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Physcio-chemical Characterization of Rafin-Kada Clay Deposits of Wukari Ward-Taraba State

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Abstract
Physcio-chemical analyses were used to characterize the clay deposits in Rafin-Kada ward of Wukari, Taraba State with the view to establishing its suitability for industrial usage. The physical parameters considered were moisture content, bulk density, particle density, pH and loss on ignition. Chemical analysis was performed using X-ray fluorescence spectrometer. The result of the physical analysis showed a moderate moisture content of 4.08%, bulk density of 1.56 g/cm^3, pH of 7.68 and loss on ignition of 13.18%. The result of the chemical analysis showed an elemental composition in the clay samples of 54.68% (SiO_2) > 6.50% (Al_2O_3) > 1.896% (Fe_2O_3)> 0.98% (K_2O) as the major components while the minor components included P_2O_5, SO_2, CaO, TiO_2, V_2O_5, Cr_2O_3, MnO, CoO, CuO, ZnO, PbO, WO_3, Au_2O_3, Rb_2O, Nb_2O_5, MoO_2, SnO, Sb_2O_5 and ZrO_2. The results of the physical parameters were found to be within the acceptable limits. Also due to the high silica content of the clay deposits as shown in the results, it can be inferred that the Rafin-Kada-Wukari clay deposits could be used as source of silica for ceramic industry for the production of floor tiles, building bricks and in the synthesis of zeiolite and zirconia gemstones.

1. Introduction

Clay is an earthly material that is plastic when moist but hard when fired or dried, that is composed mainly of fine particles of hydrous aluminium silicates and other minerals. Clay and its associated minerals have played major roles in anthropogenic activities. [1]. The low cost of clay and its relative abundance in nature its high sorptive properties, high electric charges, ion exchange ability and its compatibility with materials gives it a wide range of applications in bricks, tiles and pottery etc. Clay materials are known for their distinctive properties such plasticity, shrinkage under firing and under air drying, finest of grain, colour after firing, hardness, cohesion and capacity of the surface to take decoration. [2, 3]

Clay is a fine textured earth that is plastic when wet but hard and compact when dry. Clay occurs most abundantly in nature in soils, sediments, sedimentary rocks and hydrothermal deposits [4]. There are two general types of clay namely; expandable and non-expandable clay. Expandable clay swells up when water is added to it and can become liquid when enough water is added to it. Non-expandable called Bentonites is used to make drilling mud in petroleum industry. It is also used in the ceramics industry to make bricks, tiles pottery and porcelains [5].

Clay materials present layer and sheet orientations and the several possible structural presentations of the elements in clay results in different classes of clay such as Kaolinite, Serpentine, pylophylite (talc), smectite (Bentonite /montroillonite, sepiolite) sepiolite and vermiculite [6]. The particle size, surface area and high charge density of clay materials are some of the properties that accounts for the adsorption capacity of clays [7].

The characterization of clay is done in order to known the composition or the elements present and the level in which they occur in a given sample. There are many methods of characterizing clay as reported in the literature. The commonest are atomic Absorption Spectrophotometry, X-ray Fluorescence, Fourier transform infrared, UV-visible analysis and X-ray diffraction methods. XRF technique has variously been used to determine the concentration of major metallic elements such as Na, Al, Si, K, Fe, Cu, Mg, Ca and toxic elements such as As, Pb, and Cd as well as other contaminants in the form of Ag and Hg. Many clay materials are used as fillers, pigments, and additives. [8]. Although silica, aluminium and water are the basic components of clay, iron, alkalis, and alkaline earth metals may be present in good measures [9].

Clay is structured at an atomic, molecular and macro level and these structures interact to produce the variations in observed behaviour [10]. The atomic lattice of clay minerals present two unique structural units of octahedral and tetrahedral conformations. The octahedral confirmation involves oxygen and hydroxyl groups that are linked to aluminium, iron and magnesium atoms at equidistance from six oxygen or hydroxyl species and the tetrahedral silica conformations, where the units are oriented into hexagonal network, which is repeated continuously, forming a sheet of silica. The difference ratios of the basic components of clay and the several possible combinations of the orientations of layers sheets in conjunction with the particular metal present, determines the mineral type of clay [11].

In view of this natural architectural design of clays, it is imperative to always characterize them before putting it into use. There is however paucity of literature reports on the characterization of the huge clay deposits in Taraba State of Nigeria. Particularly, the physcio-chemical characterization of the clay deposits at Puje-Wukari have not been reported in the literature in spite of its local use for bricks and earthen pots purposes. This study is therefore set to use standard methods to characterize the Rafin- Kada, Wukari clay deposits with the view to providing a baseline for future studies and for ascertaining its industrial applications.

2. Materials and Methods

2.1. Sampling

Two composite clay samples denoted as C and D were collected into two different polythene bags. The samples were collected in such a way that contamination was minimized as far as possible by avoiding the use of metallic tools for sampling. On collection, stones and other particles were removed from the clay samples. Samples C and d were collected from northern and southern Rafin -Kada ward of Wukari respectively. The origin, location and physical appearance of the clay samples is as listed in Table 1.

2.2. Sample Preparation

The clay samples (C and D) collected were sun dried separately and were grounded using mortar and pestle into powdered form. They were further sieved through a 30µm mesh to remove the larger non-clay fractions from the finer particles. The essence of for grinding to this size was to bring the samples to a pulverized form in order to expose the clay to a greater surface area. The grounded and sieved portion of each sample was then used for analyses and characterization using EDX3600B X-ray fluorescence spectrometer.

2.3. Physical Analyses

Moisture content, pH, bulk density, particles density, loss on ignition (L. O. I) were carried out on the prepared clay samples.

2.3.1. pH Determination

The pH of the sample was determined by weighing 10g of each of the clay samples into 100 cm^3 beaker and was followed by addition of 20 cm^3 of distilled water. The mixture was stirred for 10 minutes and the volume made up to 50 cm^3. The sample pH was the measured with an electronic pH meter and the average values recorded.

2.3.2. Bulk Density Determination

The bulk density of each of the clay samples was determined according to the procedure described by [12, 13] as follows: A known quantity of clay (100g) was placed in a 100 cm^3 measuring cylinder and a little vibration was applied until no particle space and constant level of clay was observed in the cylinder and the volume recorded. Triplicate measurement were carried out and average readings recorded. The bulk density was calculated using the relation"

$$\text{Bulk density} = \frac{\text{Weight of clay}}{\textit{Volume} \text{ of clay}} \quad (1)$$

2.3.3. Moisture Content Determination

A quantity of wet clay sample was weighed in a beaker of known weight and oven dried at a temperature of 110°C for 2hr, removed and was cooled an reweighed following the procedure of [14]. Triplicate measurements were performed and the average readings recorded. The percentage moisture content was calculated from the relation:

$$\text{Percentage moisture content} = \frac{(\text{Wm- Wd}) \text{ x } 100}{\text{Ws}} \quad (2)$$

Where

Wm = weight of wet sample + beaker, Wd = weight of dry sample + beaker, Ws = weight of clay sample

2.3.4. Particle Density

A quantity of oven dried clay sample (20g) was placed into a measuring cylinder, the cylinder was gently tapped and the volume recorded as V_1. Then 50 cm^3 of distilled water were added slowly by the side of the cylinder to soak the clay completely and the final clay and water volume in the cylinder was noted as V_2. The particle density was then calculated according to the equation of [14].

$$\text{Particle density} = \frac{\text{Weight of clay}}{\text{Volume of clay}} = \frac{W}{V2\text{-}V1} \tag{3}$$

2.3.5. Determination of Loss on Ignition (L. O. I)

Some clay sample (1g) was weighed into a clean dried crucible of known weight and was placed inside an oven at 110°C for 1hr and the crucible was removed from the oven and allowed to cool in a desiccator and reweighed. The process was repeated until a constant weight was obtained [15].

The percentage loss on ignition was calculated as follows:

$$\%\text{ loss on ignition} = \frac{W1 - W2}{Ws} \tag{4}$$

Where

W_1 = Weight of crucible + sample, W_2 = Weight of sample + crucible after ignition, Ws = Weight of sample.

2.4. Chemical Analysis Using XRF

X-ray fluorescence spectrometer applies XRF technique to conduct fast and accurate analysis of complex compositions clay and other substances. A voltage of 40kv and a current of 350mA were applied to generate the X-ray needed to irradiate the clay samples in this study for a preset period of 100 seconds for each sample. The system detected elements between (Na Z= 11 and Uranium, Z = 92) with high resolution and fast analysis. The spectra from the samples were analysed and concentrations of the elements determined expressed in percentage Element and oxides respectively as shown in Tables 3 and 4.

$$\text{Percentage element} = \frac{\%\text{Oxide x } 100}{\text{Relative molecular mass}} \tag{5}$$

3. Results and Discussion

Table 1. *Description of the Clay Samples used in the Study.*

Sample	Origin	Location	Physical Appearance and texture
C	Rafin-KadaWard, Wukari	Rafin-Kada North	Dark brown, poor stickness
D	Rafin-KadaWard, Wukari	Rafin-Kada South	Dark, slightly sticky

Table 2. *Results of Physical Analysis of Clay Deposits Samples of Rafin Kada Ward of Wukari.*

Samples	Bulk density (g/cm^3)	Particle density (g/cm^3)	pH	% Moisture	% LOI
C	1.57	0.46	7.07	4.19	13.90
D	1.45	0.46	7.45	3.91	13.51

Table 3. *XRF Elemental Analysis of Rafin Kada - North Clay Deposits (Sample C) of Rafin Kada Ward - Wukari Showing the percentage Elemental and Oxides.*

Element	Oxide	Intensity	%Oxides	%Element
Mg	MgO	0.0000	0.0000	0.0000
Al	Al_2O_3	0.0404	6.5753	6.4464
Si	SiO_2	0.2299	39.5781	65.9635
P	P_2O_5	0.0028	0.1800	0.1268
S	SO_2	0.0035	0.2587	0.4042
K	K_2O	0.0166	0.9219	0.9807
Ca	CaO	0.0158	0.0548	0.0979
Ti	TiO_2	0.0025	0.3375	0.4219
V	V_2O_5	0.0004	0.0093	0.0051
Cr	Cr_2O_3	0.0002	0.0021	0.0014
Mn	MnO	0.0013	0.0305	0.0429
Co	CoO	0.0010	0.0102	0.0136
Fe	Fe_2O_3	0.0851	3.0272	1.8920
Ni	NiO	0.0013	0.0660	0.0880
Cu	CuO	0.0024	0.0635	0.0799
Zn	ZnO	0.0035	0.1012	0.1249
As	As_2O_3	0.0005	0.000	0.0000
Pb	PbO	0.0000	0000	0.0000
W	WO_3	0.0003	0.0675	0.0291
Au	Au_2O_3	0.0000	0.0000	0.0000
Ag	Ag_2O	0.0000	0.003	0.0013
Rb	Rb_2O	0.0036	0.0074	0.0039
Nb	Nb_2O_5	0.0011	0.0080	0.0030
Zr	ZrO_2	0.0834	3.0167	2.453
Mo	MoO_2	0.0039	0.01916	0.1497
Cd	CdO	0.0000	0.0003	0.0002
Sn	SnO	0.0072	1.2463	0.9232
Sb	Sb_2O_5	0.0100	1.1714	0.3615

Table 4. *XRF Elemental Analysis of Kada - South Clay Deposits (Sample D) Rafin - Kada Ward - Wukari Showing the Percentage Elemental and Oxides.*

Element	Oxide	Intensity	%Oxides	%Element
Mg	MgO	0.0000	0.0000	0.0000
Al	Al_2O_3	0.0419	9.0131	8.5664
Si	SiO_2	0.2852	34.5835	44.8322
P	P_2O_5	0.0041	0.1919	0.0913
S	SO_2	0.0046	0.3133	0.3341
K	K_2O	0.0193	1.5669	1.4317
Ca	CaO	0.0124	0.2403	0.5634
Ti	TiO_2	0.0034	0.5270	0.4111
V	V_2O_5	0.0004	0.0191	0.0099
Cr	Cr_2O_3	0.0001	0.0028	0.0041
Mn	MnO	0.0009	0.0601	0.1265
Co	CoO	0.0006	0.0164	0.0372
Fe	Fe_2O_3	0.0640	6.1582	5.1016

Element	Oxide	Intensity	%Oxides	%Element
Ni	NiO	0.0012	0.0685	0.0993
Cu	CuO	0.0022	0.0598	0.0843
Zn	ZnO	0.0039	0.1331	0.1463
As	As_2O_3	0.0007	0.000	0.0000
Pb	PbO	0.0006	0.0213	0.0097
W	WO_3	0.0004	0.0213	0.0277
Au	Au_2O_3	0.0001	0.0984	0.0155
Ag	Ag_2O	0.0000	0.000	0.0000
Rb	Rb_2O	0.0041	0.0273	0.0108
Nb	Nb_2O_5	0.0010	0.0079	0.0031
Zr	ZrO_2	0.0151	1.5387	1.2511
Mo	MoO_2	0.0048	0.1486	0.1375
Cd	CdO	0.0000	0.000	0.0000
Sn	SnO	0.0061	1.366	0.9981
Sb	Sb_2O_5	0.0083	1.0358	0.3866

Table 1 showed the physical appearance of the clay samples A and B that were collected from northern and southern parts of Rafin-Kada ward of Wukari. Sample C is dark-brown coloured while sample D is brownish – grey with smooth texture. The particle sizes of both samples passed through 30µm mesh, indicating their fine nature. These are comparable to the acceptable properties of clays characterized US Geological Agency [16].

Table 2 showed the mean values of the physical analyses of the two Rafin – Kada clay samples C and D as follows:. The moisture contents (4.19 and 3.91%) bulk density (1.57 and 1.45g/cm^3), pH (7.07 and 7.45), Loss on ignition (13.90 and 13.51%). The results showed slightly higher values for sample C compared to sample D but correlates with the values obtained by [17] which were moisture content (4.25%), bulk density (1.15g/cm^3), pH (7.10) respectively. The percentage loss on ignition values were also found to be within the range specified by the British International Standard of clay specification. The percentage loss on ignition values also indicate that the clay samples have low carbonaceous matter and higher mineral matter contents [15].

Tables 3 and 4 showed the XRF analysis values of the two Rafin-Kada clay composites. The results revealed that the clay deposits contain mainly Silica, Alumina Iron and potassium oxides along with some important mineral elements in trace but appreciable quantities. The order of the major components is as follows: SiO_2, >Al_2O_3, Fe_2O_3 > K_2O while the minor mineral elements order is P_2O_5,> SO_2> CaO>, V_2O_5>, SnO >, ZrO_2, >Sb_2O_5 >MoO_2, TiO_2>, ZnO. The ealier observed higher values in sample C against sample D was repeated in the results of the XRF analysis. This clearly show that there exist a difference in soil formation along with mineral composition between these two locations within the sample area. The quantity of silica in the two different samples C and D is (39.5781 and 34.5835%) and correspond to the result obtained for Arrirasho clay deposit as reported by [1]. The high content of silica in the two clay composite samples suggests the existence of quartz in the Rafin –Kada- Wukari clay deposits and could be used as a source of silica for the production of floor tiles and as a binder in place of standard binders [15]. According to [18] clay samples containing high quantity of silica can be utilized in the synthesis of zeolite, a catalyst mostly used in the catalytic cracking of petroleum. The iron contents of the Rafin-Kada clay deposits ranged between (3.0272- 6.1582%) and could give it a dark brown colour when pulverized [1]. Also the low quantity of alkali metal oxides in the clay samples showed that the clay deposits would not be suitable for making ceramic materials [19].

Two of the minor mineral elemental oxides found in the Rafin – Kada clay deposits are however of great industrial application they are zirconium oxide and Zinc oxide. It is reported that one of the reasons why interest in zirconium continues to grow is that, unlike many of the other metals in common usage, zirconium has a low toxicity and is classified as being non-hazardous to the environment and thus majorly used in ceramics industry for various applications [20]. Zirconium is used in alloys as Zircaloy, which is used in nuclear applications since it does not readily absorb neutrons. It is also used in catalytic converters, percussion caps and bricks Beddeleyite an impure zirconium which has iron, titanium and silicon oxide impurities is used in lab crucibles. Zircon is also marketed as a natural gemstone used in jewelry. The metal also has many other uses, among them are in photographic flashbulbs and surgical instruments etc. [21]

Zinc oxide is an inorganic compound with the formula ZnO. It is a white powder that is insoluble in water and it is widely used as an additive in numerous materials and products including rubbers, plastics, ceramics, glass, cement, lubricants, paints, ointments, adhesives, sealants, pigments, foods, batteries, ferrites, fire retardants, and first-aid tapes. It occurs naturally as the mineral zincite, but most zinc oxide is produced synthetically. Crude zinc oxide is a yellow-gray granular solid with no odor. It is insoluble in water. It is mild astringent and topical protectant with some antiseptic action. It is also used in bandages, pastes, ointments, dental cements, and as a sunblock.

Zinc oxide can be used in ointments, creams, and lotions to protect against sunburn and other damage to the skin caused by ultraviolet light. It is also widely used to treat a variety of other skin conditions, in products such as baby powder and barrier creams to treat diaper rashes, calamine cream, anti-dandruff shampoos, and antiseptic ointments. The primary hazard is the threat posed to the environment. Immediate steps should be taken to limit its spread to the environment. Prolonged inhalation of the dust may result in metal fume fever with symptoms of chills, fever, muscular pain, nausea and vomiting [22].

4. Conclusion

(a) This study established that the characterized Rafin-Kada clay deposits of Wukari, Taraba State are suitable for industrial usage particularly, they could be used as source of silica for ceramic industry
(b) The characterized clay samples could be used in the production of floor tiles and building bricks,
(c) The characterized clay samples could be used as zirconia gemstones and in the synthesis of zeolite.

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