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Studies of Effects of Hydrochloric Acid Treatment on the Chemical Composition of Kaolin Clay

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

The effect of hydrochloric acid treatment on the chemical composition of kaolin clay from Awgu Town in Awgu Local Government Area of Enugu State was studied in this work. The raw clay was mined, soaked in water to remove dirt, and sun-dried, followed by grinding to a particle size of 0.075mm. The fine sized sample was then treated with 1M hydrochloric acid. Characterization of the untreated and treated clay samples with x-ray fluorescence (XRF) spectrometry revealed that the samples consist mainly of silica (SiO_2), alumina (Al_2O_3), and iron oxide (Fe_2O_3) with potassium oxide (K_2O), titanium oxide (TiO_2), manganese oxide (MnO) and other oxides occurring as minors. The study further revealed that the percentage composition of SiO_2, Al_2O_3 and MnO increased with hydrochloric acid treatment, while Al_2O_3, TiO_2 and K_2O were removed/decreased appreciably with hydrochloric acid treatment. The acid treatment using HCl enhanced the chemical composition of kaolin clay. Kaolin clay from Awgu possesses some industrial potentials for the manufacture of glass, ceramics, refractory bricks, paint and high melting clay based on its chemical composition. More studies should be carried out using other clay treatment processes apart from HCl activation, and characterization techniques like atomic absorption spectroscopy (AAS), scanning electron microscope (SEM), Fourier transform infrared (FTIR), x-ray diffraction (XRD) and energy-

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dispersive x-ray (EDX) spectroscopy in the determination of the mineralogical phases/compositions of kaolin clay from Awgu Town, and how they relate to its application, as Awgu clay is one of the unidentified clays in Nigeria.

Keywords: Acid treatment; hydrochloric acid; kaolin; treated clay; x-ray fluorescence.

1. INTRODUCTION

Most clay materials spread across different regions of the earth have been identified by many researchers as kaolin [1-5]. Kaolin is a soft, earthy clay material produced by chemical weathering of aluminum silicate minerals like feldspar [2]. Kaolin has a pink, orange or red rust hue depending on the quantity of iron oxide present in it. Clay materials, particularly kaolin, has been widely used for a large number of applications such as in ceramics, paper coating, paper filling, paint extenders, rubber filler, cracking catalyst or cements, oil refinery and water treatment [6].

The chemical and physical behaviors of clay minerals, due to their adsorbing and catalytic properties have been reported [7], [8]. The nature of the external surface of the clay minerals which can be improved by treatment techniques is responsible for this behavior. Two broad treatment methods of clay minerals have been studied by different researchers such as physical and chemical treatments/modifications [7], [8]. According to [7], chemical treatment technique (usually done by acids, bases or organic compounds) involves altering the structure, surface functional groups and surface area of clays, while physical treatment (also known as thermal treatment) involves altering the chemical composition and crystalline structure of clays by the effects of high temperature.

Chemical clay treatment also known as acid activation leads to modification of clays with improved properties such as enhanced surface area, pore diameters, number of acid sites, and catalytic activities [9]. The treatment of clay with hot mineral acid replaces exchangeable cations with H^+ ions, and gradual leaching of Al^{3+} out of both tetrahedral and octahedral sites occurs, but the silicate groups (SiO_2) remain largely intact. Such acid-activated clay minerals are, therefore, partially delaminated and exhibit higher surface area, pore volume, pore diameter and higher surface acidity [9,10].

Studies on the acid treatment of kaolin clay have been reported [1,2,3,4,7,11,12,13]. The different acids types suitable for chemical treatment of clays include hydrochloric, sulfuric and nitric acids and organic acids such as acetic, citric, oxalic and lactic. Out of all these group of acids, hydrochloric (HCl) and sulfuric acids have gained prominence due to their strong attraction for process factors and high results in specific surface area, porosity and good adsorption efficiency [14].

The type of clay found in Awgu local government area of Enugu State, Nigeria is shale clay [4], [15]. The shale clay sometimes referred to as Awgu shale/formation is a laminated sedimentary rock that is formed by the consolidation of clay, mud, or silt. It is one of the sedimentary formations in the Southern Benue Trough which is located east of the Anambra Basin. The formation consists mainly of shale, shelly limestone, siltstone and sandstone [15]. The term shale is often used as a very general term for all kinds of clay rich sedimentary rocks. Shales are the most abundant kind of all sedimentary rocks accounting for around 60% of the stratigraphic column. As such, most of the time spent drilling oil wells is spent drilling through shales [16].

The study done by [4] and [15] revealed that HCl treatment of kaolin clay improved its mineralogical composition, making it a source of raw material for the production of refractory bricks, ceramics of highly attractive quality, various glass products such as sheet glass, for windows, bottles, mirrors, optical instruments, chemical apparatus, electrical insulation and condensers, pipes, doors, crucibles, automobile and craft bodies, filters and building blocks, on account of its high iron oxide content, high silicon oxide content, and high melting clay materials.

[7,14,17,11,12,13], have reported on the acid treatment of kaolin clays from different parts around the world and their subsequent characterization. However, studies on XRF characterization of untreated and HCl treated kaolin clay from Awgu Town of Enugu State, Nigeria, have not been documented to the best of our knowledge. Therefore, in this work, kaolin clay was treated with HCl in order to reveal and analyze the effects of the acid treatment on the following dominant oxides: SiO_2, Al_2O_3, Fe_2O_3, K_2O, TiO_2 and MnO, and how they relate to clay industrial applications.

2. EXPERIMENTAL METHODOLOGY

2.1 Sampling Location

Geographically, Awgu local government area (LGA) is located approximately between latitudes 06 00' and 06 19' North of the Equator and longitudes 07 23' and 07 35' East of the Greenwich Meridian. Awgu LGA is bounded in the north by Udi and Nkanu West LGAs, in the west by Oji River LGA , Aninri LGA and Ivo LGA of Ebonyi State in the East and share border with Umunneochi L.G.A of Abia State in the south (Wikipedia). The local clay was got from Awgu Town in Awgu local Government Area of Enugu State, Nigeria. Field sampling exercise of the local clay sample was done during the dry season. Fresh samples were collected in lump form from one sample point pit dug to depths of 1.5m at a choice deposit of the clay sample.

2.2 Sample Preparation

The local clay from Awgu mined from pits dug to depths of 1.5m was soaked in water for 72hours. It was stirred every 24hours to release organic materials. Water was then decanted from it. The concentrated clay was then transferred to a jeans bag for dewatering, after which the resulting sample was spread on a pan and sun-dried for a period of 5days. The dried clay was ground to a fine size of 0.075mm with mortar and pestle while continuously sieving with a 75µm Tyler sieve until a homogenous sample was obtained.

2.3 Acid Treatment

Hydrochloric acid was used for the acid treatment/activation of the clay through leaching process. One mole of hydrochloric acid was prepared in a 1000ml of volumetric flask. 50g of the fine homogeneous clay sample was poured into a flat bottom flask, and then 250ml of 1MHCl was added to it. The mixture was heated for 1 hour at a temperature of 95˚C on a magnetic stirrer. After 1 hour, the mixture was washed several times with distilled water so as to wash the acid out completely and acid removal was confirmed by testing it with a blue litmus paper. The resulting slurry was filtered, sun-dried and ground to powder form.

2.4 Characterization of the Clay Sample

The XRF characterization was performed to know the chemical composition of the minerals that are present in the untreated and hydrochloric acid treated clay samples. X-ray fluorescence spectrometer (Philips PW 2400) in Ahmadu Bello University (ABU) Zaria, Kaduna State, Nigeria, was used to determine the chemical composition of the untreated and treated clay. The sample cups were assembled using oxford instruments, Poly-M XRF sample film. The powdered samples were pressed in the cups using a set of dies and a press machine. Then, the cups containing the samples were placed on the auto sampler using individual and removable secondary safety windows, which is provided in case of samples leakage. The samples were irradiated with high energy x-rays from the controlled x-ray tube. After the first few seconds of measurements, live results were displaced, allowing a rapid assessment of product quality to be made. The results were continually updated till the end of the measurements. XRF peaks with varying intensities were created and presented in the spectrum – graphical representation of x-ray intensity as a function of peaks (Figs. 1 and 2).

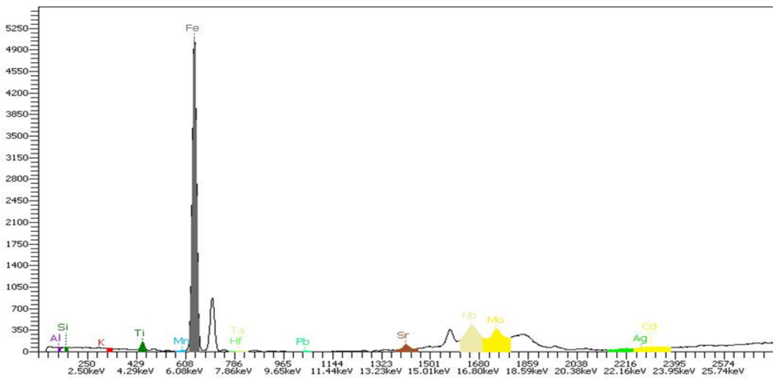

Fig. 1. XRF Spectrum of the Untreated Clay

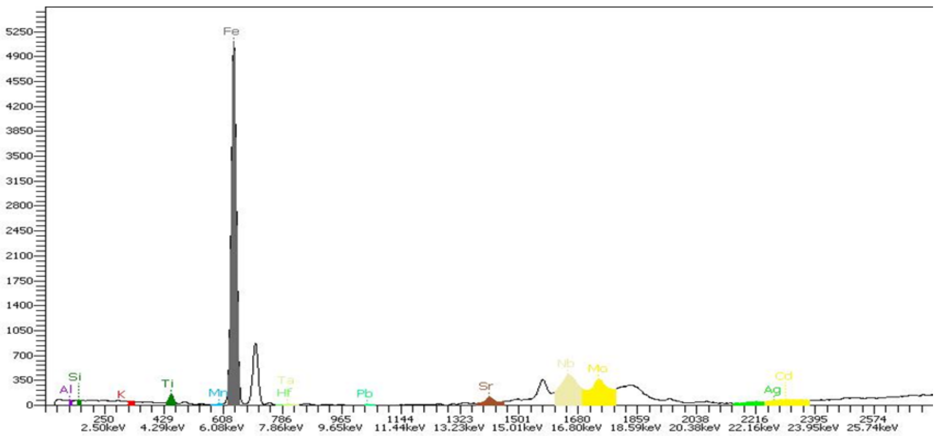

Fig. 2. XRF Spectrum of the treated Clay

Table 1. The XRF results of the untreated and treated clay samples

Oxides	Untreated clay (%)	Treated clay (%)
Al_2O_3	21.42	14.45
SiO_2	64.26	68.54
K_2O	0.19	0.05
TiO_2	0.78	0.69
MnO	0.01	0.08
Fe_2O_3	12.54	13.36
NiO	<0.01	-
CuO	<0.01	-
SrO	0.01	0.01
Nb_2O_5	0.01	0.01
MoO_3	0.03	0.06
Ag_2O	0.02	0.01
CdO	0.06	0.08
Sb_2O_3	<0.01	-
HfO_2	<0.01	<0.01
PbO	<0.01	<0.01
TaO	-	<0.01
Total	99.27	97.34

3. RESULTS AND DISCUSSION

Figs. 1 and 2 show the different peaks and /or spectral line patterns of different mineral elements in the clay samples. By interpretation, the following elements are traceable in both spectra; Al, Si, K, Ti, Mn, Fe, Hf, Pb, Sr, Ag, Cd, etc, with Fe having the highest peak/intensity. The number of elemental minerals measured were as detected by equipment in line with the assertions of previous authors [18,5].

The XRF results of the untreated and treated clay samples are presented in Table 1. From Table 1, it could be observed that the dominant oxides for both clay samples are Al_2O_3, SiO_2 and Fe_2O_3 . These oxides have a combined percentage composition of 98.22% and 96.35% for the untreated and treated clay samples, respectively. The total oxide compositions for the untreated and treated clay samples sum up to 99.27% and 97.34% respectively. This decrease in total oxide composition is an indication that activation of the clay with HCl enhanced its chemical composition. The very high percentage of SiO_2 for the treated clay sample which is slightly higher than the value (64.50%) obtained by [11] and within the range of values (53 - 73%) suggested by [12] and [13], indicates that the clay sample is more of silica (quartz) which is typical of kaolin [19]. Such clay is suitable for the manufacture of refractory bricks, ceramics and high melting clays [11], [12], [13]. As revealed in Table 1, SiO_2 is not removed, but increased. This increase could be as a result of the depletion of the cation (Si^{4+}) from the interlayer and octahedral sheet of the clay [19]. Also, the difficulty in the removal of silica (SiO_2) may be as a result of the position it occupies in the clay structure [2]. Al_2O_3, K_2O and TiO_2 present in the untreated clay sample were appreciably removed as can be seen from the results of the treated clay sample. The value of Al_2O_3 for the treated clay sample is lower than the value (16.30%) obtained by [11] but within the range of values (12 - 17%) obtained by [12] and [13], making the clay sample suitable for the manufacture of glass. No traces of K_2O and TiO_2 were reported by [12] and [13] in their respective studies, although [17] reported 0.74% for K_2O and 0.17% for TiO_2. The iron oxide (Fe_2O_3) and manganese oxide (MnO) present in the untreated clay sample were not removed but rather increased. This could be as a result of increase in surface area of the clay which brought out the metals (Fe and Mn) and made them easier for leaching [20]. The clay sample can be a source of raw material for paint production as the value of Fe_2O_3 is within the standard range (13.4 – 13.7%) for paint production as obtained by [11] and [12]. It is important to note that such high level of iron oxide usually imparts rust hue or reddish colouration to clay when fired, hence, making it very attractive as a ceramic raw material [21].

4. CONCLUSION

From the analyses of the experimental results, the following conclusions were made:

i. Untreated and treated kaolin clay samples contain the following prominent oxides: SiO_2, Al_2O_3, K_2O, TiO_2 , Fe_2O_3 , MnO and others in traces.
ii. Al_2O_3, K_2O and TiO_2 present in the untreated clay sample were appreciably removed
iii. The silica (SiO_2), iron oxide (Fe_2O_3) and manganese oxide (MnO) present in the untreated clay sample were not removed but rather increased.
iv. Acid treatment using HCl enhanced the chemical composition of kaolin clay.
v. Based on the studies of the chemical composition of clay from Awgu, kaolin possesses some industrial potentials for the manufacture of glass, ceramics of attractive quality, refractory bricks, paint and high melting clay.

5. RECOMMENDATION

Awgu clay is one of the unidentified clays in Nigeria, and this study is probably the first work on Awgu clay deposit. Hence, there is need for geological survey to determine the extent of the deposit and if mined and harnessed, it will no doubt provide internal raw material for a variety of industrial purposes. Also, more studies should be carried out using other clay treatment processes apart from HCl beneficiation and characterization techniques like atomic absorption spectroscopy (AAS), scanning electron microscope (SEM), Fourier transform infrared (FTIR), x-ray diffraction (XRD) and energy-dispersive x-ray (EDX) spectroscopy in the determination of the mineralogical phases of kaolin clay from Awgu Town, and how they relate to its applications.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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