Characterization and Evaluation of Inyi Clay Deposit in Enugu State, Nigeria

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ABSTRACT

Characterization and evaluation of Inyi clay mineral deposit in Enugu State, Nigeria was investigated to assess it suitability for use in water purifications and other industrial applications. Samples of the clay mineral were randomly collected from the excavated sites and analyzed in triplicates for physicochemical properties such as pH, moisture content, surface area, loss-on-ignition, cation exchange capacity using standard (AOAC) methods, while alumina, silica, iron, titanium, potassium, calcium contents were evaluated using Atomic Absorption Spectroscopy (AAS). Fourier Infra-red Spectroscopy (FTIR) analysis revealed the presence of functional groups characteristics of kaolinite or montmorillonite and smectite minerals while the X-ray diffraction (XRD) analysis showed a predominantly quartz composition with kaolin and albite phases as minor constituents. The scanning electron microscopy (SEM) analysis confirmed honeycomb-like hexagonal structure patterns with a heterogeneous, irregular and highly aggregated surface structure. The findings show that Inyi-Clay mineral possesses desirable mineralogical and physicochemical attributes, making it a promising candidate for use in ceramics, water remediation and other environmental applications.

KEYWORDS
Characterization, Evaluation, Heterogeneous, Mineralogical, Physicochemical

I. INTRODUCTION

Clay minerals can be said to be soil particles of the less than 5 micrometers and/or rock consisting of clay minerals (Anton et al., 2017). They occur naturally on the earth crust mainly through geological weathering, hydrothermal alteration and the diagenesis processes (Daumier et al., 2020). It ensures good and proper porosity of soil, good water retention and acts as a natural source for nitrogen, calcium oxide and potassium oxide minerals in the soil (Daumier et al., 2020). Clays are widely distributed in nature and serve as important raw materials for numerous industrial applications. Their use in industries and other environmental applications were found, from numerous studies (Murray, 2007; Aramide et al., 2014), to depend largely on their physicochemical properties and mineralogical compositions. Nigeria in general and Enugu State in particular, is endowed with abundant clay deposits, many of which are underdeveloped, underexplored and inadequately characterized, especially in rural areas like Inyi, in Enugu State which are known for her agrarian and significant clay rich soils. Aside the work of Ugwoke and Amalu (2017), no comprehensive research has been conducted on Inyi clay deposit to assess its suitability for commercial or industrial uses. Physicochemical composition and structural characterization of Inyi clay deposit can be the precursor to essential data for determining its applicability in industries and environmental applications (Olatunji et al., 2019). This study, therefore, seeks to characterize the Inyi clay deposit through physicochemical analysis, mineralogical evaluation using advanced analytical techniques such as: x-ray diffraction (XRD), scanning electron microscopy (SEM), fourier transform Infra-red spectroscopy (FTIR) and other standard techniques or test. Findings from this study, will be used to establish industrial relevance of the Inyi clay and also guide its potential utilization strategies.

II. LITERATURE REVIEW

Clay minerals are naturally occurring inorganic earth materials weathered by geological processes and composed primarily of silica (SiO_2), alumina (Al_2O_3), varying proportions of other oxides such as Fe_2O_3, MgO, K_2O and CaO (Onyedoh et al., 2023). They are extremely fine particles that make up colloidal fractions of soils, sediments, rocks and water (Clay mineral group, 2011) which exhibit significant industrial and environmental importance due to their varying physicochemical and mineralogical compositions (Kovo et al., 2005). The industrial viability of any clay deposit is largely a function of its mineral content, structural morphology, chemical constituents and physicochemical behavior (Moshoeshoe et al., 2017).

They can be broadly classified into Kaolinite, Montmorillonite, Illite and Chlorite groups based on their crystal structure and exchangeable properties. Clays comprise of two major groups, sheets or building blocks (Pooja et al., 2020; Bergaya and Lagaly, 2013): silica tetrahedral sheet and silica octahedral sheet (-di or-octahedral) bonded together through sharing of oxygen with silicon and aluminum in their respective sheets to form a unit of clay. The alumina octahedral and silica tetrahedral sheets are arranged in such a manner that gives rise to having groups of clay minerals (Inegbenebor et al., 2016) namely: Kaolinite, Chlorite, Illite and Smectite. Hence most clay minerals are porous phyllosilicates or layered silicates with spacing between the two layers of the clay crystals known as interlayer space. These interlayer spaces hold significant amount of water and other substances and comprised of large surface area that allows for swelling and shrinking (Daniel et al., 2015; Aramide et al., 2014 and Orodu, 2017). Studies (Mokwa et al., 2019; Moshoeshoe et al., 2017) have shown that clay minerals have well known structural, adsorptive, rheological and thermal characteristics that have made them suitable for industrial and environmental applications or management. They have been applied in pharmaceutical, material and agricultural industries. They have also been applied in water treatment and environmental clean-up as adsorbent supports and catalysts for hazardous compounds (Olaremu, 2021). Their high acidity, high surface area, cation exchange capacity, chemical and mechanical stability, abundance, low costs, surface and structural properties (Maciver et al., 2020; Perego and Carati, 2008; Peng et al., 2020) have made them significantly important for wide applications and uses in industry environmental management (Mamudu et al., 2020). For instance, clays with high kaolinite content, low Fe_2O_3 and low quartz impurities are preferred for ceramic applications while clays with high surface area, high CEC and negative surface charge are required for water treatment (Adebowale et al., 2005).

Nigeria in general and Enugu State in particular is endowed with significant clay deposits yet many remain under-characterized and under-utilized. Recently, the demand for locally sourced clays has increased due to their application in ceramics, water treatment, construction, catalysis synthesis of nanocomposite derivatives (Vincent et al., 2013; Crini et al., 2010 and Rao et al., 2013). Clay deposits are wide spread in Nigeria. Studies have identified deposits in regions such as Ogun, Ekiti, Enugu and Anambra as being rich in industrial quality clay minerals (Inegbenebor et al., 2016; Igwe et al., 2005). Enugu State in particular, has been noted for Kaolinitic clays suitable fir ceramic and water treatment (Ugwoke and Amalu, 2017). Noteworthy is the fact that each clay deposit has unique properties or characteristics that can be tailored towards a particular industrial uses and applications. For instance, studies in the southeast have shown that clays from locations such as Nsu (Imo State), Afuze (Edo State) and Nsukka (Enugu State) exhibit properties suitable for ceramics, refractory bricks and oil drilling (Ihekweme et al., 2021; Ikhane et al., 2020). However, little has been documented about Inyi clay deposit despite anecdotal reports of its use in local pottery. Inyi clay deposit in Oji-River L.G.A., Enugu State has remained relatively untapped, unexplored, uncharacterized and under- studied. Besides the works of Ugwoke and Amalu (2017), it has not been adequately and comprehensively characterized. A detailed characterization in literature is required to ascertain its mineralogical identity and industrial viability especially in the area of water treatment and wastewater remediation.

While numerous studies on clay deposits in Nigeria have been evaluated, knowledge gap still exist, particularly in localized and unexplored regions like Inyi-achi in Enugu state. Given the global shift towards sustainable materials and local resources utilization, evaluating the Inyi-achi clay deposit could reveal valuable industrial potentials. This study seeks to characterize the Inyi clay deposit through physicochemical, mineralogical, textural, structural and other standard techniques or tests. Advanced standard techniques such as x-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier transformed infra-red spectroscopy (FTIR) were used. Findings from this study aims to establish the industrial relevance of this clay and also guide potential utilization strategies. Besides, it will contribute to the sustainable exploitation of local clay resources as a competitive and substitutive alternative to similar imported materials.

III. MATERIALS AND METHODS

A. Materials

Sample Collection and Preparation:

The clay sample from Inyi-Achi was obtained or mined from an excavated swampy site having established geological deposits of natural clay mineral situate at "Enugu-Inyi" village in Inyi town with the help of the locals (villagers). Samples were placed in a polyethylene bag and transported to the laboratory.

In the laboratory, the sample was washed thoroughly first with water by suspending it in ordinary water with continuous stirring for 10mins in order to remove soluble salts and impurities; the slurry was allowed to settle for 12hours. At the end of this period, the suspended material was removed by wet-sieving method. The solid sample was dried for 24hours at 60oC using air-oven method. The dried solid sample was crushed with pestle and mortar, sieved to <12μm fine size. The fine particle powdered clay was treated with 0.5M HN03 for 8hours (Mekewi et al., 2015) to oxidize any organic matter still remaining in the sample.

Finally, the resulting clay sample was dried again in an oven (60oc for 24hours) crushed, grounded or pulverized and sieved to a fine powder and texture. The now purified clay sample was covered with a sieve clothing material to prevent dust and contacting other solid impurities. The clay sample was labeled as raw clay and kept for analysis and characterization.

Chemicals and Reagents:

All the chemicals used in this work were of standard analytical grade and were used without further purification.

Equipment:

All the equipment, chemicals, analytical grade, reagents, solid granules and powders used in this work were the properties of Graceland Analytical Laboratory Ltd, Awka, Anambra State and Federal Analytical Global Concept, 77 Pipeline Road, Onuogba Nike Off Old NNPC Depot, Abakaliki Express Road, Enugu, Nigeria.

B. Methods

The physicochemical analysis was performed on the raw analytical clay sample (RC) based on the principles and procedures outlined for examination of physicochemical characteristics of solid samples (AOAC, 2005) and as described in previous studies for: pH (Daniel et al., 2015); specific surface area (Osmanliogolu, 2007; Bhattacharyya and Gupta, 2009), moisture content (Hameed et al., 2008); mineral constituents (Struijk et al., 2017) loss on Ignition (Struijk et al., 2017)) and cation exchange capacity (Daniel et al., 2015). The elemental was determined using. Atomic Adsorption spectroscopy (AAS) after digestion of the sample with nitric acid and hydrofluoric acid (Akpomie and Dawodu, 2016). The X-ray diffraction (XRD) was done using model MD 10Ramdicon diffractometer, 25kv and 20mA; Fourier Transform Infra-red spectroscopy was done using (FTIR, Shimadu 8400s) spectrophotometer to investigate the surface functional groups and scanning electron microscopy (SEM) using (SEM Hitachi 54800) to access the morphology and porosity.

IV. RESULTS AND DISCUSSION

A. Result of Physicochemical Analysis

The physicochemical result is presented in table 1. A pH of 6.55 indicates slight acidic nature of the clay. It has very low surface area and would require modification to enhance the physical properties. The low surface area may be due to impurities such as quartz and calcite present in the clay mineral (Khenif et al, 2007). This value coupled with pH (6.35) and CEC (17.52 C.mol/kg) suggests the clay has low activity with high geological weathering (Agbai et al., 2022). Cation exchange capacity (CEC) refers to the ability of the clay mineral to exchange positively charged ions (cations) from aqueous solution (Daniel et al., 2015). A high CEC suggests a great capacity of the clay to adsorb and retain cations. Thus, Inyi clay mineral has the potential to adsorb heavy metal ions from wastewater or effluent, therefore can be applied in water purification. The high loss-on-ignition content (15.60%) suggests presence of occluded matter (i.e organic matter, CO_2, water trapped in pores and edges), while the moisture content (10.44%) indicates more adsorption sites retaining water than being available as site for contaminant adsorption. Moisture content is a measure of the amount of water retained by the clay after treatment or purification.

The chemical constituent influences her ability to remove toxic ions from aqueous solution. Silica (SiO_2), alumina (AL_2O_3) and irons (Fe_2O_3) are the major chemical components of the clay mineral. The observed values agree very well with the ones found in literature (P. Souza Santos, 2022). The low content of CaO (3.70%) suggests low amount of calcium carbonate (Sadki et al., 2014). The presence of the mineral as shown in table indicate that the clay mineral has the potential for heavy metal remediation from contaminated media due to her exchangeability properties. Therefore, the clay soil can be applied in adsorption technology.

The $Si0_2/Al_2O_3$ ratio (1.72%) indicate the presence of alumino-silicate minerals, specifically those of a 2:1-layer structure (eg; Illite, vermiculite and montmorillonite). Since montmorillonite is a dominant and prominent example of a 2:1 clay mineral mostly found in soils, Inyi clay mineral could be said to be montmorillonite clay type. The high contents of silicon, aluminium and iron indicate high adsorption capacity potentials due to strong electrostatic interactions, cation exchange and surface complexation properties.

Table 1: Physicochemical Result of Inyi Clay

Property	**Raw Clay (% wt)**
pH	6.55
CEC (C.mol/kg)	17.52
Surface area (m 2/g)	49.0
Loss on Ignition (%)	15.60
Moisture (%)	10.44
Silica	37.48
Alumina	21.84
Iron	11.48
Zinc	10.22
Titanium	9.32
Magnesium	6.01
Manganese	2.31
Calcium	3.70
Copper	0.55

B. Scanning Electron Microscopy Result.

The SEM micrograph of the raw clay is shown in figure 1. The image shows a heterogeneous, regular and highly aggregated surface structure with multiple pores, cracks and voids distributed across the surface and contributing to high surface area (i.e., adsorption sites). Also, it has coarse and rough texture indicating poor purification, and white crystalline particles, indicating salt, iron oxide and carbonate impurities typically found in raw clays (Wilfred and Akinwunmi, 2016). The highly uneven morphology and void spaces provides active sites for physical adsorption and a well enhanced diffusion and retention of pollutants in water. These features suggest that lnyi clay has naturally rough and porous structure with potential adsorption capacities (Ihekweme et al., 2020).

C. XRD Analysis Result

The XRD analysis of the raw clay sample reveals a complex mineralogical composition, highlighting the dominance of quartz and albite and other minor minerals including Orthoclase, Kaolinite, Muscovite and Goethite. The diffractogram showed multiple sharp and moderate peaks indicating a well-ordered crystalline structure. Several strong peak patterns corresponding to quartz were observed at 2θ at about 26.6^0, 33.4^0, 39.4^0, 42.5^0, 50.1^0, $54,8^0$, and 60.1^0, and Albite appeared at about 28.1^0, 31.7^0, 32.1^0, and 44.5^0. Secondary peak patterns corresponding to orthoclase was observed at about 27.8^0, 28.9^0, 32.1^0, 35.9^0, 39.2^0, and 43.3^0, Kaolinite mineral phase at 2θ was observed at about 12.5^0, 25.0^0, 35.2^0, and 39.6^0, while Muscovite mineral phase was observed at about 2θ at 27.1^0, 35.2^0, 44.8^0, and 46.4^0. Goethite peaks were observed at 33.3^0, 36.0^0, and 49.9^0

Figure 2b is the pie chart representing (quantitatively) the relative abundance of each mineral phase in lnyi clay. It revealed a complex mineralogical composition highlighting the dominance of quartz constituting 46(10) % and albite, 20(4) %, including other minor mineral phases such as kaolinite 14(5) %, muscovite 79(19) % a layered structure mineral, goethite 7(3) % an iron-oxide hydroxide mineral that influences redox reactions and metal ion adsorptions and orthoclase 4.5(10) %. The quantitative analysis shows that the raw clay contains a combination of highly adsorptive (kaolinite, Goethite, muscovite) and structurally stable (quartz, albite, orthoclase) mineral phase. However, the relatively low percentage of kaolinite and Goethite, suggests the raw clay is good ceramic industry, but may not be highly efficient in its natural state, therefore requires modification for use in water treatment.

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D. FTIR Analysis Result

Result from the FTIR Spectrum (Figure 3) shows absorption bands between 4000cm^{-1} and 500cm^{-1} The bands of 3882 cm^{-1} and 3435cm^{-1} corresponds to the inner – OH stretching vibration of alcohol functional group which facilitates contaminants (e.g. heavy metal) adsorption by providing additional binding sites through hydrogen bonding (Li, Y. et al 2014), while the peaks at 2516cm^{-1} and 1412cm^{-1} represents outer –OH stretching vibration typical of carboxylic acid particularly associated with Kaolinite minerals, suggesting the clay is kaolinite (Sdiri et al, 2018; Bukalo et al.,2017). However, the strong intensity and sharp peak at 2516cm^{-1} strongly indicate –OH stretching vibration of carboxylic acid group (Ihekweme et al, 2020).

V. CONCLUSION

The main aim of this work is to investigate the inherent characteristics of Inyi clay sample to access its suitability, particularly for use in water purifications and other industrial and environment applications. From the results obtained, it follows that Inyi clay is a slightly acidic clay with silica/alumina (SiO_2/Al_2O_3) ratio 1.72% indicating alumino-silicate minerals of 2:1-layer structure, suggesting that Inyi clay mineral deposit is mainly Montmorillonite dominated type of clay which is suitable for many industrial and environmental management applications. The high content of silicon, aluminum and iron signify its high adsorptive characteristics and potentials due to strong electrostatic interactions, cation ion exchange and surface complexation. The FTIR spectra bands revealed that the clay contains inherent admixtures and functional groups characteristics of Kaolinite or Montmorillonite clay mineral while the X-ray diffraction analysis revealed a complex mineralogical composition, highlighting the dominance of quartz and albite and other minor minerals. Images obtained from SEM analysis showed a heterogonous, irregular and highly aggregated surface structure and crystalline in nature. Generally, the clay possesses desirable mineralogical and physicochemical attributes for use in water remediation, catalysis and other environmental and industrial applications.

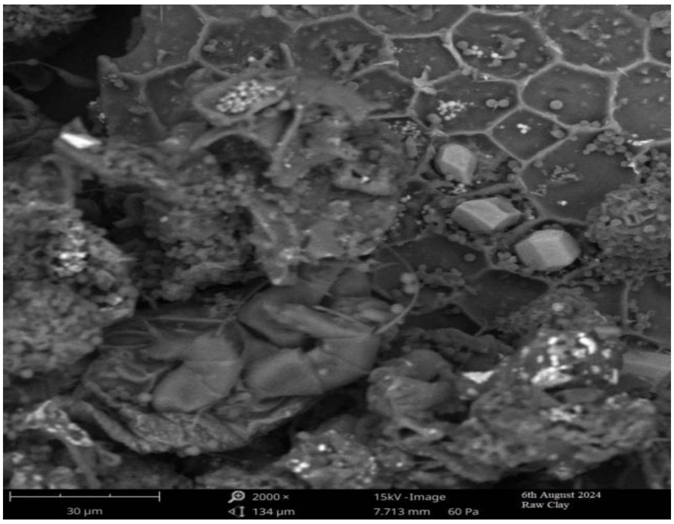

Fig.1: SEM Image of Raw Inyi Clay

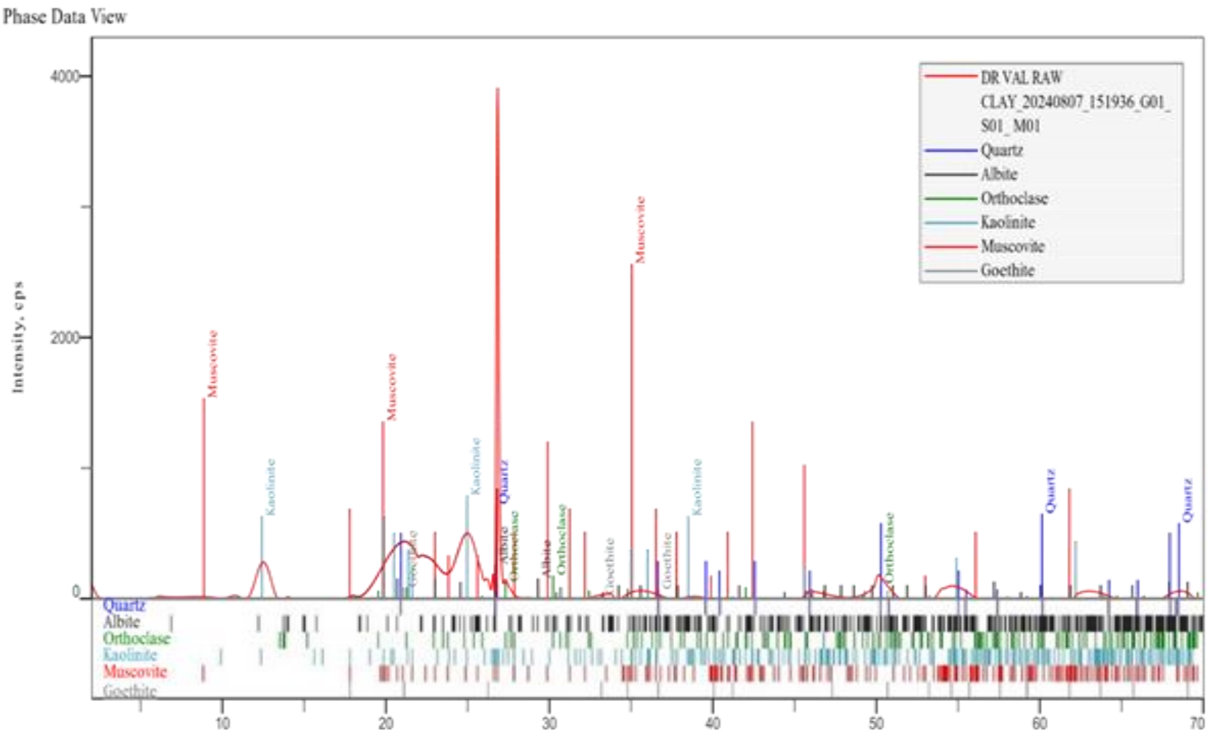

Fig.2a: XRD Diffractogram of Raw Inyi Clay

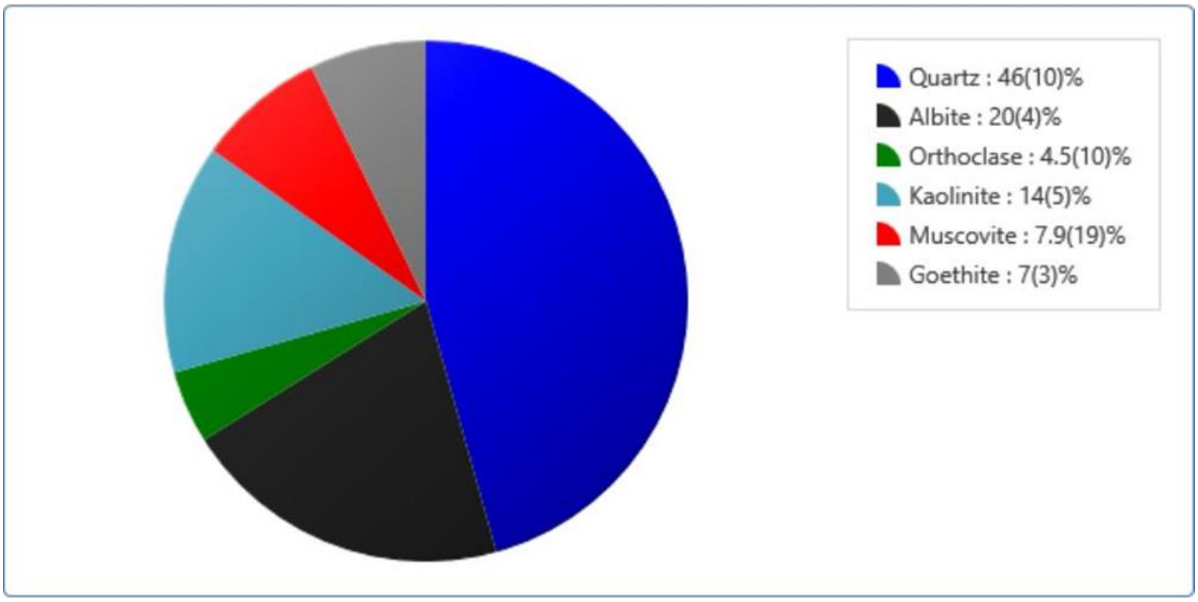

Fig. 2b: XRD Phase diagram of Raw Inyi Clay

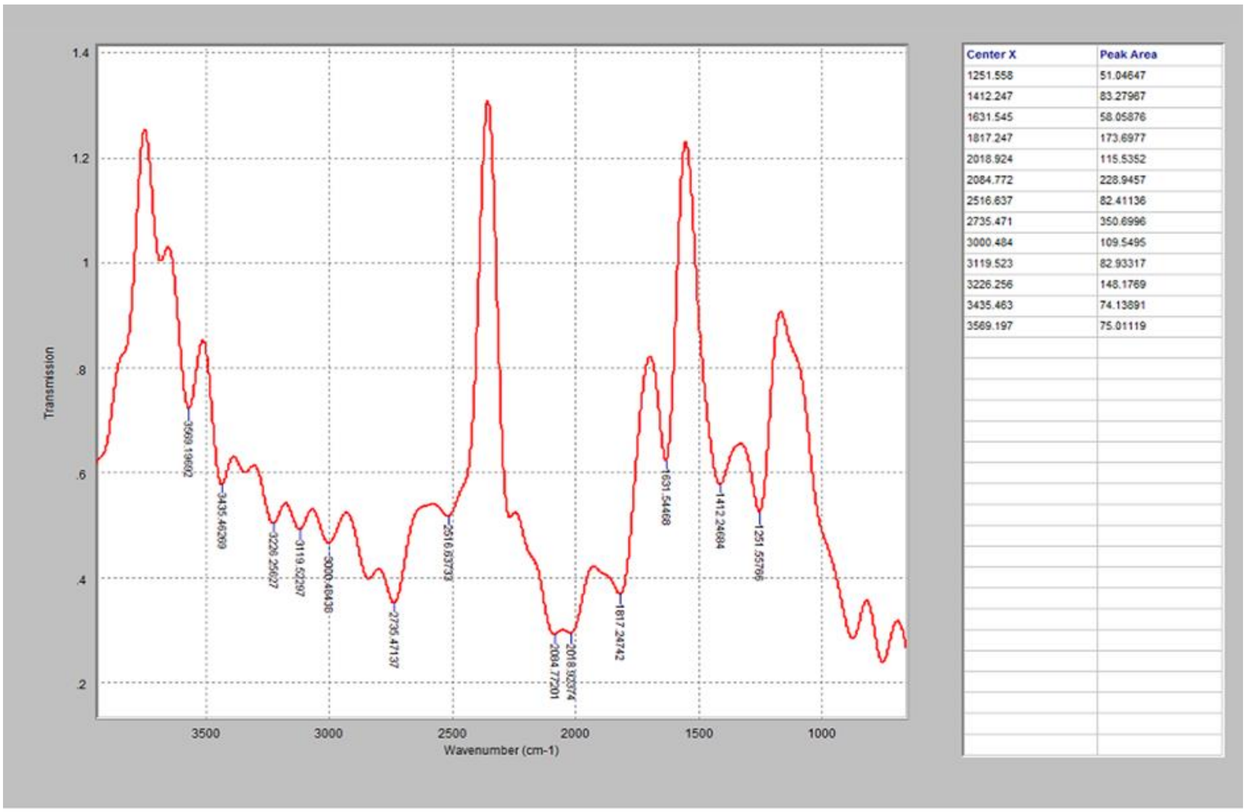

Fig. 3: FTIR Spectrum of Raw Inyi Clay

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