

SYNTHESIS AND CHARACTERIZATION OF PURE AMORPHOUS SILICON OXIDE FROM TREATED KAOLINITIC CLAY USING CHEMICAL EXTRACTION

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ABSTRACT

Pure silicon oxide was produced in this study utilizing a sodium silicate solution made from Kankara clay as a precursor. The Kankara clay that was obtained from Nigeria was first beneficiated to produce pure dried powder clay. After that, the dried powdered clay was treated with heat activation and acid leaching, respectively. In a 500 mL Erlenmeyer flask, appropriate amounts of each clay (raw, thermally treated clay, and leached clay) were reacted with 3M NaOH solution. The flask was heated to 200°C and stirred continuously for 3 hours on a magnetic stirring hot plate connected to a reflux condenser. The solution was filtered to yield sodium silicate solution, which was then precipitated with 3M HCl while constantly stirring to produce a gelly-like white substance. The gel was aged for 18 hours, then washed with de-ionized water several times before being dried at 80°C for 12 hours to get pure white silica particles, which were subsequently described. The XRD analysis revealed that the silicon oxide synthesized is amorphous, but the microstructure evaluation revealed particles aggregation, which is usual in sol-gel synthesized powder.

Keywords: kaolinitic clay, chemical extraction, pure silicon oxide, amorphous.

INTRODUCTION

Silica, also known as silicon dioxide, is found in the form of quartz in nature. In many parts of the world, silica is an essential component of sand. Silica is a mineral and manufactured product composite that belongs to one of the most intricate and abundant material families. Silica is a mineral that can be found in abundance in the earth's crust. Glass, beach sand, silicone, and granite are all examples of silica materials. There are two types of silica: crystalline and amorphous. The crystalline form of quartz contains the most appreciable amount of silica in the earth's crust, yet it has a low reactivity [1].

Due to its benefit of being highly reactive, amorphous

silica, on the other hand, finds greater uses in a variety of areas [2]. The classic method of synthesizing pure silica from natural quartz sources is costly and energy intensive [3]. The nature of amorphous silica, on the other hand, allows it to be extracted at much lower temperatures. As a result, it ensures a low-energy approach as an alternative to the current high-energy-consuming conventional silica extraction method [4].

As a result, concentrated efforts are presently being made to extract pure silica from other silica-bearing minerals as precursors. Silica has been extracted and investigated from a variety of sources, including waste glass, bagasse ash (waste sugarcane), wheat husk, and rice husk. Amorphous silica has been produced

extensively using TEOS [5], sodium silicate [6], and water glass [7], as well as rice husks, maize cobs, wheat husks, rice straws, and other agricultural wastes [8 - 11]. However, there has been little or no research on the use of kaolinite clay, which is known to be abundant and inexpensive compared to most other documented sources.

Kaolin is a clay mineral that belongs to the group of industrial minerals and has the chemical formula $Al_2Si_2O_5(OH)_4$. Kaolin is a type of rock that contains a lot of kaolinite. Kaolin is a fine-grained white clay with a hydrated aluminum silicate classification. Kaolin is a low-cost source of silica that is readily available and abundant in Nigeria. Kaolin clay is widely used as a filler and pigment in a few materials, including rubber and resins, paints, and paper coatings, while its usage as a precursor for amorphous silica extraction has yet to be completely investigated.

The current study aims to synthesize pure amorphous silica particles from both raw and treated (thermally and acid leached) kaolinitic clay in this regard.

EXPERIMENTAL

Materials

Raw kaolinite clays and sodium hydroxide pellets (purity 98 %) were employed as starting materials in this study. The kaolinite clay was obtained from Kankara, which is located at 11.9313°N and 7.4138°E in Katsina State, Nigeria. To remove unwanted organic matter and other earth items that had adhered to the clay, it was first soaked in water for 72 h, then washed and wet sieved. The clay slurry was sieved and dried in an electric oven at 105°C until all the water had evaporated. The dried clay is allowed to cool inside a desiccator to obtain processed raw Kankara clay. The raw clay was processed both thermally and chemically to increase the silica concentration and improve the purity.

The thermal treatment was carried out by pouring part of the beneficiated raw clay into a crucible and placing it inside a muffle furnace at 850°C for 1 h at a rate of 10°C min⁻¹. The acid leaching was conducted by reacting the clay with 3M HCl in a volumetric heating flask, and the solution was then heated and stirred continuously for 3 h using a magnetic stirrer pellet in the solution. The clay-acid solution was then allowed to cool completely before being filtered. After that, the clay was washed several times until no trace of acid

remained. This was determined using blue litmus paper. The leached clay was then dried in an oven. After that, the three clay samples labeled raw clay, thermally treated clay, and leached clay were obtained for use as silica synthesis precursors.

Synthesis of sodium silicate from the clay samples

In accordance with Nittaya and Apinon, the hydrothermal process used in this work is an open system under atmospheric pressure [12]. To keep the reaction mixture at a constant volume, the system uses a glass reaction vessel, a heating source, a temperature detection device, and a reflux condenser. In this experiment, 50 g of processed raw clay, thermally treated clay, and leached clay were mixed with 400 mL of 3M NaOH solutions in a 500 mL Erlenmeyer flask. At a temperature of 200°C, the mixture was placed in a flask on a hot plate connected to a reflux condenser and spun constantly with a magnetic stirrer at 40 rpm for 3 h. Constant stirring was necessary to dissolve the clay and generate sodium silicate solutions. After filtering the sodium silicate solutions with Whatman No. 41 filter paper, the leftovers were washed with 100 mL boiling water. After that, the sodium silicate solutions were kept in a glass beaker until they were utilized to make silica particles.

Extraction of pure silicon oxide

3 M hydrochloric acid was prepared and carefully added to the sodium silicate solution, stirring frequently until a white gel-like material (pH 10) was achieved. The sodium silicate solutions derived from the heat treatment and the leaching process followed the same steps. To make silica gel, the gelly mixture was allowed to settle for 18 h before being filtered and dried in an 80°C hot air oven for 12 h. The silica gel was then washed many times to remove NaCl, which is commonly found in silica xerogel, and dried in an electric oven at 80°C for 12h to achieve highly pure silicon oxide powder with a pure white color.

Characterization of pure silicon oxide

An X-ray diffractometer (Rigaku miniflex 600, Japan) was used to investigate the phase constituent, Fourier transform infrared spectrometry (FT-IR- Pelkin Elmer) was used to investigate the silica functional groups, and scanning electron microscopy (SEM, JSM-6100 JEOL, Japan) was used to investigate the

morphology of the as-prepared SiO₂ powder from each clay sample, raw clay, thermally treated clay, and leached clay.

RESULTS AND DISCUSSION

Phase evaluation (clay samples)

Fig. 1 (a) - (c) showed the phase composition of raw clay, heated clay, and leached clay samples, respectively,

while Table 1 displays the quantitative phase report obtained from the spectra. Sharp peaks in all the XRD spectra indicate that the samples are crystalline, as evidenced by the presence of sharp peaks. Quartz, illite, montmorillonite, and orthoclase, which are known to exist with kaolinite clay, can also be seen in the raw clay samples. The raw clay shows a well-defined reflection of 12° and 25° at 2 theta value, which is typical of kaolinite clay, as previously described [13]. The raw clay, on the

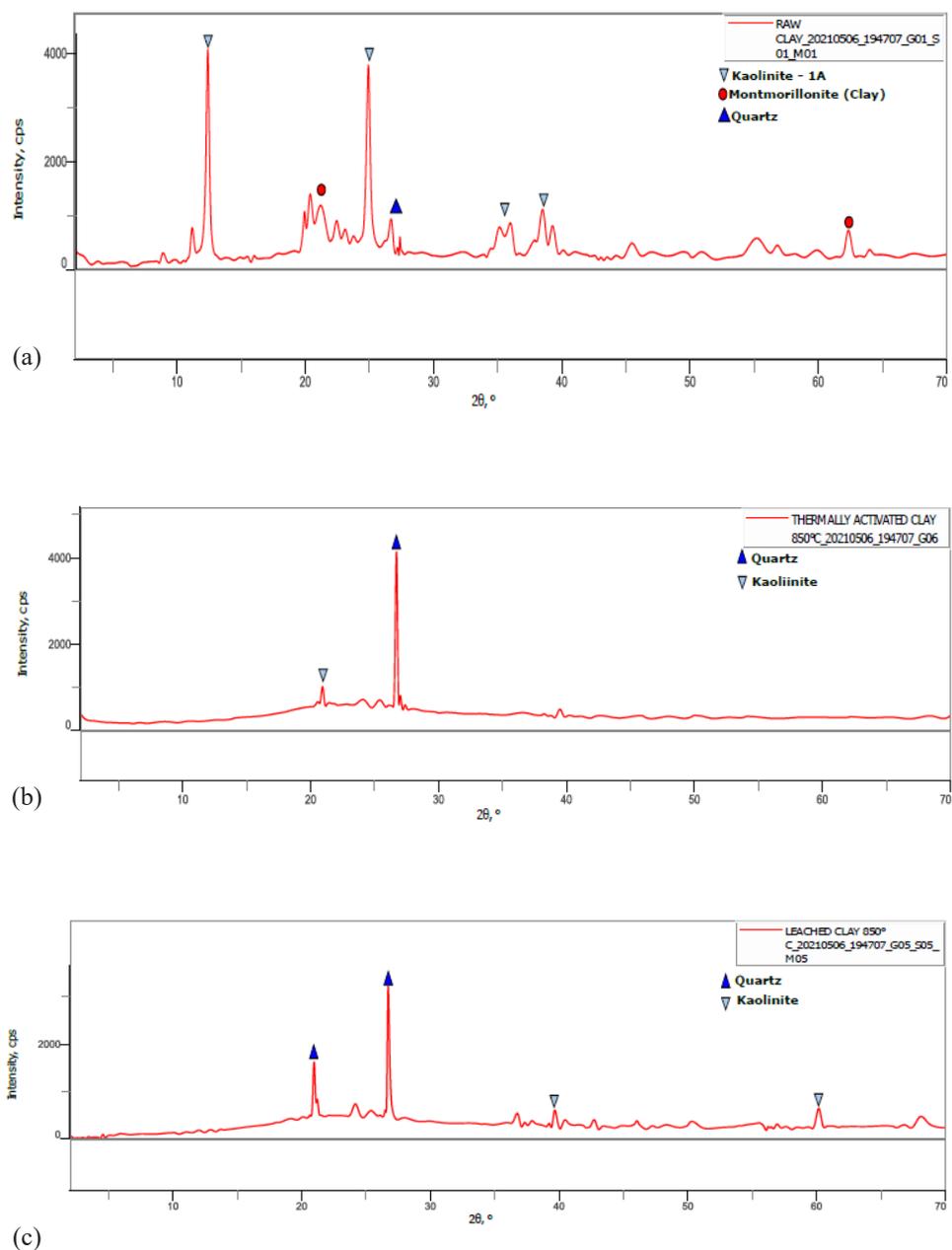


Fig. 1. XRD spectra of (a) raw clay, (b) thermally treated clay, (c) leached clay.

other hand, has a low Quartz (SiO_2) percentage. The quartz (SiO_2) peaks are well evident in both thermally and chemically (leached) clay samples, with the thermally treated clay sample having the largest quartz peak.

According to the quantitative phase analysis report, raw clay has the lowest quartz concentration (4.58 %), while thermally and chemically treated clay has 75.9 % and 51 % quartz, respectively, justifying the importance of the treatment performed on the clay prior to its use as a precursor for pure silica synthesis. Although heat activation renders clay alumina acid soluble, leaching removes more iron from the clay [14]. The lower quartz peak intensity in the leached clay compared to the thermally treated clay could be due to structural disorder generated by the acid leaching, which alters the clay's crystalline structure [14].

Functional group analysis (clay samples)

The FT-IR spectra of raw clay, thermally treated clay, and leached clay samples are shown in Fig. 2 (a - c), respectively. IR spectra with wavenumbers ranging from 500 to 4000 cm^{-1} were captured using the FT-IR technique. Fig. 2 (a) displays the FT-IR spectra for raw clay and showed bands at 3686 and 3619 cm^{-1} , which could be due to Al-OH stretching. The IR peaks at 909, 790, and 749 cm^{-1} respectively indicate the existence of Al-OH, Al-Mg-OH, and Si-O-Al vibrations in the clay sheet [13]. Fig. 2 (b) and (c) show high peaks of 849, 969 cm^{-1} for heated clay and 775, 1043 cm^{-1} for leached clay, which could be attributed to symmetric and asymmetric stretching of Si-O-Si. The IR peak found at 1636 cm^{-1} for leached clay sample can be attributed to the bending vibration mode of physisorbed water on the surface of the free silica formed by leaching. Based on the functional groups discovered by the FT-IR, it can be determined that the material is an alumino-silicate.

Phase evaluation (Pure Silica obtained from clay samples)

Fig. 3 (a) - (c) showed the phase identification of silica particles synthesized from clay samples using X-ray diffractometer. In contrast to the crystalline peaks found in their individual clay samples, all the pure silica samples produced from their individual clay samples had a similar diffractogram with a broad band between 22° and 27°, confirming the amorphous band of silica particles without any trace of crystallization.

This broad band diffractogram reveals the amorphous nature of the silica particles produced. The NaCl signal (peak) peculiar with xerogel as previously reported is also completely absent in the silica samples, confirming the efficiency of the washing and extraction procedures [15]. Amorphous silicon oxide has been found to have a similar pattern in previous research [2, 16].

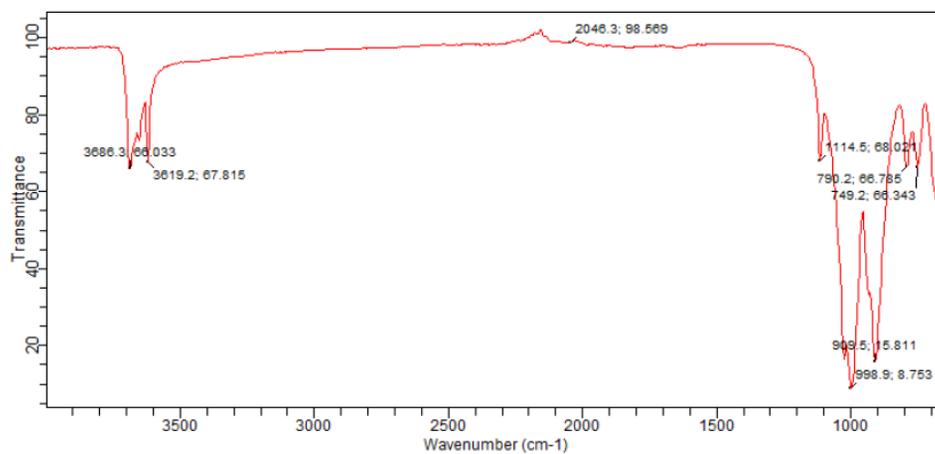
Functional group analysis (silica powders)

Fig. 4 (a) - (c) showed the functional groups present in the generated pure silicon oxide using Fourier transform infrared spectroscopy. IR spectra with wavenumbers ranging from 500 to 4000 cm^{-1} were captured using FT-IR. The transmittance peak observed at 972, 969, and 984 cm^{-1} for raw clay, thermally clay, and leached clay, respectively, has been attributed to Si-OH symmetric stretching vibration, while the absorption band observed at 1640 cm^{-1} for all silica powders has been attributed to H-O-H bending vibration [8]. Peaks recorded for silica particles at 853, 849, and 857 cm^{-1} could be attributed to symmetric bond stretching between Si and O [17]. The band identified at 3388, 3365, and 3410 cm^{-1} for the three silica powders obtained could be attributable to an O-H bond from the silanol group (Si-OH), according to Mohanraj et al. [8].

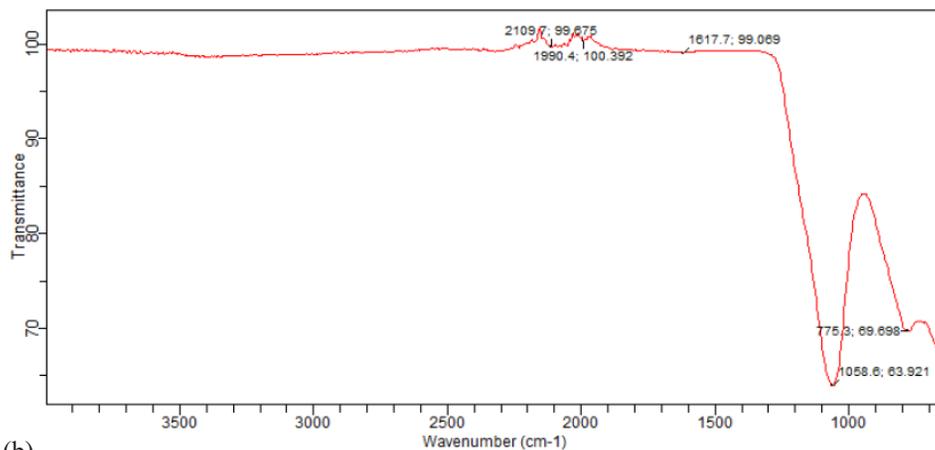
Microstructure evaluation

Raw and treated clays

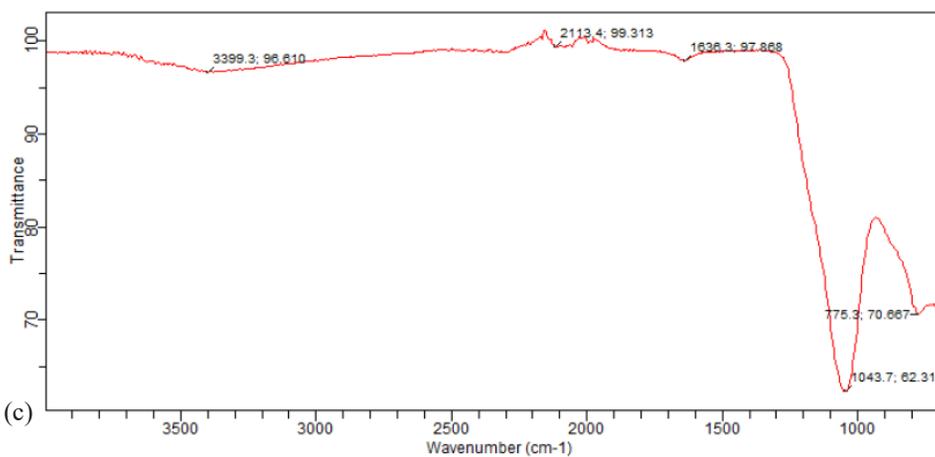
Fig. 5 (a) - (c) showed the findings of scanning electron microscopy (SEM) microstructure examinations on raw and treated clays (thermally and acid leached), respectively. The morphology of the raw clay revealed somewhat agglomerated particles that looked to have been created by multiple flaky or plate-like particles typical of natural kaolinite clay, as previously documented in prior investigations [13, 18]. The treated clays' SEM pictures contrasted sharply with the raw (untreated) clay sample. The agglomerated flaky-like particles in the thermally treated clay shown in Fig. 5 (b) have changed to spherical-like particles, though still agglomerated, consisting of partly bonded and detached particles, which can be attributed to the thermal activation of the raw clay resulting in a meta-kaolin product. The thermally treated clay also has a whitish look on the surface of the morphology, which could imply that there is more silica present as a result of the thermal activation, which is accompanied by a drop in alumina concentration [18].



(a)



(b)



(c)

Fig. 2. FT-IR Spectra of (a) raw clay sample, (b) thermally clay sample, (c) leached clay sample.

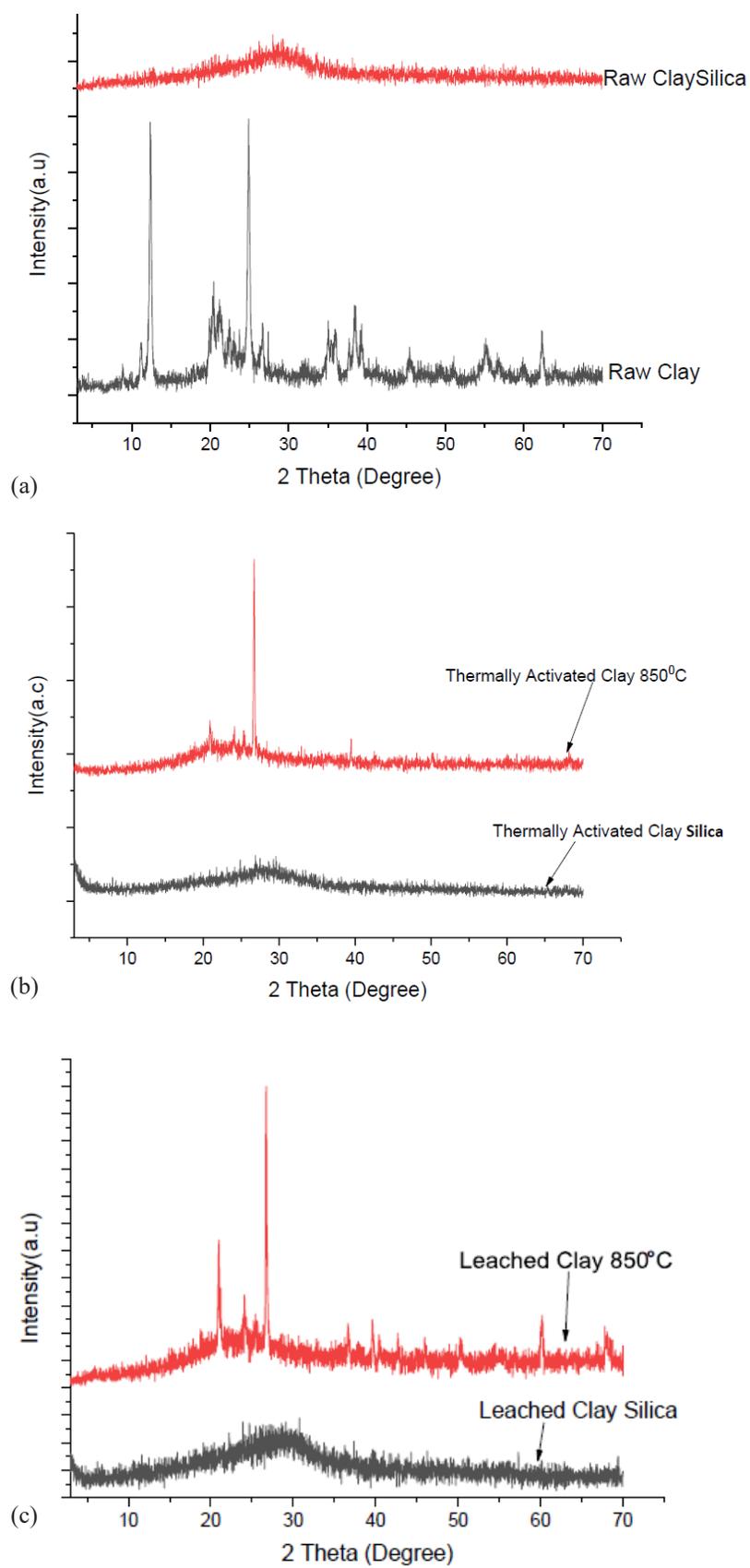


Fig. 3. XRD spectra of pure silicon oxide powders obtained from (a) raw clay, (b) thermally treated clay, (c) leached clay.

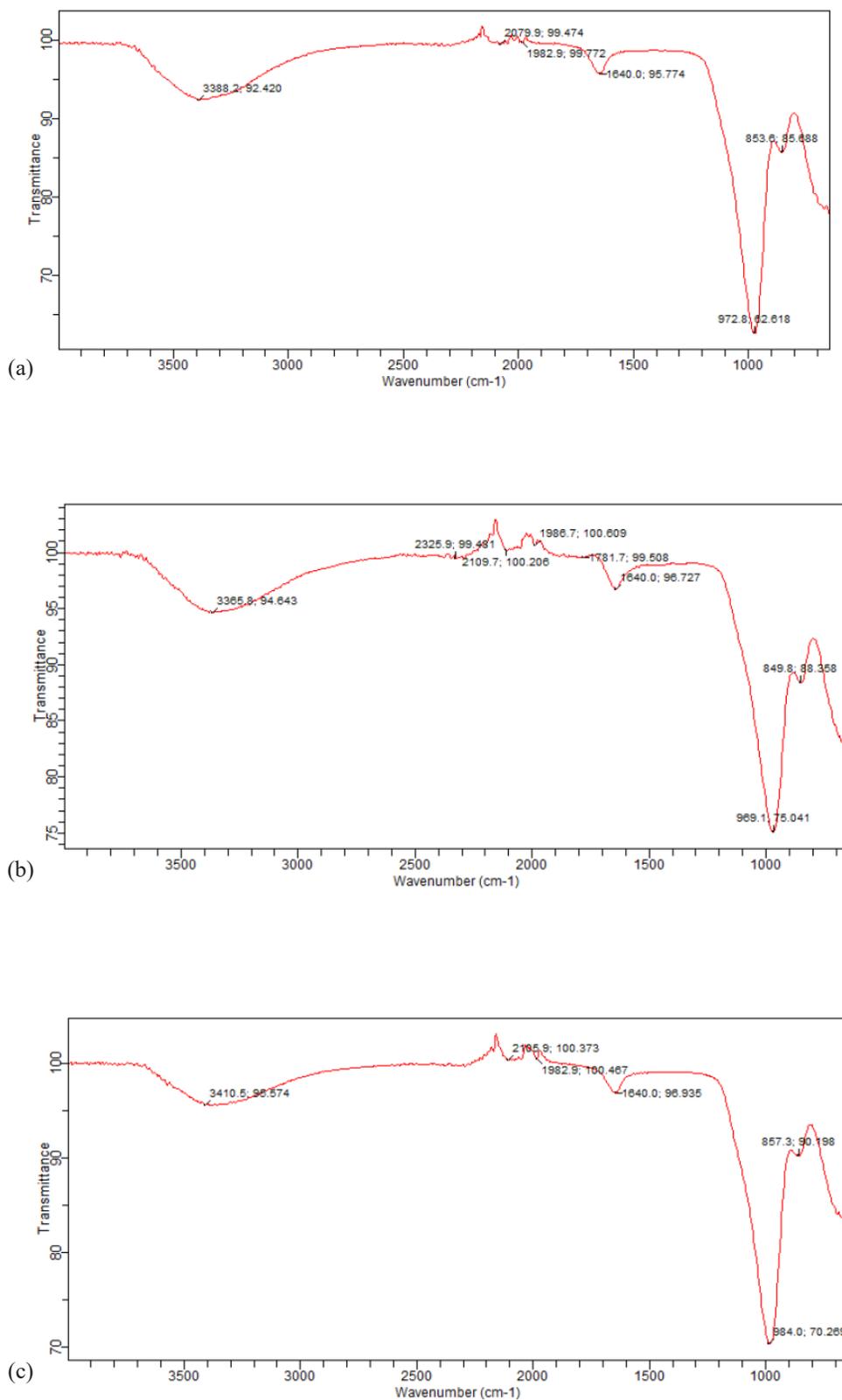


Fig. 4. FT-IR spectra of pure silicon oxide powders obtained from (a) raw clay, (b) thermally treated clay, (c) leached clay.

The morphology of the acid leached clay shown in Fig. 5 (c) is similar to that of thermally activated clay, but the spherical particles observed for the leached clay are well-bonded, and the whitish appearance of the particles is more pronounced, which could be attributed to the acid's leaching effect, indicating a higher concentration of silicon oxide. Despite meta-kaolin breakdown in acid, white rims of silica (SiO_2) emerged around and inside the crystals, implying that amorphous silicon oxide is maintained [19].

Extracted pure silica

Fig. 6 (a) - (c) illustrated the findings of representative microstructure investigation using scanning electron microscopy (SEM) on manufactured pure silica particles for samples raw clay, heated clay, and leached clay. All the produced silica particles have a slightly uneven but spherical form and are evenly distributed throughout the matrix. Particle aggregation was also seen in the silicon oxide morphologies. Several authors have also mentioned this arrangement [2, 8, 16].

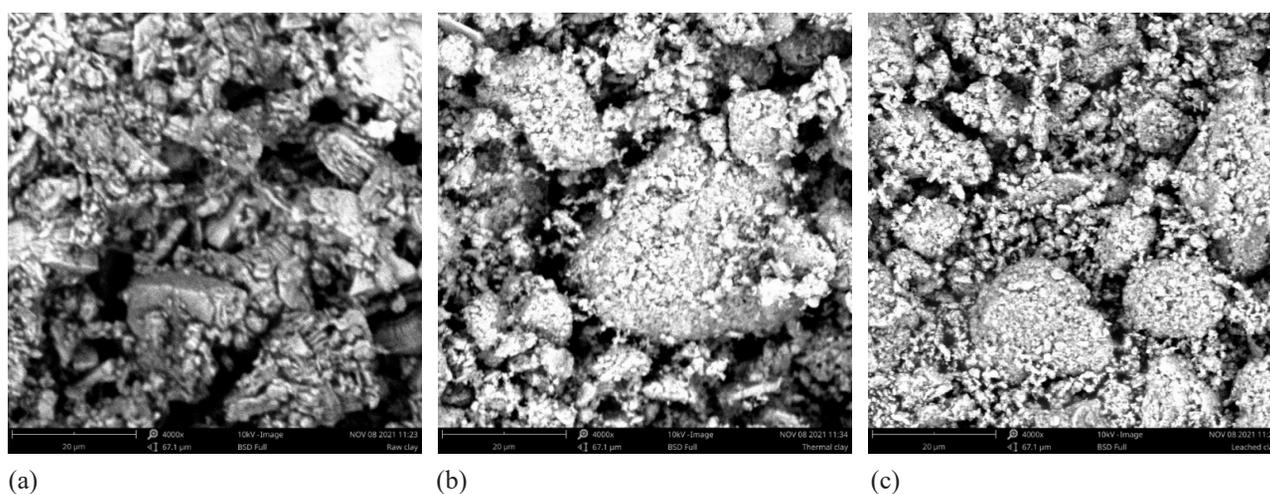


Fig. 5. Representative SEM image of (a) raw clay, (b) thermally activated clay, (c) leached clay.

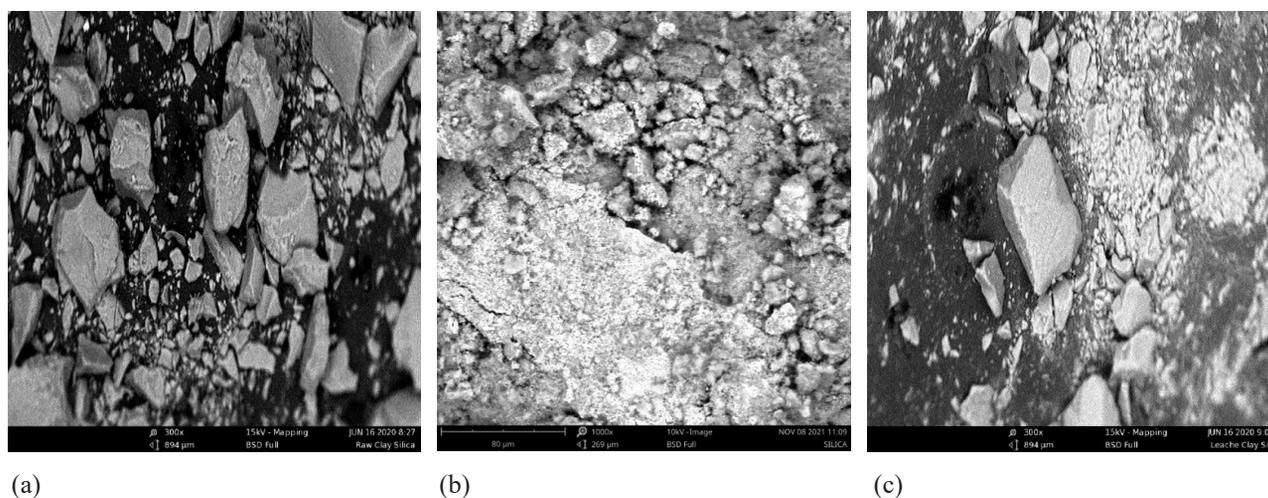


Fig. 6. Representative SEM image of the synthesized silica powder from (a) raw clay, (b) thermal clay (c), leached clay.

CONCLUSIONS

The preparation and characterization of pure amorphous silica particles from raw kaolinite clay and treated kaolinite clays generated by thermal activation and acid leaching were studied. It is concluded that kaolinite clay can be fully utilized in the production of highly pure amorphous silica. However, the morphological analysis revealed that all the synthesized silica particles are somewhat irregular but spherical in shape, evenly scattered throughout the matrix, and have a high degree of particle aggregation, as described by various publications.

The XRD examination revealed that all the generated pure silica samples had a broad band between 22° and 27°, confirming the characteristic amorphous band of silica nanoparticles without any trace of crystallization. The treatment (thermal and acid leaching) carried out on the treated clays enhances high purity silica compared to raw clay (untreated clay).

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