

Production of Amorphous Silica Nanoparticles from Cassava Periderm using Modified Sol-Gel Approach

Jeleel Adekunle-Adebisi^{1,2,*}, Johnson Olumuyiwa Agunsoye¹, Sefiu Adekunle Bello³, M Haris⁴, Mercy Munyadziwa Ramakokovhu⁵, Michael Olawale Daramola⁶, and Suleiman Bolaji Hassan¹

¹Department of Metallurgical and Materials Engineering, University of Lagos, Nigeria

²Department of Materials and Metallurgical Engineering, University of Ilorin, Nigeria

³Department Materials Science and Engineering, Kwara State University, Malete, Nigeria

⁴Department of Physics, Karunya University, Karunya Nagar, Coimbatore 641 114, India

⁵Department of Chemical, Metallurgical and Materials Engineering, Tshwane University of Technology, Pretoria, South Africa

⁶School of Chemical and Metallurgical Engineering, Faculty of Engineering and the Built Environment, University of the Witwatersrand, Johannesburg, South Africa

Corresponding author's contact: 08030422330, adebisijeleel@gmail.com

Abstract

Modified sol-gel synthesis of amorphous silica nanoparticles from cassava periderm (CP) was investigated. Cassava periderm wastes are generated and disposed indiscriminately or burnt due to nil economic value. The wastes were pretreated with HCl to remove soluble metallic impurities. Both treated and untreated CP flakes were calcined at 700 °C to obtain their respective ashes. The ashes were leached with HCl to remove soluble metallic oxides and thereafter sol-gelled to obtain silica gel modified with ethylene glycol. The gel was dried at 80 °C for 18 hours and then characterized using SEM, EDX, FT-IR and XRD. The SEM micrographs showed that silica modified with ethylene glycol is less agglomerated with higher silica yield and lower particle sizes. All the silica produced showed similar functional groups and non-crystallinity. The silica nanoparticles could be used as feedstock for synthesis of silicon nanoparticle.

Keywords: cassava periderm, acid pretreatment, sol-gel, amorphous silica, agglomeration.

INTRODUCTION

Agricultural wastes have been utilized for production of several useful materials to reduce their disposal challenges. Agricultural wastes have been used for production of solid fuel briquettes, adsorbents, cellulose, activated carbon, silica, silicon, refractory and ceramic products, livestock feed, inhibitors, biofuels, construction materials, lignin, and composite reinforcement [1-9]. Most often, these wastes are generated and disposed indiscriminately or burnt which results in

environmental pollution with adverse effects on climate [10]. Nigeria is the largest producer of cassava and generates cassava periderm as a complete waste with no known value [11].

Silica has been employed in biomedical, archaeology, pharmaceuticals, electronics and feedstock in silicon production [12]. It has been used as intensive blue light emitter, fining agent in food industry, powder flow agent in pharmaceutical industry, extra-terrestrial particles collectors, DNA and RNA extractors, hard abrasives in toothpaste, inhibitor of human breast cancer, desiccant, oil absorption, capacitors, hydrogen storage and silicon production [13-18].

It has also been produced from agricultural wastes [8, 19]. Adepoju et al. [8] synthesized silica nanoparticle from cassava periderm with average grain size of 62.69 nm using sol-gel method. The particles were reported to be lumpy and observed to be highly agglomerated. This work investigates the effect of acid pre-treatment and ethylene glycol as capping agent in modified sol-gel method for size control.

MATERIALS AND METHODS

A. Materials

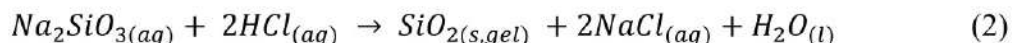
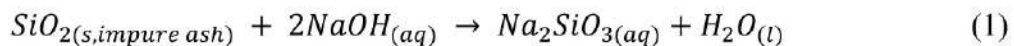
Cassava periderm (CP) used was extracted from cassava purchased from traders at Better Life market, Isale-Osun, Osogbo, Osun State. Reagents used include sodium hydroxide (NaOH), hydrochloric acid (HCl) and ethylene glycol ($\text{CH}_2\text{OH}.\text{CH}_2\text{OH}$). All reagents used are analytical grades. Rinsing was done with double distilled water (DDW).

B. Methods

Cassava periderm was prepared as described in Adebisi et al. [20]. The cassava periderm (CP) was treated in 0.1 M HCl at 45 ± 5 °C for 90 min to remove some soluble compounds and rinsed five times to remove the leachate. The untreated and treated CP flakes were oven dried at 105 °C for 5 hours and then labelled untreated cassava periderm (UCP) and treated cassava periderm (TCP), respectively. UCP and TCP were calcined separately at 700 °C for 4 hours to obtain their respective ashes, labelled untreated cassava periderm ash (UCPA) and treated cassava periderm ash (TCPA). 25 g each of UCPA and TCPA were separately leached in HCl solution at 42.5 ± 5 °C for 75 min, stirred at 600 rpm. The mixtures were filtered and residues rinsed five times to remove traces of the acid. The residues were then dried at 80 °C for 18 hours and labelled leached untreated cassava periderm ash (LUCPA) and leached treated cassava periderm ash (LTCPA).

LUCPA and LTCPA, in different 1000 ml Erlenmeyer flasks, were leached in boiling 2.0 M NaOH which was magnetically stirred at 700 rpm for 2 hours. The mixture was allowed to cool before filtration with Whatman No 41-filter paper to get sodium silicate (see Equation 1). LUCPA and LTCPA sodium silicates were separately stirred at 900 rpm at room temperature and titrated with 1.0 M HCl to precipitate silica. The mixtures were allowed to age for 18 hours before filtration to obtain silica gels. The gels were rinsed five times to remove NaCl (see Equation 2). For the modified sol-gel approach, 20 v/v% ethylene glycol (EG) was added to freshly prepared LTCPA sodium silicate prior to the titration. Rinsing was repeated five times before addition of 50 % EG followed by further stirring before filtration.

The three gels were oven dried at 80 °C for 24 hours. Modified gel was thereafter dried in two stages at 130 °C for 60 min to remove water of hydration and then 250 °C for another 60 min to vapourize EG. All the silicas were labelled LUCPA silica, LTCPA silica and silica (EG). Silica (EG) was finally thermally treated at 1000 °C for 2 hours to examine the crystalline phases present.



Scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and X-ray diffractometry (XRD) were used to investigate morphology, elemental composition and phases of compounds in all the samples. Silica (EG) was finally characterized with Fourier transform infrared spectroscopy (FT-IR).

RESULTS AND DISCUSSIONS

A. XRD Analysis

X-ray diffraction patterns for UCP and TCP with further processing conditions are shown in Figure 1. The patterns for UCP and TCP indicate amorphous phases with few crystalline phases at 24.7, 26.9, 35.2, 44, 64.3 and 77.5 diffraction angles with significant difference at 24.7 and 26.9°. Calcination of both UCP and TCP suppressed their amorphous natures with identifiable crystalline phases. The effect of acid treatment is prominent at this stage since fewer peaks shown for TCPA confirm removal of some phases during acid pre-treatment. Leaching of UCPA and TCPA with HCl further purified the residues. The XRD peaks detected correlate with Joint Committee on Powder Diffraction Standards (JCPDS) reference numbers of SiO₂ (78-1254), KAlSi₃O₈ (83-1604), NaAl(SiO₃)₂·3H₂O (03-0234) for LUCPA while only SiO₂ and CaAlAlSiO₆ (70-2129) are

observed for LTCPA. Also, crystallinity of the residues is improved by the post calcination acid treatments.

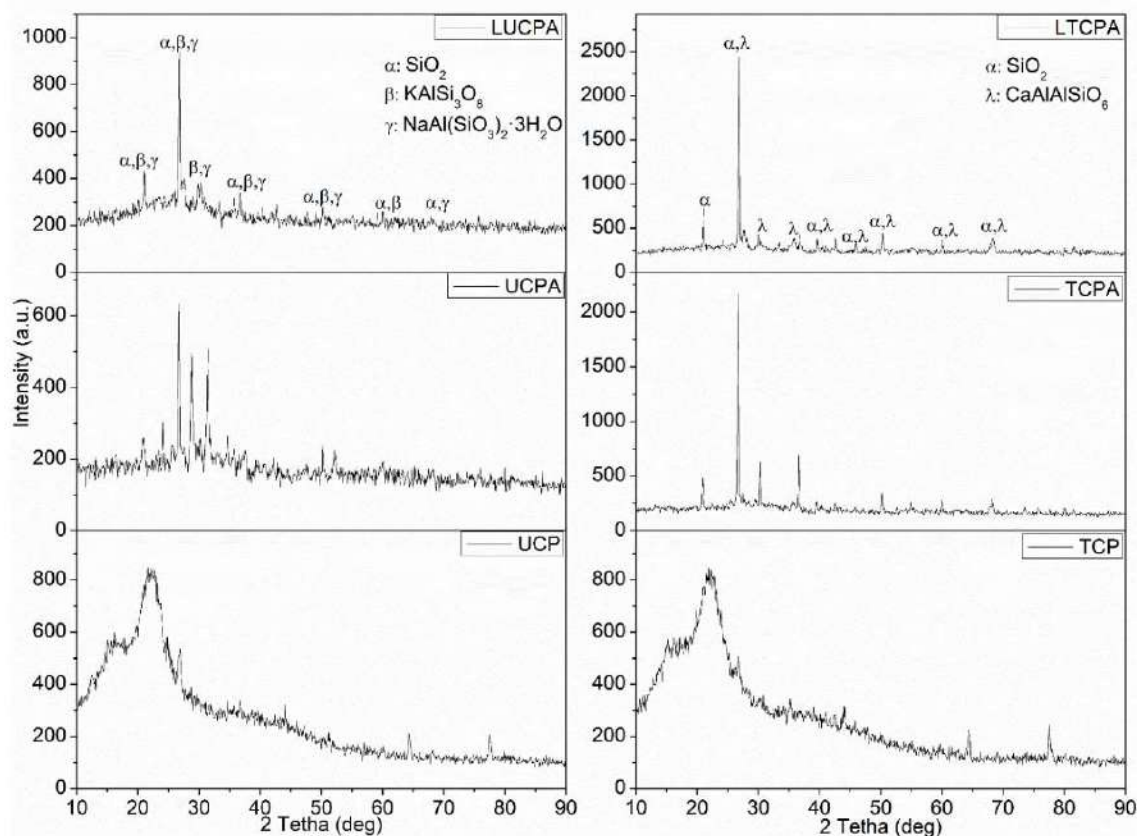


Figure 1: XRD of untreated and treated cassava periderm (UCP and TCP), cassava periderms calcined at 700 °C (UCPA and TCPA) and acid leached chars (LUCPA and LTCPA).

Silicas obtained from LUCPA, LTCPA and silica (EG) after several rinsing with DDW and drying (up to 250 °C for silica with EG) showed similar amorphous natures as shown in Figure 2. Amorphous nature of silicas obtained by chemical methods have been reported [21]. Ethylene glycol retained some NaCl, even after several rinsing, as observed from the XRD peaks before vapourization of the EG. Annealing of the silica at 1273 K transformed the amorphous silica to crystalline silica with JCPDS reference code 82-0512 which is found to be cristobalite with tetragonal crystal system [22]. This enables easy calculation of crystal size of amorphous powders

using Scherrer equation. The crystallite size of the silica produced is given in Table 1 with average crystal size of 16.98 nm.

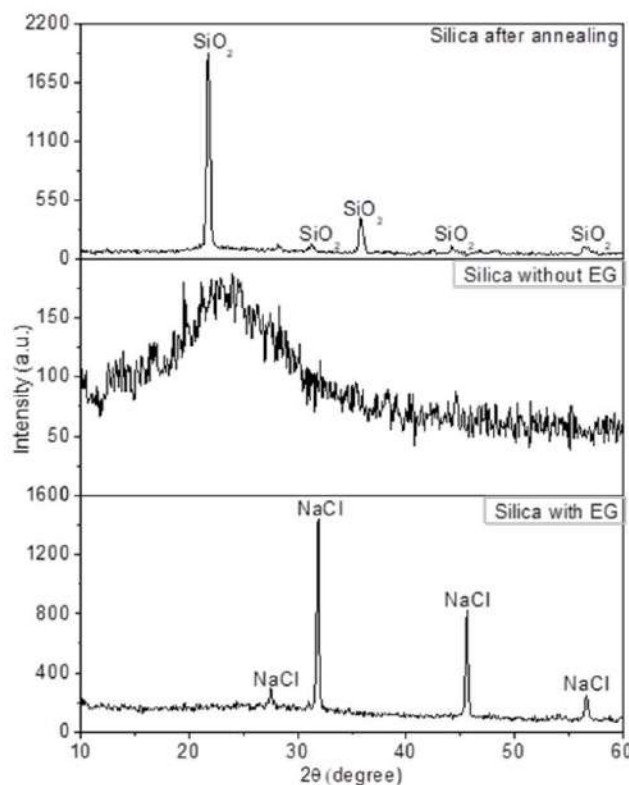


Figure 2: Silicas obtained without/with ethylene glycol (EG) and after annealing at 1273 K.

Table 1: Crystal size of silica produced using Scherrer equation

	Peak pos.	FWHM	Rel. Int.	Crystallite
No.	[$^\circ 2\theta$]	[$^\circ 2\theta$]	[%]	size (nm)
1	21.78	0.30	100.00	27.4
2	28.29	0.59	2.41	14.6
3	31.26	0.59	2.62	14.8
4	35.82	0.39	17.39	21.2
5	44.34	0.59	2.65	14.5
6	56.57	0.96	3.36	9.4

B. Scanning Electron Microscopy (SEM)

Figure 3 shows the SEM micrographs of cleaned CP (a_1), treated CP (b_1), calcined UCP (a_2) and TCP (b_2), leached UCPA (a_3) and TCPA (b_3). It is observed that UCP and TCP have nonporous

and bulky tissues. Calcination of both UCP and TCP produced fine particles of UCPA and TCPA but TCPA is less fragmented due to its higher thermal stability. This is more pronounced after leaching of UCPA and TCPA as can be observed in Figure 3 (a₃ and b₃).

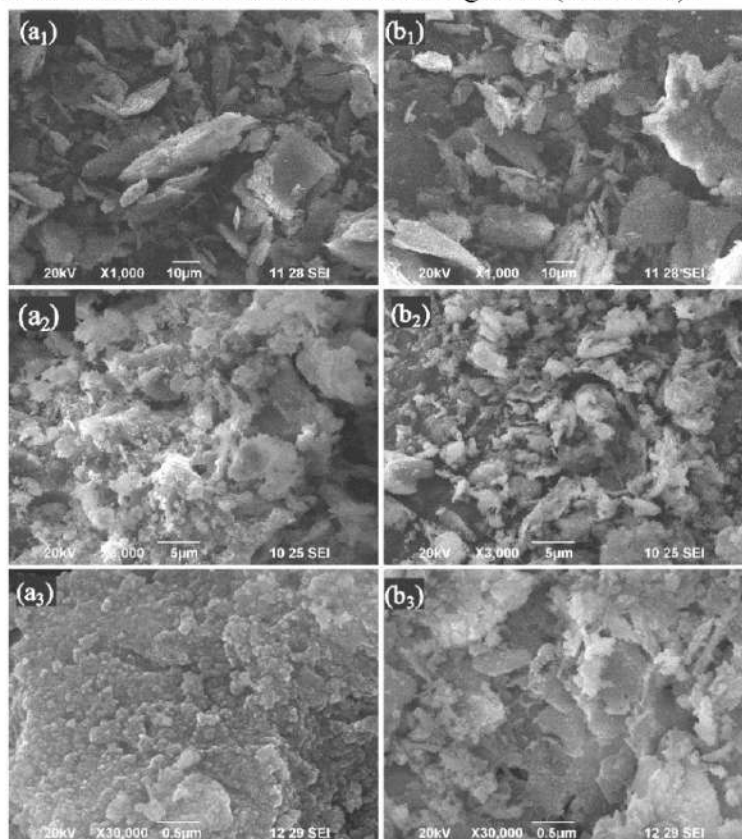


Figure 3: SEM micrographs of (a) untreated CP, (b) HCl treated CP for (1) as received/treated, (2) calcined at 700 °C, and (3) HCl leached calcines.

The SEM micrographs of silicas produced are shown in Figure 4. Degree of agglomeration is highly influenced by processing conditions of the silicas. LUCPA silica in Figure 4(a) has high degree of agglomeration but silicas produced from pretreated CP in Figure 4(b) are less fused together. Drying at 105 °C seems not effective in removing ethylene glycol from silica (EG) particles as shown in Figure 4(c). Vapourization of ethylene glycol above its boiling point, at 250 °C left dispersed small agglomerates (Figure 4(d)). The morphology of the amorphous silicas produced revealed no definite shape in all the processing routes. This implies that particles formed are still agglomerated irrespective of methods of production.

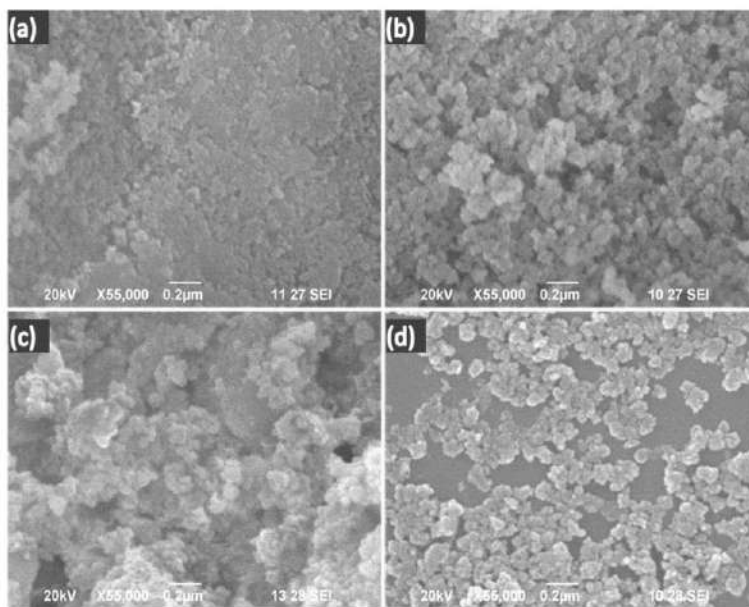


Figure 4: SEM micrographs of silica obtained from (a) as-received CP, (b) HCl treated CP, (c) ethylene glycol modified silica, and (d) silica after vapourization of EG

C. *Energy Dispersive Spectroscopy*

Figure 5 shows the elemental composition of CP through the various processes such as acid pre-treatment, calcination and post calcination acid leaching. Silicon was not detected in UCP (see Figure 5(a₁)) which was improved by acid leaching to a slight detectable level in TCP as shown in Figure 5(b₁). Calcination produced residues composed mainly of elements Na, Mg, Al, Si, K, Ca and Fe. The high oxygen proportions indicate presence of oxides of the elements. Figure 5(a₂ and b₂) revealed higher silicon percent in both UCPA and TCPA. Silicon percent increased after post calcination treatment and removal of soluble impurities. Both acid pre-treatment and post calcination leaching are effective in removing Na completely while post calcination treatment is effective for Mg removal. The acid treatments reduced Mg, K and Ca while Al and Fe are unaffected. Acid treatments have been reported to improve quality of silica produced from agricultural wastes [23]. Highest silicon proportions are obtained after post calcination treatments with/without acid pre-treatments [Figure 5(a₃ and b₃)].

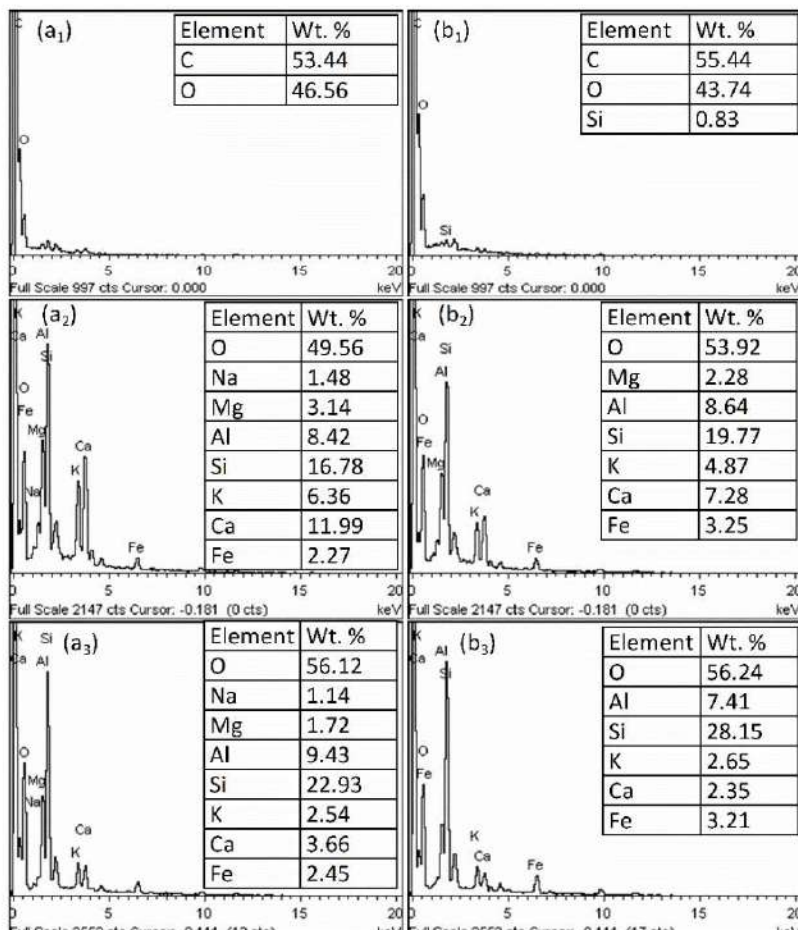


Figure 5: Energy Dispersive X-Ray spectra and composition of (a) untreated CP, (b) HCl treated CP for (1) as received/treated, (2) calcined at 700 °C, and (3) HCl leached calcines.

Table 2 shows the chemical compositions of silica obtained from three different routes. Presence of Na could be attributed to those retained from unrinsed NaCl from precipitation process. Al present in the modified silica is very low compared to other silicas produced. Both acid pre-treatment and introduction of ethylene glycol improved the purity of silica. Chakraverty et al. [24] has reported effectiveness of acid treatments on purity of silica.

Table 2: Chemical composition of silica produced from as-received/treated CP and ethylene glycol (EG) modified sol-gel precipitated silica

Elements	O	Na	Al	Si	K	Ca	Fe	Cu
LUCPA silica	54.7	10.03	10.97	24.3	ND	ND	ND	ND
LTCPA silica	54.95	5.69	9.15	29.75	0.47	ND	ND	ND
Silica (EG)	56.48	2.52	3.01	36.89	0.09	0.08	0.65	0.29

D. Functional groups analysis in modified silica by FT-IR

The FT-IR spectrum of silica produced by morphological modification with ethylene glycol is shown in Figure 6. Silica is characterized by band between 400 and 1300 cm^{-1} [25, 26]. The spectra from prepared silica exhibits bands at 448, 796 and 1085 cm^{-1} , corresponding to characteristics rocking of the Si-O bond, its bending and stretching (symmetric and asymmetric) of Si-O-Si bond, respectively [27]. Drying the samples at 65 °C left the samples with OH and H-O-H bonds for silanol and adsorbed water [25]. The band at 1642 cm^{-1} corresponds to H-O-H twisting while band spreading from 2600 to 3800 cm^{-1} represent stretching vibrations of the surface silanols (Si-OH) groups excited by hydrogen bonds of either water adsorbed or those between Si-O molecules [25].

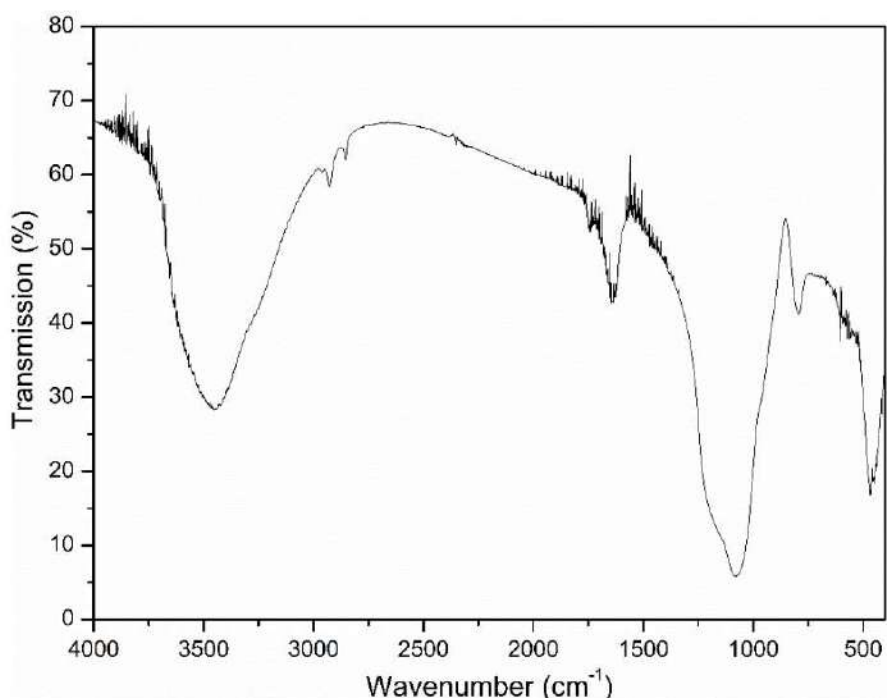


Figure 6: FT-IR spectrum of silica (EG) after drying at 250 °C.

CONCLUSION

Silica has been produced from cassava periderm using three different routes. Acid treatments before and after calcination were found to be effective for reducing or eliminating soluble metallic impurities. Silica obtained from acid pre-treatment, post-calcination treatment and ethylene glycol modified sol-gel methods are found to yield higher purity products with nano range particle sizes.

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