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Synthesis and Characterization of Novel Nanosilicates from Kenyan Indigenous Microporous Clay

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Abstract

This study reports the synthesis of novel sodium nanosilicates extracted from locally available Kenyan clay. The synthetic method involved thermal calcination of the clay at 1000 ^{0}C followed by alkaline extraction with sodium hydroxide (NaOH) at 75 ^{0}C. The calcination temperature of 1000 ^{0}C was ideal for enhancing the conversion of silica components and decreasing the alumina components by making them soluble in the extracting base. Different concentrations of extraction medium (NaOH) were evaluated. The clay and the synthesized nanosilicates were characterized by X-ray fluorescence (XRF), Energy Dispersive Spectroscopy (EDS), Fourier infra-red (FTIR) spectroscopy, Field emission scanning, and transmission electron microscopy (FESEM & FETEM), and X-ray diffraction (XRD). 20% (w/v) NaOH was found to be the most appropriate concentration as revealed by XRF and EDS data which showed better silica content.

Keywords: Sodium nanosilicates; Microporous clay; thermal calcination; Base extraction.

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1. Introduction

Over the last century nanoscience, research and application have unlocked massively in various fields of sciences including nanochemistry, drug delivery systems [1**]**, chromatography, sensors, and biomedical research [2**]**. For instance, Silicon nanoparticles have been used in drug delivery and gene therapy [3], Various opportunities and challenges that are related to nanoscience have been identified periodically. In materials science, the use of nanosilicates has shown significant improvement in the construction industry [4], while as in environmental remediation, the advent of nanotechnology has formed an enormous projection of producing desired nanomaterials for that purpose [5]. Mesoporous silica has been used as a catalyst for various specialized catalysis reactions [6]. Elsewhere, silica nanoparticles have been used in plants to ameliorate the effect of salinity so that they can last through drought periods and saline atmospheric conditions [7]. Bentonite clay contains mainly silicates alongside alumina components [1], and various methods are normally used to synthesize silica nanoparticles from different sources [8]. Preparation of silica nanoparticles via the Sol-gel process using precursor tetraethylorthosilicate (TEOS) has been reported [9]. The use of sodium silicate solution (SSS) as a cheap precursor for the synthesis of silicates from rice husks, bagasse ash, rice straw ash by precipitating SSS with mineral acids such as hydrochloric acid (HCl) has also been reported [10]. The use of both acid and alkali in the leaching of silicates from clay sources is a commonly used technique in the preparation of silicates [11]. Due to the presence of alumina in all clay samples, calcination of the clay is an important step for its removal since the solubility of alumina in alkaline solution decreases with thermal treatment at temperatures exceeding 600^0C [12]. A combination of both acid and thermal treatments processes has been employed and yielded to micro-scaled silicates from clay [9], Sequential acid-alkali leaching of silicates from coal fly-ash and direct-alkali leaching has also been used in the synthesis of silica nanoparticles [13], Optimization of different extraction parameters such as extraction medium, temperature, and extraction time has been studied extensively and reported [14], An increase in temperature during the synthesis of silica from barley grain waste showed improvement in the mechanical properties of the silica nanoparticles. [15].

The study presents an easy method of synthesis of novel sodium nanosilicates particles from indigenous Kenyan clay sampled from Kimathe Valley. The method employed a thermal process with sodium hydroxide used as a leaching agent. The concentration of sodium hydroxide and duration of extraction was used to achieve an optimum yield of extraction. The untreated clay and the extracted samples were characterized using XRF, EDS, FTIR, FESEM, FETEM and XRD.

2. Materials and Methods

2.1 Study Area

Natural clay was collected from Kimathe Valley, Mukurweini in Nyeri County (Kenya) as shown in Fig.1. Sampling was done by both grab and composite sampling techniques. The area was selected due to the interest of international firms to mine clay from the area.

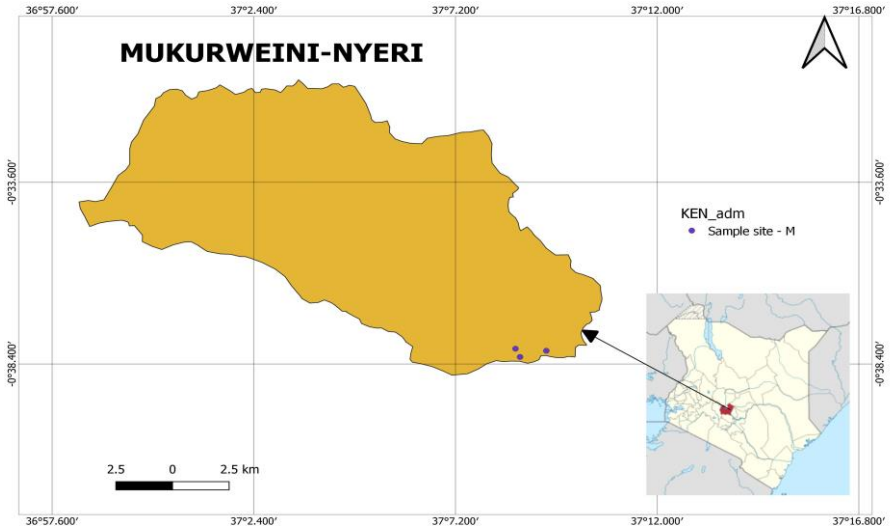

Figure 1: Sampling area location of Kimathe Valley, Mukurweini in Nyeri County-Kenya.

2.2 Materials

The sodium hydroxide used was analytical grade and purchased from Chemoquip Limited. The calcination was done with a furnace (Daihan FHX, Digital Muffle Furnace, Standard-type, 1200°C, FHX-03/05/12/14/27/63) while locally available deionized water was used in the whole process.

2.3 Method

The collected clay was subjected to pre-treatment to remove impurities. The raw clay was washed with a sufficient amount of deionized water and left for 24 hours. The clay was decanted till the decanted water became perfectly clear and then air-dried. The dried clay was thereafter crushed and sieved. The clay was calcined at 1000˚C for a period of one hour. The temperature and wait period is suitable for the conversion of components of silica in the clay to a form that is soluble in a considerable amount that will avoid recrystallization of the clay. The extracting agent used was sodium hydroxide at a temperature of 75^{o}C.

25g of calcined clay sample was weighed and a solution comprising 20% excess NaOH (w/v %) was added into it to dissolve the silicate contents in a flask. The flask was placed in a bath of water and magnetically stirred. The extraction was carried out for 20 minutes and subsequently filtered. The remainder/residue was placed in an oven at 65 ^{o}C for four hours to dry. The measurement of the dried sample weight was taken. The procedure was repeated using different concentrations of NaOH (20% and 40% (w/v%)) and different time duration in order to achieve an optimum yield.

2.4 Characterization

The synthesized silicate was characterized using FTIR (Nicolet 6700 FTIR system, Model: 16F PC), TEM (JEM-2100F), SEM (Model; Quarto S), XRF, EDX, and XRD (Rigaku powder XRD-model ultima IV with

conditions of; start angle 5 and stop angle 70; scan speed 5). Elemental compositional analysis of the natural clay and synthesized silicates was done with XRF and EDX. X-ray diffraction of silicates was performed to determine the phase analysis. Morphology investigation and measurement of size was carried out by Field Emission Scanning Electron Microscopy (FESEM), and Transmission Electron Microscopy (TEM). To ascertain the Chemical structure pellets were made by using KBr and FTIR was used for the analysis.

3. Results and Discussion

Limitations of the study

The study research was limited in terms of previous studies of the clay in the chosen area of research and the type of the clay silicates extraction with NaOH base and no other bases or acids limited the specific result product obtained from the extraction process.

Elemental analysis of calcined clay and extracted silicates composition was determined by XRF and EDX. Results are shown in table 1 and figure 1 respectively. The XRF analysis showed that the method of extraction gave a significant percentage improvement in the content of silicates extracted. After the extraction, the pattern reveals that the % composition of nanosilicates was majorly composed of sodium silicates and increased concentration of the alkali (NaOH) reduced the % composition of silica. 20% NaOH gave the best result. The chemical reaction of the process is as shown in the equation below;

$$SiO_{2\ (Calcined\ clay)} + NaOH_{(aq)} \longrightarrow NaSiO_{3\ (aq)} + H_20_{(l)}$$

Table 1: Percentage composition of calcined clay and silicate extract by XRF.

Composition	Calcined Clay	Silicate extract (20%)	Silicate extract (40%)
Al_2O_3	32.4	5.1	8.2
SiO_2	55.0	83.6	72.3
K_20	1.1	5.0	8.5
CaO	1.1	1.3	4.1
Fe	6.1	1.0	2.2
P_2O_5	0.5	0.6	0.5
Others	3.8	3.4	4.2

From EDX results Figure 2 it is clear that synthesis of silicates was successful but the use of 20% NaOH concentration gave better yield as compared to 40% NaOH. It has been reported that the higher the concentration of the extracting medium the lower the yield of the silicates extracted [16]. This is due to the fact that the extraction medium reacts with available alumina thereby forming a complex. The synthesized nanosilicates were also characterized with FTIR and it depicted almost the typical structure of sodium silicates in the literature [17]. The Infrared bands of 1000, 1500, 1700, and approx. 3500 cm^{-1} clearly describes the bands of silicates as shown in figure 3 below.

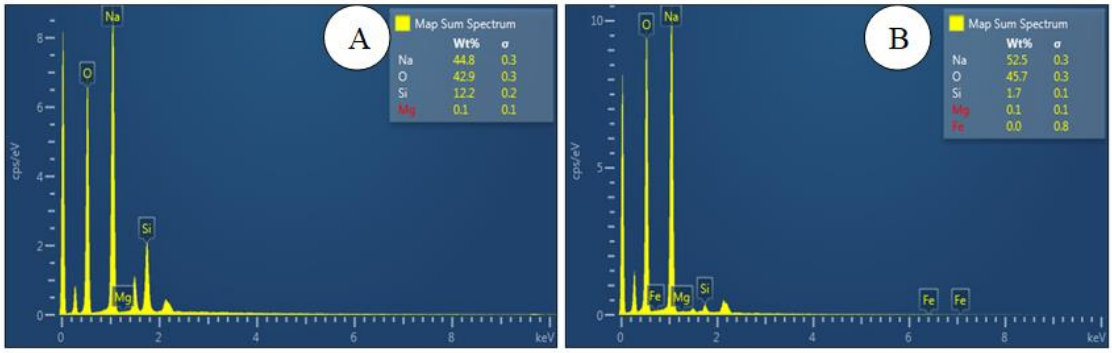

Figure 2: EDX patterns of nanosilicates extract with (a) 20% NaOH and (b) 40% NaOH.

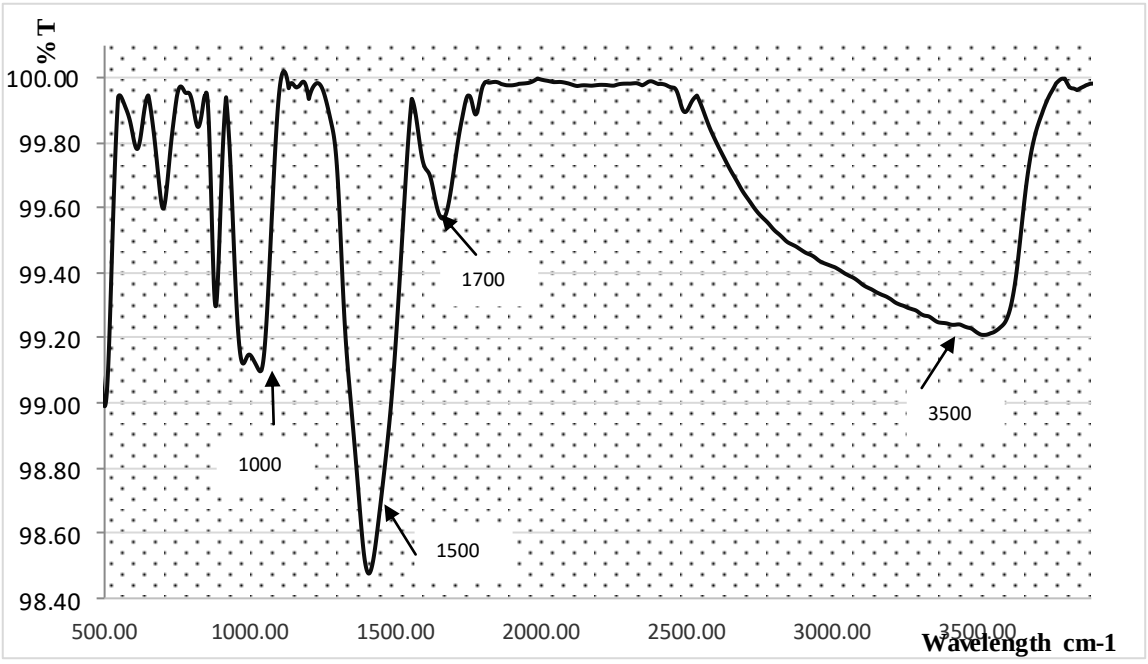

Figure 3: FTIR spectra of synthesized silicate nanoparticles.

Figure 4 and figure 5 show the size and morphological characterization of the synthesized nanosilicates using FESEM and FETEM as shown below respectively. SEM analysis showed the synthesis of agglomerated spherical shape nanosilicates which were synthesized with 20% and 40% (w/v %) molar concentration of sodium hydroxide solution, collision, and coalescence of the nanoparticles are the main factors that determine the extent of agglomeration in a nanoparticle powder system. The intense aging process that occurs during the drying of the silicates can lead to complex agglomeration behavior resulting from the polycondensation reaction. The structure and shape of the synthesized nanosilicates is well reported in the literature and as well observed in the SEM analysis. [18]. The average particle diameter size of the nanosilicates was about 80-90 nm.

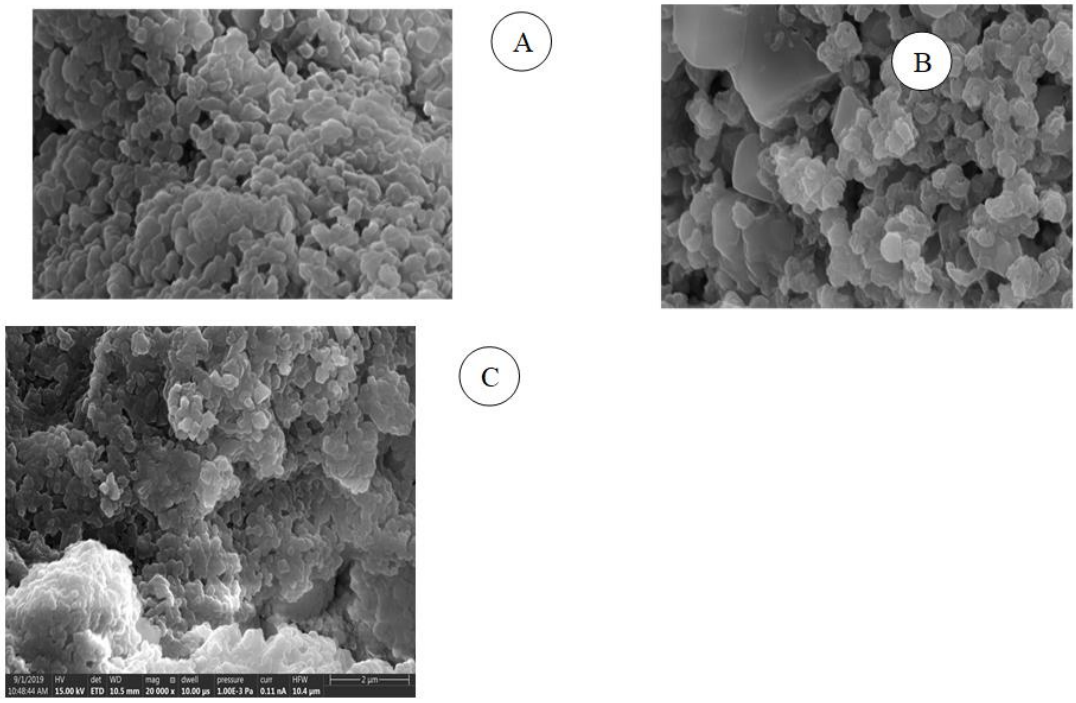

Figure 4: FESEM images of synthesized silicate nanoparticles using 20% NaOH (w/v%) (A) 2 µm, (B) 5 µm, and 40% NaOH (w/v%) (C) at 2 µm.

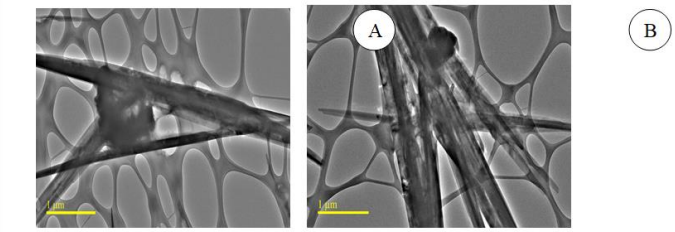

Figure 5: FETEM images of synthesized silicate nanoparticles using (A): 20% NaOH (w/v%) and (B): 40% NaOH (w/v %).

The phase analysis with XRD revealed the synthesis of silicate nanoparticles and corresponded to the sodium silicates since the medium of extraction was sodium hydroxide (NaOH). Figure 6 and Figure 7 shows XRD results for silicates based on the 20% NaOH and 40% NaOH extraction medium respectively. The synthesized silicates nanoparticles displayed a 2θ=30o that showed the presence of silicates nanoparticles with peak positions agreeing with the reference peaks (JCDPS, No. 29-1233). The intense diffraction sharp peaks from 25.26 ^{o} to 65.93 ^{o} are usually related to sodium silicate [19]. The comparison of the two concentrations depicted more intensity of silicates with 40% as compared with 20% NaOH solution with almost the same peaks at the same 2θ degree level for nanosilicates.

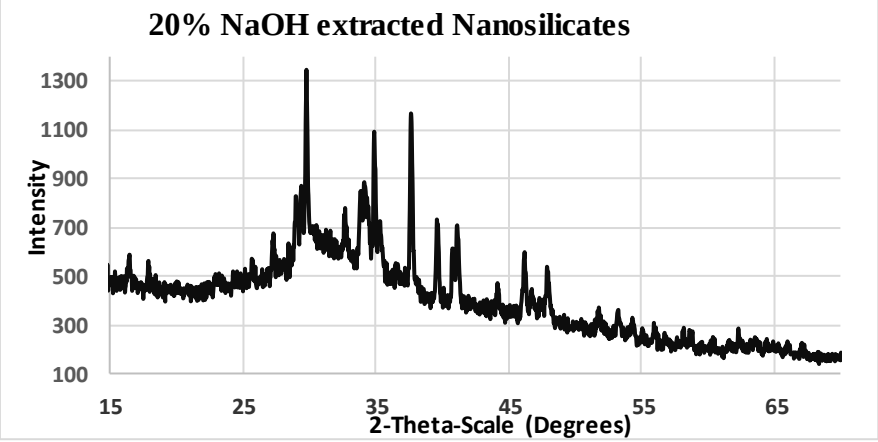

Figure 6: XRD pattern of synthesized silicate nanoparticles using 20% NaOH.

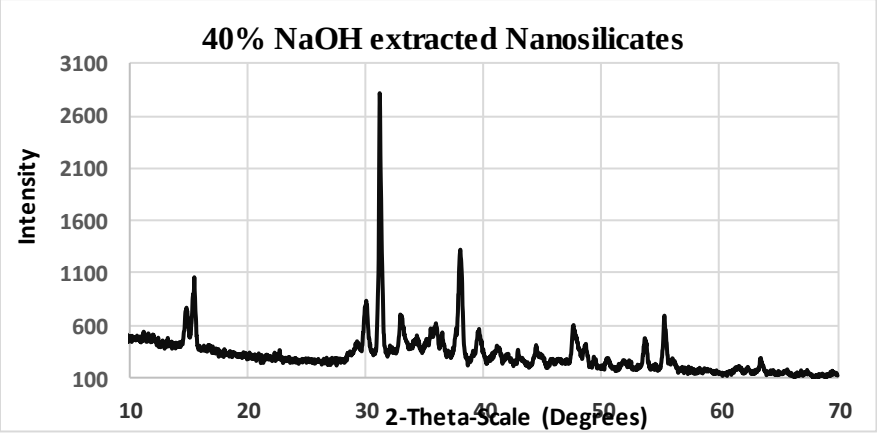

Figure 7: XRD pattern of synthesized silicate nanoparticles using 40% NaOH.

4. Conclusion

A simple and novel synthesis of nanosilicates from indigenous clay was performed. The basic alkali extraction of silicates from clay at average temperatures was done and subsequently slow drying at 65oC temperature for a longer period resulted in the synthesis of agglomerated spherical shape nanosilicates as shown by the SEM and TEM analysis. The optimum concentration of extracting medium was found to be 20% NaOH which lead to more alumina/magnesia dissolution and this can be seen from the EDX results since some other metals like Mg and Fe are seen in the final composition of synthesized nanosilicates with 40% NaOH. The percentage composition showed silicates synthesized contained more % composition of silicates as compared with original clay as evidence of elimination of alumina from the clay and drastic reduction in composition.

5. Funding support

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6. Conflict of interest

All authors declare no conflict of interest

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