Characterization of Primitive Clays from Katsina-Ala and Makurdi, Benue State - Nigeria

Donald Kukwa[1,2*], Rose Ikyereve[1,3] and Chris Ikese[1]
1. Department of Chemistry, Benue State University Makurdi – Nigeria
2. Department of Chemical Engineering, University of Benin, Benin City – Nigeria
3. Department of Chemistry, Loughborough University, Loughborough, Leicestershire – United Kingdom
*E-mail of the corresponding author: dkukwa@bsum.edu.ng

Abstract

Clay samples sourced from Katsina-Ala and Makurdi were characterized using x-ray fluorescence (XRF), X-ray diffraction (XRD), and Fourier transform infrared (FTIR). The XRD of both clays revealed the presence of halloysite and quartz as the major phyllosilicate mineral crystals in both clays. An IR spectral analysis identified Al-OH, Al-O, Si-O and Si-O-Si functional groups in the high frequency stretching and low frequency bending modes of the clays respectively. A comparison of the physicochemical properties of both clays showed that clay samples from Makurdi have a marginally higher moisture content, porosity, and cation exchange capacity (17.65 %, 4.2, 0.32 and 3.1 meq/100g respectively) than that from Katsina-Ala which had the following respective values of 14.21 %, 2.4, 0.17 and 2.9 meq/100g. Thus clay samples from Makurdi show better characteristics of efficient low cost adsorbents than those from Katsina-Ala.

Key words: Primitive clay, characterization, XRF, XRD, FTIR

1. Introduction

Primitive clays are naturally occurring hydrous alluminosillicates which are composed of mixtures of ultra-fine grained clay minerals, crystals of other minerals and metal oxides (Guggenheim and Martin, 1995). The different minerals present in primitive clay account for its different properties, plasticity being one of these (Wikipedia, 2011). The various clay properties in turn account for their wide range of industrial and domestic applications.

Plasticity, adsorptivity, cation exchange and shrink-swell capacity are perhaps the most important properties of clay as they are the most frequently exploited for industrial purposes; plasticity in pottery (Amethyst Galleries, 2011), adsorptivity and ion exchange in water purification (Mockoviakova and Orolinova, 2009) as well as the removal of heavy metal pollutants and other unwanted substances from the environment., industrial waste effluents and other media in which they are present. One study (David, 1976) which investigated the interaction of petroleum heavy-end with montmorillonite reported that the adsorption of asphaltenes onto montmorillonite occurred rapidly, and to a large extent, irreversibly under near anhydrous laboratory conditions and that the adsorption was influenced by exchangeable ions on the clay, neighbouring molecules and the solvent. In similar studies (especially with cationic sorbates), clays seem to be receiving tremendous attention as the preferred adsorbent. Studies abound where clays or their modified forms have been used for metal removal from aqueous solutions. Illite has been used for the removal of Cd^{2+} (Echeverria *et al*, 2002), natural and Na-exchanged bentonites have been used for Cr^{3+}, Zn^{2+} and Cu^{2+} adsorption (Alvarez and Garcia, 2003). Sepiolite has been used for Co^{2+} (Kara *et al*, 2003)], and kaolinite for Mn^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} removal (Bhattacharyya and Sengupta, 2006).

The largest application of kaolinite is in the manufacture of glossy paper. This is because Kaolinite is soft, earthy and usually white dioctahedral clay (Agbende, 2010). It is also used as food additive, in white incandescent light as well as in cosmetics (Bear, 1978). Smectites on the other hand are known for their ability to absorb significant amounts of water molecules between their tetrahedral and octahedral sheets thus causing a significant expansion of their crystal lattice than observed for other clay types and as such they have found application in the oil industry as a component of drilling mud (Bear, 1976). Montmorillonite has also been used to hold soil water in drought–prone soils (Mukherge and Biswas, 1974).

Because the chemical composition of a given clay accounts for its chemical and physical properties and by extension its application, it has become necessary to characterize clay samples from different locations with a view to sourcing and identifying the most suitable clay for different applications. This study is aimed at sourcing efficient low-cost materials for informed industrial applications.

2. Materials and Methods

2 kg each of clay samples were collected from Katsina-Ala (K_{un}) and Makurdi (M_{un}) in Benue State, Nigeria at a depth of 30 cm from their respective clay deposits using a spade and meter rule. The clay samples were then separately beneficiated by the wet method (Balabin and Syuyaev, 2008).

The physicochemical properties determined for the unmodified primitive clays were: bulk density which was determined by up-thrust, moisture content by oven drying method (Masooleh *et al*, 2010), pH using a pH meter, porosity and cation exchange capacity (CEC) by ammonia ion selective electrode method (Alvarez and Garcia, 2003).

Mineral compositions of the beneficiated and unbeneficiated clay samples were determined by XRF analysis which involved presenting the sample as 32 mm diameter fused beads prepared from a 1:5 ratio of sample to lithium tetraborate mixture.

FTIR spectral analysis of the samples was performed using a Perkin-Elmer 10.00.00 FTIR spectrophotometer (David, 1976) and the resulting peaks were obtained using He-Ne as the reference at a 4 cm^{-1} resolution.

XRD Analysis of the unmodified clay samples was performed using the method described by Dutrove and Clark (Echeverria *et al*, 2002)]. 10 g of the clay sample was ground into powder using an electric homogenizer and sieved using $> 10\ /200\ mesh$. This was done in a fluid to minimize inducing extra strain (surface energy) that might offset peak positions and randomize orientation.

3. Results and Discussion

3.1 Physicochemical Analysis

The physicochemical properties of the clay samples are summarized in Table 1.

3.1.1 Bulk Density

The bulk density of pure clay and other fine textured soil minerals range between 1.1-1.4 g cm^{-3} (Cha *et al*, 1991). Table 1 gives the bulk density of clay samples from Makurdi and Katsina-Ala as 1.8 and 2.2 g cm^{-3} respectively. These values are an indication of some physical properties of the clay samples such as shrinkage-swell potential, available water capacity and pore space, all of which bear on its sorption ability. The values obtained from the clay samples indicate the presence of coarse non-clay minerals in both clay samples. This is especially so with clay samples from Katsina-Ala. With a bulk density of 1.8 g cm^{-3}, the clay sample from Makurdi probably has higher clay content, than that from Katsina-Ala with a bulk density of 2.2 g cm^{-3}.

3.1.2 Moisture Content

As shown in Table 1, the moisture contents of clay samples from Makurdi and Katsina-Ala were found to be 17.65 % and 14.21 % respectively. This signifies that clay samples from Makurdi are expected to have a higher degree of inter-layer hydration and swelling capacity than that from Katsina-Ala, thus allowing a much freer movement of the clay structure than in the latter. The effect would be an enhancement in adsorption and ion exchange capacity over the clay sample from Katsina-Ala.

3.1.3 pH

The pH of clay samples from Makurdi and Katsina-Ala were found to be 4.8 and 2.4 respectively. In clays, the percentage adsorption of cations has been reported to increase with increase in pH and obtains a maximum at about pH 7.0 (Rmamurthi *et al*, 2009) and thereafter, it does not change significantly with increase in pH. This is because the higher the pH, the more favoured would be the exchange or replacement of Al^{3+} centres in the crystal structure. The adsorption characteristics of clay are influenced by ion exchange and precipitation and the adsorbed ions will be precipitated at extremely high basic pH. Low percentage adsorption at lower pH may be due to an increase in competition for adsorption sites by H^+ ions (Rmamurthi *et al*, 2009).

3.1.4 Clay Porosity

The porosity of clay samples from Katsina-Ala and Makurdi were found to be 0.17 and 0.32, respectively (Table 1). Being a measure of the void in clay matrix, the implication is that, the greater the porosity of a given clay sample, the greater the relative size of molecules it can adsorb onto its crystal structure. This way the ion exchange characteristics of clay are determined also by the size and geometry of its pore spaces.

3.1.5 Cation Exchange Capacity (CEC)

Table 1 show that the CEC of unmodified clay from Makurdi and Katsina-Ala are 3.1 and 2.1, respectively. This shows that M_{un} posseses more exchangeable cations than K_{un}, thus showing a greater adsorption capacity for the former.

3.2 Mineral Composition of Beneficiated and Unbeneficiated Clay Samples

Table 2 shows the percentage mineral composition of beneficiated and unbeneficiated clay samples from Katsina-Ala ($K_{beneficiated}$ and $K_{unbeneficiated}$) and Makurdi ($M_{beneficiated}$ and $M_{unbeneficiated}$). There is a marginal decrease in the percentage mineral composition of beneficiated clay for both locations with specific reference to SiO_2, Al_2O_3, Fe_2O_3, Na_2O and K_2O. However, there was a marginal increase in the concentration of CaO and MgO after beneficiation (Kovo and Edoga, 2005).The observed decrease in the mineral composition of beneficiated clay may be attributable to the fact that more of the minerals may have been associated with the more coarse-sized particles that were unable to go through the mesh during beneficiation. Also, some of the metal ions may have been washed off or lost in the deionised water used during the beneficiation.

From the percentage composition of SiO_2, and Al_2O_3 (Table 2), the Al: Si ratio of clay samples from Katsina-Ala and Makurdi are 0.17 and 0.10, respectively, indicative of more tetrahedral sheets than there are octahedral sheets in the mineral structure of both clay samples. Such clay samples will show a remarkable degree of isomorphous substitution of Si^{4+} for Al^{3+} in their tetrahedral and octahedral sheets. These isomorphous substitutions induce a net negative charge on the clay structure (Reynolds, 2004). This is expected to promote significant attraction and adsorption of cations.

3.3 Infrared Spectral Analysis

Infrared spectra of unmodified clay samples from Katsina-ala (K_{un}) and Makurdi (M_{un}) in the range of 200–4000 cm^{-1} are presented in Figures 1 and 2. From the individual spectrum of the clay samples, the assignments of the observed peaks are as shown in Table 3. These were found to be in consonance with Masooleh *et al* (2010). The infrared spectra show that both clay samples gave absorption peaks at about the same wave numbers (3695, 33701; 3620, 3524; 3430, 3424; 1636, 1634; 1032, 1022; 915, 910; 797, 778; 698, 696; 541, 535; 471, 466; 430, 428; 214 and 220 cm^{-1}) except that in most cases, the peaks varied in intensity. This is an indication that both samples, contain essentially the same functional groups but in different amounts. Both clays are expected to have different cation exchange capacities to the extent of the observed variation in Si-O-Si, Si-O-Al and Si-OH composition. The IR-Spectra of both clay samples showed no intense peak corresponding to organic matter. This is consistent with similar work (Masooleh *et al*, 2010).

3.4 X-ray diffraction

The diffractograms of unmodified clay from Katsina-Ala (K_{un}) and Makurdi (M_{un}) are presented in Figures 3 and 4 respectively showing the individual patterns for the clay minerals. Comparing the generated d-spacings at 2θ with a reference data base of d-spacings identified quartz (01-085-1780) and halloysite (00-029-1487) as the major minerals in both clay samples. Of these minerals, the hallyosites are the most important. This is because they are cylindrical in structure (Wikipedia, 2012) and are characterized by ultra tiny nanotubes (Natural Nano, 2012) thus significantly improving the sorption capacity of clays where they are found.

4. Conclusion

The XRD analysis showed that quartz and halloysites are the major phyllosilicate mineral crystals in primitive clay samples from Katsina-Ala and Makurdi. The IR analysis revealed Al-OH, Al-O, Si-O, and Si-O-Si functional groups occurring in varying amounts in both clay samples. However, there is a marginal difference between the physicochemical properties of clay samples from Katsina-Ala and Makurdi; with the clay samples from Makurdi showing greater promise for adsorption applications.

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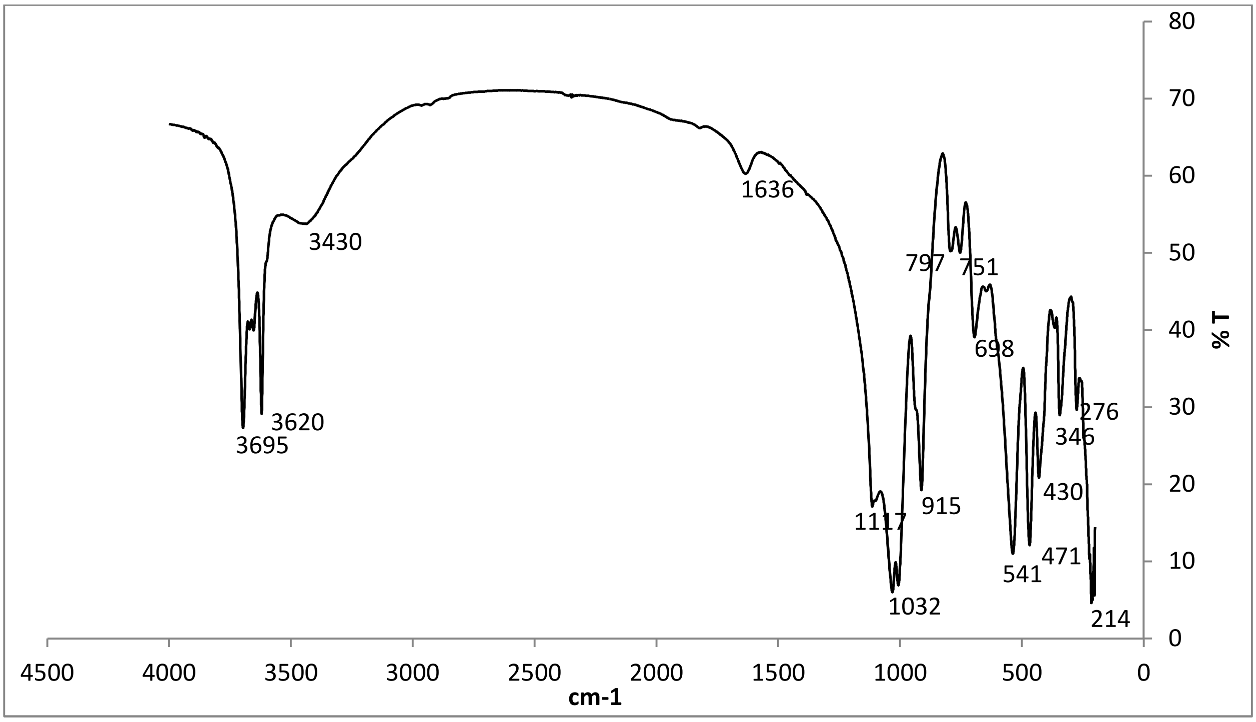

Figure 1: FTIR-spectra of K_{un} clay

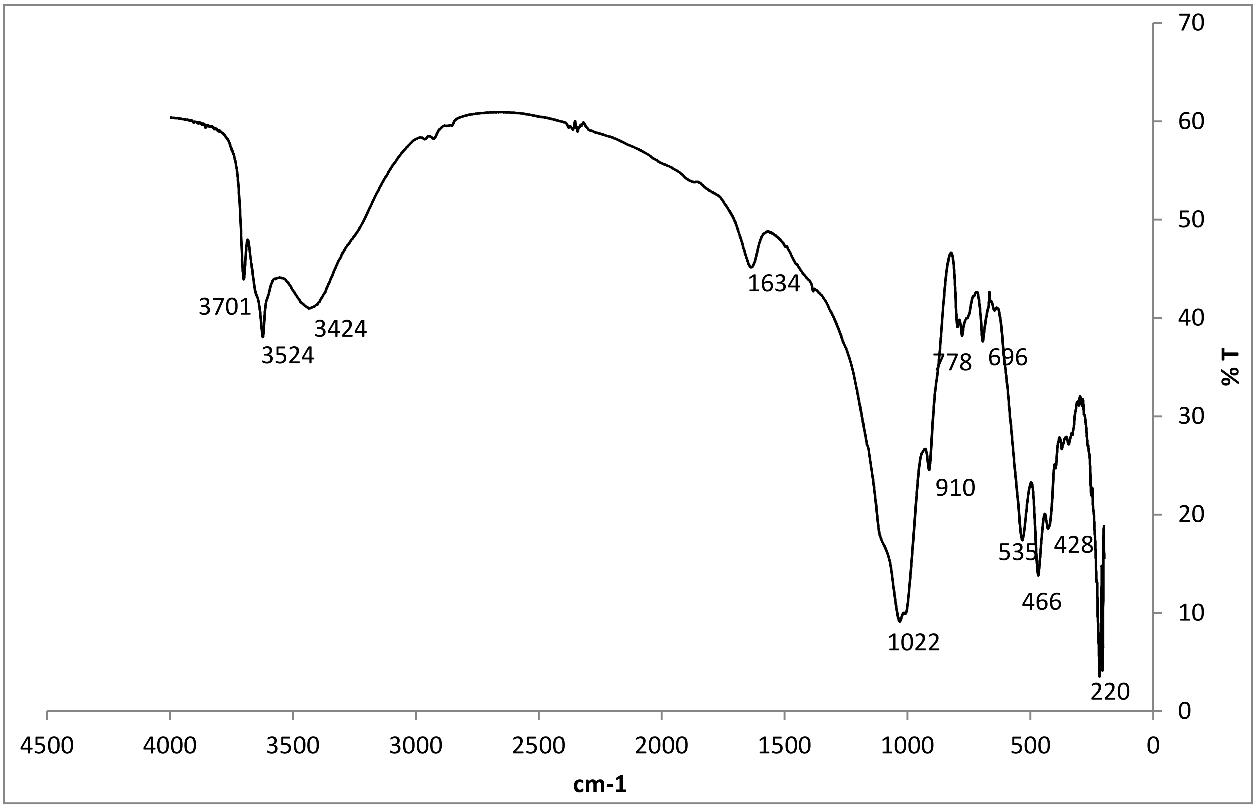

Figure 2: FTIR-spectra of M_{un} clay

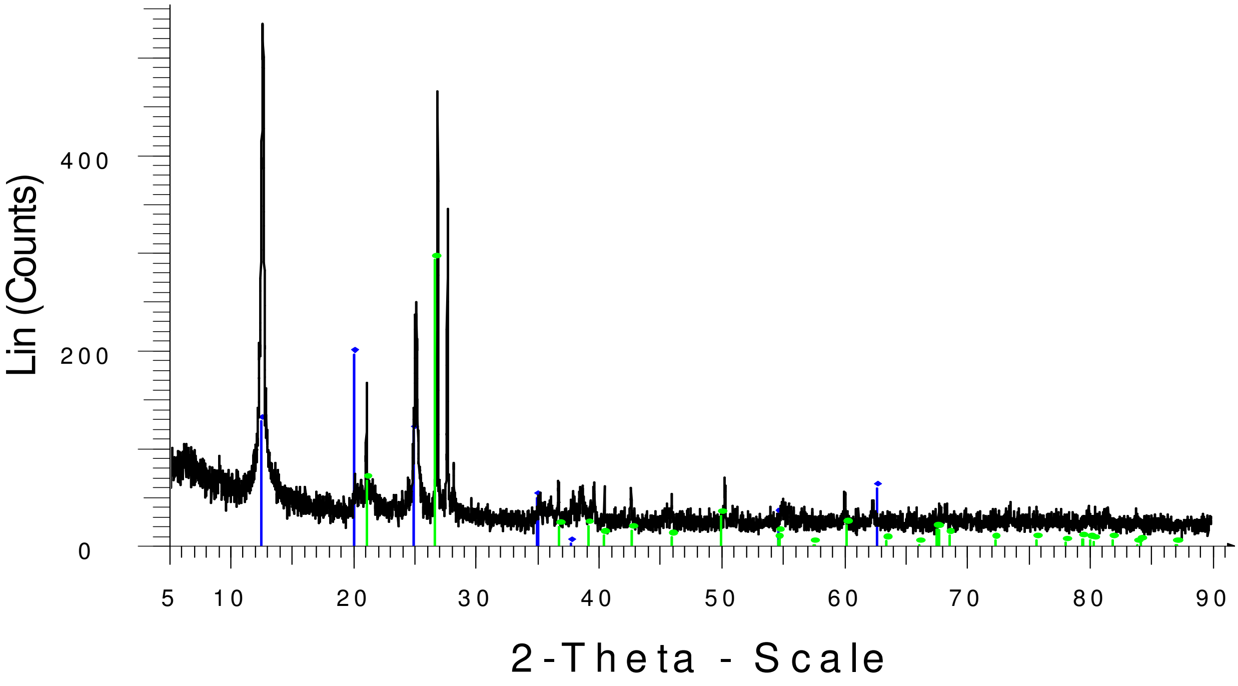

Figure 3: X-ray Diffractogram of K_{un} clay

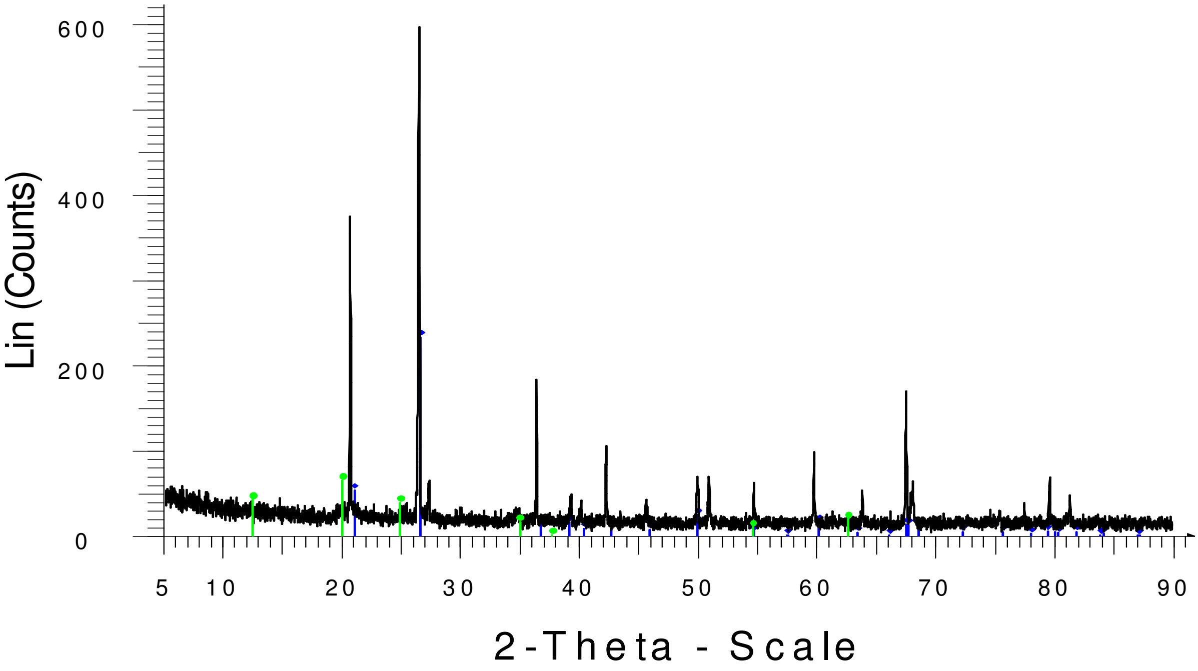

Figure 4: X-ray Diffractogram of M_{un} clay

Table1, Physicochemical Properties of Clay Samples collected from Katsina-Ala and Makurdi

Source	Bulk density (g cm^{-3})	Moisture content (%)	pH	Porosity	CEC (meq/100g)
Katsina-Ala	2.2	14.21	2.4	0.17	2.9
Makurdi	1.8	17.65	4.8	0.32	3.1

Table 2 Percentage mineral composition of beneficiated and unbeneficiated clay samples

Sample	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O
$K_{unbeneiciated}$	60.60	18.81	5.75	1.18	0.42	0.23	1.53
$K_{beneficiated}$	58.36	18.39	5.42	2.26	0.44	0.13	1.47
$M_{unbeneficiated}$	82.64	13.86	4.79	0.99	0.71	0.07	2.44
$M_{beneficiated}$	78.94	13.68	4.68	2.32	0.77	0.01	2.42

Table 3. FTIR-Spectral frequency designations for K_{un} and M_{un}

Wave number (cm^{-1})	Assignments
3695- 3620	Al-O-H stretching
3430, 3424	H-O-H stretching of absorbed water
1636, 1634	H-O-H bending of water
1032, 1022	Si-O stretching in clay mineral
915	OH deformation linked to $2Al^{3+}$
778, 696	Si-O quartz
541, 535	Fe-O, Fe_2O_3 and Si-O-Al stretching
471- 428	Si-O-Si bending