H_2O \quad (1)$$

Analysis of the Raw and Modified Clay Samples

The morphological, chemical composition and molecular properties of the raw and modified clay samples were assessed using SEM, EDX and FTIR, techniques.

Scanning Electron Microscopy/Energy Dispersive Xray Spectroscopy (SEM-EDS) Characterization of the Clay Samples

The surface characteristics and morphology of the raw and modified clay samples were observed using scanning electron microscopy Phenom world proX G6 model (PhenomWorld Eindhoven Company, Netherlands) coupled energy dispersive Xray spectroscopy at room temperature. The SEM micrographs and EDX results were used to compare changes between the raw and modified clay samples.

Fourier-transform Infra-red (FTIR) Analysis of the Clay Samples

FTIR analysis was conducted using a NicoletTMisTM 10 FTIR spectrometer (ThermoFisher Scientific, Holland). Samples weighing 0.01 g were homogenized with 0.01g KBr anhydrous using a mortar and agate. The mixtures were then pressed using vacuum hydraulic pressure (Graseby Specac) at 1.2 psi to obtain transparent pellets. The scanned samples were subjected to infrared radiation, and the resulting waveforms were detected and recorded.

RESULTS AND DISCUSSION

Alkali Modification of the Clay Samples

The clay samples were subjected to surface treatment using different concentration of NaOH solution. Comparatively, visible colour and texture changes were observed between the raw and individual modified clay samples. The modified clay samples appeared to be lighter brown as compared to the dark brown of the raw clay sample. Also, the coarse particles of the raw clay samples changed to fine and smooth particles after the modification using NaOH solution. Additionally, the 20% NaOH modified clay exhibited a finer and softer texture compared to the 15% NaOH modified clay sample. This outcome showed that the 20% NaOH acted more on the clay samples by altering the surface morphology compared to the 15% NaOH. Also, the natural impurities in the clay samples were removed after the NaOH treatment. In addition, the NaOH treatment of the clay samples led to increased surface area that will make it effective for adsorption during industrial wastewater treatment.

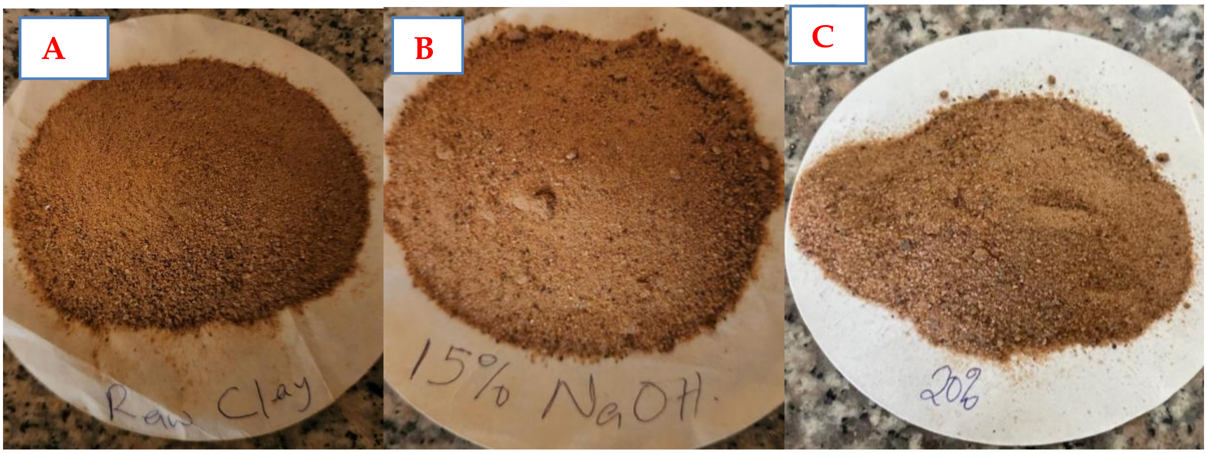


Fig. 1: (A) Raw Clay (B) 15% NaOH Modified Clay (C) 20% NaOH Modified Clay

Assessment of Surface Characteristics (SEM Analysis)

SEM was employed in investigating the surface morphologies of the raw and modified clay samples. The SEM micrographs obtained at magnification of 1500 are displayed in Figure 2.

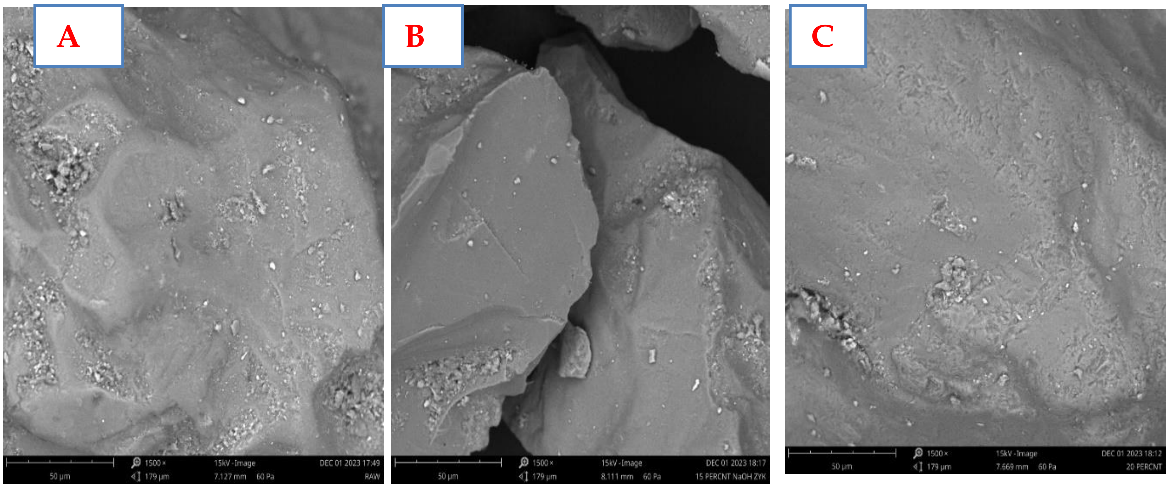


Fig. 2: SEM Micrographs (A) Raw Clay (B) 15% NaOH Modified Clay (C) 20% NaOH Modified Clay at 1500 Magnification

From Fig. 2, the SEM diagrams of the raw clay present a network structure in which the particles are cemented and bonded together. However, the micrographs of the 15% and 20% NaOH modified clay samples clearly showed that the treatment removed the cementing substances. The rough surface topography observed in the photomicrograph will offer a good clay/matrix interface for preparation of composite in wastewater treatment. Therefore, the results showed that the 15% and 20% NaOH treatment improved the surface of the clay samples.

Furthermore, the micrographs of the raw clay showed that the particles were not fully dispersed into individual layers. While for the modified clay samples, stacks of clay particles were observed with good dispersion. Additionally, these findings were similar to the work of Jiang et al. (2009), who reported that closely packed layers of particles and flaky dispersed fraction with more micro-sized particles of larger surface area was obtained after acid treatment of kaolin clay. Furthermore, Angaji *et al.* (2013) reported that the dissolution of octahedral aluminium layer was affected at lower acid concentration while that of the tetrahedral silica in the clay structure was affected at higher acid concentration due to the stable nature of the tetrahedral layer.

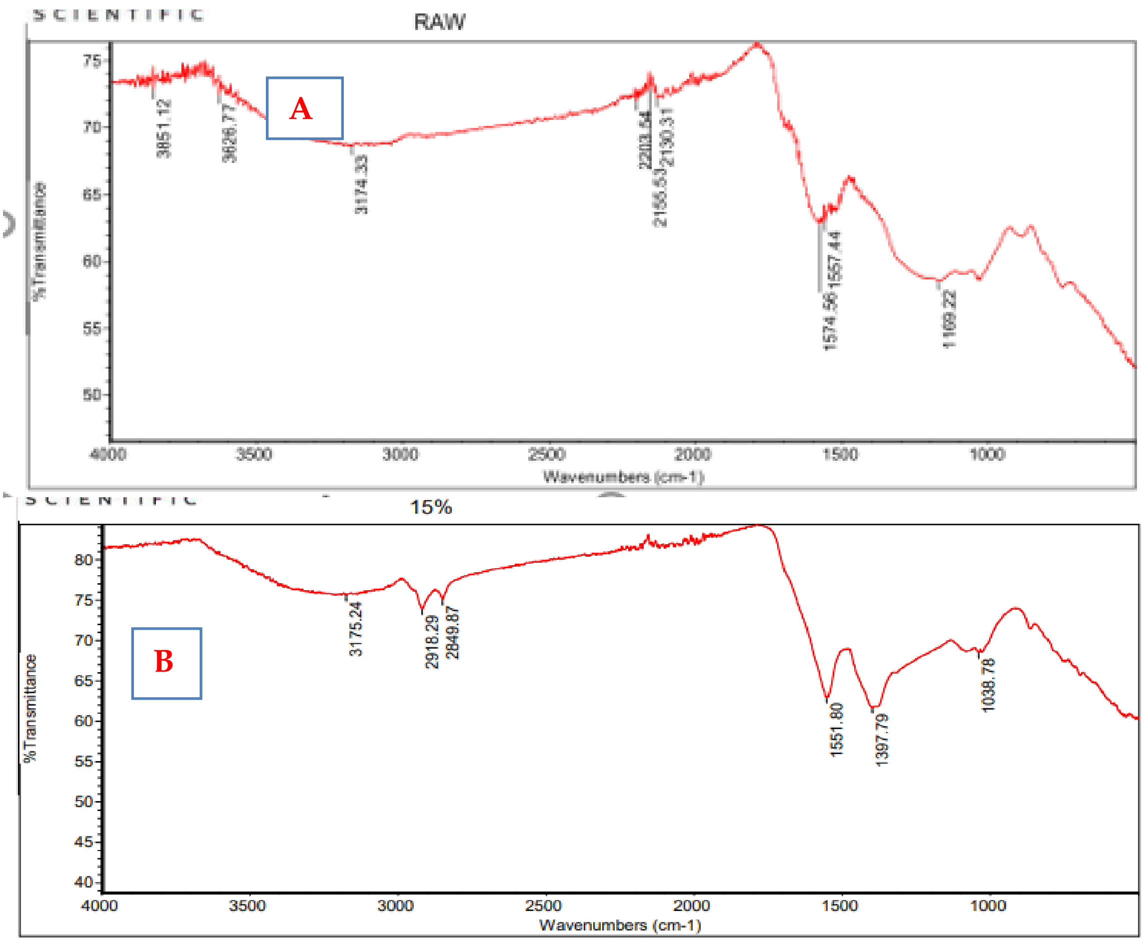
Additionally, Table 1 presents the results of the EDX for the raw, 15% and 20% NaOH modified clay samples. Kaolin clay is majorly comprised of silicon, aluminium and little magnesium. The EDX analysis indicated that clay sample was made up of five elements namely; Si, Al, Fe, Mg, Na and Ca. Additionally, it was observed the aluminium content of the clay decreases as the silicon content increases with greater acid concentration (Table 1). Thus, aluminium content continues to decline proportionally to acid content. This findings is in agreement with that of (Sengupta *et al.*, 2008; Yahaya *et al.*, 2017).

Table 1: EDX Analysis

Element Name	Weight Concentration (%)		
	Raw	15%	20%
Silicon (Si)	74.25	79.04	82.98
Aluminium (Al)	9.89	6.54	5.99
Iron (Fe)	8.66	6.42	4.13
Calcium (Ca)	2.21	1.90	0.54
Sodium (Na)	1.15	2.21	1.68
Magnesium (Mg)	1.09	1.30	1.13

FTIR Analysis of the Clay Samples

The FTIR spectra for clay minerals involves the identification of various functional groups present in the clay structure. These functional groups are associated with specific vibration modes, which can be identified by the characteristic absorption bands in the FTIR spectrum. Figure 2 shows the FTIR spectra for the raw and modified (15% and 20%) clay samples.



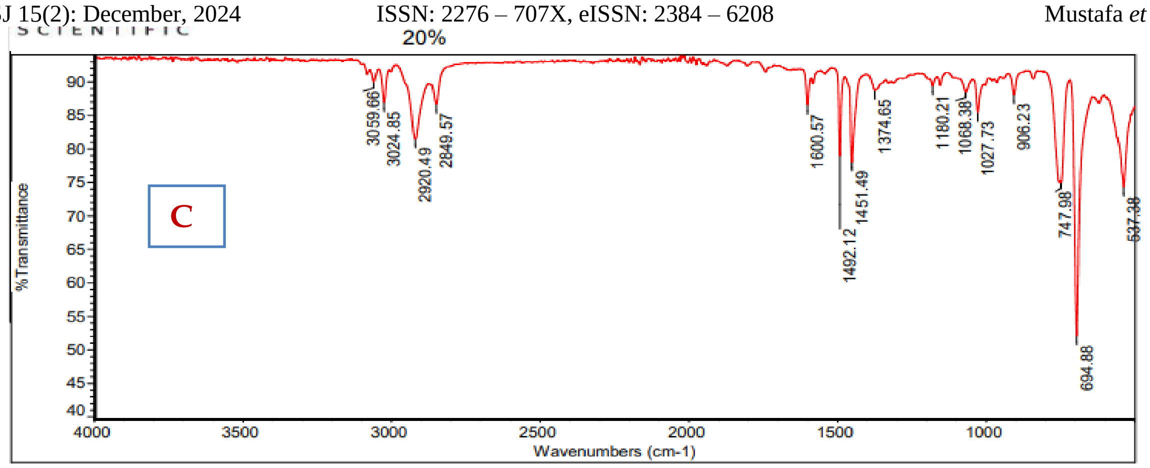


Fig. 3: FTIR SPECTRA (A) Raw Clay (B) 15% NaOH modified Clay (C) 20% NaOH modified Clay

From Fig: 3, the FTIR was used to study the molecular structure of both the raw and modified clay samples. The FTIR spectra of the raw clay exhibited peaks at wavelengths of 3851, 3626, 3174., 2203, 2155, 2130, 1574, 1557, and 1169 cm^{-1}. Notably, the region between 1027-1068 cm^{-1} displayed strong absorption bands attributed to Si=O bonds, indicative of the silicate structure. Peaks at 3175, 2918, 2849, 1551, 1397 and 1038 cm^{-1} were recorded for 15% NaOH modified clay sample. In contrast, the 20% NaOH modified clay exhibited peaks at 3059, 3024, 2920, 2849, 1600, 1492, and 1451 cm^{-1}. However, the absence of the peak at 3059 cm^{-1} in the raw clay spectrum was notable, as it corresponds to O-H bending due to adsorbed water. Peaks observed between 3200-2500 cm^{-1} indicate O-H bending and C-O stretching vibration of a chelate compound, while those between 2160-2120 cm^{-1} signify N stretching vibration. Furthermore, the FTIR absorption band at 3059 cm^{-c}orresponds to the stretching vibration of C-H bonds, which suggests the presence of organic compounds in the clay sample. The absorption bands at 3024 and 2920 cm^{-1} correspond to C-H bonds in aliphatic compounds, while the absorption band at 1600 cm^{-1} corresponds to the C=O stretching vibration of carboxylic acid. These results suggest that the modified clay sample contains carboxylic acids and aliphatic compounds. Furthermore, the spectra of the raw clay revealed different bands between 3851 and 3600 cm^{-1} characteristics of the triclinic layer structure of kaolinite clays. The band at 3626 cm^{-1} was due to stretching vibrations of Al-OH groups. The Si-O in plane and out of plane stretching vibrations bands appeared at 906 and 1180 cm^{-1}, respectively. These finding corresponds with the work of Otieno *et al.* (2021). Other bands at 537 and 1027 cm^{-1} were due to Si-O-Si bending and stretching vibrations.

CONCLUSION

This study demonstrated that NaOH treatment can alter the chemical and physical properties of kaolinite clay, which could make it more effective for use in wastewater treatment. The FTIR and SEM results showed that the treatment caused changes in the hydroxyl groups and surface morphology of the clay, respectively. Also, through the modification of the surface properties and introduction of functional groups, the modified clay will improve the adsorption capacity for various contaminants present in wastewater. The findings of this study highlight the potential of NaOH modified clay as an effective adsorbent in wastewater treatment. Also, NaOH treatment can be used to obtain rough surface morphology that will enhance clay/matrix interface for composite in wastewater treatment application. Thus, the application of NaOH modified clay materials as reinforcement in the synthesis of nanocomposite for wastewater treatment will offer a sustainable and cost-effective solution for environmental remediation.

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