



## EVALUATION OF GASTROPOD SHELL AS A GREEN PRECURSOR IN THE SYNTHESIS OF ANIONIC CLAY MINERAL

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### ABSTRACT

*In order to add value to an abundant waste biogenic resource, the ability of the shell of a Gastropod was appraised as a green precursor in the synthesis of an anionic clay (Ca-Al-layered double hydroxide). Using the co-precipitation method, different ratios (1, 2 and 4) of gastropod shell (GS) to AlCl<sub>3</sub> salt were reacted to obtain anionic clay samples (AC1, AC2, AC4,) of different M(II) and M(III) ratios. The XRD analysis of the samples showed that only the reactant combination ratios of 2 and 4 produced the Hydrocalumite minerals (i.e. AC2 and AC4). The surface architecture of the samples showed that the particles of the Hydrocalumite were of irregular shapes and the pore locations and sizes were asymmetrical. The prominence of Ca, Al, Cl and O in the samples were identified with the EDAX. The FTIR spectra showed vibration characteristics that are similitude of layer double hydroxides (LDHs). The values of the surface charge of the samples, determined via the determination of the point zero charge, were also synonymous with that of the LDHs*

**Keywords:** Gastropod shell; anionic clay; co-precipitation method; layer double hydroxides, hydrotalcite

### 1.0 Introduction

Anionic clays, usually referred to as layered double hydroxides (LDHs) or hydrotalcite-like compounds, are natural or synthetic lamellar hydroxides with two or more kinds of metallic cations in the main layers and hydrated interlayer domains containing anionic species (Martin and Pinnavaia, 1986). The reference to the LDH as anionic clay indicates a complementarity with the more usual cationic clays, whose interlamellar domains contain cationic species. The mineral hydrotalcite, which was discovered in Sweden around 1842, is a hydroxycarbonate of magnesium and aluminum and can be considered a prototype of this class of materials. LDHs are described by the general formula  $[M^{(II)}_{1-x}M^{(III)}_x(OH)_2]^{x+} (A^{n-})_{x/n} \cdot mH_2O$ , where  $M^{(II)}$  and  $M^{(III)}$  are di- and trivalent metals

respectively, and  $A^{n-}$  is an anion (Cavaniet al., 1991). The structure is based on brucite-like layers, in which a divalent metal cation is located in the center of oxygen octahedral and two-dimensional infinite layers are formed by edge-sharing of the octahedral. Partial isomorphous substitution of trivalent cations for divalent ones results in a positive charge on the layers.

Recently, LDHs have received considerable attention because of their layered structures, anion exchange properties and high positive charge density of their layers. They have important anion exchange and intercalation properties, which make them potentially useful materials for a wide variety of technological applications in various fields, such as industrial catalytic processes, electrochemistry, separation technology, pharmaceuticals, polymer reinforcement,

and environmental clean-up by ion exchange, or adsorption process (Cavani et al., 1991; DeRoy et al., 1992). Their physicochemical properties, such as ion exchange ability, the extent of hydration and ionic conductivity, as well as their reactivity are largely determined by the interactions between the hydroxylated sheets and the interlayer species (Aisawa et al., 2005; Chang et al., 2005). LDHs may be synthesized with a wide range of compositions and a large number of materials with a wide variety of  $M^{(II)}/M^{(III)}$  cation combinations as well as  $M^{(I)}/M^{(III)}$  cation pairs (e.g. Li/Al), with different anions in the interlayer. The interlayer domains contain anions, water molecules and sometimes other neutral or charged moieties. Relatively weak bonding occurs between the interlayer ions or molecules and the host sheets. A key feature of these materials is therefore their anionic exchange capacity, which makes them unique as far as inorganic materials are concerned. A number of synthetic techniques have been successfully employed in the preparation of anionic clays but the most commonly used are simple coprecipitation methods. The other methods that have been reported include: the classical ion exchange process; reconstruction method; sol-gel synthesis using ethanol and acetone solutions; and a fast nucleation process followed by a separate aging step at elevated temperatures (He et al., 2006).

In the present studies, a green approach is adopted in the synthesis of anionic clay (Ca-Al layered double hydroxide) mineral. Gastropod shell was chosen, as a source of  $M^{2+}$  ( $Ca^{2+}$ ) for the anionic clay (AC) synthesis from the perspective of green and sustainable approach, value addition to waste and cost minimization in material synthesis. A Gastropod shell (GS), African Land Snail (*Achatina achatina*) shell, is being proposed as a source of  $Ca^{2+}$  specie because of the inherent chemical and mineralogical assemblage (Oladoja, and

Aliu, 2009, Oladoja et al., 2011). Gastropods have worldwide distribution from the near arctic and Antarctic zones to the tropics and they are very striking in their extraordinary diversification of habitats. Mollusks make up the phylum Mollusca and Gastropoda (snails and slugs) is a class under the phylum Mollusca. The snail shell (SS) has got the same basic construction as other Mollusk shells and it contains, mainly,  $CaCO_3$ , as well as various organic compounds (Oladoja, and Aliu, 2009, Oladoja et al., 2011). Large tonnes of GS are discharged annually, as waste from food processing industries, which made it a low cost and abundant material that could be harnessed for deriving  $Ca^{2+}$  (Oladoja et al., 2012). The use of SS as a  $Ca^{2+}$  ion source in environmental remediation and material synthesis have been reported (Oladoja et al., 2013a and 2013b).

In order to achieve the aim of the present study, GS shall be used as a green precursor in the synthesis of a Ca-Al- LDH mineral, using different ratios of GS to Al salt. The products obtained shall be characterised via the determination of the mineralogical assemblage, surficial architecture, elemental composition, functional groups and surface charge.

## 2.0 Materials and Methods

### 2.1 Material synthesis

Solution of  $CaCl_2$  was prepared from the GS by adopting the protocol described by Oladoja et al., (2012). Aluminium chloride ( $AlCl_3$ ) salt (Merck KGaA, Germany) was used as the source of  $Al^{3+}$ . The anionic clay was prepared via the co-precipitation method thus: mixed solutions containing the appropriate mass ratios of  $Ca^{2+}:Al^{3+}$  (1, 2 and 4) were prepared and stirred to obtain an even mix. The mixture was agitated thoroughly before another solution containing 2 M NaOH was added, under vigorous stirring. The slurry was allowed to gelate in the mother liquor for 24 h, at ambient temperature, before it was washed, severally with copious deionized water. The

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slurry was collected and allowed to dry to constant weight in the drying oven at 80°C. The synthesized AC were labeled AC<sub>1</sub>, AC<sub>2</sub> and AC<sub>4</sub>, the subscript showing the Ca<sup>2+</sup>:Al<sup>3+</sup> ratio used in the synthesis.

### 2.2. Material Characterization

#### 2.2.1 X-Ray Diffractometry Analysis

The crystallinity and mineralogical assemblage of the AC samples were determined via X-ray diffraction (Philip PW 1820 diffractometer). Diffraction patterns of the samples were recorded with Cu K $\alpha$  radiation ( $k = 1.54060 \text{ \AA}$ ) and recorded in the range of 5–90° (2 $\theta$ ) with a scanning rate of 2°/min and a step size of 0.01.

#### 2.2.2 Scanning Electron Microscopy and Energy Dispersive Analysis of X-Ray Analysis

The surface morphology and elemental composition were determined by scanning electron microscopy (SEM) equipped with energy dispersive analysis of X-ray (EDAX). The analysis was carried out using a scanning electron microscope (Model EMJEOL-JSM6301-F) with an Oxford INCA/ENERGY-350 microanalysis system. The EDAX microanalysis system (Oxford INCA 400, Germany) was connected to the SEM machine. The EDAX analysis used Mn K $\alpha$  as the energy source operated at 15 kV of accelerating voltage, 155 eV resolutions and 22.4° take off angle.

#### 2.2.3 Fourier Transform Infra-Red Analysis

Fourier transformed infrared spectroscopy (FTIR) analyses were performed on the samples to determine the functional groups present. The samples and analytical grade KBr were dried at 100°C overnight, prior to the FTIR analysis. A mixture of 0.25 mg of each sample and 100 mg of KBr was ground to fine particles and was placed in a manually operated hydraulic press operated at 8 Mbar to obtain a translucent disc of 12.7 mm diameter and about 1 mm

thickness. The instrument used was Perkin–Elmer Spectrum GX Infrared Spectrometer with resolution of 4 cm<sup>-1</sup> operating in the range of 4000–400 cm<sup>-1</sup>.

#### 2.2.4 Determination of Surface Charge

The pH<sub>PZC</sub> was determined via a batch equilibrium procedure described by Oladoja et al., (2009) viz: Into a series of 100 ml conical flasks, 45 ml of 0.1 M KNO<sub>3</sub> solution was transferred. The pH<sub>0</sub> values of the solution were roughly adjusted from 2 to 12 by adding either 0.1 N HNO<sub>3</sub> or NaOH. The total volume of the solution in each flask was made exactly to 50 ml by adding the KNO<sub>3</sub> solution. The pH<sub>0</sub> of these solutions were then accurately noted. GS (1 g) was added to each flask and securely capped, immediately. The suspension was then manually agitated. The pH values of the supernatant liquid were noted. The difference between the initial and final pH (pH<sub>i</sub>) values ( $\Delta\text{pH} = \text{pH}_0 - \text{pH}_i$ ) was plotted against the pH<sub>0</sub>. The point of intersection of the resulting curve at which  $\Delta\text{pH} = \text{zero}$  gave the PZC.

### 3.0 Results and Discussion

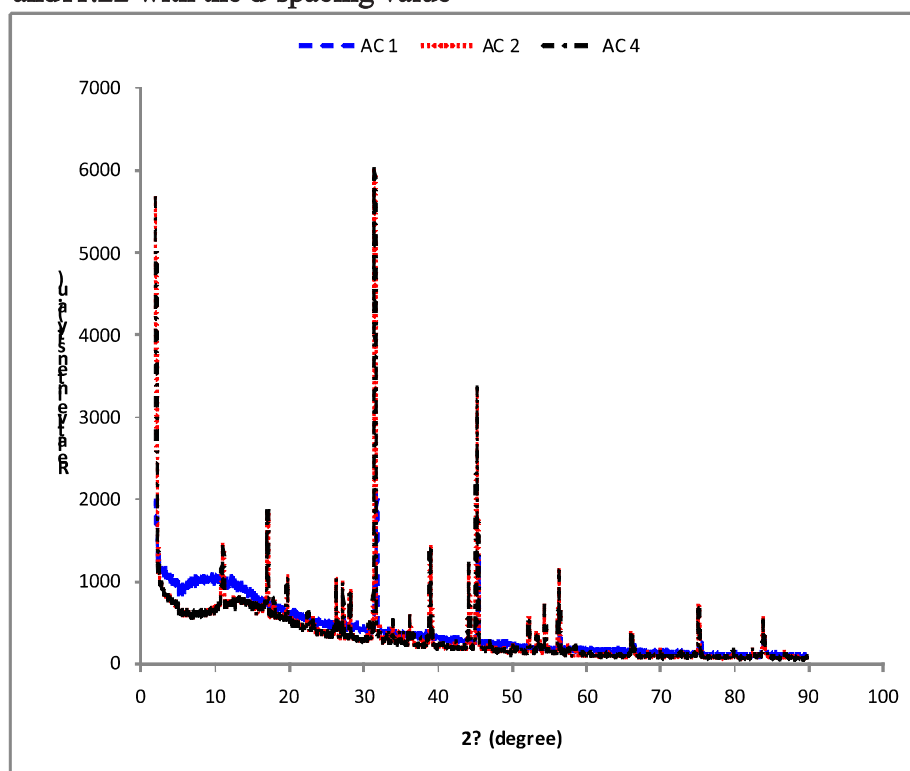
The Ca-Al layered double hydroxide, which is also known as Hydrocalumite, is a member of an emerging material of choice in diverse uses. Hydrocalumite [Ca<sub>2</sub>(Al,Fe)(OH)<sub>6</sub>]<sup>+</sup>X<sup>-</sup>·mH<sub>2</sub>O] has the same lamellar structure as natural hydrocalcite, where X<sup>-</sup> is an anion, such as OH<sup>-</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and CO<sub>3</sub><sup>2-</sup> (Braterman, et al., 2004). The results of the characterization of the synthesised Hydrocalumite samples are presented below.

#### 3.1 Mineralogical Assemblage

The XRD pattern (Fig. 1) of AC<sub>2</sub> and AC<sub>4</sub> samples agreed with that recorded in the database of the International Center for Diffraction Data, which confirmed that these materials are Hydrocalumite mineral. Series of sharp and intense symmetric peaks at low 2 $\theta$  values and small

symmetric peaks at high  $2\theta$  values revealed characteristic basal reflections, which has been ascribed to the LDH-type materials (Zhou, et al., 2011). The values of the d-spacing, obtained for samples AC<sub>2</sub> and AC<sub>4</sub>, were typical of that of the synthesized Hydrocalumite samples reported by other workers, (Pavan, et al., 2000, Wu, et al., 2011, Zhou, et al., 2011). The positions and the relative intensity of the peaks shown by samples AC<sub>2</sub> and AC<sub>4</sub> were very similar while sample AC<sub>1</sub> differed in both the relative intensity and peak positions and value of lattice spacing. Samples AC<sub>2</sub> and AC<sub>4</sub> showed the characteristic  $2\theta$  reflection at 11.07 and 11.22 with the d-spacing value

at 7.99 Å and 7.88 Å, respectively, while sample AC<sub>1</sub> did not show any of these peaks and lattice spacing values. The other major reflections of AC shown by AC<sub>2</sub> and AC<sub>4</sub> are 3.95 Å and 3.93 Å at  $2\theta$  values of 22.52, and 22.60 and 2.84 Å and 2.88 Å at  $2\theta$  values of 31.52 and 31.04 respectively. Some other peaks that are uncharacteristic of the LDH were also observed and these were attributed to the presence of impurities in the samples, originating from the biogenic precursor.



**Figure 1: X-Ray Diffractogram of the synthesised anionic clay samples**

The size of the particles of the synthesized AC samples were calculated using Scherrer equation;  $D = 0.9\lambda/\beta \cos\theta$ , where  $\lambda$  is the wavelength of X-rays,  $\beta$ , is the half width at full maximum and,  $\theta$ , is the diffraction angle. The average grain size of the particles (nm) was found to be 135.26, 116.12, and 121.60 for AC<sub>1</sub>, AC<sub>2</sub> and AC<sub>4</sub>, respectively.

### 3.2 Surficial Architecture and Elemental Composition

The results of the SEM and EDX analysis of the AC samples are represented in Fig. 2a–c. The SEM analysis showed that the samples are made up of particles of irregular shapes and sizes. The pore locations and sizes are also asymmetrical. Sample AC<sub>1</sub> (Fig. 2a) appeared as a fusion of relatively larger particles, whereas the other two samples (sample AC<sub>2</sub> (Fig. 2b) and AC<sub>4</sub>

(Fig. 2c) appeared as being derived from smaller particle sizes. The results of the EDX analysis revealed the prominence of Ca, Al, Cl, and O in all the samples synthesised. The presence of Na observed in all the samples was attributed to the residual Na from the NaOH solution, used as precipitant, while the trace of Si observed was attributed to the biogenic precursor.

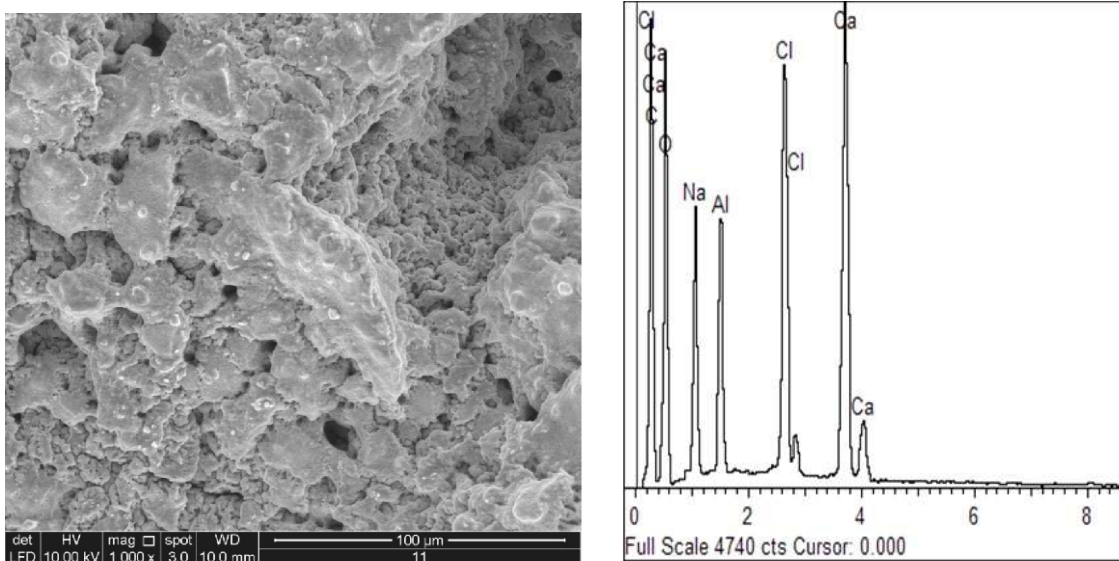
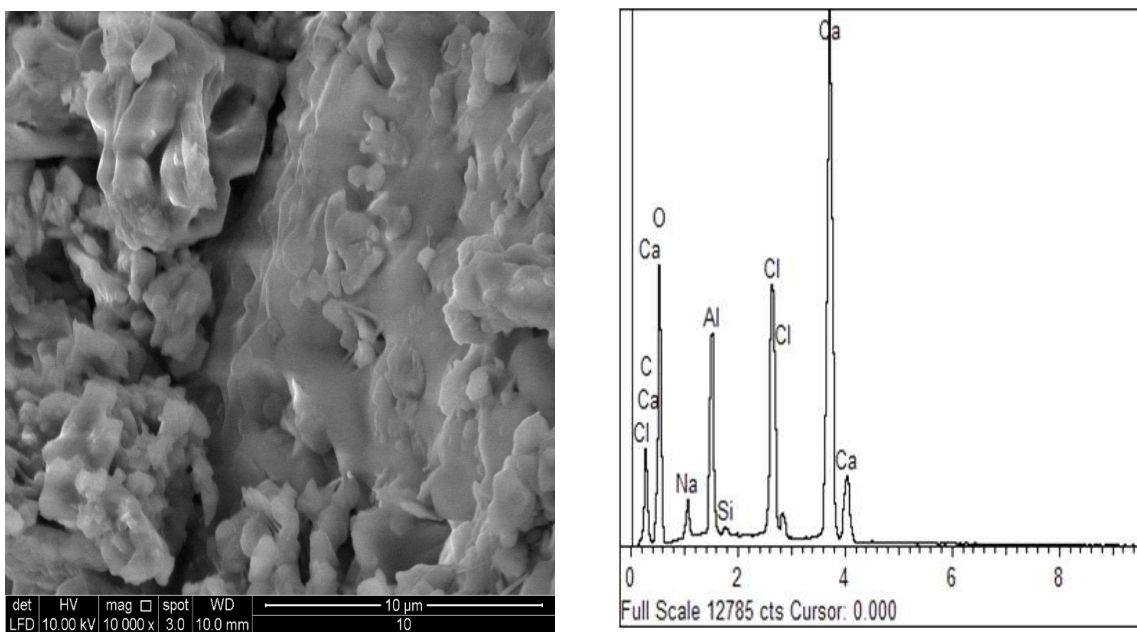
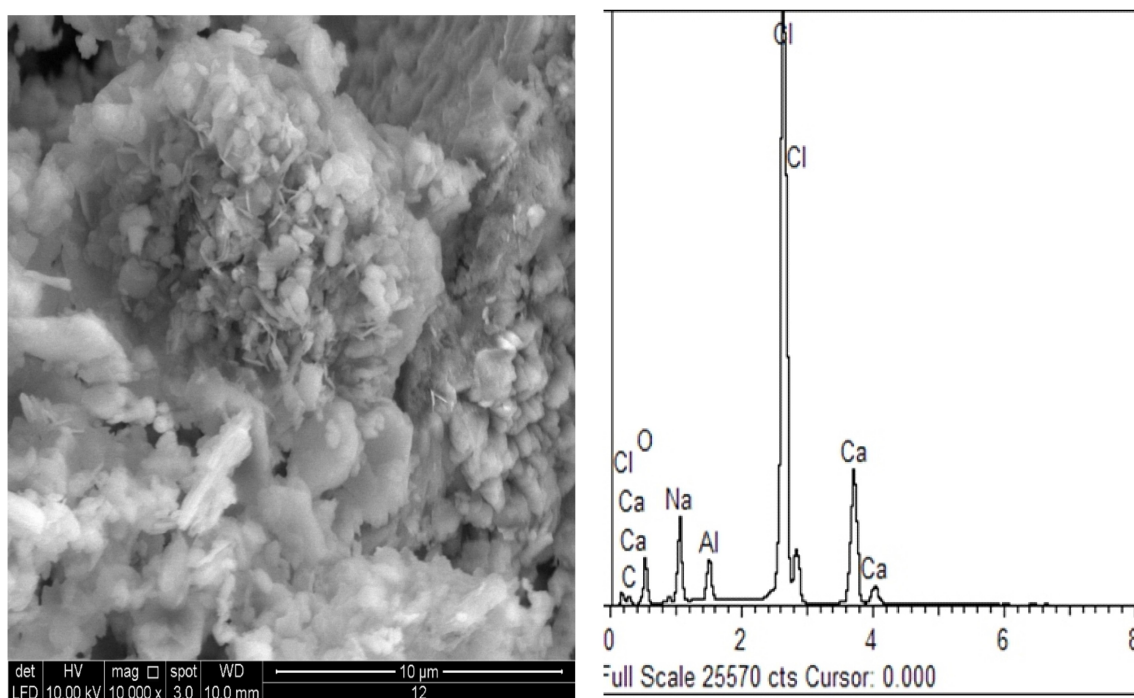


Figure 2a: Surficial and elemental composition of AC<sub>1</sub>



Surficial and elemental composition of AC



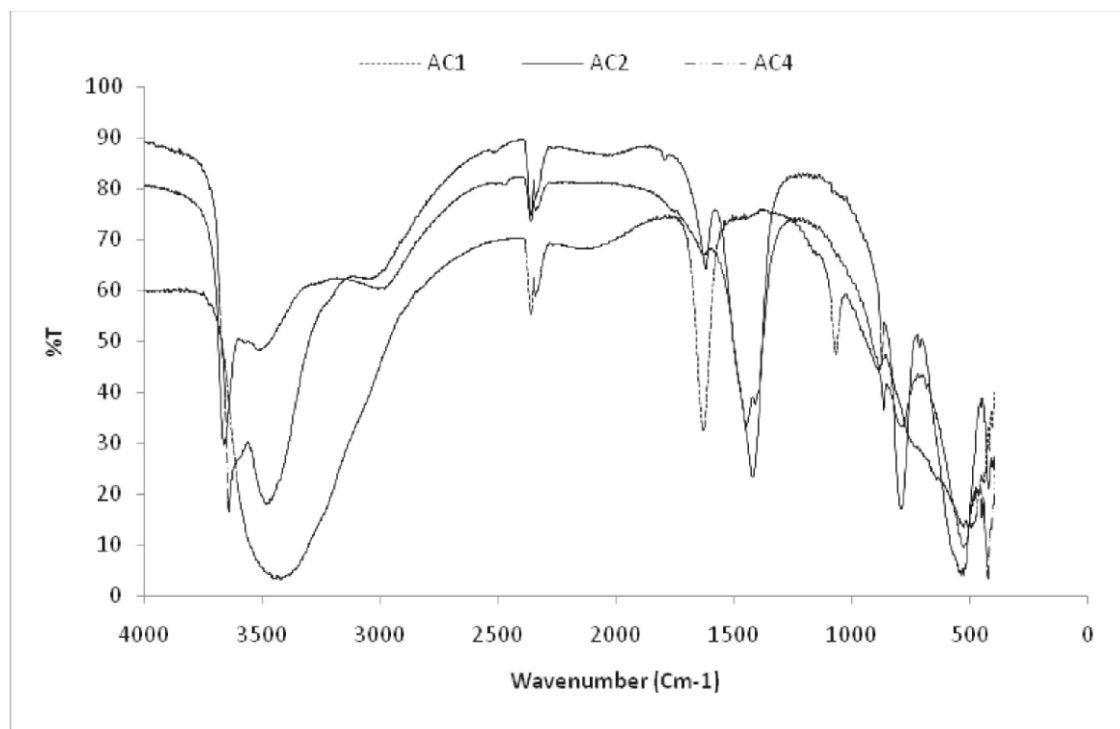
**Figure 2c: Surfacial and elemental composition of AC<sub>4</sub>**

### 3.3 Surfacial Functional Groups

The FTIR spectra of the AC samples, presented in Fig 3, show the similar vibrations characteristics of the LDH structures. These include the band of H–O–H bending in water molecule at 1550–1700  $\text{cm}^{-1}$  and the vibrations of metal–O (or metal–OH) bond at 500–750  $\text{cm}^{-1}$ . The strong overlapping bands at 3443 in AC<sub>1</sub>, 3662 and 3641 in AC<sub>2</sub> and 3475 in AC<sub>4</sub> were attributed to the stretching vibrations of lattice water and structural OH groups in the samples. This intense and broad absorption band regions also correspond to metal–OH stretching vibrations, in this case, Al–OH<sub>str</sub> (octahedral structural hydroxyl groups). The broadening of this band has been ascribed to hydrogen bond formation (Birnin-Yauri, and Glasser, 1998). The H–O–H bending

vibrations of the interlayer water molecules were shown by the peak at 1631 in AC<sub>1</sub> and AC<sub>2</sub> and 1620 in AC<sub>4</sub>. The peak at 532 in AC<sub>1</sub>, 528 and 788 in AC<sub>2</sub> and 528 and 792 in AC<sub>4</sub> was ascribed to bending vibration of Al–OH and stretching vibration of Al–OH respectively (Birnin-Yauri, and Glasser, 1998). In addition, the peak at 1448, observed in AC<sub>2</sub> was assigned to the anti-symmetric stretching vibration of CO<sub>2</sub><sup>3-</sup> while the bending vibration of CO<sub>2</sub><sup>3-</sup> was shown at 885 in AC<sub>1</sub>, 866 in AC<sub>2</sub> and 873 in AC<sub>4</sub>. The presence of CO<sub>2</sub><sup>3-</sup> peaks was ascribed to the CO<sub>2</sub> captured from air during the AC preparation. No vibration peaks of chloride ions appear in the range of 400–4000  $\text{cm}^{-1}$  due to the ionic nature of the chloride bonding with the positive charge layer.

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**Figure 3: Results of the FTIR analysis of the AC samples**

### 3.4 Surface Charge

The results of the determination of the  $pH_{PZC}$  of the HC samples showed that the  $pH_{PZC}$  of AC<sub>1</sub> ( $pH = 3.8$ ) was lower than the  $pH_{PZC}$  values of the HC<sub>2</sub> and HC<sub>4</sub> ( $pH = 12.0$ ) samples. This showed that the nature of surface charge of sample AC<sub>1</sub> differs, at different pH values, from that of samples AC<sub>2</sub> and AC<sub>4</sub>. The  $pH_{PZC}$  values of samples AC<sub>2</sub> and AC<sub>4</sub> showed that the surface charges were predominantly positive over the pH range studied (2–12), while AC<sub>1</sub> surface was predominantly positive, until pH 3.8, when the surface charge changed and became predominantly **negative**.

### 4.0 Conclusion

Using the co-precipitation method, with different ratios (2 and 4) of a green precursor, GS, to AlCl<sub>3</sub> salt, the anionic clay, Hydrocalumite (Ca-Al-layer double hydroxide), can be prepared with different  $M^{(II)}$  and  $M^{(III)}$  ratios.

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