Analysis And Characterization of Clay Earthy Mineral Aggregate Deposit from Nyeri County for Removal of Nitrates, Phosphates and Heavy Metals from Water

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https://doi.org/10.62049/jkncu.v5i1.417

Abstract

It is important to characterize clay minerals in order to be able to determine their applications. Knowing the characteristics of clay minerals can help us to understand their potential use in various fields, such as agriculture, construction, and manufacturing. Characterizing clay minerals can help us to identify the best possible applications for them, which can be beneficial for both the environment and society. To investigate the characteristics of the Nyeri County Clay minerals, various methods were used, such as X-ray diffraction (XRD), energy-dispersive X-ray fluorescence spectroscopy (EDXRF), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FT-IR). Before the characterization, the clay mineral was calcined at 700°C for 2 hours, then it was hydrothermally treated for 3 hours using an 8M NaOH solution and finally recalcined at 650°C for 2 hours. The paper aims to give suitable remediation for removal of heavy metals phosphates and nitrates in wastewater using natural clay soil.

Keywords: Fluorescence, Hydrothermal, Calcined, Microns, Alkalization, Porosity

Introduction

Clay minerals are a group of hydrous aluminium silicates that form from the alteration of other minerals, typically feldspar and mica[1].Clay minerals are found in soils, sediments, and sedimentary rocks, and are an important component of the Earth's crust[2].They are used in a wide range of industries, from pottery and ceramics to construction and agriculture. Clay minerals are composed of tiny particles of silicate minerals, which are held together by strong hydrogen bonds. The particles are typically less than two microns in size, making them very fine and allowing them to be easily manipulated. Clay minerals are generally categorized into different groups: kaolinite, smectite, and illite. Each of these groups has different properties and is used for different purposes [3].

Modifying clay mineral surfaces is a process used to improve the properties of clay minerals for a variety of applications [4]. The modification process involves treating the clay mineral surfaces with a variety of chemicals, such as surfactants, acids, and polymers. These chemicals are able to interact with the clay mineral surface and modify its properties [5,6,7& 8]. Alkalization of clay minerals is a process by which clay minerals are chemically altered by the addition of alkali metals. This process is used to modify the properties of clay minerals, such as their porosity, permeability, and surface area [9]. Alkalization can also be used to increase the reactivity of clay minerals, making them more suitable for use in various industrial applications [10]. The alkalization process involves the addition of alkali metals, such as sodium, potassium, and calcium, to clay minerals. These metals react with the clay minerals, causing them to become more soluble and more reactive. The resulting solution can then be used to modify the properties of the clay minerals. For example, the addition of sodium can increase the porosity of the clay, while the addition of potassium can increase the permeability. By understanding the process of alkalization, it is possible to create clay minerals with the desired properties for a variety of applications [11].

Characterization of clay mineral is the process of determining the physical and chemical properties of clay minerals. This includes identifying the mineral composition, chemical composition, particle size, and other physical properties. Clay minerals are important components of soils and sedimentary rocks and are used in a variety of industries, from construction to agriculture. Characterizing clay minerals is important for understanding their behavior in various environments and for predicting their use in various applications [12]. For example, clay minerals can be used as adsorbents for pollutants, and understanding their characteristics can help determine their effectiveness in this role. Characterization can also help to identify the source of clay minerals, which can be useful for understanding the geologic history of an area [13]. Characterizing clay minerals involves a variety of techniques, including X-ray diffraction, scanning electron microscopy, and chemical analysis. X-ray diffraction can be used to identify the mineral composition of clay minerals, while scanning electron microscopy can be used to determine particle size and shape. Chemical analysis can be used to determine the chemical composition of clay minerals, which can provide information about their reactivity and adsorption capabilities. Additionally, other techniques, such as thermal analysis, can be used to characterize clay minerals.

Materials and Methods

Materials

The clay mineral was collected in Nyeri County, Kenya, a site that had been explored by the Chinese some years back. Without any further treatment, the clay was placed in a sealed plastic bag in order to preserve its natural state. Once in the lab, the clay mineral underwent a calcination process at 700°C. Following this, it was hydrothermally treated with a very strong alkali solution. Alkali treatment was used to increase the surface area of the clay mineral, making it more reactive and easier to use in certain applications. The chemicals used were analytical grade.

Methodology

The clay mineral was first dried in an oven at 80°C for 12 hours. It was then finely ground using a motor and a pestle. The finely ground clay mineral was then calcined at 700°C using a muffle furnace for 2 hours. After that, 50 g of the clay mineral was mixed with 20 ml of 8M Sodium Hydroxide and placed in a pressurized cooker for 3 hours. Finally, the clay mineral was recalcined at 650°C for 2 hours using a muffle furnace.

For EDXRF analysis, a Malvern Panalytical Epsilon 4 X-ray Fluorescence Spectrometer was used to collect data. This spectrometer was equipped with a 15 W silver anode X-ray tube, a ten-sample changer, and a helium gas flush option. An energy dispersive silicon drift detector was also used. The samples were finely ground using a motor and a pestle and then packed into 4µm polypropylene XRF cups. The cups were placed in the beam, and the data was collected using Epsilon Software.

The XRD measurements were performed at room temperature, with the angle fixed between 4 and 90 ºC in 2θ. The diffractometer was equipped with a sealed copper tube X-ray radiation source (=1.5406) and the Soller had apertures on both sides of the incident receiving optics. The detector used was the PixCel3D Medipix. The particles were finely grinded and packed in a metal sample cup, which were placed in a monochromatic x-ray beam. The XRD doors were opened and the samples were loaded, then the doors were closed and the parameters were set to a step size of 0.5 -0.1 – 2q and a set time of 1s. The samples were then scanned and the data were recorded.

A FEI Nova NanoSEM (WSLR S044) scanning electron microscope was used to analyse the samples 'morphology. Before the analysis, the samples were sprinkled on a double-sided carbon and polished with epoxy. The samples were then dried in an oven for 3 hours at 65°C. After drying, the samples were loaded into the SEM holder, and the doors were tightly closed. The parameters were then set to an acceleration voltage of 20kV and lowest magnification of 30X. As the samples were being scanned, the images were previewed and saved.

To prepare the samples for FTIR analysis, they were first dried in an oven for 3 hours at 90 ºC. Pellets were made using KBr in the ratio of 1:100 (samples: KBr) by weighing 100 mg of KBr and mixing it with 1mg of the sample, which was then grinded in a mortar using a pestle until it was thoroughly mixed. The samples were then placed in the sample holder and pressed using a hydraulic press at a pressure of 15psi for 90 seconds. After the pressure was released, the sample was gently placed in the FT-IR beam, which was

purged using nitrogen gas. Finally, the spectrum was recorded in the computer connected to the FT-IR instrument and plotted using excel.

Results and Discussions

EDXRF

Table 1 presents elemental composition EDXRF results for the analysed Soil.

Table 1: Elemental composition of kaolinite in percentage.

Kaolinite												
Si	Al	Fe	Ti	K	Ca	Mg	V	Mn	Sn	Cr	Ba	Nb
48.37	28.892	12.539	6.815	1.256	0.633	0.412	0.111	0.108	0.082	0.069	0.085	0.052
Zn	Na	Cu	Ni	Sr	Zr	Y	Ga	Te	Pb	Rb	Sb	As
0.051	0.05	0.048	0.035	0.035	0.27	0.021	0.017	0.015	0.013	0.012	0.006	0.002

Table 2 represents Metakaolinite percentage levels of various elements in the clay soil.

Table 2: Represents Elemental composition of alkali-modified kaolinite in percentage.

Metakaolinite												
Si	Al	Fe	Ti	K	Ca	Mg	V	Mn	Cr	Sn	Na	Ba
46.125	30.719	12.749	6.961	1.331	0.625	0.442	0.112	0.11	0.07	0.056	0.065	0.072
Nb	Zn	Cu	Ni	Sr	Zr	Y	Ga	Rb	Te	Pb	Sb	As
0.051	0.051	0.048	0.035	0.035	0.267	0.021	0.017	0.012	0.012	0.011	0.005	0.001

Table 3: Elemental composition of alkali-modified kaolinite in percentage

Alkali-Modified Kaolinite												
Na	Si	Al	Fe	Ti	K	Ca	Zr	Mn	V	Sn	Ba	Cr
36.102	26.625	19.426	10.233	4.893	1.433	0.449	0.237	0.088	0.078	0.075	0.058	0.054
Zn	Nb	Ni	Sr	Cu	Y	Ga	Te	Rb	Pb	Th	Sb	As
0.047	0.042	0.03	0.03	0.023	0.018	0.014	0.015	0.011	0.008	0.006	0.006	0.001

EDXRF was used to identify the different elemental compositions represented in Table1 after calcination of the clay mineral at 700 ºC, the clay mineral entered a dehydroxylated phase, which occurs when the clay mineral is heated between 400-800 ºC [14], resulting in the loss of the hydroxide group. Si and Al were the predominant elements in the raw clay mineral, identified as kaolinite 1A, and occupied 77.26% of the total elemental composition, indicating a high level of kaolinite purity in this clay mineral[15].The Si/Al ratio of the raw clay mineral (kaolinite 1A) was 1.6, which is slightly lower than the standard kaolinite Si/Al ratio of 1.8. Other minor elements such as Fe, Ti, K, and Ca were also identified as kaolinite impurities. After calcination at 700 ºC, the Si/Al ratio was reduced to 1.5 as the kaolinite transformed into metakaolinite, and the presence of Fe was detectable due to the sudden change in color of the clay mineral from pale grey to red [16]. Several studies have indicated that the average percentage of silicate in clay mineral varies between

47-48% [17]. However, during the hydrothermal treatment with sodium hydroxide, a huge shift was observed as the Si elemental composition was greatly reduced from 48.37 % to 26.625%. This is due to the precipitation of SiO_2^- making Na predominant with 36.1%.

XRD

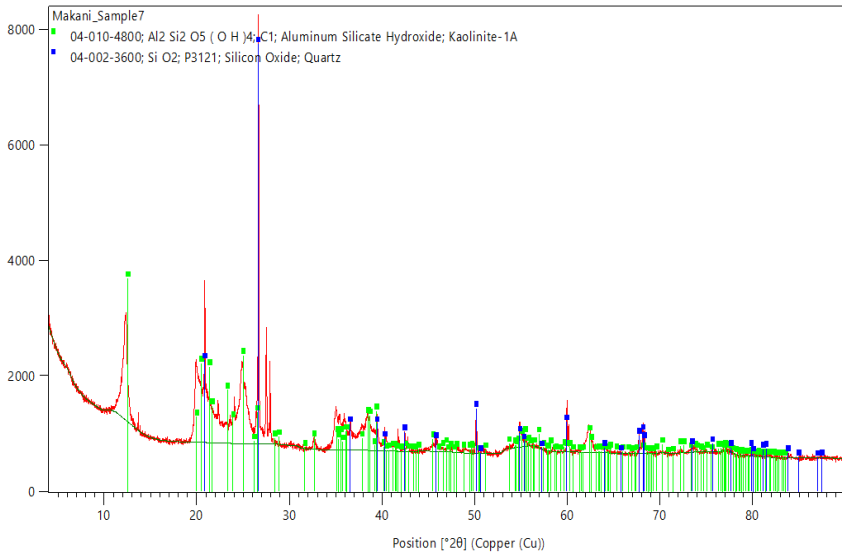

Figure 1: XRD patterns for kaolinite

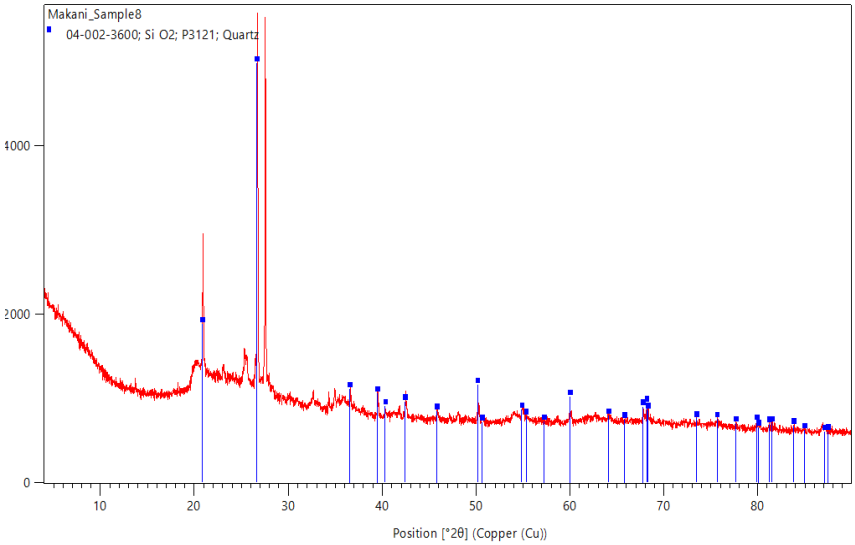

Figure 2: XRD patterns for Metakaolinite

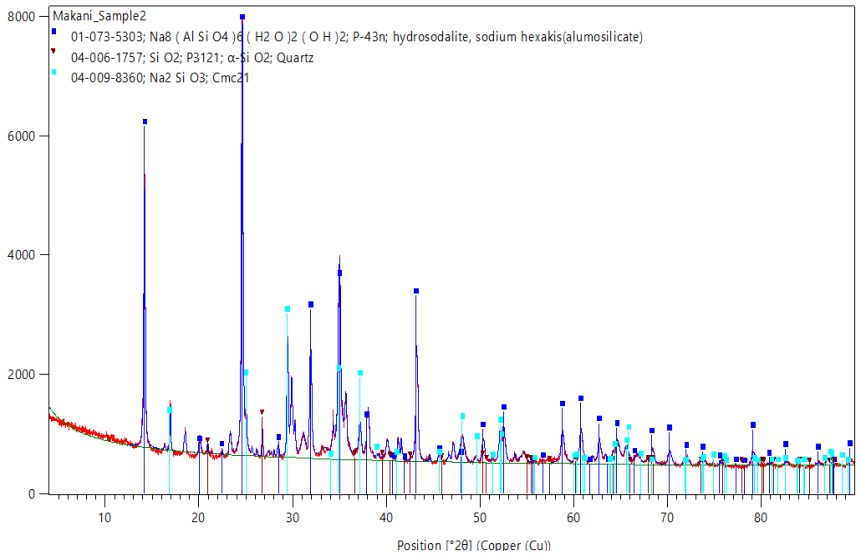

Figure 3: XRD pattern for Alkali-modified kaolinite

XRD is an important technique used in the characterization of clay minerals for determining their structural composition. It was used to deduce precise cell unit, size, peak position, intensity, and atomic arrangements from X-ray powder patterns. Using the Panalytical Data Collector Software, different types of clay mineral and non-clay were identified. Kaolinite 1A was the major crystalline point for the raw clay mineral (RK) which were detected in the 2θ range of 10-25°C, followed by quartz (figure 1). In 2016, Ombaka characterized samples of clay minerals in the neighbouring area and found that kaolinite was among the main clay minerals. After calcination at 700°C, the kaolinite X-Ray powder patterns disappeared due to the removal of the hydroxide group as water molecule and the formation of metakaolinite, also known as low quartz (figure 2) [18]. Finally, after the hydrothermal treatment of metakaolinite using NaOH at 8M concentration, the characteristic peak was able to be detected around… indicating the presence ofhydrosodalite, sodium hexakis ($Na_8(AlSiO_4)_6(H_2O)_2(OH)_2$). Lapides and Zhang [19:20] found similar results. The alkalinization of the metakaolinite transformed the metakaolinite surface, as its amorphous structure was altered to a crystalline structure. This transformation is observed through the sharpness of the peaks in the X-ray diffraction pattern.

SEM

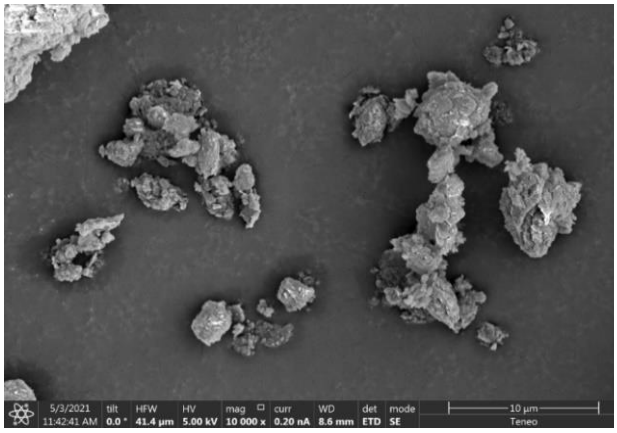

Figure 4: Kaolinite

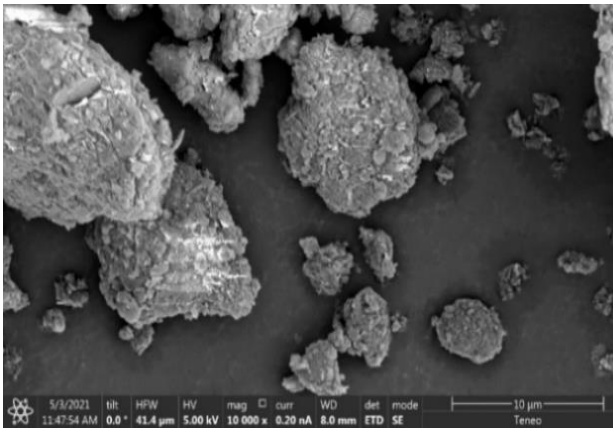

Figure 5: Metakaolinite

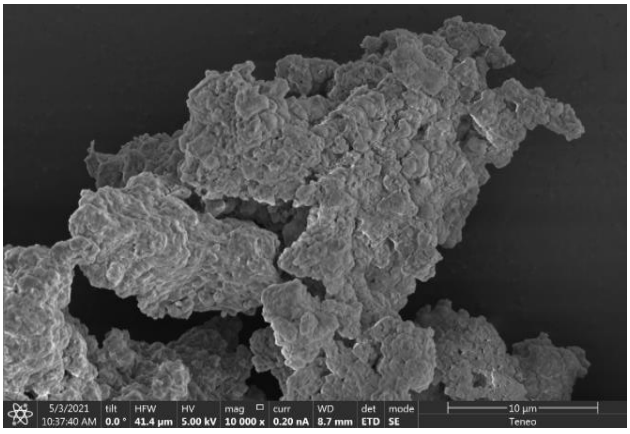

Figure 6: Alkali-modified kaolinite

The particle size and distribution of clay minerals are important factors in their application. For adsorption, smaller particle sizes have higher adsorption capacity. The raw clay mineral (Figure4) had particle sizes below 2µm with an irregular, disordered surface area, similar to other kaolinite studies [21]. The calcined clay mineral (Figure 5) had a similar irregular, disordered surface area, but with particle sizes less than 2µm. The difference between the Kaolinite and the Metakaolinite was observed at the agglomeration levels, with the kaolinite having particles gathered in smaller quantities compared to the Metakaolinite.The surface morphology of Metakaolinite was greatly affected by alkalinization. It was observed that the particles of Metakaolinite were drawn together, forming larger agglomerations which tend to have crystal structure rather than the original amorphous structure. This result collaborates with the XRD's finding as it was observed that the kaolinite and the metakaolinite had broad peaks, amorphous structure, and the alkali modified kaolinite had sharp peaks (crystalline structure). The alkali-modified kaolinite had an irregular; heterogeneous surface closely agglomerated with very small pores of less than 0.5 µm.

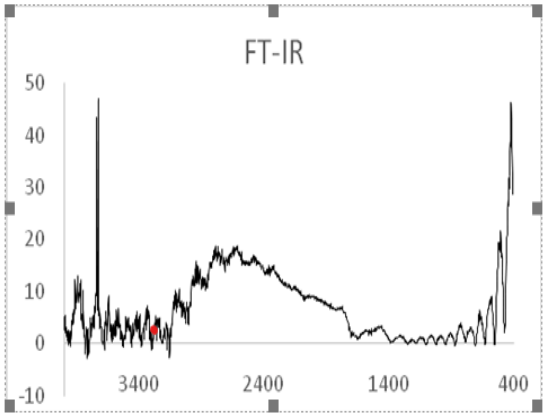

Figure 7: FT-IR Kaolinite

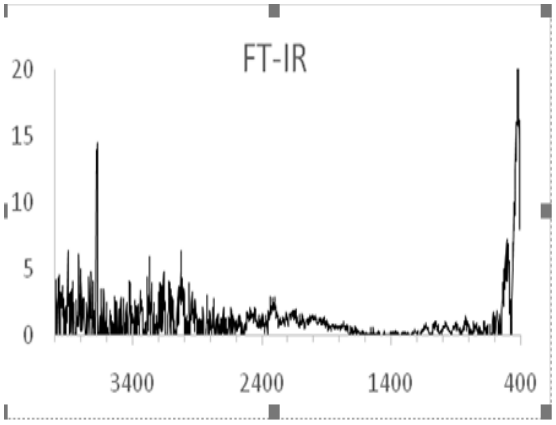

Figure 8: FT-IR metakaolinite

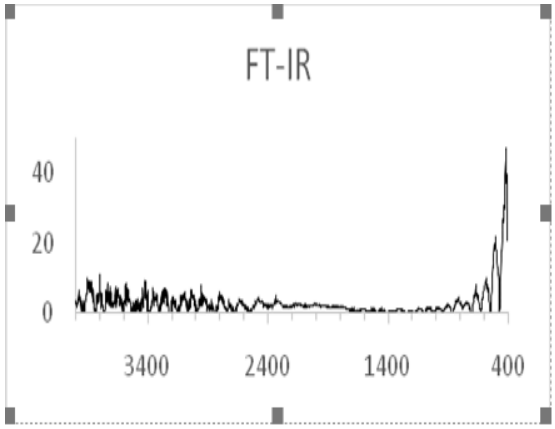

Figure 9: FT-IR alkali-modified kaolinite

The FT-IR spectrum of the three samples showed similar profiles, with the presence of O-H stretching at 3732- 3400 cm^{-1} and Si-O stretching at 418cm^{-1}. However, there was a difference in the O-H stretching. For kaolinite (figure 7), the peaks were at 3743 and 3729 cm^{-1} and had a high intensity, indicating an O-H free stretching, which is similar to other kaolinite studies [15;22]. Metakaolinite had weak peaks at 3646 cm^{-1} (figure 8), suggesting that the O-H bonds were not free, but were H-bonded due to the water molecules lost during the calcination process. Finally, for the hydrothermal treated clay mineral spectrum, some weak peaks were detected around 3400cm^{-1} (figure 9), indicating an O-H, H-bonded stretch.

Conclusion

The natural clay found in Nyeri County was identified as kaolinite 1A using X-ray diffraction (XRD). The purity level of the kaolinite was determined to be 77.26% using energy-dispersive X-ray fluorescence spectroscopy (EDXRF). Further analysis using scanning electron microscopy (SEM) revealed an irregular heterogenous surface morphology and Fourier transform infrared spectroscopy (FT-IR) analysis deduced a high intensity peak between 3743 and 3729 cm^{-1} indicating the presence of kaolinite O-H free stretching. After calcination at 700°C, the kaolinite was transformed to metakaolinite, also known as low quartz, as the OH was lost as water molecules. From the FT-IR analysis after calcination, weak peaks were detected

around 3646 cm^{-1} suggesting that the O-H bonds were not free but were hydrogen-bonded due to the water molecules lost during the calcination process. After alkanilization, sodium became the predominant element (EDXRF), as the alkali-modified kaolinite was able to be identified as hydrosodalite, sodium hexakis (XRD). Additionally, the particles became more agglomerated (SEM), making them easier to handle for variousapplications.

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