

Preparation and Characterization of Amorphous Silica Nanoparticles from Cassava Waste

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Abstract— Agricultural waste recycling has attracted researchers in order to reduce their undiscerning disposal to our environment which poses environmental challenges. Cassava is cultivated in large quantities by several developing countries, led by Nigeria, with lots of waste generation. Cassava periderm (CP) is among the wastes generated in cassava processing industries. In this work, silica nanoparticles were produced from CP using a pyro-hydrometallurgical approach. Acid leaching followed CP sample preparation, calcination and lastly sol-gel. The silica nanoparticles obtained were characterised using SEM, EDS, XRD and PSA. The results showed an amorphous silica with Na, Al and P as impurities. The particle sizes were observed to be in nano-range but with agglomeration. Silica produced can be used in production of refined oil, detergents, adhesives as well as in pharmaceutical industry.

Keywords— Amorphous silica, cassava periderm, sol-gel, agricultural wastes, nanoparticles

I. INTRODUCTION

There are numerous agricultural wastes generated annually across the world with little or no utilization except rice husk that caught interest of early researchers in 1980's. Owing to their renewability nature, the wastes continued to pile up with majority burnt to provide space for yet produced by-products. The earlier use was for compost or as direct green manure for local farmers. Later researchers found their utilization as solid fuel briquettes, adsorbents, cellulose, activated carbon, silica, silicon, refractory and ceramic products, livestock feed, inhibitors, biofuels, construction materials, lignin, and composite reinforcement [1-16]. These are approaches that converted waste to wealth; creating jobs and thus enhance the living standard of interested personnel.

Researches have established the production of silica from various agricultural wastes [13, 17-20]. Methods of extraction

of silica from agricultural wastes could be obtained from reviews [21, 22]. All the various approaches produced amorphous silica as either silica gel, xerogel or aerogel. They are very useful in various applications such 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, desiccant, capacitors and silicon production [17, 23-32].

This work present production of silica from cassava periderm. Adepoju, Adebisi [13] produced silica nanoparticles from this source employing sol-gel approach with average particle size of 62.69 nm and a yield of 61.53%. An improved sol-gel approach has been used in this report. Cassava periderm is the outermost brown thin layer covering fleshy cassava tuber. It is usually generated as waste during cassava transit and processing. Typical processing routes to obtain this waste have been highlighted in the review by Adebisi, Agunsoye [21]

II. MATERIALS AND METHODS

A. Materials

Cassava periderm (CP) used was sourced from Betterlife market, Osogbo, Nigeria. Reagents used are analytical grades of NaOH and HCl.

B. Methods

Preparation and Acid Pre-treatment of the Agricultural Waste (AW)

CP was manually removed from cassava, washed several times until fine sands were not obvious from the rinsing water. CP was then sun dried for 7 days and then oven dried at 105

°C for 5 hours. Three different portions each of 100 g dried CPs were treated with 1.5 M HCl at 60 °C for 150 min and rinsed with distilled water. They were then sun dried for 5 days and finally oven dried at 105 °C for 5 hours to obtain treated cassava periderm (TCP). The initial and final masses with pH were recorded.

C. Calcination and Acid Leaching

TGA analysis of cassava periderm showed that temperature above 500 °C is suitable for pyrolysis of CP. CP and TCP were burnt in muffle furnace at heating rate of 6 °C/min for 2 hours and held at 700 °C for another 2 hours. The ashes obtained after cooling to room temperature, CPA and TCPA, were thereafter leached with 1.0 M HCl to remove soluble oxides. These were filtered, rinsed with distilled water until free from acid to get LCPA and LTCPA, respectively.

D. Chemical Extraction of Silica

8 g each of LCPA and LTCPA were leached with 3.0 M NaOH to form a silicate solution. The amounts leached were calculated and recorded. The silicate solutions were obtained after filtration. Titration of the solutions with HCl produced white precipitates of silica below pH 10. The titration was stopped at pH 7 to show acid neutralization. The colloidal silica suspensions were left to age for 18 hours. Clear silica concentrate and NaCl supernatant were observed. The supernatant was decanted and the concentrate rinsed repeatedly with distilled water during filtration. Silica gels obtained were later dried at 75 °C for 6 hours.

E. Characterization

To determine the thermal behaviour of CP, with heating rate of 10 °C/min in inert gas (N₂ (g) atmosphere), TGA was measured and determined from room temperature to 825 °C. Silica xerogels obtained from both LCPA and LTCPA were thereafter characterized with SEM, EDS and XRD.

III. RESULTS AND DISCUSSION

Thermal Behaviour

The thermogravimetric analysis (TGA) of CP shows that three main stages of mass losses. The early stage is characterized with moisture loss below 100 °C and a stable mass till around 200 °C. This stage represents a mass loss of about 10 %. The second stage is the main stage with two folds' decomposition of volatile matters. The first is decomposition of hemicellulose and cellulose between 200 and 380 °C but could occur simultaneously with second fold of first rapid stage of lignin decomposition between 300 and 500 °C [33-35]. The last stage of the volatilization is very slow decomposition of lignin from 500 to 800 °C [34].

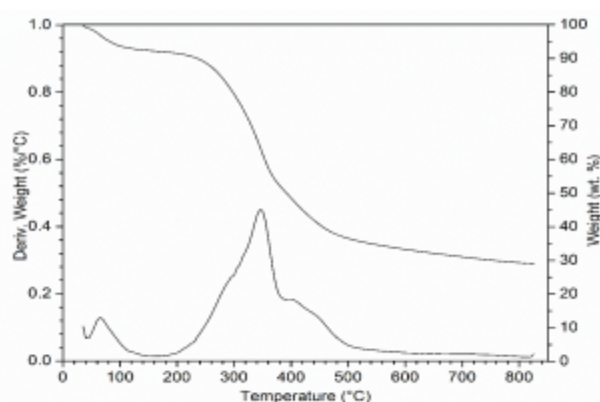


Figure 1: Thermographs (DTG and TG) of cassava periderm

Acid Pre-treatment

There is observable colour change in the leachate but with no change in pH (Table 1). This implies that cassava periderm is a neutral substance unlike the fleshy portion of the cassava tuber always associated with hydrocyanic acid. The colour change was from colourless to light orange which is similar to its natural colour. An average mass loss of 7.83 % showed that some constituents were soluble in HCl. The results from the EDX from Table 2 also confirmed removal of some metallic ions as reported by Rafiee, Shahebrahimi [36]. This is similar to the phases eliminations or reduction at peaks 50, 60 and 68 diffraction angles in Figure 2.

Table 1: pH of leachate before and after leaching with mass leached

	pH		Mass (g)	
	Initial	Final	Initial	Final
Sample 1	-0.24	-0.24	1.000	0.923
Sample 2	-0.24	-0.24	1.000	0.921
Sample 3	-0.24	-0.24	1.000	0.921

Table 2: Composition of treated and untreated cassava periderms

	Composition (at. %)					
	C	O	Na	Mg	Al	Si
CP	55.75	35.01	<<	<<	2.66	3.68
TCP	54.86	40.07	0.38	0.05	1.73	2.16
	Composition (at. %)					
	S	Cl	K	Ca	Ti	Fe
CP	<<	<<	<<	1.86	<<	1.04
TCP	0.08	0.14	0.29	0.06	0.04	0.12
<< below detection						

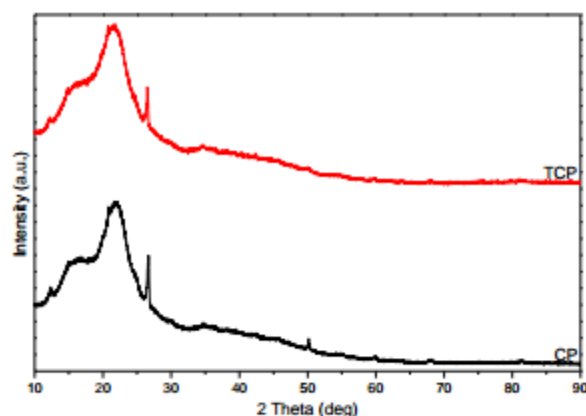


Figure 2: XRD of treated and untreated cassava periderms

Calcination and Acid Leaching

Table 3 shows the compositional analysis of CP ashes for both untreated (CPA) and treated (TCPA) samples. The percentage of silicon in the treated samples is more than that of treated samples. This is because of the metallic ions removed during acid pre-treatment. This procedure has been confirmed by previous researches to increase the silica yield in their ashes [37, 38]. This initial high silicon content in TCPA was reduced after leaching with HCl. Leached TCPA (LTCPA) increased by 47 % which is rather small when compared with leached CPA (LCPA) that gave about three folds' increment. This phenomenon may be due to loss of some silicon compounds during the pre-treatment process. Figure 3 shows the X-ray diffractometric analysis of the ashes and leached residues. The main peak of silicon dioxide is located at 27° but with lower intensities at positions 21, 29 and 50°.

Silica

12 and 45 % of LCPA and LTCPA were dissolved to form the silicate solution. This implies that the initial acid pre-treatment increased the overall yield of silica. Silica obtained from LTCPA was also found to uniform shapes and sizes as can be observed from Figure 4 (b). Though there is agglomeration in both procedures (Figure 4), the agglomerates in (b) formed lumps of micron sizes but the boundaries of individual particles in (a) are clearly defined.

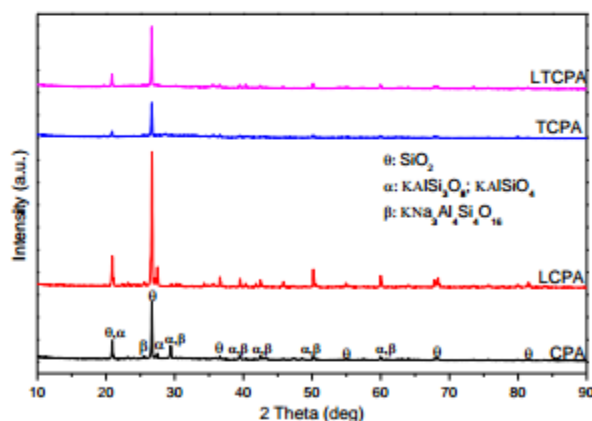


Figure 3: XRD of untreated and treated cassava periderm ashes before and after leaching with HCl

Table 3: Compositions of ashes (CPA and TCPA) and leached residues with 1.0 M HCl

	Composition (at. %)							
	C	O	Na	Mg	Al	Si	P	S
CPA	9.23	66.13	0.56	2.11	3.89	5.96	0.36	0.24
LCPA	6.86	70.68	<<	0.43	3.59	15.04	<<	<<
TCPA	5.96	65.70	0.47	1.83	5.56	8.38	0.41	0.29
LTCPA	5.51	72.68	<<	0.43	5.42	12.29	0.49	<<
	Cl	K	Ca	Ti	Fe	Cu	Zn	
CPA	0.15	3.96	6.44	0.22	0.75	9.23	<<	
LCPA	<<	1.68	<<	0.26	1.46	<<	<<	
TCPA	0.26	4.72	5.13	0.20	1.08	<<	<<	
LTCPA	<<	0.86	0.34	0.45	1.16	0.18	0.20	
	<< below detection							

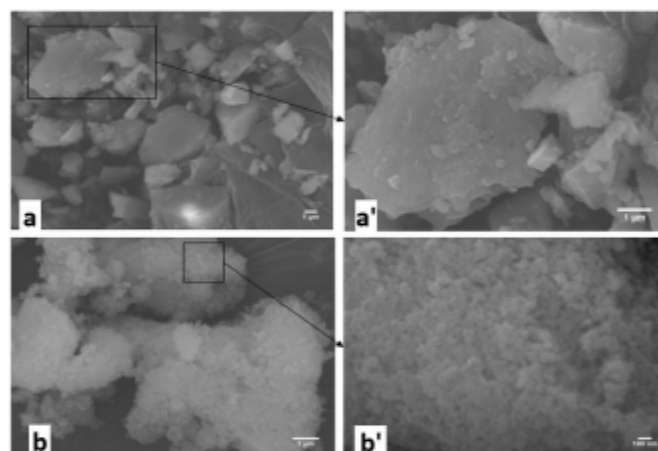


Figure 4: SEM micrographs of silica xerogel from (a) LCPA, (b) LTCPA and (a' & b') higher magnification showing degree of agglomeration

The purity of silica obtained from cassava periderm is quite low (Table 4) compared to those reported for several other agricultural wastes. The presence of high aluminium and sulphur contents impairs the possible application of this silica. Figure 5 shows X-ray diffractographs of the silica indication production of amorphous silica. This span of the broad peaks is similar to those reported by Liou and Yang [39] and Ning, Zhai [40].

Table 4: Compositions of the silica xerogels from treated and untreated leached cassava periderms

	Composition (at. %)					
	C	O	Na	Al	Si	P
CP-Silica	5.21	71.54	-	4.18	17.6	1.46
TCP-Silica	10.65	61.9	0.83	10.39	13.95	2.29

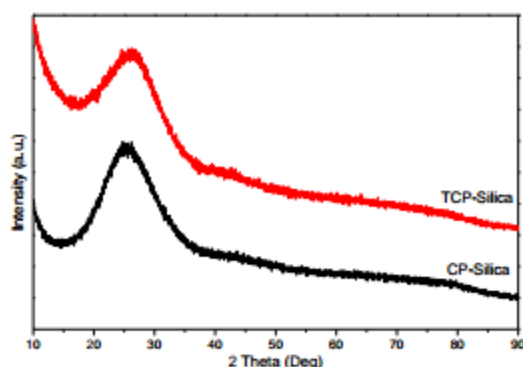


Figure 5: XRD of silica xerogels from LTCPA (TCP-Silica) and LCPA (CP-Silica)

CONCLUSION

Silica nanoparticles has been produced from cassava periderm using the sol-gel method. However, more investigation needs to be conducted to establish the form in which aluminium exists in the silica obtained as this impairs its purity. This will inform where this material can be applied.

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