

Extraction and Characterization of Biosilica from *Raphia Africana* Fruit Shells and *Borassus aethiopum* Leaves

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Abstract: Agricultural wastes which include leaves, shells, husk, stalks, bagasse and ash of plants are often residues of processing or growing of raw agricultural products [1]. These wastes may contain materials that are beneficial to man despite their contribution to environmental pollution. Increase in human population has led to increase in agricultural expansion with exponential increase in waste generation [2]. Converting these wastes to useful forms is of great significance. In this study, biosilica was extracted from the ash of *Borassus aethiopum* leaves (BALA) and *Raphia africana* fruit shells (RASA) using precipitation method. The ashes obtained were characterized using Atomic Absorption Spectrophotometry (AAS). Scanning Electron Microscope (SEM), Fourier Transform Infrared Spectroscopy (FTIR) and X-Ray Fluorescence (XRF) were used to characterize the extracted silica. Morphology of the extracted biosilica using SEM revealed fine globules of various sizes formed from aggregates of biosilica at different magnifications: 150x, 500x and 1000x. FTIR spectra of the extracted biosilica revealed the presence of hydroxyl (OH), silanol (Si-O-H) and siloxane (Si-O-Si) functional groups recorded at absorption bands: 3395.6, 1636.3 and 1062.3 cm^{-1} respectively for BALA and 3388.2, 1640.0 and 1058.6 cm^{-1} respectively for RASA. XRF of the extracted biosilica showed two major peaks which correspond to the presence of silicon and oxygen atoms respectively. Percentage extraction of biosilica from the two precursors was between 70-90%. AAS result revealed that BALA had biosilica 67% while RASA showed 82% biosilica content. This study revealed that the leaves of BALA and fruit shells of RASA are good sources of silica and as such, converting waste to wealth thereby reducing green-house gases like CO_2 released into the atmosphere when left to decompose naturally.

Keywords: Biosilica, *Borassus aethiopum*, Leaves, *Raphia Africana*, Fruit Shells, Ash, Extraction, Characterization

1. Introduction

One of the basic materials and valuable inorganic multipurpose chemical compound is silicon dioxide (SiO_2) commonly known as silica. It is known to occur in nature as sand, quartz or flint and exists as gel, crystalline and amorphous forms [3]. It is also one of the most abundant materials on the earth's crust [4]. Extraction process has been employed for the production of silica making use of quartz or sand as raw materials [3]. Smelting quartz and sand with sodium carbonate at 1300°C is currently used in manufacturing sodium silicate, the precursor for silica production [5].

The International Union of Pure and Applied Chemistry

(IUPAC) defined Green Chemistry as the invention, design and application of chemical products and processes to reduce or eliminate the use and generation of hazardous substances [6, 7]. Synthetic materials based upon fossil fuels and oil has pushed aside none food raw materials from agriculture and other land-based industries [8]. Much attention has been attracted to agro-industrial wastes in recent times due to its potential sources of novel green alternatives such as biotransformation for fuels and other materials [9].

Agricultural products and residues attract widespread attention for renewable energy generation and their large-scale combustion. Many agricultural products as well as their by-products which include palm oil, sugarcane bagasse and waste

like ashes produced from palm oil fuel, rice husk ash or wheat-straw/husk are considered potential raw materials for preparing valuable products. Silica is one of such products. Herbaceous plants cultivated by irrigation method and fertilizer application has led to higher content of inorganic species compared to wood or coal, with ash content of between 3-12 weight percent (wt%). [7, 10, 11] There is therefore urgent need to extract, recover, recycle and reuse inorganic species or elements. Combustion of herbaceous biomass results in the production of fly ash and bottom ash. The fly ash is mainly composed of potassium, sodium, sulfates, chlorides and phosphates while the bottom ash is rich in silica or silicates [12]. Research has shown that bottom ashes from biomass (rice husk) and biomass power station waste could be used for reforming silicate solutions by alkaline extraction, to obtain higher value end-products [13].

Currently, especially in developing countries like Nigeria, most of the waste agricultural biomass is left in the field to decompose naturally, which releases CO₂ and the high global warming greenhouse gas, methane. These agricultural wastes when burnt openly, releases gaseous emissions such as CO (a poisonous gas) as well as a black carbon which also has high global warming potential [14].

Manjula *et al.* [15] reported the extraction of Silica from cow dung using precipitation method. Cow dung ash was mixed with sodium hydroxide to produce sodium silicate which was filtered and the residue thoroughly washed with double distilled water. The filtrate: sodium silicate was acidified with 5 N H₂SO₄ to precipitate silica gel. The silica gel was washed with double distilled water to free the filtrate from alkali and oven dried at the temperature of 110°C yielding nano sized amorphous silica. Manjula *et al* [15] characterized the product using SEM, EDX and XRD.

Precipitation method has also been reported [9] for production of silica nanoparticles from coconut shell ash. After heating the coconut shell in a furnace at 700°C to produce coconut shell ash (CSA), 2.5 M NaOH was added and stirred with it to form sodium silicate. Upon treatment of the sodium silicate with 5N H₂SO₄, silica gel precipitated out which was washed and dried in an oven to produce amorphous silica which was later refluxed with 6 M HCl and washed to remove the alkali. The solution was treated with 2.5 M HCl and H₂SO₄ to give white precipitate which was dried to obtain silica nano particles. The silica nano particles were characterized by FTIR, XRD and SEM [9].

Citric acid leaching treatment has been reported for extraction of silica from palm ash, [7]. The heating temperature, reaction time and concentration parameters on palm ash for silica extraction by leaching process were investigated. The effect of acid concentration on palm ash showed an increase percentage of extracted silica as the concentration increases [7]. Silica in micro and nano size forms find application in industries as precursor in ceramic production, synthesis of highly active silica gel, pharmaceutical products and as semiconductors, etc. [8].

2. Materials and Methods

2.1. Materials, Reagents and Equipments

Borassus aethiopum leaves (BAL), *Raphia africana* fruit shells (RAS), hot air oven, weighing balance, muffle furnace, 2.5 mol/dm³ sodium hydroxide solution, 2.5 mol/dm³ H₂SO₄ solution, 6 mol/dm³ HCl solution, 2.5 mol/dm³ HCl solution and concentrated H₂SO₄, Fourier transform infrared spectrophotometer (FTIR), X-ray fluorescence spectrometer (XFS), Atomic Absorption Spectrometer and Scanning electron microscope (SEM).

2.2. Sample Collection

BAL was harvested from a farm in Kusuv along Tyowanye – Jor Mbatyough Road in Buruku Local Government Area, Benue State, Nigeria. RAS was purchased from a market at Tyowanye, Shorov, Buruku Local Government area of Benue State, Nigeria where the fruit is marketed for commercial purpose.

2.3. Preparation of Sample

BAL and RAS were washed with distilled water thoroughly to remove dirt and other impurities. The washed precursors were dried in hot air oven for 2 hours at 100°C [9].

2.4. Preparation of *Borassus aethiopum* Leaves Ash (BALA) and *Raphia africana* Fruit Shells Ash (RASA)

Three portions (20 g each) of dried BAL were combusted in an electric furnace with air at 650°C for 4 hours. The temperature was maintained throughout this process to prevent crystallization of silica to form cristobalite and tridymite. The ash was collected, labeled as BALA and analysed. A similar procedure was used for RAS to produce the ash, RASA [16]

2.5. Extraction of Biosilica

The BALA and RASA were separately made into fine powder using mortar and pestle. The powder (10 g each) was stirred with 2.5 mol/dm³ NaOH solution using 250 mL beaker for 4 hours at 100°C to produce sodium silicate solution. The solution was filtered and the residue washed with boiling water. The filtrate was stirred with 2.5 mol/dm³ H₂SO₄ at 100°C to precipitate the silica gel. The gel was washed with deionized water to remove sulphate impurities and heated in an oven at 70°C for 15 hours to form amorphous silica. The amorphous silica was refluxed at 90°C with 6 M HCl for 6 hours and washed with distilled water to remove alkali or minerals such as Al, Na etc. The sample was treated with 2.5 M NaOH and stirred continuously using a magnetic stirrer for 10 hours at 90 - 100°C. The formed sodium silicate was acidified with concentrated H₂SO₄ to adjust the pH to the range 7.5 - 8.5 to form white precipitate. The white precipitate was filtered and dried in hot air oven at 110°C for 30 hours to obtain silica particles [8, 15, 17].

2.6. Characterization of Biosilica

The chemical bonds in extracted biosilica obtained from BASA and RASA were determined using FT-IR spectrophotometer 8400s Shimadzu 4000-450 cm^{-1} [18] at the Joseph Sarwuan Tarka University Makurdi-Nigeria and Ahmado Bello University, Zaria-Nigeria.

The morphologies of BASA and RASA were determined using Scanning Electron Microscope while their chemical compositions were determined using X-ray fluorescence [19, 20].

BALA and RASA (5 g, each) were separately first digested with 1N HCl at 90°C and mixed properly, filtered and kept in polyethylene bottle before transferred to atomic absorption spectrophotometer for determination of their chemical composition [21].

3. Results and Discussion

3.1. FTIR

Fourier transformed infrared (FTIR) spectra for biosilica from BAL and RAS respectively are shown in figures 1 and 2, respectively. Broad bands due to the stretching vibration of the H-O-H bond from the silanol groups were observed at 3395.60 and 3388.20 cm^{-1} . This is attributed to the adsorbed water molecules on the surface of the silanol [5, 22-24] group. Bending modes of water molecules trapped in the matrix of silica reported by Music, S., Filipovic, V., and Sekvanic, L. [25] and Faizul C. P., Abdulah C., and Fazhul B. [5] showed vibrational bands at 1636.3 and 1640.0 cm^{-1} . Asymmetric bending modes or vibration of siloxane (Si-O-Si) were observed at the bands: 1062.3 and 1058.6 cm^{-1} . Bands at 957.9 and 957.9 cm^{-1} correspond to symmetric bond stretching modes of siloxane (Si-O-Si) while band at 797.7 and 793.7 cm^{-1} correspond to its bending modes [23]. Vibrational frequencies at 1871.1, 1986.7, 2109.7, and 2165.6 cm^{-1} could be attributed to impurities or the gel's vibration mode [15].

3.2. Scanning Electron Microscopy (SEM)

The morphologies of biosilica from BALA and RASA at different magnifications were determined using SEM. The

micrographs for BALA are shown in figures 3, 4 and 5. The micrographs for RASA are shown in figures 6, 7 and 8. The results showed that the silica particles formed aggregates of various sizes with a broad range of size distribution. This agrees with the report by Napierska, D., Thomassen, L. C.J., Lison, D., Martens, J. A., and Hoet, P. [26]. The aggregate formation or agglomeration is attributed to the hydrogen bonding between silanol groups on the surface of silica [9, 27-29].

3.3. X-ray Fluorescence (XRF)

Figures 9 and 10 show the XRF spectra for biosilica obtained from BALA and RASA, respectively. The spectra showed two major peaks corresponding to the presence of silicon and oxygen which confirms predominant in biosilica from the samples and other traces due to impurities. Manjula K. R, Palamsamy P. N and Sivakumar [15] and by Music, S., Filipovic, V., and Sekvanic, L. [25] reported similar results.

3.4. Chemical Composition

The chemical composition of the extracted biosilica obtained from BALA and RASA at 650°C are shown in Tables 1 and 2. The results showed that BALA contained approximately 88% silica while RASA has 70% silica. In both samples, silica was obtained as the component with highest concentration in wt% while other components were obtained in trace percentages [30].

Tables 3 and 4 report the chemical composition of raw BALA and RASA at 650°C. The results revealed that BALA has 80% while RASA has about 67% silica. This is in agreement with the report by Faizul C. P., Abdulah C., and Fazhul B. [5, 28]. The concentration of the extracted biosilical in BALA (87.9%) is higher than that obtained from the ash content (82%). Similarly, for RASA, the extracted showed 70.3% silica while its ash recorded 67.7%. This is in agreement with the observations of Vaibhav, V., Vijayalakshmi, U., and Roopan, S. M. [31] and Khushbu G. P, Rakshith R. S, and Nirendra M. M. [32] as the major mineral component found in rice husk. The other components were found in very trace percentages.

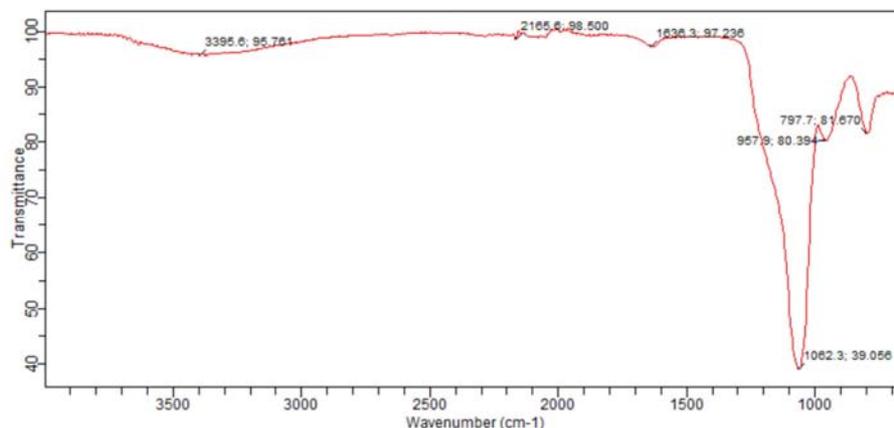


Figure 1. FTIR Spectra of Biosilica from *Borassus aethiopum* Leaves Ash.

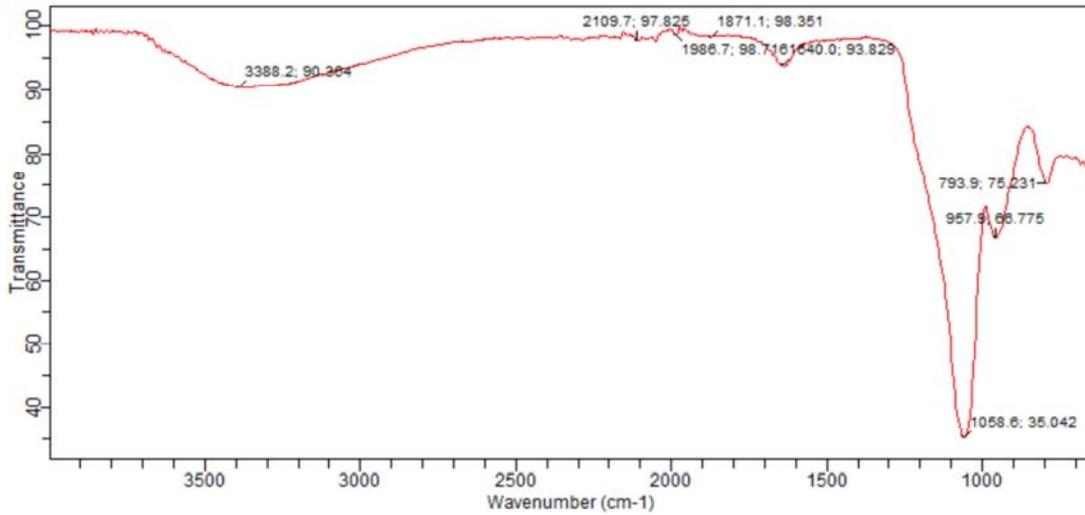


Figure 2. FTIR Spectra of Biosilica from *Raphia africana* Fruit Shells Ash.

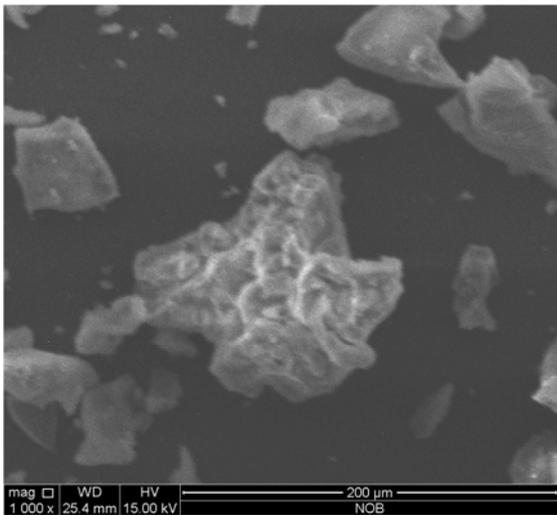


Figure 3. Scanning Electron Microscope Image of Biosilica Extracted from *Borassus aethiopicum* Leaves Ash at mag. 1000x.

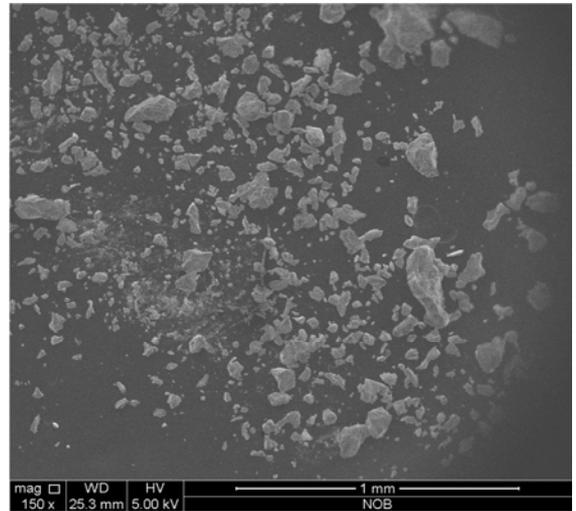


Figure 5. Scanning Electron Microscope Image of Biosilica Extracted from *Borassus aethiopicum* Leaves Ash at mag. 150x.

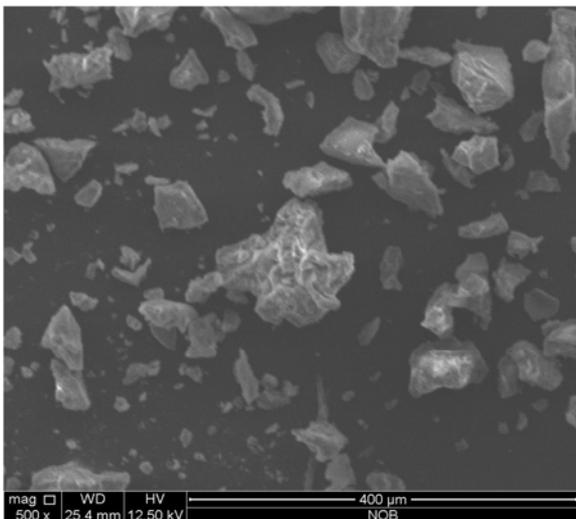


Figure 4. Scanning Electron Microscope Image of Biosilica Extracted from *Borassus aethiopicum* Leaves Ash at mag. 500x.

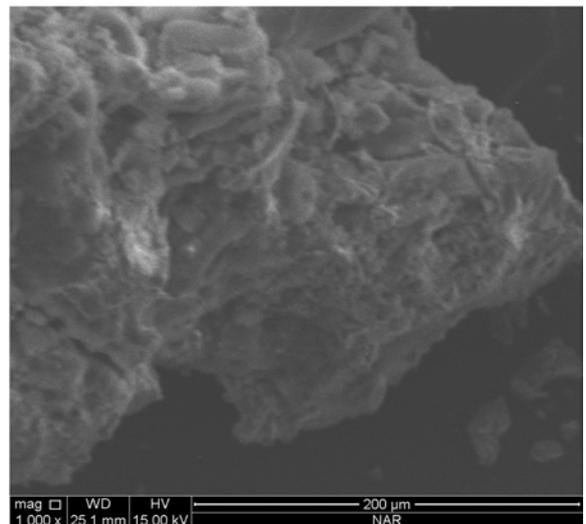


Figure 6. Scanning Electron Microscope Image of Biosilica Extracted from *Raphia africana* Fruit Shells Ash at mag. 1000x.

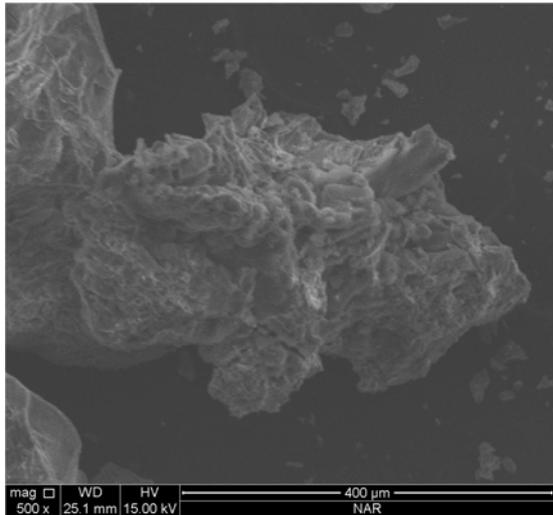


Figure 7. Scanning Electron Microscope Image of Biosilica Extracted from *Raphia africana* Fruit Shells Ash at mag. 500x.

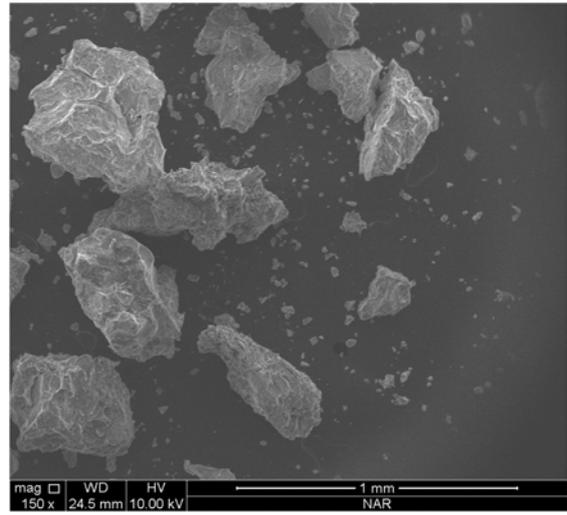


Figure 8. Scanning Electron Microscope Image of Biosilica Extracted from *Raphia africana* Fruits Shells Ash at mag. 150x.

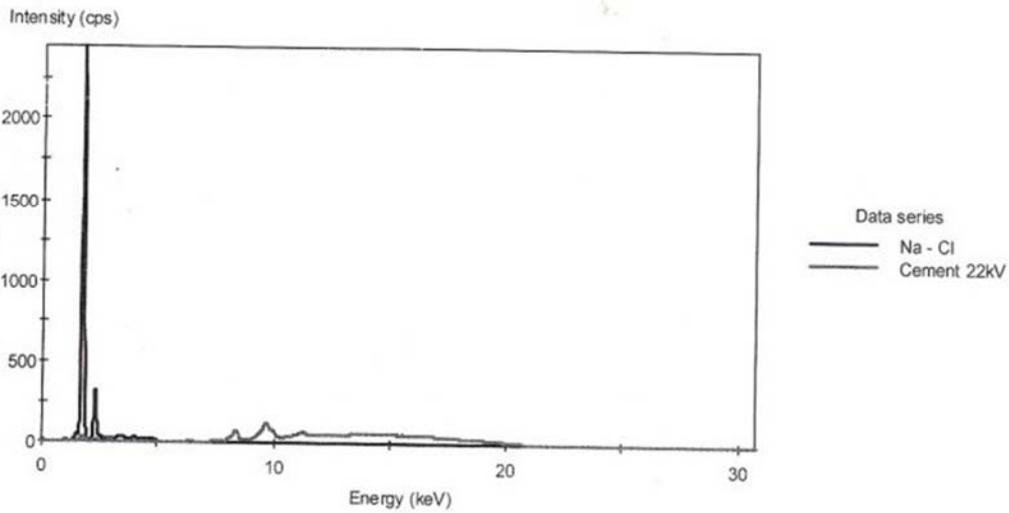


Figure 9. X-Ray Fluorescence Spectra of Biosilica from *Borassus aethiopum* Leaves As.

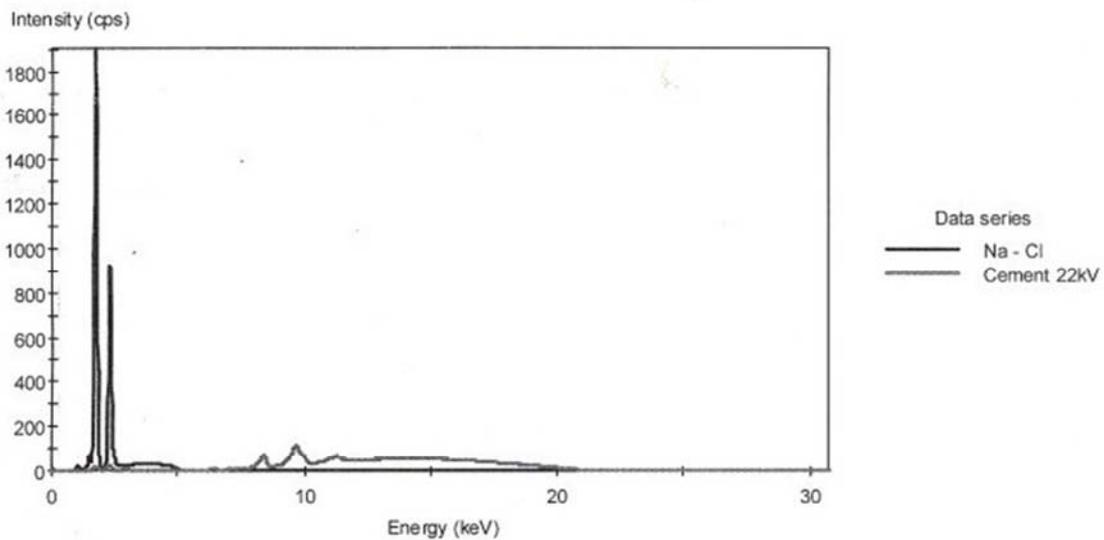


Figure 10. X-Ray Fluorescence Spectra of Biosilica from *Raphia africana* Fruit Shells Ash.

Table 1. Composition of Extracted Biosilica from BASA at 650°C.

Elements	Concentration (wt%)
Na ₂ O	3.483
MgO	0.047
Al ₂ O ₂	1.256
SiO ₂	87.961
P ₂ O ₂	0.100
SO ₂	7.038
Cl	0.056
K ₂ O	0.024
CaO	0.005
TiO ₂	0.003
Cr ₂ O ₃	0.002
MnO ₂	0.002
Fe ₂ O ₂	0.022
ZnO	0.000
SrO	0.000

Table 2. Composition of Extracted Biosilica from RASA at 650°C.

Elements	Concentration (wt%)
Na ₂ O	7.795
MgO	0.073
Al ₂ O ₂	1.900
SiO ₂	70.316
P ₂ O ₂	0.093
SO ₂	19.720
Cl	0.031
K ₂ O	0.027
CaO	0.007
TiO ₂	0.005
Cr ₂ O ₃	0.002
MnO ₂	0.002
Fe ₂ O ₂	0.027
ZnO	0.000
SrO	0.000

Table 3. Composition of Biosilica from BASA (Raw) at 650°C.

Elements	Concentration (wt%)
Na ₂ O	0.653
MgO	0.169
Al ₂ O ₂	4.730
SiO ₂	82.900
P ₂ O ₂	0.308
K ₂ O	2.339
CaO	3.605
TiO ₂	0.243
MnO ₂	0.021
Fe ₂ O ₂	0.021
ZnO	0.018

Table 4. Composition of Biosilica from RASA (Raw) at 650°C.

Elements	Concentration (wt%)
Na ₂ O	0.181
MgO	0.827
Al ₂ O ₂	5.407
SiO ₂	67.706
P ₂ O ₂	0.405
K ₂ O	3.970
CaO	2.330
TiO ₂	0.562
MnO ₂	0.164
Fe ₂ O ₂	0.030
ZnO	0.004

4. Conclusion

The study revealed that 70-90% silica can be extracted from BALA and RASA by precipitation method. These common wastes burnt at controlled temperature produced large amount of ashes. These ashes can be subjected to chemical treatment to extract silica particles. Particles obtained from precipitation method contain mainly silica and OH groups. Based on FTIR and SEM analysis they present a trend toward a spherical morphology [5, 26]. AAS results showed that the ashes are highly rich in silica due to low level of impurities. The high silica content can be used to prepare silica compounds and can minimize the environmental impact of BAL and RAS as such, converting waste to wealth and reducing the concentration of greenhouse gases like CO₂ which are released when plant wastes are left to decompose on their own.

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