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XRD Analysis and Mineralogical Composition of Sodium/Copper Nanocomposite Clay of Nigerian Origin

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Abstract **Original Research Article**

The study investigated the mineralogical and crystallogical structures of natural and sodium/copper nanocomposite modified clay derived from a Nigerian clay deposit for potential application in adsorption process. The aim is to evaluate their structural and textural modifications and suitability for use in water purifications. The raw clay sample was purified and afterwards modified through sodium activation and subsequent impregnation of copper nano particle to obtain sodium/copper nanocomposite clay (Na/Cu-NC) by simple green method. The raw clay and the modified clay were subjected to some physicochemical analysis using standard (AOAC) methods, while the mineralogical composition was determined using XRD to confirm surface modification and structural integrity. The physicochemical analysis result revealed a successful functionalization of the raw clay with increase in surface area (49 – 123 m2/g), cation exchange capacity (17.52 - 21.54 mol/kg) and lowering of loss-on- ignition (15.60 – 11.95%), indicating enhanced surface reactivity and improved adsorption potential. The XRD result revealed presence of quartz (46%), albite (20%), kaolinite (14%) as the dominant minerals in the raw clay while quartz (37%) and goethite (39%) were the dominant minerals in the nanocomposite derivative. Modification led to major significant shifts in peak intensities and basal spacing, indicating successful intercalation and structural rearrangements. The reported mineral composition and structural data suggest that sodium/copper nanocomposite clay exhibited improved physicochemical properties compared to the raw clay and is also highly functionalized for adsorption applications with strong presence of goethite, clinochlore and magnetite minerals contributing to its high adsorption capacity; making it a promising low-cost adsorbent for the removal of heavy metal ions from aqueous effluents and other environmental applications. These findings support the utility of locally available Nigerian clay as a viable precursor for the development of efficient adsorbents for water treatments.

Keywords: Composition, Crystallographic, Mineralogical, Modification, Nanocomposite.

1.0 Introduction.

The contamination of water resources with heavy metals (HMs) remains a significant environmental challenge due to its extreme toxicity and persistence in the environment (Abatal et al., 2021; Kinuthia et al., 2020; Ibupoto et al., 2018). Exposure to these HMs even at low concentration led to severe health issues such as cancer, ulcers, central nervous system disorder (CNS) and organ damage (Wang et al., 2016; Sudo et al., 2020). Therefore, the removal of HMs from effluents or contaminated water gained attention by researchers, scientists and water treatment experts. Among various treatment methods, adsorption technique was highly favoured because of its simplicity both in design and operations. Also, among diverse adsorbents used for HM removal, natural clay minerals gained popularity because they are naturally abundant, cheap, non–toxic and has wide applications due to surface reactivity and multifunctional properties (Yuan et al., 2011; Uddin et al., 2017; Pooja et al., 2021), therefore offer excellent choice adsorbent for the removal of HMs from water systems. Their use as adsorbent in water purification and heavy metal removal in effluents has proved effective (Adebowale et al., 2006; Boumedience et al., 2020). The use of clay-based materials in sorption technology is very much linked to their mineralogical composition, surface area, CEC, and crystallinity (Malu et al., 2017; Adekola and Abdue-Salam, 2015). Thus, detailed characterization of the mineral phases present in both the natural and modified clays is critical to understanding and optimizing their adsorption behavior/characteristics.

Nigeria in general and Enugu state in particular is endowed with diverse clay deposits many of which are underutilized. Research (Murray, 2007; Agu, 2025; Ugwoke and Amalu, 2017) shows that clay deposit from this region has promising potentials as adsorbent for both metallic and organic pollutants from aqueous media and comprise typically of minerals such as kaolinite, illite, montmorillonite and quartz whose properties influence their adsorptive efficiency (Abdus-Salam and Itiola, 2012; Iwuozor, 2019). However natural clay has its limitations (low surface area, high loss-on-ignition, low CEC) compared to its modified derivatives (Aggarwal et al., 2006; Hundal et al., 2001). Research (Adebowale et al., 2005; 2006) shows that the dominant mineral phase in clay significantly affects the physicochemical properties such as the porosity, CEC, surface area, etc., which in turn influences the adsorption capacity. For instance, kaolinite-rich clay is less reactive but thermally stable while montmorillonite-dominant clays show higher swelling and high ion- exchange properties (Olatunji et al., 2019; Murray, 2007).

Modification of clay minerals enhances the physicochemical properties and adsorption potentials (Okoya et al., 2021). Recent development in modifying clays with nanoparticle have shown some promising advancement or improvement in adsorption capacity and selectivity of metals (AL-Saadi et al., 2020) due to increased surface area, CEC, and surface chemistry between metal ions and adsorbent surface (Okoya et al., 2020).

Specifically, the use of copper nanoparticles (Cu-NPs) supported on sodium modified clay has emerged as a promising approach for enhancing HM removal from effluents. Copper nanoparticles (Cu-NPs) exhibit high reactivity and have been shown to effectively and efficiently adsorb HMs due to their large surface area, high surface-to-volume ratio (Mohan et al., 2014; Salavati-Niasari et al., 2013), redox reaction, availability of more adsorption sites, enhanced electrostatic interaction (Zhang et al., 2020; Eze and Obasi 2017) and metal ion complexation due to the presence of copper particles (Nassar et al., 2020; Santos et al., 2015). In Nigeria few studies have explored copper modified clays but available report indicates improved performance compared to its sodium modified variant (Umaru et al., 2022). The interactions of HMs with the adsorbent can be effectively studied by carrying out the mineralogical analysis (i.e., XRD analysis). The XRD analysis provides insight into the crystalline structure and phase mineral compositions of the clay material (Peters and Iyiola, 2021; Eze and Amusiem, 2020). Changes in peak positions and peak intensities reveal the alterations in crystal structure and interlayer spacing after modification. For example, shifts in basal spacing after modification suggests successful intercalation which correlates with enhanced adsorption properties (Malu et al., 2017). This analysis helps in evaluating the suitability of both the raw and modified (modified) clays for environmental applications such as heavy metal adsorption.

In this study the mineral phases of both (raw and nanocomposite) clay were determined and compared to understand the effects of chemical treatment and nanotechnology in adsorption systems. Transforming Nigerian natural clay into sodium/copper nanocomposite clay significantly improved the adsorption potential. Findings from this study would provide baseline data for selecting and optimizing Nigerian clays for water treatment and environmental remediation. Moreover, it is expected that findings from this study would also contribute, expand and validate the development of cost effective and efficient adsorbent for the removal of HMs from industrial effluent, thereby addressing environmental and public health concerns associated with HM pollution.

2.0 Materials and Methods

2.1 Materials

2.1.1 Sample Collection and Preparation

The clay sample from Inyi, Oji-River L.G.A., was obtained or mined from an excavated swampy site having established geological deposits of natural clay mineral situate 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 clay sample was washed thoroughly first with ordinary water with continuous stirring for 10mins in order to remove soluble salt and impurities and the slurry is 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 24 hours at 60^{o}C using air-oven method. The dried solid sample was crushed with pestle and mortar, sieved to ≤ 12 microns fine size. The fine particle powdered clay was treated with 0.5M HNO_3 for 8 hours (Mekewi et al., 2015) to oxidize any organic matter still in the sample.

Finally, the resulting clay sample was dried again in an air oven at 60^{o}C for 24 hours, crushed, grounded or pulverized and sieved to a fine powder and texture. The now purified clay sample was covered with a sieving cloth material to prevent dust and contacting other solid impurities. The clay sample was labeled as raw clay (RC) and kept for analysis and characterization.

2.1.2 Preparation of Na-Clay (Sodium clay).

In order to obtain the nanocomposite clay, the raw clay was modified first with NaCL solution by method of Anirudham and Ramadran (2015). 25g of the raw clay (RC) was carefully dispersed in a 500mL, 1M NaCL and agitated for 12 hrs. at room temperature using mechanical stirrer. The suspended clay was filtered using Whatman No. 1 filter paper. The wet clay was dispersed again in another 500mL, 1M NaCL and agitated for 12 hrs. and the whole process was repeated five more times. The wet clay obtained was washed repeatedly till no trace of chloride ion was detected in the filtrate by conducting a simple $AgNO_3$ test for chloride. In this way sodium clay was obtained. The resultant wet sodium modified clay was oven-dried at 60^{o}C for 72 hours; grounded using pestle and mortar, sieved to obtain a fine texture and labeled sodium clay (Na-C) sample.

2.1.3 Preparation of Cu-Nanoparticle (Cu-NPs)

The Cu-nanoparticle was synthesized by method of Borah et al., (2010). Into a conical flask add 0.03g of copper chloride solution ($CuCL_2.2H_2O$) and 10 mL of distilled water, stir thoroughly till complete homogenization and keep. Into another conical flask dissolve 0.03g of Cetyltriammoniumbromide (CTAB) in 10 mL of distilled water and stir till homogenous mixture is obtained. Mix the two solutions together with a gentle drop-wise addition of ammonium hydroxide (NH_4OH) solution till a pH solution = 10 is obtained with the formation of a dark –blue precipitate. Label this solution 1. In another conical flask disperse 0.03g CTAB in 25mL of distilled water, mix thoroughly with 0.05 ml of hydrazine hydrate ($N_2H_2.2H_2O$) solution and label this solution 2. Finally mix solutions 1 and 2 together with continuous stirring under heat (80^{o}C). On homogenous mixing, color changes from colorless to light yellow to orange to brown and finally to red color. Formation of red colloidal suspension infers formation of copper nanoparticle.

2.1.4 Preparation of Sodium/Copper Nanocomposite (Na/Cu-NC) Clay.

The prepared copper nanoparticle was converted or modified to the corresponding nanocomposite by mixing 1g of Na-clay with 10mL of copper nano particle colloidal solution and heated to 80oC while stirring till formation of a metallic paste (Sodium/copper nanocomposite clay). The resulting wet metal/clay nanocomposite was dried for 24 hrs. at 70^{o}C to obtain sodium/copper nanocomposite clay adsorbent. This sample was kept under seal for further analysis and characterization.

2.1.5 Chemicals and Reagents

All the chemicals used in this work were of standard analytical grade except otherwise stated and were used without further purification. Sodium chloride (NaCl), Sodium hydroxide (NaOH), Hydrogen Peroxide (H_2O_2), Hydrochloric acid (HCL), Nitric acid (HNO_3), Ammonium hydroxide (NH_4OH), Sodium acetate (CH_3 COONa-3H_2O), Copper Chloride ($CuCL_2.2H_2O$), Hydrazine Hydrate ($N_2H_2.2H_2O$), Sulphuric Acid (H_2SO_4), Cetyltriammoniumbromide (CTAB)

2.1.6 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 State.

2.2 Methods

The physicochemical analysis was performed on the raw clay (RC) and sodium/copper nanocomposite clay (Na/Cu-NC) samples 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 composition was determined using Atomic Absorption 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 Randicon diffractometer (Model MD 10, 25kv and 20mA).

3.0 Results and Discussion

3.1 Result of Physicochemical Analysis

The physicochemical analytical result is presented in table 1. Both adsorbents are slightly acidic to neutral pH (6.35 – 6.55) with nanocomposite adsorbent being the most acidic (6.35). They are both suitable for heavy metal adsorption, but the slight variation in pH may affect the rate of adsorption. The surface area increased from 49 m^2/g (raw) to 123m^2/g (Na/Cu-NC). This is desirable and suggest higher propensity of the nanocomposite for metal ion adsorption. Modification of clay minerals enhance the physical properties (Adebowale et al, 2005); removes impurities such as quartz and calcite (Khenit et al., 2007); increase surface area due to decomposition of the smectite structure within the clay lattice (Eze and Obasi; Onyedoh et al., 2023). The low surface area of the raw clay may be due to presence of impurities such as quartz and calcite (Khenit et al., 2007). The low surface area, low pH and low CEC (17.52 C. mol/kg) suggests the raw clay has very low activity with high geological weathering (Agbai et al., 2022) unlike the Na/Cu – NC. The higher CEC (21.5 C.mol/kg) of Na/Cu- NC may be due to high level of isomorphic substitution (Grim In WHO, Geneva, 2005) and is typical of clay with TOT structure (Mekewi et al., 2016) coupled with the potential role of copper ions in chelation and complexation with heavy metals, giving rise to increased availability of exchangeable cation sites. Notwithstanding, both adsorbents has the potential to adsorb heavy metals wastewater or industrial effluent, therefore can be applied in water purification. The high loss-on-ignition content (15.60 %) for raw clay suggests presence occluded matter (i.e., organic matter, CO_2, H_2O trapped in pores and edges, while the high moisture content (10.40 %) unlike Na/Cu-NC (6.54 %) indicates more adsorption sites retaining water than being available as site for contaminant adsorption. Therefore, the raw clay is more likely to have lower removal efficiency and low adsorption capacity than Na/Cu-NC clay adsorbent.

The chemical constituents influence the ability of the material (adsorbent) to remove toxic ions from aqueous solution. Silica (SiO_2), alumina (Al_2O_3), and iron (Fe_2O_3) were the major chemical components common to the adsorbents, with the raw clay having the highest compositions of SiO_2 (37.48%), Al_2O_3 (21.48%), and Fe_2O_3 (11.48%). The observed values agree with the ones found in literature (P Souza Santos, 2022). The average compositions of Al_2O_3, MgO, MnO_2, CaO and CuO significantly vary among the clay minerals due to lixiviation of the oxides (Vasconcelos et al., 2014). Ca, Mg, Fe, Ti, P, K and Na were present in both clay samples. Their presence shows that both clay samples have potential for remediation of heavy metals from contaminated media due to their exchangeability properties with Na/Cu-NC being more efficient and effective. Therefore, the adsorbents can be applied in sorption technology (Awokunmi and Asaolu, 2017; Adekeye et al., 2009). The SiO_2/Al_2O_3 ratio of the adsorbents: raw (1.72%) and Na/Cu-NC (1.51%) indicate the presence of alumino-silicate minerals, specifically those of a 2:1 layer structure (e.g., illite, vermiculite and montmorillonite) (Nesse, 2000). The high contents of silicon, aluminum and iron in the raw clay indicates good adsorption capacity due to electrostatic interactions, cation exchange and surface complexation properties (Cao et al., 2019 and Gao et al., 2017). However, the high content of copper, phosphorus manganese, sodium and magnesium in Na/Cu-NC provide enhanced environment for ion exchange (i.e., higher CEC) and the potential catalytic properties of copper (Chakraborty et al., 2020), therefore making it more effective and efficient adsorbent HM ions in solution.

Table 1: Result of physicochemical analysis of Clay

Property	Raw Clay	Na/Cu-NC
pH	6.55	6.35
CEC (C. mol/Kg)	17.52	21.54
Surface area (m^2/g)	49	123
Loss on Ignition (%)	15.60	11.95
Moisture (%)	10.40	6.54
Silicon	37.48	22.64
Aluminum	21.84	15.08
Iron	11.84	11.42
Zinc	9.22	-
Magnesium	6.01	7.30
Manganese	2.31	2.80
Titanium	9.22	0.76
Phosphorus	1.01	1.53
Potassium	1.21	0.45
Sodium	5.54	18.15
Copper	0.53	19.42

3.2 Mineralogical Composition

3.2.1 XRD Analysis Result of Raw Clay.

The XRD analysis of raw clay sample revealed a complex mineralogical composition, highlighting the dominance of quartz and albite and other minor accessory minerals including orthoclase, kaolinite, muscovite and goethite. The diffractogram (fig.1a) 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^{o}, 33.4^{o}, 39.4^{o}, 42.5^{o}, 50.1^{o}, 54.8^{o}, and 60.1^{o} 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 2Θ at about 12.5^{0}, 25.0^{0}, 35.2^{0}, and 39.6^{0} while muscovite mineral phase was observed at 2Θ at about 27.1^{0}, 35.2^{0}, 44.8^{0}, and 46.40^{0}. Goethite peaks were observed at 2Θ at about 33.30, 36.00 and 49.90. The dominant quartz and albite minerals provide structural stability and mechanical strength for the material, suggesting high silica content (confirming the physicochemical result) which may affect adsorption selectivity. Kaolinite presence indicates good surface reactivity, which is typical of tropical soils and cation-exchange capacity (CEC), suggesting good adsorptive potentials, low shrink- swell potential and chemical stability (Olugbenga et al., 2019), while muscovite (a mica group mineral), goethite (an iron oxyhydroxide) and orthoclase (feldspar mineral) phases add some ionic contributions, strong affinity towards metal ions and contribute to slight variation in the physicochemical properties of the clay (Adebowale et al., 2016).

Quantitatively, figure 1b is the pie chart representing the relative abundance of each mineral phase. The chart confirms the raw clay consists of primarily quartz 46(10) %, indicated by several strong peaks with high intensity (fig.1a) most notably around 26.69^{0} at 2Θ. This was followed by albite 20(4) % with a distinct peak around 27.80^{o} and 28.00^{0}. Kaolinite 14(5) % was confirmed by notable peaks at about 12.50^{0} and 25.00^{0}. Muscovite 7.9(19) %, a layered structural mineral (Olu-Owolabi et al., 2017) with peak around 27.10, goethite an iron-oxide hydroxide mineral that influence redox reactions and metal ion adsorption with peak at 29.9^{0} and orthoclase, 4.5(10) % with a distinct a distinct peak at 27.90^{0}.

Summarily the XRD analysis of the raw clay shows that it contains a combination of highly adsorptive minerals (kaolinite, goethite, muscovite) and structurally stable (quartz, albite, orthoclase) minerals. The relative low contents of kaolinite and goethite suggests the raw clay may not be highly efficient in its natural state, therefore requires modification for adsorption applications, catalysis and other environmental remediation purposes (Olugbenga et al., 2019).

3.2.2 XRD Analysis of Sodium/Copper Nanocomposite clay (Na/Cu- NC)

The diffractogram (fig. 2a) displays sharp intense peaks, suggesting the presence of well crystallized phases. The XRD result shows a complex composition of quartz and goethite as dominant minerals, while magnetite, clinochlore and hematite as minor or secondary phase minerals. The characteristic peaks of 20.9^{0} and 26.6^{0} (2Θ) indicate strong presence of quartz which is common in many geological samples, providing the composite structural integrity. Peaks near 22.5^{0} and 33.1^{0} (2Θ) indicate goethite, suggesting iron-rich environment, signifying strong potential for heavy metal ion or contaminant adsorption. The presence of these minerals (quartz and goethite) increased with the deposition of copper nanoparticles. The emergence of a new mineral phase (hematite) observed with peaks at 24.10 and 32.2^{0} (2Θ) and magnetite enhanced the nanocomposite adsorption efficiency, magnetic properties and catalytic reactivity. The peak at about 7.4^{0} (2Θ) indicate clinochlore, a chlorite mineral commonly found in volcanic ash deposit. Clinochlore formation suggests a minor structural re-ordering, improving surface area and cation exchange capacity of the nanocomposite thereby aiding metal adsorption. The incorporation of copper nanoparticles seeks to induce the nucleation of iron oxide related phases such as magnetite whose peak was observed at 36.4^{0}. The presence of multiple peaks signify that the sample is a mixture of different crystalline phases with goethite, quartz and clinochlore appearing to be the dominant phases. The broad peaks indicate presence of nanoparticles, since smaller particles leads to broadening of peaks (Zhang et al., 2013).

The pie chart (fig.2b) illustrates the relative abundance of mineral phase within the nanocomposite clay. The reported mineral composition and structural data shows that Na/Cu-NC has large surface area leading to increased adsorption capacity, contain iron oxides which facilitates redox reactions and possess porous structures that enhance metal ion diffusion to active sorption sites. Compared to the raw clay, the nanocomposite clay has higher goethite content (increased reactivity of redox-based adsorption), lower quartz content (increasing active sorption sites) and presence of magnetic properties which allows easier recovery and re-use in water treatment.

Conclusion

The sodium/Copper nanocomposite clay exhibits a mineralogical composition conducive for effective heavy metal adsorption. The analysis report suggests that Na/Cu-NC clay are highly functionalized for adsorption applications with the strong presence of goethite and magnetite, contributing to their high metal binding capacity (or adsorption capacity), q_e. The mineralogical profile showed improved structural and adsorptive properties compared to the raw clay, making Na/Cu-NC clay a better adsorbent for heavy metal ion removal from contaminated water, thereby highlighting the importance and relevance of clay modification and nanotechnology in wastewater remediation process.

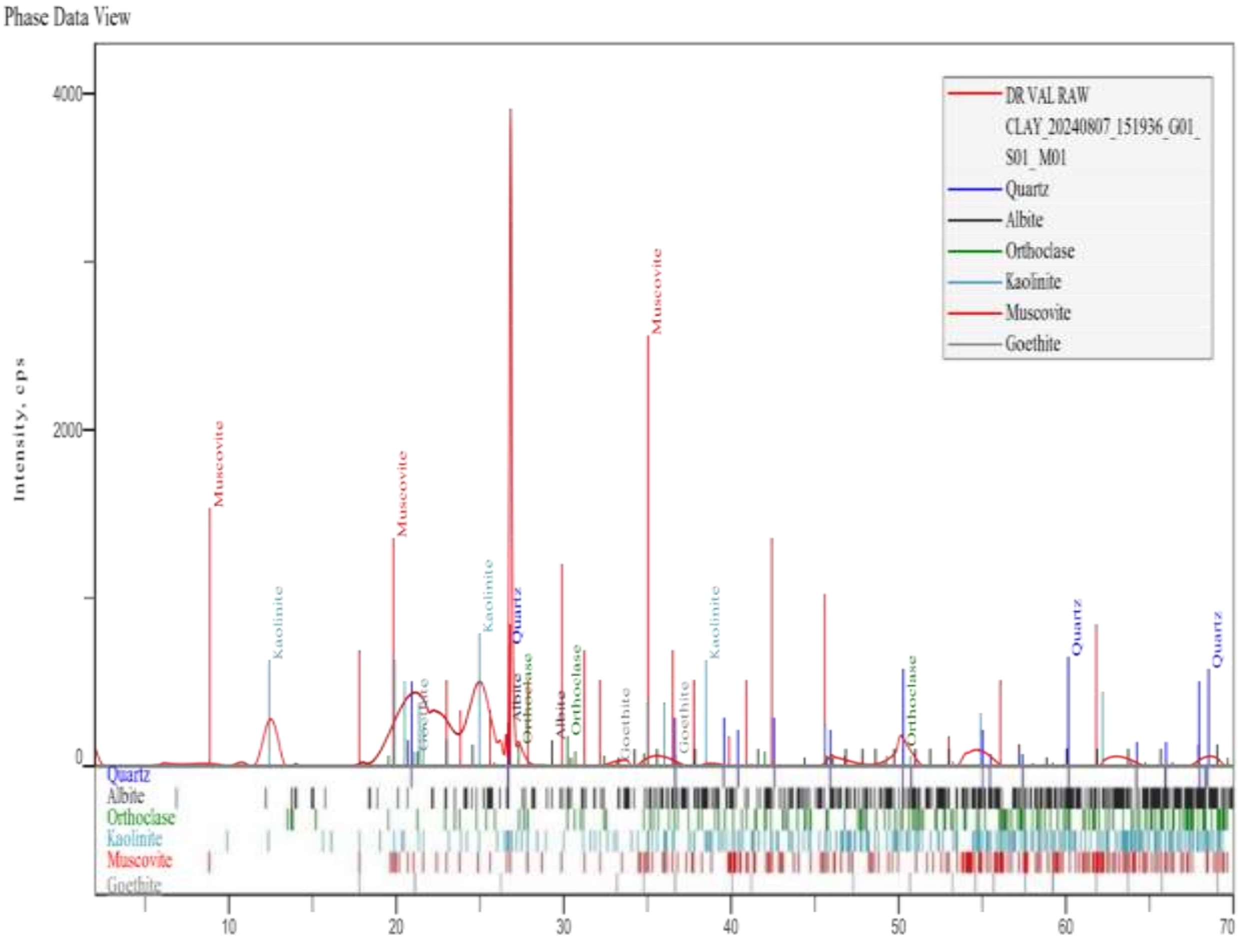

Fig. 1a: XRD diffractogram of Raw Inyi Clay

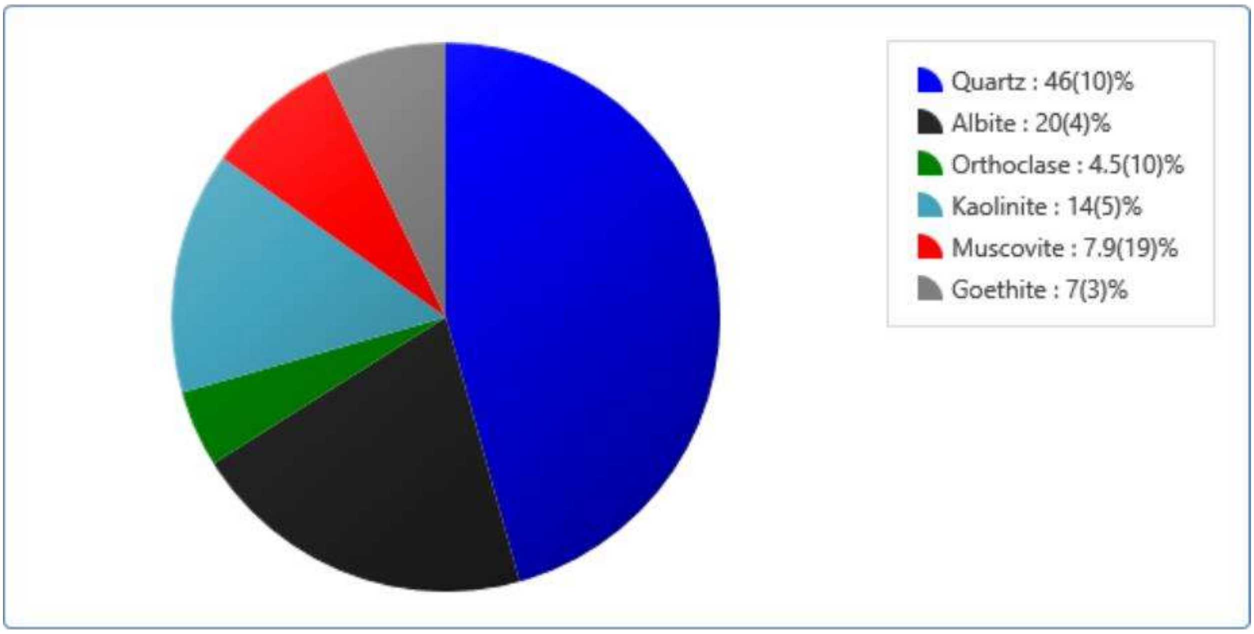

Fig.1b: XRD Mineral Phase of Raw Inyi Clay

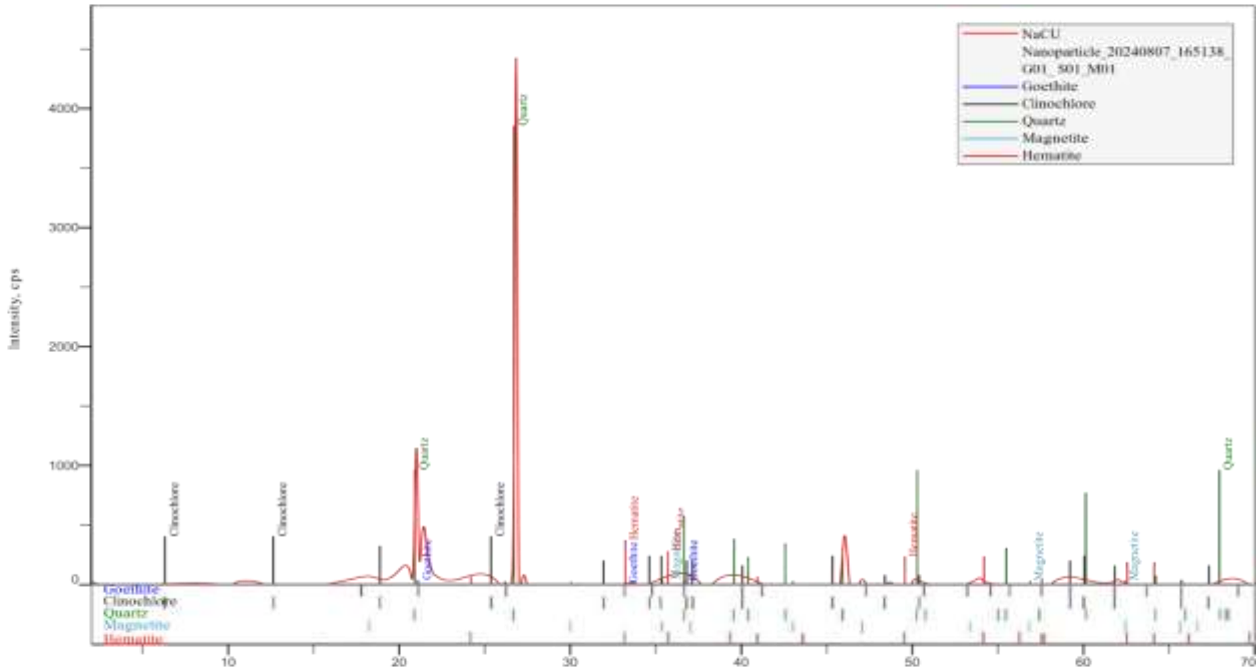

Figure. 2a: XRD Diffractogram of Na/Cu-NC clay

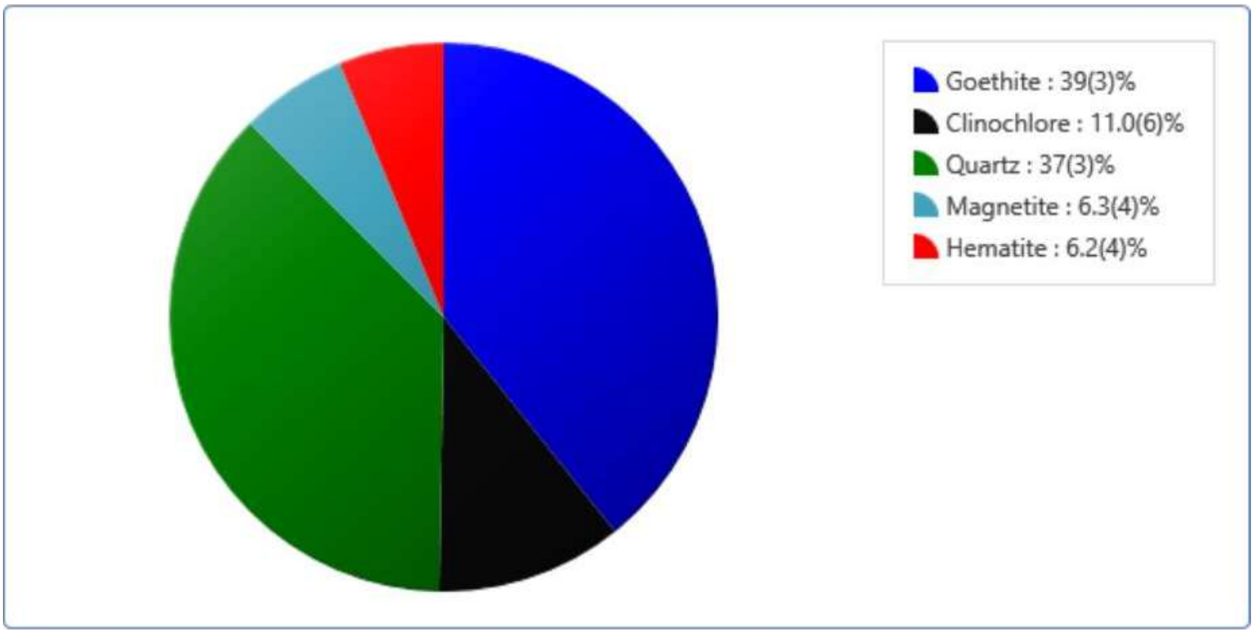

Fig. 2b: XRD Mineral Phase of Na/Cu-NC

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