

Silica-derived materials from agricultural wastes: characterization and comparative studies

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The management and disposal of agro-wastes are the major environmental problems now-a-days and presence of substantial quantity of silica in agro-wastes made them possible to convert waste into valuable fertilizer materials. The present study aimed to extract silica from various agro-wastes such as paddy straw (PS), sugarcane bagasse (SB), maize cobs (MC) and coconut husk (CH) by exposing to various calcination temperatures (500°C, 600°C and 700°C) and characterized through XRF, FESEM-EDAX, TEM, FT-IR, XR-D and other basic properties. The recovery of silica from paddy straw calcined at 700°C was higher than that of other temperatures and sources tested.

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1. Introduction

Huge waste generation, its inadequate disposal and lesser rate of transformation into value-added products are the major aspects that needs to be addressed in the perspective of circular economy [1-3]. As per the records of FAO, 1.3 billion tons of agro-wastes are generated every year [4], with an annual growth of 10%. The main technologies to valorise these wastes are generation of bioenergy, bio-fertilizers, chemical products, and materials of high economic value [5]. The productions of materials by these approaches are based on traditional extraction techniques from raw materials [6]. The silica obtained from agricultural biomasses has advantages (ecological and economic) over silica compounds produced using chemical precursors. Applications of eco-friendly siliceous materials has multiple uses in the manufacturing of super capacitors, drug delivery, sensors, catalysts and adsorbents [7,8].

Acid leaching is one of the major step in synthesis of silica for reducing the metallic impurities. Researchers employed different acids like HCl, sulphuric acid (H₂SO₄), oxalic acid (C₂H₂O₄) and citric acid (C₆H₈O₇) for acid leaching to check their effect on surface area of silica and maximum surface area was predominantly achieved with HCl [9]. Calcination of agricultural wastes at higher temperature produce ash and has comparatively pure composition, with reduced metallic impurities because of evaporation of all the organic constituents [10]. The quality of ash produced during calcination is influenced by temperature and heating rate [11]. Silica particles synthesized from green precursor exhibit diverse shapes at different calcination temperatures, including spherical [9], irregular [12], spherical agglomerates [13], irregular agglomerates [14], and needle-like [15].

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The silica extracted from calcinated pine needles (600°C) and rice husk (700°C) exhibited porous and spherical morphology with agglomeration and confirmed the presence of siloxane bonding with hydroxyl groups [15,16]. Higher calcination temperatures is associated with reduced particle aggregation [17]. Silica synthesized from maize stalks calcined at 650°C, 700°C and 750°C showed spherical morphology with agglomeration [18]. The FTIR results also confirmed the presence of siloxane bonding and hydroxyl functional groups, which is characteristic peak for silicon based materials and also revealed the presence of more intense peaks with increasing temperature [11] and depicted higher purity (80-95%) with least impurities [19,20] and amorphous structure [10]. Additionally, silica synthesized from rice husk have good biocompatibility with human cells [21,22].

Moreover, most studies focus on rice husk, as the main sources of silica [8], even though agricultural by-products such as maize cobs, sugarcane bagasse and coconut husk also contains higher silica content which are available in plenty and causes issues in agricultural solid waste management [23]. The basic properties of silica, such as pH, EC, bulk density (BD), moisture content, specific gravity, solubility are also expected to vary with different calcination temperatures. However, these differences have not been documented yet. Hence, to understand the influence of thermal decomposition on the properties of silica derived from agricultural wastes is crucial for applications in agricultural sector. The current study investigates the impact of thermal decomposition on the properties of silica synthesized from agricultural wastes to understand the relationship between temperature and resulting properties.

2. Materials and methods

2.1. Raw materials

The agricultural wastes were collected from farmlands of Tamil Nadu Agricultural University (TNAU), Coimbatore. All reagents used were of analytical grade, and their solutions were prepared with double distilled deionized water. The analytical grade HCl was used for acid leaching and neutralization of sodium silicate. The AR grade chemicals like NaOH and CaO were purchased from M/s. Merck & Co., Inc., Mumbai, India and used for alkali extraction and lime reactivity respectively.

2.2. Preparation of agricultural waste ash

2.2.1. Washing and acid treatment

The residues were washed with water followed by distilled deionized water to eliminate soluble particles, dust, and other contaminants. During this process, heavy impurities were removed and dried in hot air oven at 110°C for 24 hours [24] and for further purification, it was refluxed using 2M HCl for 90 minutes with intermittent stirring. Subsequently, the acid was decanted, and washed with distilled water until the rinse became free from traces of acid.

2.2.2. Thermal treatment

A known quantity of residues were subjected to varied thermal treatment by placing inside a programmable furnace (Nabertherm controller B 170, Nabertherm GmbH, Lilienthal, Germany) and calcinated at 500°C, 600°C and 700°C with a heating rate of 10°C per minute.

2.3. Characterization of ash

2.3.1. Composition

Quantitative chemical analysis of ash treated thermally at various temperatures (500°C, 600°C and 700°C) were accomplished using X-ray fluorescence (XRF, Philips, model PW 1480) by loading samples in calibrated spectrometer, applying X-ray excitation, and quantitatively analysing emitted characteristic X-rays.

2.3.2. Basic properties

The pH and electrical conductivity (EC) was determined in a sample: water ratio of 1:2.5 using the pH meter and conductivity bridge as suggested by Jackson [25]. The reactivity was determined by a chemical method outlined by Rao et al. [26] where a small quantity of ash (approximately 0.3 g) was suspended in 50 mL of saturated lime solution with constant stirring for 24 hours. The unused Ca was estimated by titration with 0.001M EDTA and expressed as mg CaO g⁻¹.

The bulk density (BD) depends on moisture, shape and size of ash and was calculated using Eq. (1) outlined by Nayak and Datta [27]. A measuring cylinder of 100 ml volume was filled with ash and the mass was weighed. The density was determined in triplicates and the average was taken.

$$\text{Bulk density} = \frac{\text{Weight of agri wastes ash}}{\text{Volume}} \text{ ----> Equation (1)}$$

2.4. Extraction of silica

About 5.0 g of ash was taken and added with 50 mL of 2.0 M sodium hydroxide (1:10 ratio) solution and heated for 120 minutes by stirring constantly. The viscous, transparent and colourless solution (Na₂SiO₃) obtained after filtration was permitted to cool at room temperature. Subsequently, the solution was neutralized with 2M HCl under slow and constant agitation using stirrer for gelation. After ageing for 24 hours, the gel was smoothly fractured and washed twice with distilled water in centrifuge at 3000 RPM for 5 min. and dried in a laboratory dryer (model SP-10032/1001, SP LABOR Ltd., BR) at 100 ± 5 °C, for 24 h [24]. Further, it was crushed in pestle & mortar and used for further characterization.

2.5. Characterization of silica

The newly synthesized silica from various agricultural residues were calcined at different temperatures viz., 500°C, 600°C and 700°C and characterized for its basic properties, morphology (FESEM-EDAX, TEM), structure (XRD) and Functional groups (FTIR).

2.5.1. Basic properties

The pH and electrical conductivity (EC) of materials were determined in a sample : water ratio of 1:100 using the pH meter and conductivity bridge as suggested by Liang and Wu [28]. Reactivity and bulk density (BD) of newly synthesized silica particles were determined using the aforementioned procedures outlined in the basic properties of ash.

The angle of repose is the angle at base of fertilizer heap obtained by allowing a material to fall onto a horizontal flat surface. Standard protocol described by International Fertilizer Development Centre [29] was used to measure the angle of repose by passing 100 g of material through funnel to form a cone on flat surface. The circumference of cone was measured at four corners and the angle of repose was determined using the following equation 2.

$$\text{Angle of repose (degree)} = \text{Arctangent} \frac{2h}{\bar{d} - d_i} \text{ ----->Equation (2)}$$

where 'h' is the height of cone, \bar{d} is the arithmetic mean of four diameters (cm), 'd_i' is the internal diameter of funnel spout (cm).

The moisture content was estimated by drying 20 g of material in hot air oven at 40°C until there was no appreciable change in its weight and expressed in percentage [30]. The solubility is defined as the maximal amount of material that can be soluble in a litre of water which was estimated by continuously dissolving a known quantity of material in one litre of water until it attain saturation and expressed in g L⁻¹ [31]. The specific gravity is calculated by measuring the weight of material and quantity of water displaced [31]. The silica yield for each of the residues processed at various calcination temperatures were determined by the following equation 3.

$$\text{Silica yield (\%)} = \frac{\text{Weight of silica obtained (g)}}{\text{Weight of processed residue (g)}} \times 100 \text{ ---->Equation (3)}$$

2.5.2. Morphology

The morphological and compositional analysis of silica particles were done using a field emission scanning electron microscope (MERLIN FE-SEM) coupled with Energy-dispersive X-ray analysis (EDAX). The powder samples were dispersed in distilled water and sonicated using ultrasonicator probe operated at a frequency of 20 ± 3 kHz for 5 minutes. The suspension was drop-casted against coverslips followed by vacuum drying and storage in vacuum desiccator until use. The coverslips were mounted to SEM stub using carbon tape followed by Au/Pd sputter coating to enhance the conductivity. The working distance (WD) for capturing images was kept at ≈ 5 mm while for EDAX analysis, it was kept at >8 mm.

Transmission Electron Microscopy (TEM) was used for microstructural characterization using ZEOL JEM-2100F Field Emission Electron Microscope. A small quantity of sample was dispersed properly in acetone using ultrasonicator probe (frequency 20 ± 3 kHz; time 10 min) and a tiny drop was pipetted onto a carbon coated 300 mesh Cu grid followed by natural drying. The images were obtained using microscope operated at a voltage of 120 kV.

2.5.3. X-Ray diffraction

The structural characterization of newly synthesized silica particles were analysed using X-Ray Diffraction (XRD) technique by acquiring a spectra using D2 PHASER X-ray diffractometer (Brooker, Germany) operated with Cu K- α radiation ($\lambda=1.55$ Å) at 30 kV and 10 mA. The samples were scanned between 2θ angle at 10° to 60° with a scanning step of 0.05 degree and a fixed counting time of 0.10 s step^{-1} . The graph was prepared using OriginPro 8.1 (OriginLab Corporation, MA, USA).

2.5.4. Functional groups

Functional groups in the silica sources were studied using Fourier transform infrared spectrometer (Nicolet™ 6700, TESIC, USA). Powder samples of silica calcined at various temperatures (500°C , 600°C and 700°C) were ground with KBr in a ratio of 1:100 (w/w) and pressed using an hydraulic press to form pellets. The IR spectra was obtained in $400 - 4000$ cm^{-1} wavenumber which gives information on the nature of surface hydroxyl groups and types of chemical bonds associated with newly synthesized silica. The graph was prepared using OriginPro 8.1 (OriginLab Corporation, MA, USA).

3. Results and discussion

3.1. Characterization of agricultural waste ash

3.1.1 Elemental composition

The chemical composition of ash from agricultural wastes calcined at different temperatures (Table 1) confirms the coexistence of elements such as SiO_2 , K_2O , CaO , MgO and Al_2O_3 . Composition of silica and other constituents are variable with sources because of their differential composition and recovery [12]. The silica contents varied from 78.4 to 92.1% in paddy straw ash, 69.1 to 80.8% in maize cob ash, 57.9 to 70.5% in sugarcane bagasse ash and 19.9 to 30.6% in coconut husk ash. Paddy straw yielded higher content of silica, which exceed the other agricultural wastes. The coconut husk ash yields very low silica content and having comparatively lesser potentials for producing silica. In the current study, silica content displayed a significant increasing trend with increasing pyrolyzing temperature from 500°C to 700°C . This rise in silica content corresponds with a decline in impurities, potentially attributed to the evaporation of volatile matter at higher temperatures [12]. A notable reduction in impurities was observed owing to increasing temperature (500°C to 700°C) which was proved in attaining economically pure material [10,20,32].

Table 1. Elemental Composition of ash derived from agricultural wastes at various calcination temperatures.

| Element | Paddy straw | | | Maize cobs | | | Sugercane bagasse | | | Coconut husk | | |
|--------------------------------|-------------|-------|-------|------------|-------|-------|-------------------|-------|-------|--------------|-------|-------|
| | 500°C | 600°C | 700°C | 500°C | 600°C | 700°C | 500°C | 600°C | 700°C | 500°C | 600°C | 700°C |
| SiO ₂ | 78.4 | 84.7 | 92.1 | 69.1 | 74.7 | 80.8 | 57.9 | 64.7 | 70.5 | 19.9 | 26.7 | 30.6 |
| K ₂ O | 1.92 | 1.81 | 1.22 | 3.17 | 3.04 | 2.63 | 3.02 | 2.87 | 2.56 | 12.1 | 11.6 | 11.4 |
| CaO | 2.51 | 1.26 | 0.81 | 4.31 | 3.67 | 3.15 | 3.57 | 3.29 | 2.98 | 20.7 | 19.3 | 19.1 |
| P ₂ O ₅ | 2.01 | 1.79 | 1.16 | 3.14 | 2.98 | 2.54 | 2.36 | 1.99 | 1.93 | 1.17 | 1.08 | 0.97 |
| MgO | 0.62 | 0.39 | 0.17 | 2.15 | 1.95 | 1.77 | 3.72 | 3.31 | 3.16 | 3.45 | 3.31 | 3.02 |
| MnO | 0.21 | 0.12 | 0.08 | 0.19 | 0.12 | 0.04 | 1.45 | 0.93 | 0.46 | 2.41 | 2.12 | 1.93 |
| Na ₂ O | 0.81 | 0.54 | 0.21 | 1.43 | 1.17 | 0.92 | 0.27 | 0.22 | 0.13 | 1.62 | 1.38 | 1.11 |
| Al ₂ O ₃ | 2.96 | 2.53 | 1.75 | 2.22 | 1.95 | 1.43 | 4.26 | 3.94 | 3.32 | 0.76 | 0.36 | 0.24 |
| Fe ₂ O ₃ | 2.93 | 1.78 | 1.02 | 2.02 | 1.86 | 1.46 | 4.24 | 3.98 | 3.31 | 1.19 | 1.14 | 0.99 |
| ZnO | 0.10 | 0.08 | ND | 0.55 | 0.18 | 0.09 | 0.94 | 0.87 | 0.34 | 0.72 | 0.59 | 0.43 |
| Cl | 0.32 | 0.25 | 0.21 | 0.29 | 0.19 | 0.15 | 1.25 | 0.93 | 0.56 | 15.0 | 14.7 | 14.3 |
| SO ₃ | 0.04 | 0.01 | 0.01 | ND | ND | ND | 2.21 | 0.91 | 0.52 | 3.11 | 2.89 | 2.67 |
| Carbon | 7.16 | 4.68 | 1.29 | 11.4 | 8.20 | 5.02 | 14.8 | 12.0 | 10.2 | 17.8 | 14.8 | 13.2 |

*ND: Not Detected

3.1.2. Basic properties

Selected physico-chemical properties of ash obtained from agricultural wastes at calcination various temperatures were depicted in figure 1. The pH of calcined agricultural wastes ash ranged from 7.04 to 7.51, 7.18 to 7.43, 6.87 to 7.12 and 8.31 to 8.91 for paddy straw, maize cobs, sugarcane bagasse and coconut husk respectively. The lowest pH was recorded with the ash of sugarcane bagasse followed by paddy straw at all calcination temperatures whereas higher pH was recorded with the ash from coconut husk. Lesser pH in sugarcane bagasse ash attributed to higher concentration of Al₂O₃ and Fe₂O₃, whereas the neutral to slightly alkaline pH of paddy straw and maize cob ash might be due to slight dominance of basic cations which was evident from the composition of ash. Conversely, higher pH of coconut husk ash may be due to the dominant presence of K₂O in the ash. The lowest pH was recorded in all the ashes calcined at 700°C, while the highest pH was recorded at 500°C which might be attributed to the effective removal of basic soluble cations at higher calcination temperatures. Electrical conductivity (EC) of calcined agricultural wastes ranged from 0.31 to 0.51 dS m⁻¹, 0.38 to 0.56 dS m⁻¹, 0.64 to 0.87 dS m⁻¹ and 0.71 to 0.98 dS m⁻¹ for paddy straw, maize cobs, sugarcane bagasse and coconut husk respectively. The highest EC was recorded in coconut husk ash (0.98 dS m⁻¹) followed by sugarcane bagasse ash (0.87 dS m⁻¹), maize cobs ash (0.56 dS m⁻¹) and the lowest in paddy straw ash (0.51 dS m⁻¹) at 700°C. The highest and lowest EC in coconut husk ash and paddy straw ash might be attributed to presence of more and less soluble salts (mainly K₂O and Chloride) in ashes respectively. The EC decreased with increasing temperature in all sources, which might be due to incomplete combustion at lower calcination temperatures, where all the soluble salts were not fully eliminated.

Reactivity of the calcined agricultural waste ash at various temperatures varied from 50.9 to 61.7, 48.9 to 54.9, 40.2 to 53.4 and 27.2 to 29.8 mg CaO g⁻¹ for paddy straw ash (PSA), maize cobs ash (MCA), sugarcane bagasse ash (SBA) and coconut husk ash (CHA) respectively. Increasing calcination temperature increased the reactivity of ash due to higher calcination temperature, potassium ions (K⁺) and carbon were effectively removed. The weight of silica is higher than at 600 °C and 500°C which might be the reason for higher reactivity of ash [24]. Bulk density of ash varied from 0.23 to 0.27, 0.29 to 0.33, 0.31 to 0.36 and 0.33 to 0.38 Mg m⁻³ for PSA, MCA, SBA and CHA respectively, which depends on texture of agricultural waste ash. Irrespective of sources, the density showed downward trend with increasing calcination temperature and attributed to melting of particles at higher calcination temperature [20,27].

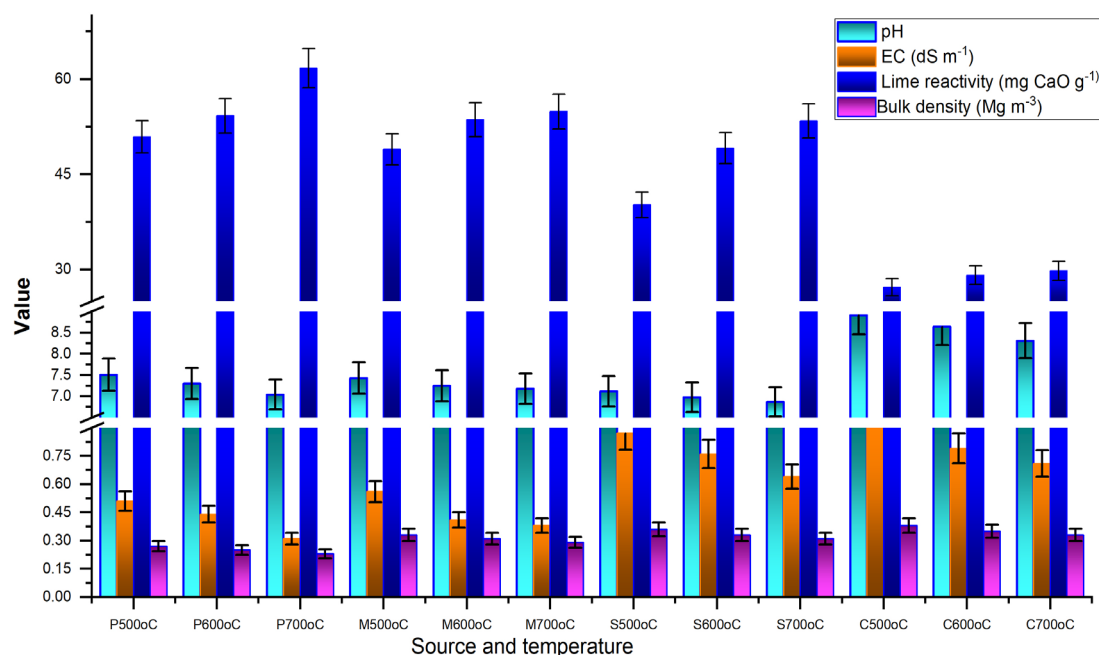


Fig. 1. Basic properties of silica derived from agricultural wastes at various calcination temperatures. (P: Paddy straw; M: Maize cobs; S: Sugarcane bagasse; C: Coconut husk calcined at 500°C, 600°C, 700°C).

3.2. Characterization of silica

3.2.1. Basic properties

Properties of silica synthesized by varying calcination temperature from agricultural wastes are presented in Figure 2 & 3. The silica obtained from all sources at all temperatures (500°C, 600 °C, 700 °C) has alkaline pH (7.72 to 8.88) which attributed to the use of sodium hydroxide (NaOH) during alkali extraction. Traces of sodium in the final product caused pH elevation, which was opined with the findings of Abboodi et al. [32]. The highest pH (8.88) was recorded in the silica particles obtained from SB calcined at 500°C attributed to the presence of more impurities. Conversely, lesser pH (7.72) was noted in silica synthesized from paddy straw calcined at 700°C. The electrical conductivity (EC) is an indicative of soluble salts which was low (0.16 dS m⁻¹) in paddy straw at 700°C among all the sources and higher EC (0.73 dS m⁻¹) was reported in silica synthesized from coconut husk calcined at 500°C which might be due to the presence of more soluble salts. Though differential increase in EC was noted at various calcination temperatures, the values are well below the threshold limit to cause salt injury.

The bulk density of silica products calcined at various temperatures were determined as per procedure described by Nayak and Datta [27] which varied from 0.09 to 0.13 Mg m⁻³ in paddy straw, 0.11 to 0.15 Mg m⁻³ in maize cobs, 0.10 to 0.14 Mg m⁻³ in sugarcane bagasse and 0.11 to 0.16 Mg m⁻³. The lowest (0.09 Mg m⁻³) and highest bulk density (0.16 Mg m⁻³) was reported in silica synthesized from paddy straw and coconut husk decomposed at a temperature of 700°C and 500°C respectively. In contrary, the angle of repose showed reverse trend attributing to the melting of silica particles and resulting in smaller particle sizes as compared to others and particles are piled steeply.

Reactivity of silica calcined from various agricultural wastes at different temperatures (500°C, 600°C, and 700°C) varied from 67.2 to 71.5 mg CaO g⁻¹ for paddy straw, 65.7 to 70.8 in maize cobs, 64.1 to 69.0 in sugarcane bagasse and 63.1 to 67.1 in coconut husk. It is worth noting that, reactivity increases with increase in silica content. The highest and lowest silica content was noted in paddy straw and coconut husk derived silica respectively. Higher reactivity was noticed in the products calcined at 700°C [24].

Moisture content of synthesized silica from all sources at all calcination temperatures was very low and not significant (0.11 to 0.13% in paddy straw, 0.12 to 0.15% in maize cobs, 0.09 to 0.13 in sugarcane bagasse and 0.10 to 0.12% in coconut husk). It was not affected by thermal decomposition which was similar with the finding reported by Abboodi et al. [33]. Lesser moisture content might be ascribed to breaking of water bond and silanol groups which resulted in condensation [34]. Higher moisture content reduce adsorption strength of silica thus, decreases the nutrient fixation by 40-90% [34]. The specific gravity of newly synthesized silica ranged from 2.19 to 2.22 g cm^{-3} in paddy straw and sugarcane bagasse, 21.8 to 2.23 g cm^{-3} in maize cobs, and 2.19 to 2.24 g cm^{-3} in coconut husk and found to be non-significant with all sources at all calcination temperatures.

The solubility of silica varied from 0.11 to 0.33 g L^{-1} in paddy straw, 0.20 to 0.43 g L^{-1} in maize cobs, 0.23 to 0.59 g L^{-1} in sugarcane bagasse and 0.37 to 0.68 g L^{-1} in coconut husk. The low solubility (0.11 g L^{-1}) was noted with paddy straw at 700°C which was due to the presence of fewer impurities. Higher solubility is noted in coconut husk calcined at 500°C which might be due to higher pH of final product. Silica is insoluble at neutral pH, and its solubility rises with increasing pH and beyond 11, it is highly soluble [35]. Higher solubility may also attributed to the presence of more soluble impurities (Na, Cl, Ca, K) because of improper calcination.

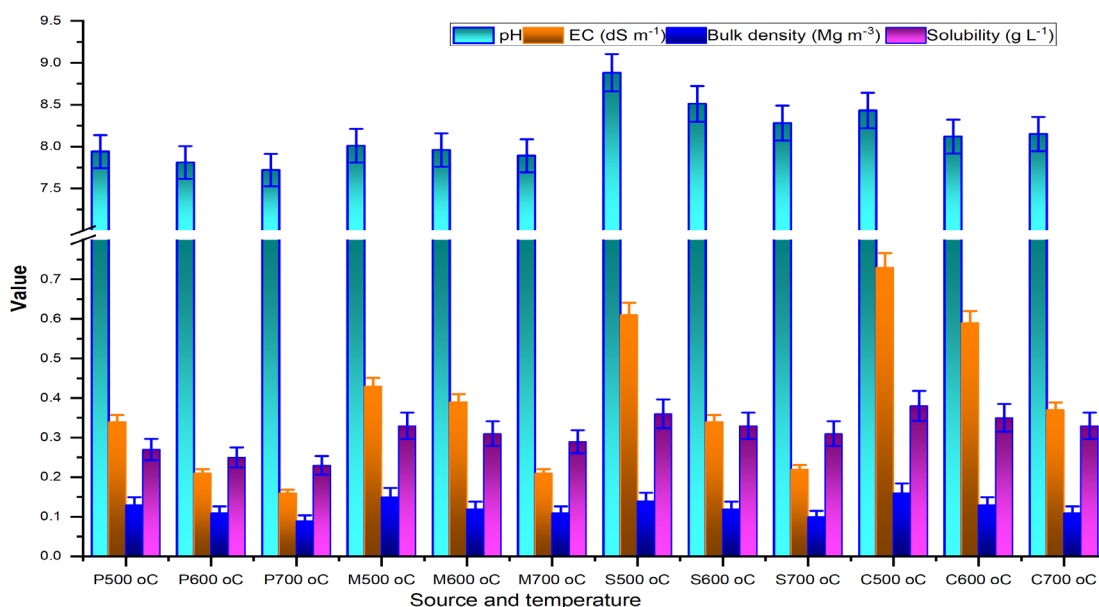


Fig. 2. Basic properties of silica (pH, EC, bulk density and solubility) derived from agricultural wastes at various calcination temperatures. (P: Paddy straw; M: Maize cobs; S: Sugarcane bagasse; C: Coconut husk calcined at 500°C, 600°C, 700°C).

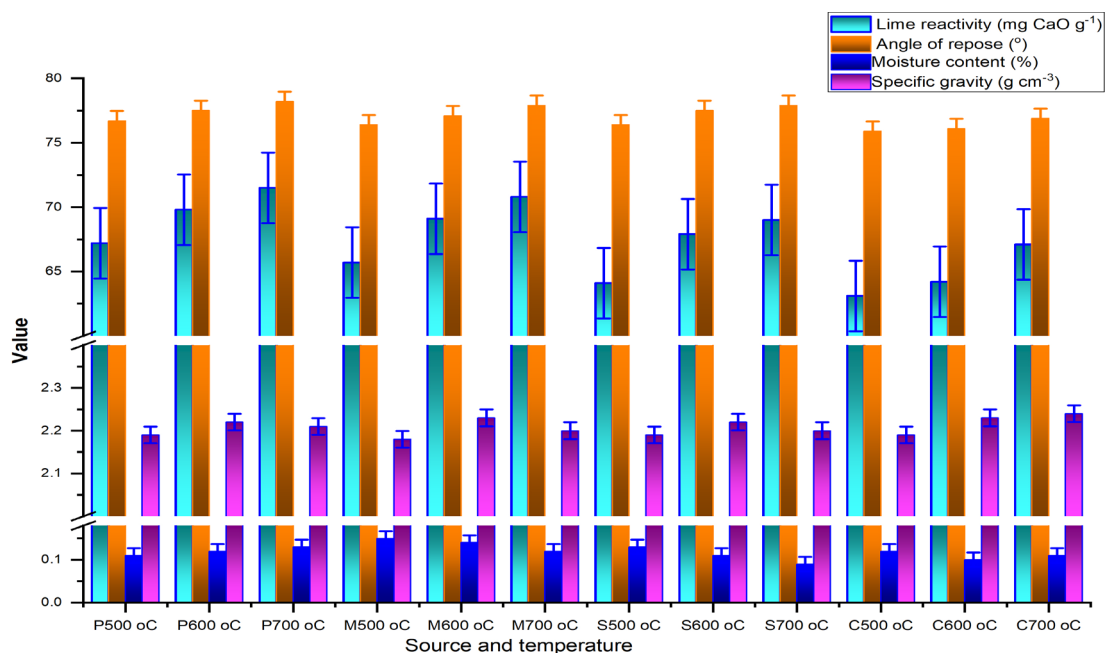


Fig. 3. Basic properties of silica (Lime reactivity, Angle of repose, Moisture content, Specific gravity) derived from agricultural wastes at various calcination temperatures. (P: Paddy straw; M: Maize cobs; S: Sugarcane bagasse; C: Coconut husk calcined at 500°C, 600°C, 700°C).

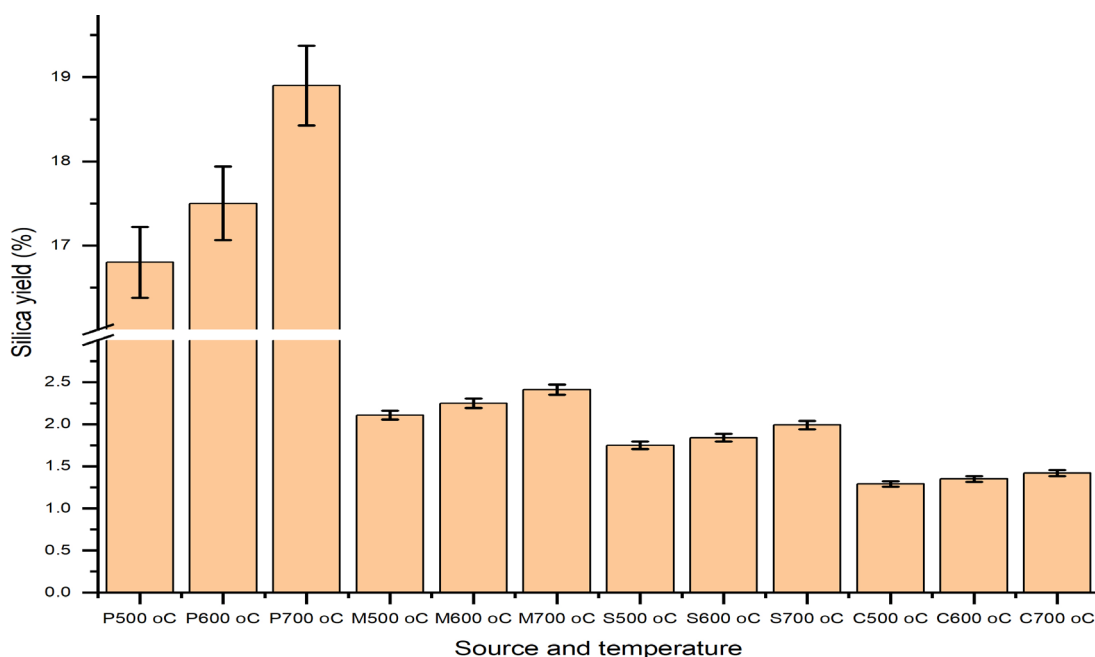


Fig. 4. Silica yield derived from agricultural wastes at various calcination temperatures. (P: Paddy straw; M: Maize cobs; S: Sugarcane bagasse; C: Coconut husk calcined at 500°C, 600°C, 700°C).

3.2.3. Morphology

The morphology of synthesized materials displayed the presence of spherical, linear, irregular and fibrous shaped particles (Fig. 5). The linear, fibrous, and agglomerated shape of silica particles obtained from sugarcane bagasse (SB) and coconut husk (CH) is related to the skeletal structure of biomasses, while paddy straw (PS) and maize cobs (MC) silica showed agglomerated particle morphology with uniform spherical arrangements, similar to their residual biomass source.

It is noted that the materials present heterogeneous morphologies among themselves so that the fibrous particles of SB and CH have hollow zones of variable size. The uniform morphological structure of paddy straw and maize cob silica is intrinsically linked to hierarchical agglomeration of SiO₂ on the external surface of material. The effect of synthesis conditions was characteristic and favoured by transformation of gel into xerogel [40]. However, considerable reduction in the agglomeration with increasing temperature was noted in paddy straw and maize cobs, whereas in sugarcane bagasse and coconut husk, agglomeration was not decreased and it was confirmed with the TEM micrographs got at 700°C of the present study (Fig. 6). The particles within these agglomerates were noticed to be in nanometric scale, ranging from 10 to 30 nm [39,40]. The silica prepared from corn residues showed spherical, agglomerated and non-porous morphology [41,42] where as in RH showed irregular and fibrous structure [43].

The EDAX analysis of silica obtained from various agro wastes confirmed the major presence of silicon and oxygen which varied from 96.6 to 99.4 wt% in paddy straw, 93.8 to 97.4 wt % in maize cob, 88.7 to 95.3 wt% in sugarcane bagasse and 88.2 to 93.6 wt% in coconut husk at various calcination temperatures (Table 2). Higher purity (99.4%) of silica and oxygen obtained from paddy straw calcined at 700°C indicates the successful removal of inorganic metallic ion impurities. The presence of small amounts of mineral impurities such as sodium, carbon, chloride, potassium and copper in the final product could be owing to the entrapment of impurities during instant gel formation, which hindered their complete removal even after crushing and washing [27]. Similarly, higher impurities were detected in silica synthesized from coconut husk at 500 and 600°C [8].

3.2.4. Functional groups

The FTIR spectrum of silica obtained from paddy straw, maize cobs, sugarcane bagasse and coconut husk are shown in fig. 7. The patterns detected in the frequency between 1050 and 1100 cm⁻¹ revealed the presence of asymmetric Si–O–Si stretching which is a characteristic feature of silicon materials. The peaks at 790-810 cm⁻¹ correspond to silanol bending (Si–OH) and Si–O coupling, due to adsorption of water on the silica surface. The bands around 1640 cm⁻¹ and 3440 cm⁻¹ represent O-H stretching for silanol (Si–OH) groups and angular vibration of water (H–O–H) molecules. Moreover, intensity of peaks increased with increasing temperature, which indicates the more quantity of silica. The absence of peaks between 1825 to 2800 cm⁻¹ in the silica obtained at 700°C confirms the successful elimination of organic substances. In contrast, at 600°C and 500°C, a slight fluctuations was noticed indicating the inadequate elimination of impurities [8,27,44,45].

3.2.5. X-ray diffraction

Structural characterization of newly synthesized silica was done through X-Ray Diffraction (XRD) technique at different calcination temperatures (500°C, 600°C and 700°C; Fig. 8). A single prominent broad peak around 2θ angle at 22° is noticed for the silica produced from all sources at all calcination temperatures [13], indicating their amorphous nature and the solid is either non crystalline or it consists of microcrystalline structures. The presence of minor peaks suggested the occurrence of trace amounts of sodium (Na), confirmed with the findings from EDAX spectrum obtained in the present study. Acid washing helped in delignification and facilitated loosening of rigid structure at a specified calcination condition. Similar observations was reported by Adebisi et al. [18], Athinarayanan et al. [21], Liou and Yang [9] and Nayak et al. [10] who synthesized silica using rice husk as raw material and found an amorphous X-RD pattern, which aligned closely with our study.

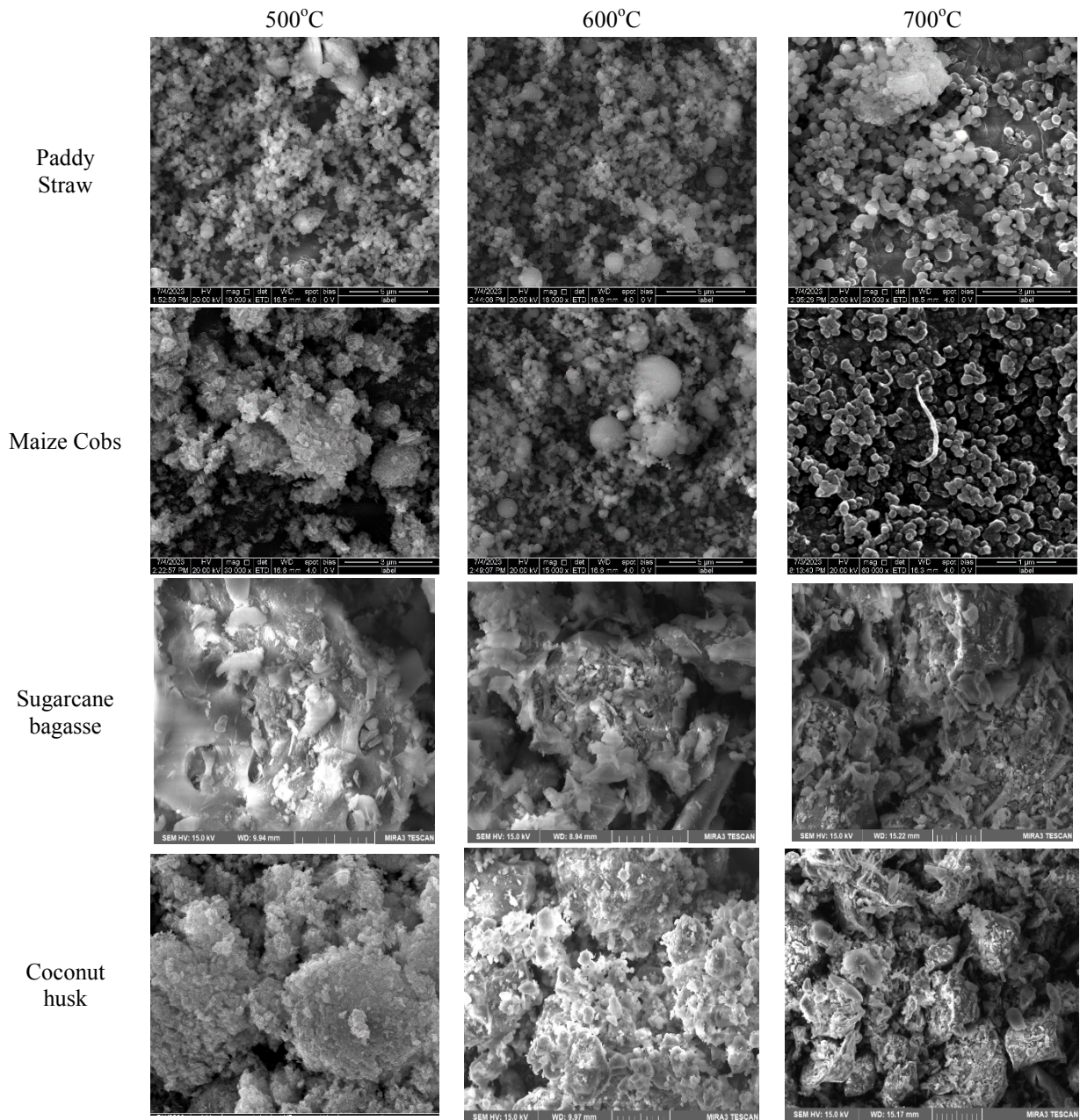


Fig. 5. SEM images of silica synthesised from agricultural wastes at various calcination temperatures

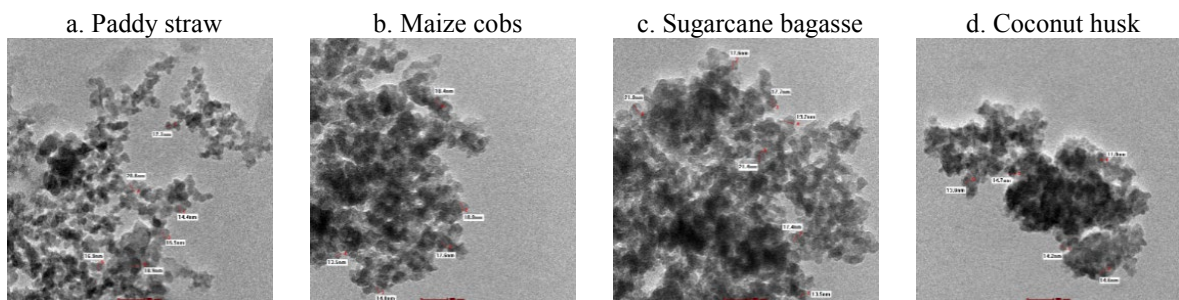


Fig. 6. TEM images of silica synthesized from agricultural wastes at 700°C.

Table 2. Composition (EDAX) of synthesized silica from agricultural wastes at various calcination temperatures.

| Sources | Calcination temperatures | Silicon | Oxygen | Carbon | Others |
|-------------------|--------------------------|---------|--------|--------|--------|
| Paddy straw | 500°C | 42.5 | 54.1 | 2.68 | 0.66 |
| | 600°C | 47.9 | 50.0 | 1.51 | 0.57 |
| | 700°C | 54.0 | 45.4 | 0.23 | 0.39 |
| Maize cobs | 500°C | 39.1 | 54.7 | 5.27 | 0.97 |
| | 600°C | 43.8 | 52.0 | 3.43 | 0.75 |
| | 700°C | 46.9 | 50.5 | 1.94 | 0.61 |
| Sugarcane bagasse | 500°C | 34.1 | 54.6 | 7.31 | 3.98 |
| | 600°C | 39.2 | 53.9 | 5.25 | 1.62 |
| | 700°C | 44.4 | 50.9 | 3.93 | 0.76 |
| Coconut husk | 500°C | 28.7 | 59.5 | 9.67 | 2.05 |
| | 600°C | 36.1 | 55.0 | 7.71 | 1.19 |
| | 700°C | 41.4 | 52.2 | 5.36 | 1.01 |

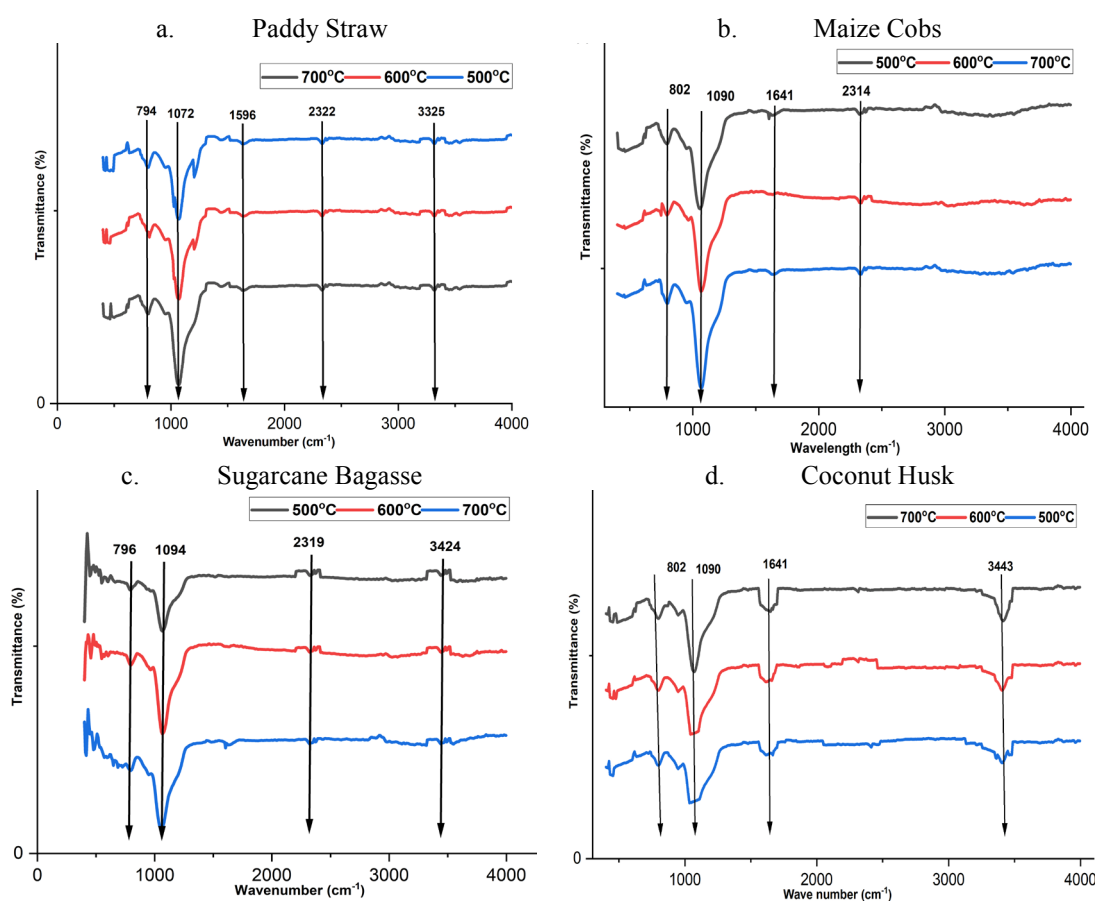


Fig. 7. FTIR spectra of silica synthesized from agricultural wastes calcined at various temperatures

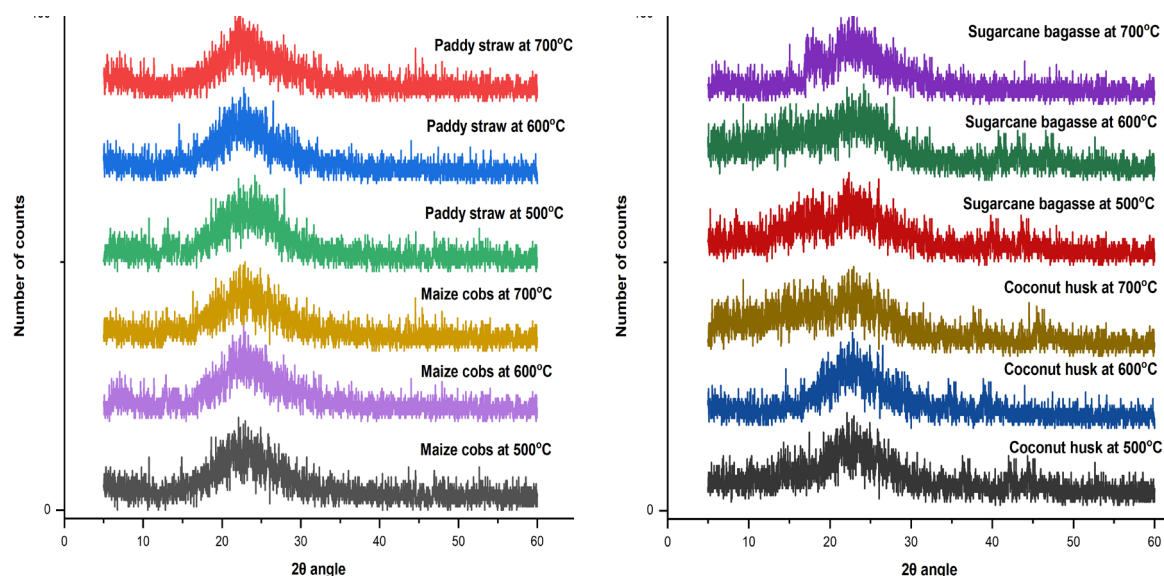


Fig. 8. X-RD spectra of silica synthesized from agricultural wastes calcined at various temperatures.

4. Conclusion

Synthesis of silica materials from agro-wastes minimizes the environmental constraints linked with existing disposal methods. The thermochemical treatment of paddy straw, maize cobs, sugarcane bagasse and coconut husk allowed their valorisation and conversion into silica. Higher recovery of ash was observed with paddy straw (PS) with lesser pH, EC, bulk density and more reactivity. The alkali extraction and acid leaching of paddy straw derived silica showed higher recovery and purity as compared to other agro-wastes. The silica particles synthesized from all the agro wastes consist of agglomerated nanometric structures having heterogeneous morphology. Agglomeration was decreased increasing calcination temperature in paddy straw and maize cobs where as in sugarcane bagasse and coconut husk, calcination temperature didn't affected the agglomeration which was confirmed in TEM micrographs. The broad characteristic peak around 1090 cm^{-1} , indicated the presence of silica in all the synthesized materials and intensity of peaks increased with increasing calcination temperatures. The X-RD peak at 2θ angle of 22° noticed for silica in all the sources at all calcination temperatures, indicates the amorphous nature. Higher calcination temperature recorded lesser pH, EC, bulk density, solubility and higher reactivity in silica synthesized from all sources which might be due to reduction in impurities. Overall, the current study emphasizes that calcination of agricultural wastes at 700°C yielded pure silica as compared to other temperatures (500°C and 600°C) and paddy straw yielded higher quantity of silica followed by maize cobs, sugarcane bagasse and coconut husk for applications in agriculture.

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