Journal of Environmental Biology
p-ISSN: 0254-8704 • e-ISSN: 2394-0379 • CODEN: JEBIDP

JEB®

Original Research Paper
Volume 45 Issue 4 July 2024 pp. 476-486
DOI: http://doi.org/10.22438/jeb/45/4/MRN-5251

J. Environ. Biol., 2024

Journal website : www.jeb.co.in ★ **E-mail :** editor@jeb.co.in

Maize stalks derived nanosilica: Synthesis, characterization and its kinetics in soil

B. Rakesh[1], C. Thiyagarajan[2]*, M. Subbu[1], J.S. Sharmila[3], S. Alagarsamy[4] and C. Narayanasamy[5]

[1]*Department of Soil Science and Agricultural Chemistry, Tamil Nadu Agricultural University, Coimbatore-641 003, India*
[2]*Department of Sericulture, Forest College and Research Institute, Mettupalayam-641 301, India*
[3]*Centre for Agricultural Nano Technology, Tamil Nadu Agricultural University, Coimbatore-641 003,, India*
[4]*Department of Crop Physiology, Tamil Nadu Agricultural University, Coimbatore - 641 003, India*
[5]*Department of Agricultural Entomology, Tamil Nadu Agricultural University, Coimbatore-641 003, India*

Received: 02 February 2024 **Revised:** 09 March 2024 **Accepted:** 04 May 2024

***Corresponding Author Email :** chitdeshwari@tnau.ac.in ***ORCiD:** https://orcid.org/0000-0001-5383-7718

Abstract

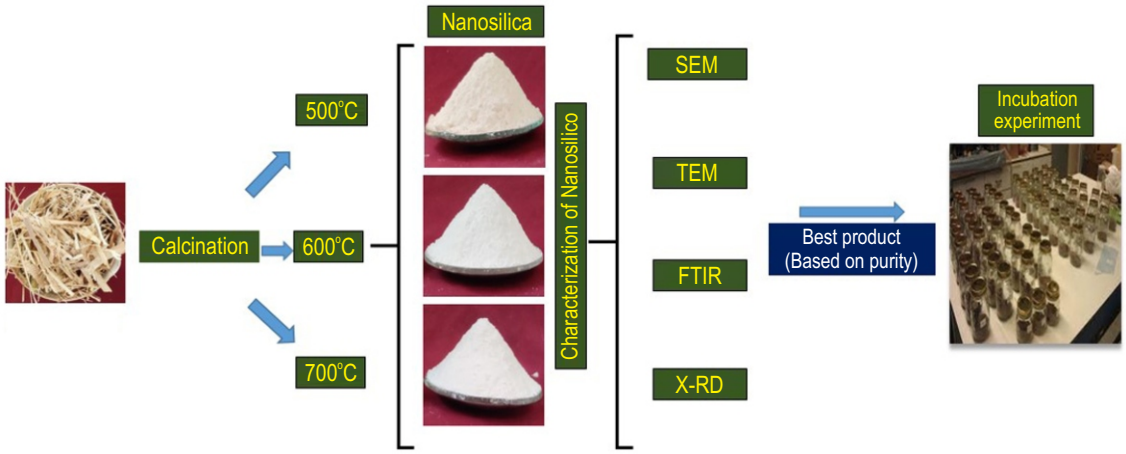
Aim: The current study aimed to synthesize nanosilica from maize stalks at various calcination temperatures and to evaluate silicon release pattern in soil.

Methodology: Nanosilica was synthesized by sol-gel method through thermal decomposition (500-700 °C) of maize stalks and evaluated for silicon release with varied levels (0, 5, 10, 15, 20, 30, 40 mg kg^{-1}) through an incubation experiment and the data obtained was fitted in various kinetic models.

Results: Nanosilica synthesized from maize stalks calcined at 700 °C showed spherical morphology with little agglomeration, amorphous nature and higher purity than the products obtained at 500 °C and 600 °C. Incubation experiment revealed that application of nanosilica at 40 mg kg^{-1} increased the available silicon upto 60 days with slight decrease at 80 days. The silicon release pattern from nanosilica was fitted in kinetic equations and observed that pseudo-second order equation describes the silicon release in a better way than other models.

Interpretation: The present study showed a sustainable approach to convert maize stalks into valuable nanosilica, addressing the pressing issue of agri-waste management. The nanosilica synthesized from maize stalks calcined at 700°C exhibited promising characteristics and good silicon release pattern which can be alternatively used as a fertilizer source in agriculture.

Key words: Agglomeration, Available silicon, Kinetics, Maize stalks, Nanosilica



How to cite: Rakesh, B., C. Thiyagarajan, M. Subbu, J.S. Sharmila, S. Alagarsamy and C. Narayanasamy: Maize stalks derived nanosilica: Synthesis, characterization and its kinetics in soil. *J. Environ. Biol.*, **45,** 476-486 (2024).

Introduction

A metalloid can be defined as an element that exhibits physical and chemical characteristics that lie between metals and non-metals. Amidst various metalloids, silicon stands as the most prevalent on our planet and ranks as the second most abundant element in the earth's crust, trailing only oxygen (Epstein, 2009). The role of silica in plants is intermediary, considered neither fully essential nor nonessential. While not crucial for most plants' survival, its presence enhances adaptation to various environmental stressors (Varsha and Chitdeshwari, 2022). In recent years, the field of nanotechnology has witnessed remarkable advancements, introducing innovative applications across various industries. One such advancement is the synthesis of nanosilica, a nanostructured form of silicon dioxide, which holds immense potential due to its unique properties and diverse applications (Mor *et al.,* 2016).

Nanosilica finds utility in areas ranging from electronics and materials science to medicine and environmental remediation, making its production a topic of significant interest (Adebisi *et al.,* 2017). Several methods have been employed to produce nanosilica in the form of gels and powders at nanoscale, which are highly porous, light weight materials with a large superficial surface area (Zaky *et al.,* 2008). Nanoscale silica materials demonstrate distinctive physico-chemical properties that contrast from their bulk counterparts (Mohd *et al.,* 2017). Nevertheless, it is crucial to highlight the chemical synthesis of nanosilica which involves the utilization of hazardous chemicals, elevated temperatures and energy-intensive procedures (Naik 2020). Consequently, the produced nanosilica may have adverse implications on soil, plants, human health, and environment (Sankar *et al.,* 2018). To reduce the adverse effects, synthesis from green materials is encouraged, which are less toxic, eco-friendly and cleaner than chemical methods (Doke *et al.,* 2021). The agricultural by-products like rice husk, maize cob and sugarcane bagasse are good sources for the synthesis of nanosilica (Karande *et al.,* 2021) through microwave heating processes which has been accomplished through sol-gel (Sarkar *et al.,* 2021), precipitation (Uda *et al.,* 2020), and calcination methods (Rafiee *et al.,* 2012). Controlled burning of raw materials yields silica with amorphous nature and high reactivity, smaller size with greater surface area (Chandrasekhar *et al.,* 2006).

Nanosilica particles synthesized from green precursor exhibit diverse shapes at different calcination temperatures, including spherical (Liou and Yang 2011), irregular (Anuar *et al.,* 2018), spherical agglomerates (Chindaprasirt and Rattanasak, 2020), irregular agglomerates (Gu *et al.,* 2015), and needle-like (Assefi *et al.,* 2015). Nanosilica extracted from calcinated pine needles (600 °C) and rice husk (700 °C) have porous and spherically shaped silica particles with agglomeration and siloxane bonding with hydroxyl groups (Assefi *et al.,* 2015; Doke *et al.,* 2021). Higher calcination temperature is associated with reduced particle aggregation (Kavaz and Vaseashta, 2019). Nanosilica synthesized from maize stalks calcined at 650 °C, 700 °C and 750 °C showed the spherical morphology with agglomeration (Adebisi *et al.,* 2020). FTIR results have also confirmed the presence of characteristic siloxane bonding and hydroxyl functional groups and the presence of more intense peaks with increasing temperature (Chandrasekhar *et al.,* 2006) and depicted higher purity (80-95%) with least impurities and amorphous structure (Adebisi *et al.,* 2020; Ananthi *et al.,* 2016).

The basic properties of nanosilica, such as pH, EC, bulk density, moisture content, specific gravity, solubility, texture, and colour are expected to vary with different calcination temperatures. However, these variations have not been documented yet. Hence, to understand the influence of thermal decomposition on the properties of nanosilica is crucial for tailoring its properties in agricultural sector. The current study investigates the impact of thermal decomposition on the properties of nanosilica synthesized from maize stalks to understand the relationship between temperature and resulting properties followed by silicon release from newly synthesized nanosilica product.

Materials and Methods

Raw materials: Maize stalks were collected from the Eastern Block, Tamil Nadu Agricultural University, Coimbatore. All reagents in this study used were of analytical grade, and their solutions were prepared with double distilled deionized water.

Preparation of Maize Stalk Ash

Washing and Acid Treatment: Maize stalks were washed with tap 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 hr (Rafiee *et al.,* 2012) and for further purification, it was refluxed with 2M HCl for 90 min with intermittent stirring. Subsequently, the acid was decanted and washed with distilled water until the rinse was free off traces of acid.

Thermal treatment: A known quantity of maize stalk was subjected to varied thermal treatment by placing inside a programmable furnace (Nabertherm controller B 170, Nabertherm GmbH, Lilienthal, Germany) and calcinated at temperatures of 500 °C, 600 °C and 700 °C with a heating rate of 10 °C per min (Morales-Paredes *et al.,* 2023). The resulting ash was referred as maize stalk ash.

Extraction of nanosilica: To 5.0 g of ash 50 ml of 2.0 M sodium hydroxide (1:10 ratio) solution was added and heated for 120 min by constant stirring. The viscous, transparent and colourless solution (Na_2SiO_3) obtained after filtration was cooled at room temperature. Subsequently, the solution was neutralized with 2M HCl under slow and constant agitation using stirrer for gelation. After 24 hrs, the gel was smoothly fractured and washed twice with distilled water in a centrifuge at 3000 rpm for 5 min (Nayak *et al.,* 2019). The xerogels obtained after drying the gels in a

laboratory dryer (model SP-102/100, SP LABOR Ltd., BR) at 100 ± 5 °C, for 24 hr (Rafiee *et al.,* 2012) were crushed in pestle & mortar and used for further characterization.

Characterization of nanosilica: The newly synthesized nanosilica from maize stalks calcined at different temperatures viz., 500 °C, 600 °C and 700 °C were characterized for its basic properties, morphology through FESEM-EDAX (MERLIN FE-SEM from Carl Zeiss), Transmission electron microscopy (TEM-ZEOL JEM-2100F Field Emission Electron Microscope), structure (X-ray diffractometer,D2 PHASER, Bruker, Germany) and functional groups (FTIR - Nicolet™ 6700, TESIC, WI, USA).

Basic properties of nanosilica: The pH and electrical conductivity (EC) of nanomaterials were determined in a sample: water ratio of 1:100 using a pH meter and conductivity bridge as suggested by Liang and Wu (2007). The reactivity was determined by a chemical method outlined by Rao *et al.* (1989), where a small quantity of ash (approximately 0.3 g) was mixed with 50 ml of saturated lime solution with constant stirring for 24 hrs. The unused Ca was estimated by titration with 0.001M EDTA and expressed as mg CaO g^{-1}. The bulk density depends on the moisture, shape and size of the maize stalk ash and was calculated using Eq. (1) outlined by Nayak and Datta (2022).

$$\text{Bulk density} = \frac{\textit{Weight of maize stalks}}{\textit{Volume}} \text{ ---->eq...(1)}$$

The angle of repose is the angle at the base of fertilizer heap obtained by allowing the material to fall onto a horizontal flat surface. Standard protocol described by International Fertilizer Development Centre (Santos *et al.,* 2019) was used to measure the angle of repose by passing 100 g of material through funnel to form a cone on the flat surface. The circumference of the cone was measured at four corners and the angle of repose was determined by eq. 2.

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

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 (Fruhstorfer, 1961). 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} (AOAC, 2000). The specific gravity was calculated by measuring the weight of the material and quantity of water displaced (AOAC, 2000).

Incubation experiment: An incubation experiment was conducted in the laboratory at the Department of Soil Science and Agricultural Chemistry, TNAU, Coimbatore to investigate the effect of various levels of synthesized nanosilica (0, 5, 10, 15, 30, 30, 40 mg kg^{-1}) at 700 °C on the silicon transformation in soil. Hundred grams of processed soil was weighed in polythene containers and mixed with the calculated quantities of nanosilica as per treatments. The experiment was conducted in Factorial Completely Randomized block Design (FCRD) with three replicates. The soil was moistened to field capacity and incubated for 80 days. Moisture corrections were carried out with double distilled water at alternate days on weight loss basis and continued up to the end of experiment. Destructive sampling was carried out at 20, 40, 60 and 80 days after incubation and used for assessing the silicon release pattern in soil.

Soil analysis: The experimental soil was sandy loam in texture with neutral pH (6.67), low electrical conductivity (0.30 dS m^{-1}), low available silicon (22.9 mg kg^{-1}) and belonged to the *Narasipuram* soil series. The soil was normal in bulk density (1.45 Mg m^{-3}), particle density (2.54 Mg m^{-3}) and low in organic carbon content (1.18 g kg^{-1}). It had low available nitrogen (176 kg ha^{-1}), medium available phosphorous (17.0 kg ha^{-1}) and high available potassium (375 kg ha^{-1}). The secondary nutrients were sufficient in quantity (800, 240 and 12.5 mg kg^{-1} of calcium, magnesium and sulphur). As regards the micronutrients, the soil was sufficient in available Cu (0.84 mg kg^{-1}), Fe (6.76 mg kg^{-1}) and Mn (3.02 mg kg^{-1}), while it was deficient in available Zn (0.80 mg kg^{-1}). Electrical conductivity and pH were analysed in a 1:2.5, soil:water extract using a conductivity probe and a glass electrode (Jackson *et al.,* 1973). Available silicon was extracted from soils with 0.5 M acetic acid and measured calorimetrically by molybdenum blue method (Korndorfer *et al.,* 2001).

Kinetic models: The data on silicon release from nanosilica in soil at different time intervals were fitted to zero-order, first order and second order kinetic models as given in Eq. 3,4 and 5

$$q_t = q_0 - k_0 t \text{ --------- (3)}$$

$$q_t = q_0 . e\text{-}k_1 t \text{--------- (4)}$$

$$1/q_t = 1/q_0 - k_2 t \text{ --------- (5)}$$

Where, 'q_0' and 'q_t' are the quantity of Si (mg kg^{-1}) released initially and at time 't' (days) respectively; k_0: zero order rate constant, mg kg^{-1} day^{-1}; k_1: first-order rate constant, day^{-1}; k_2: second-order rate constant, day^{-1} (Sparks, 2018). The data is also fitted in parabolic diffusion model proposed by Morris and Weber (1962) as below (6)

$$q_t = q_0 + k_p t^{1/2} \text{ --------- (6)}$$

Where, k_p: diffusion rate constant, $mg^{-0.5} kg^{0.5}$.

The experimental data was fitted to Elovich and power function model proposed by Aharoni *et al.* (1991) as given in Eq. 7 and 9.

$$q_t = b + k \ln t \text{--------- (7)}$$

$q_t = \alpha t^{\beta}$ --------- (8)

where, k: Elovich rate constant; b: release constant. The data is also modeled using pseudo-second order kinetic model given by Ho and McKay (1999) which was:

$t/q_t = 1/h + t/q_e$ --------- (9)

where, h: initial release rate, mg kg^{-1} day^{-1}; q_e: equilibrium concentration and calculated by

$h = kq_e^2$-------(10)

where, k is the pseudo-second order rate constant. The best fitting model was selected by considering the coefficient of determination (R^2).

Statistical analyses: The linear forms of seven kinetic equations were fitted to the kinetic experimental data. The R^2 values and release rates were subsequently acquired from the fitted equations. The constants and parameters of all the kinetic models were computed using Origin Pro 2022. The data was subjected to statistical analysis using SPSS software (Nie *et al.,* 1975) and simple variance analysis was done (ANOVA) using factorial completely randomized block design with two factorial arrangement (Si concentration and incubation interval) and three replications. The least significance test was used to uncover the variations between means at $p < 0.05$.

Results and Discussion

The properties of nanosilica synthesized by calcination of maize stalks at various temperatures are presented in Table 3. The obtained nanosilica at all temperatures (500 °C, 600 °C, 700 °C) had alkaline pH (8.62-8.91), attributing to the use of sodium hydroxide during alkali extraction, which is in line with the findings of Abboodi *et al.* (2020) who stated that, sodium impregnation in lattice holes of silioxanes might have elevated the pH, in the final product. The highest pH (8.93) was recorded in nanosilica particles obtained from maize stalks calcined at 500 °C due to more sodium, calcium and potassium impurities. Conversely, lesser pH was noted in nanosilica synthesized from maize stalks calcined at 700 °C. Electrical conductivity is an indicative of soluble salts which is found to be low (0.31 to 0.51dS m^{-1}) in all the sources and among all, higher EC was reported in nanosilica synthesized from maize stalks calcined at 500 °C. Though differential increase in EC was noted at various calcination temperatures, the values were well below the threshold limit to cause salt injury (Abboodi *et al.,* 2020). because of efficient removal of soluble impurities at higher calcination temperatures. The bulk density of new nanosilica products calcined at various temperatures varied from 0.15 to 0.11mg m^{-3}.The lowest (0.11 mg m^{-3}) and highest bulk density (0.15 mg m^{-3}) was reported in nanosilica synthesized from maize stalks decomposed at 700 °C and 500 °C, respectively, attributing to the melting of silica particles and resulting in smaller particle sizes as compared to others. Reactivity of newly synthesized nanosilica calcined at different temperatures (500 °C, 600 °C, 700 °C) varied from 68.7 to 74.1 mg CaO g^{-1}. Higher reactivity was noticed in the product calcined at 700 °C (74.1 mg CaO g^{-1}) which was in accordance with Rafiee *et al.* (2012) who stated that the silica synthesized at such temperatures are more reactive.

No significant variation was witnessed in angle of repose which ranged from 77.5 to 77.6°. The moisture content of the synthesized nanosilica at all calcination temperatures was very low (0.15 to 0.12%), which may be ascribed to breaking of water bond and silanol groups resulting in condensation (Setyawan *et al.,* 2019). The moisture content of silica must be less because higher moisture content can reduce adsorption strength of silica to phosphorus, thereby, decreases the fixation by 40-90% (Setyawan *et al.,* 2019). The specific gravity of newly synthesized nanosilica ranged from 1.18 to 1.23 g cm^{-3}, and it was not affected by thermal decomposition and the range of values are on par with commercially available nanosilica as stated by Abboodi *et al.* (2020).

The solubility of synthesized nanosilica varied from 0.12 to 0.22 g l^{-1} and low solubility (0.12 g l^{-1}) of nanosilica was noted at 700 °C which was attributed to the presence of fewer impurities. Silica is insoluble at neutral pH, and its solubility rises with increasing pH beyond 11 (Liou and Yang, 2011). In contrast, nanosilica synthesized at 500 °C exhibited comparatively higher solubility attributing to the presence of more impurities (Na, Cl, Ca, K) which are readily soluble. The texture of synthesized nanosilica was fine at all calcination temperatures and colour varied from light yellow to pure white. Light yellow colour was observed in nanosilica at 500 °C might be due to improper removal of yellow pigment in stalks at lower calcination temperatures which was reflected in the ash and resultant nanosilica (Fig. 1, 2).

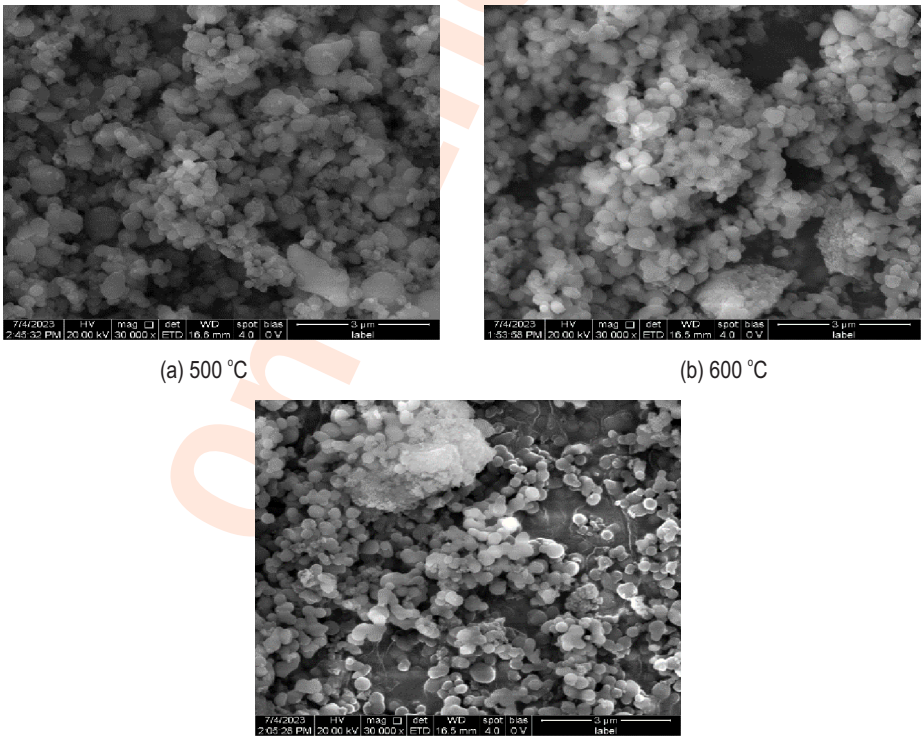
The morphological properties of synthesized nanosilica at various calcination temperatures (500 °C, 600 °C, 700 °C) were investigated using FESEM (Fig. 3), and noted that silica synthesized are spherical agglomerates which is a characteristic favoured by transformation of gel into xerogel (Adebisi *et al.,* 2020). No much differences between the obtained products was observed, however, considerable decrease in the agglomeration with increasing temperature was noted, which was confirmed with TEM micrographs of the present study. The particles within these agglomerates were noticed to be in nanometric scale, ranging from 10 to 20 nm which aligns with the findings of Uda *et al.* (2020), who synthesized silica particles from agro-wastes with size <100 nm. The EDAX analysis of nanosilica confirmed the major presence of silicon and oxygen. The silicon and oxygen contents varied from 91.1 to 98.1% at various calcination temperatures (Fig. 4). The variations in calcination temperatures were mostly associated with the purity (98.1%) of nanosilica obtained from maize stalks due to the reduction in impurities thereby slightly increasing the overall percentage of silicon in the final product. The minor peaks comprising 1.90 % variation is

(a) Raw maize stalks (b) 500 °C (c) 600 °C (d) 700 °C

Fig. 1: Visual appearance of (a) Raw maize stalks and (b) Maize stalks calcined at 500 °C (c) 600 °C and (d) 700 °C

(a) 500 °C (b) 600 °C (c) 700 °C

Fig. 2: Nanosilica synthesized from maize stalks calcined at various temperatures.



(a) 500 °C (b) 600 °C

(c) 700 °C

Fig. 3: SEM images of nanosilica synthesised at various calcination temperatures.

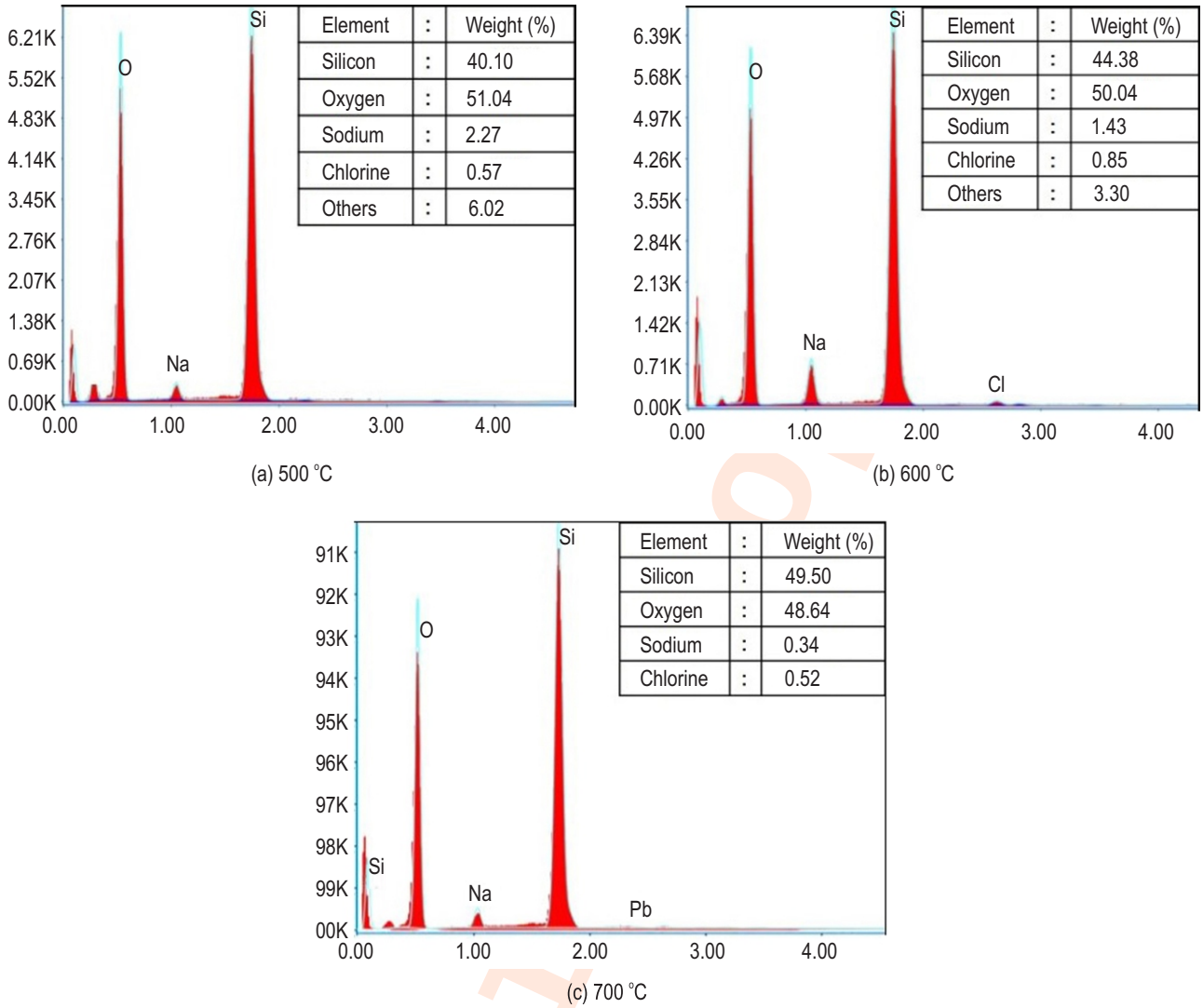
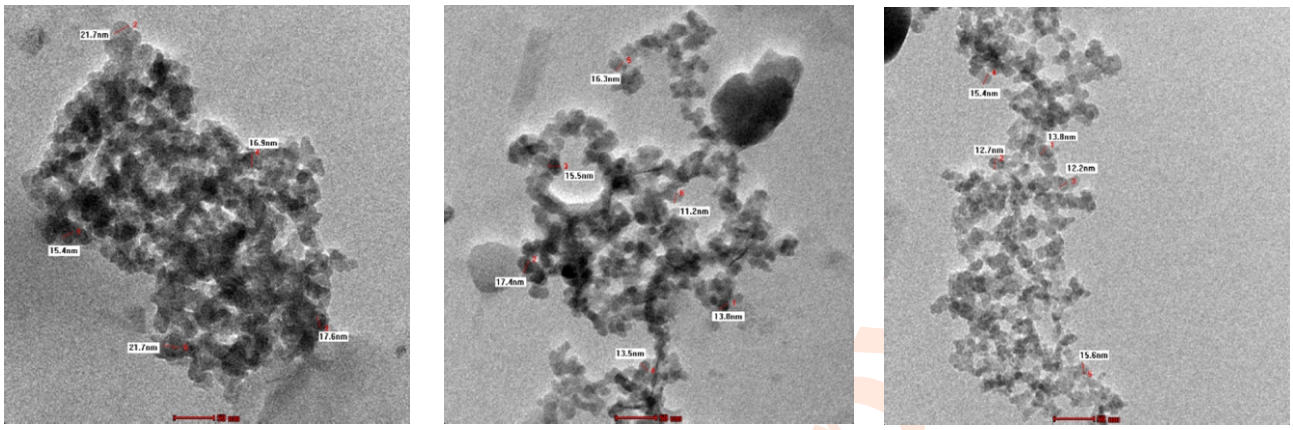


Fig. 4: EDAX spectrum of nanosilica obtained from maize stalks calcined at (a) 500 °C (b) 600 °C and (c) 700 °C.

likely to be attributed to sodium and other impurities. It is worth noting that, the presence of small amount of mineral impurities such as sodium, 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 (Nayak *et al.,* 2023). Similarly, higher impurities were detected in nanosilica synthesized from maize stalks at a calcination temperature of 600 °C (5.68%) and 500 °C (9.00%) which might be due to higher impurities present in maize stalk ash and synthesized nanosilica.

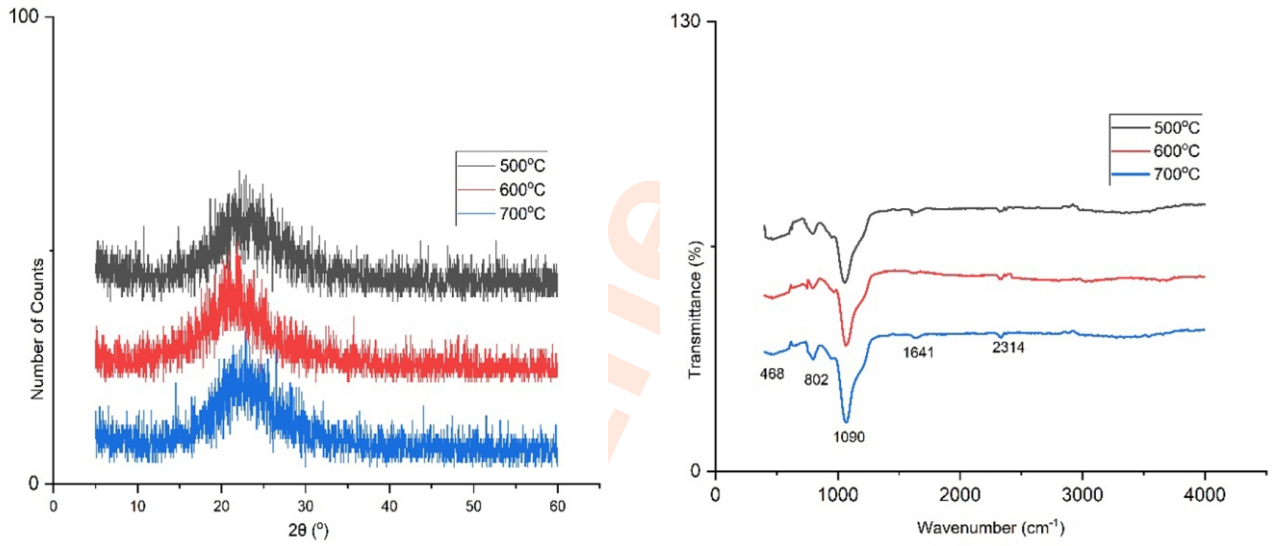
Transmission electron microscopy (TEM) provided a detailed insight into the size, shape and internal structure of silica (Fig. 5). A linked three-dimensional array of nanoparticles, a characteristic feature of sol-gel synthesis was observed with spherical shape. It also displayed decreased rate of agglomeration with increasing calcination temperature which was influenced by silicon-oxygen bonding and notably less agglomeration in nanosilica synthesized at 700 °C was similar to the findings of Adebisi *et al.* (2021) who stated the presence of less agglomeration in maize stalks at higher calcination temperatures. The presence of porous aggregated structures surrounding particles at increased temperature led to decrease in agglomeration within nanosilica (Morales-Paredes *et al.,* 2023). This parallelism among our results and the aforementioned studies support the notion that, calcination temperature plays a significant role in diminishing the level of aggregation.

Structural characterization of newly synthesized nanosilica was conducted through X-Ray Diffraction technique at different calcination temperatures (500 °C, 600 °C and 700 °C; Fig. 6a). A single prominent broad peak around 2θ angle of 22° was



(a) 500 ℃ (b) 600 ℃ (c) 700 ℃

Fig. 5: TEM images of nanosilica obtained from maize stalks calcined at (a) 500 ℃ (b) 600 ℃ (c) 700 ℃.



(a) XR-D spectra (b) FT-IR spectra

Fig. 6: (a) XRD and (b) FTIR spectra of nanosilica synthesized from maize stalks calcined at various temperatures

noticed for nanosilica at all calcination temperatures, indicating their amorphous nature and solid is either non crystalline or it consists of microcrystalline structures. The presence of minor peaks suggested the occurrence of trace amounts of sodium, 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 Nayak *et al.* (2023) who synthesized nanosilica using rice husk as a precursor and found an amorphous XRD pattern, aligning closely with our study. In addition, Chindaprasirt and Rattanasak (2020) demonstrated that the synthesis of biogenic nanosilica from sugarcane bagasse, showing a broad XRD peak at 2θ angle of 23–24° which is in line with the findings for this study.

Functional groups existing in the synthesized nanosilica at various calcination temperatures was determined by Fourier Transformed Infrared Spectroscopy (Fig. 6b). The newly synthesized nanosilica exhibit characteristic peaks at 468 cm^{-1} and 802 cm^{-1} which correspond to bending modes, symmetric vibration of siloxane (Si-O-Si) bonds, respectively (Nayak *et al.,* 2023). The sharp band at 1090 cm^{-1} is consigned to asymmetric stretching vibration of Si-O-Si which is a specific band for silica molecules (Song *et al.,* 2019).

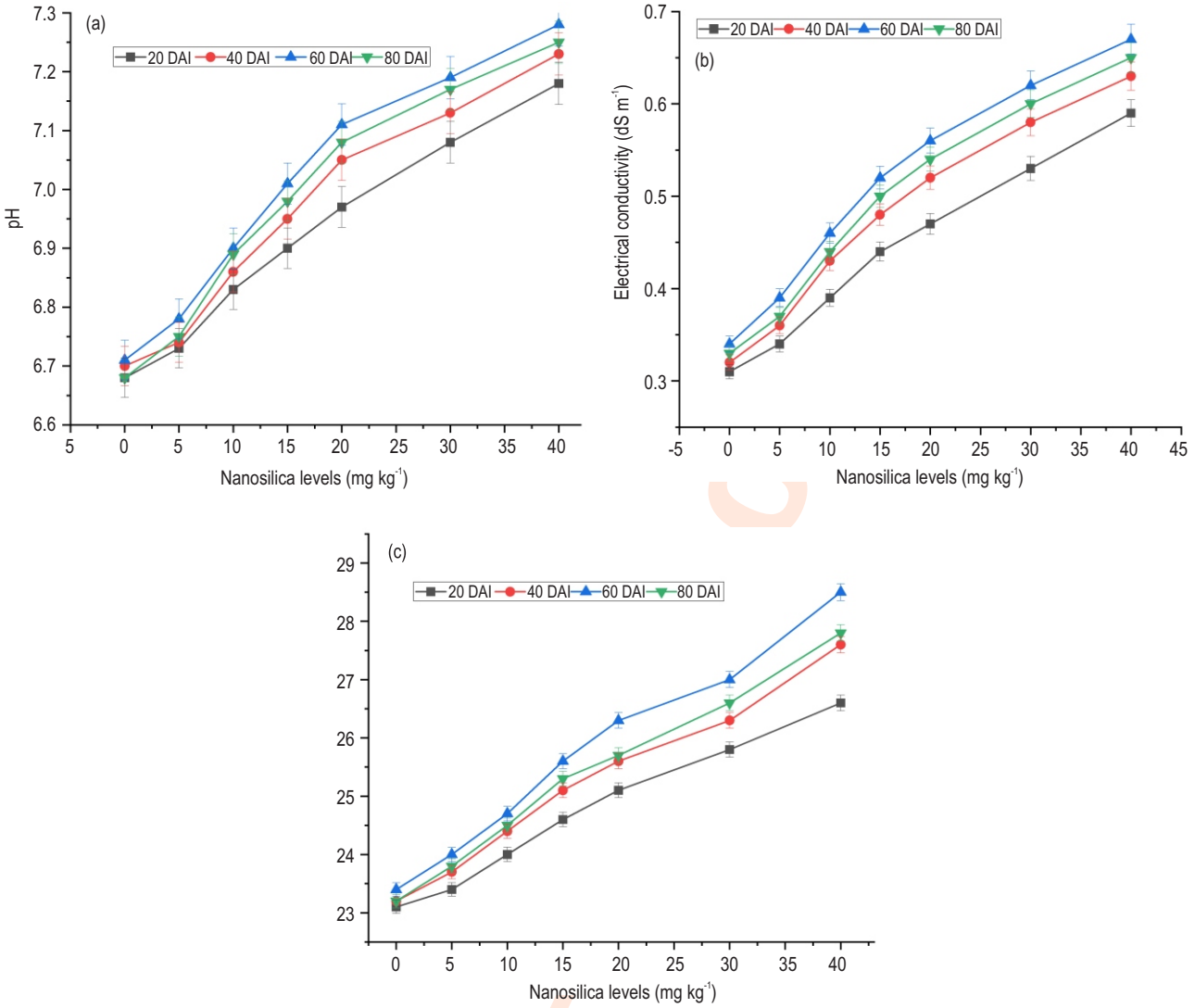


Fig. 7: Effect of nanosilica levels on a. pH; (b). Electrical conductivity and (c). Available silicon. Bars represent standard error; data are average of three replications; comparison of mean was done at 5% level.

The broad band at 1641 cm^{-1} and 2314 cm^{-1} is ascribed to the presence of O-H stretching frequency for silanol (Si-OH) group and adsorbed water, indicating the angular vibration of water molecules. The band spreading from 2600 to 3800 cm^{-1} represents vibrations of the surface silanols (Si–OH) groups (Imoisili and Jen, 2021). Because of higher purity of nanosilica at 700 °C, it is further used in incubation experiment with varied levels. The changes in soil pH and EC due to the addition of nanosilica at varying levels (0, 5, 10, 15, 20, 30, 40 mg kg^{-1}) were determined and depicted in Fig. 7a and b. A significant increase in soil pH and EC was observed up to 60 DAI (6.88 to 6.97, 0.44 to 0.51dS m^{-1}) and slightly decreased at 80 DAI (6.95, 0.41dS m^{-1}). Higher increase in the mean pH and EC values noted with 40 mg kg^{-1} nanosilica application (7.21, 0.64dS m^{-1}) whereas the lowest values of both was noted in control (6.69, 0.33 dS m^{-1}). Increase in the pH and EC values of incubated soil from 0 to 60 DAI with the application of different levels of nanosilica may be attributed to dissolution of silica into soluble monosilicic acid and also due to higher pH (8.42), presence of sodium in final synthesized product. A slight decrease in pH and EC noted at 80 DAI was attributed to the conversion of monosilicic acid to amorphous form. Available silicon content (Fig. 7c) in the soil revealed a consistent upward trend with increasing levels of nanosilica addition. Higher mean available silicon (27.6 mg kg^{-1}) was recorded with the addition of 40 mg kg^{-1} nanosilica, while the lowest Si was registered in control (23.2 mg kg^{-1}). Notably, silicon concentration elevated upto 60 days and reduced at 80 DAI. The silicon release from nanosilica fertilizer was fitted in seven kinetics equations viz., zero order, first

Table 1: Basic properties of newly synthesized nanosilica at different calcination temperatures

Properties	Nanosilica obtained at*		
	500°C	600°C	700°C
pH	8.91	8.76	8.42
EC (dS m^{-1})	0.24	0.15	0.12
Lime reactivity (mg CaO g^{-1})	68.7	73.4	74.1
Bulk density (mg m^{-3})	0.15	0.12	0.11
Angle of repose	77.5	77.6	77.5
Moisture content (%)	0.15	0.14	0.12
Specific gravity (g cm^{-3})	1.18	1.23	1.20
Solubility (g l^{-1})	0.22	0.14	0.12
Texture	Fine	Fine	Fine
Colour	Light yellow	Pure white	Pure white

*Nanosilica obtained from calcination of maize stalks at 500 °C, 600 °C and 700 °C

Table 2: Coefficient of determination (R^2) of kinetic equations

Nanosilica levels (mg kg^{-1})	Zero order	First order	Second order	Simple elovich	Parabolic diffusion	Power function	Pseudo-second order
0.0	0.13	0.10	0.11	0.07	-0.01	0.07	0.98
5	0.40	0.40	0.41	0.62	0.52	0.62	0.99
10	0.43	0.44	0.44	0.67	0.56	0.67	0.98
15	0.46	0.48	0.48	0.66	0.57	0.66	0.98
20	0.14	0.15	0.16	0.35	0.26	0.35	0.99
30	0.44	0.45	0.47	0.62	0.54	0.62	0.99
40	0.32	0.33	0.35	0.55	0.45	0.55	0.98
Mean	0.33	0.34	0.35	0.51	0.41	0.51	0.98

Table 3: Calculated rate constants for the pseudo second order model

Nanosilica levels (mg kg^{-1})	0	5	10	15	20	30	40
k	0.49	0.15	0.12	0.10	0.07	0.05	0.03
q_e	23.3	24.1	25.0	25.9	26.3	27.3	28.7
h	0.00	0.02	0.02	0.03	0.02	0.03	0.04

order, second order, simple elovich, parabolic diffusion, power function and pseudo second order kinetics equation, to understand the rate of silicon release.

The constants were estimated by fitting all equations and based on the highest coefficient of determination (R^2), the best fitted equation was selected (Table 2). Among the discussed equations, the mean coefficient of determination (R^2) values of 0.33, 0.34, 0.35, 0.51, 0.41, 0.51 and 0.98 respectively was observed for zero order, first order, power function, elovich and pseudo second order kinetics equations. As the 'R^{2}' value for pseudo second order equation was higher than others (R^2=0.98), it was considered as best fitted kinetic equation to describe silicon release from the applied nanosilica in soil. From Table 3, it was observed that, the quantity of Si released at equilibrium (q_e) increases with increasing the initial nanosilica concentration from 23.3 to 28.7 mg kg^{-1} and the intial release rate (h) also increased from 0 to 0.04 mg kg^{-1} day^{-1}. On the contrary, the release constant (k) decreased with increasing concentrations implying that, with increasing silica concentrations, the rate of silica release from the soil decreased even though the availability was found to be higher (higher q_e and h) and these results are in line with the findings of Haynes *et al.* (2020) who revealed that the major mechanism of holding silicates on the soil surfaces is specific adsorption or chemisorption.

The present study concluded that the maize stalks subjected to a calcination temperature of 700°C yielded highly

pure silica, having amorphous structure, spherical morphology, reduced agglomeration and siloxane bonding. Furthermore, the results of incubation experiment revealed that, pH, EC and available silicon increased with increasing concentration upto 60 DAI and slightly declined at 80 DAI and the data was fitted well in pseudo second order equation (R^2=0.98) indicating chemisorption as a rate controlling step behind silicon release.

Acknowledgements

The authors duly acknowledge the support rendered by the Department of Soil Science and Agricultural Chemistry, TNAU, Coimbatore and the Department of Science and Technology (DST) - INSPIRE, Government of India for funding the research.

Authors' contribution: B. Rakesh: Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Writing, Original draft preparation; **T. Chitdeshwari:** Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Supervision, Validation, Visualization, Writing and Editing; **S. Maragatham:** Editing; **J.S. Sharmila:** Reviewing and Editing; **A. Senthil:** Editing. **N. Chitra:** Editing.

Funding: This research work was financially supported by the Department of Science and Technology (DST), Government of India under INSPIRE Fellowship (IF210053) program.

Research content: The research content of manuscript is original and has not been published elsewhere.

Ethical approval: Not applicable.

Conflict of interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability: The data cannot be disclosed since it is a part of the student thesis research work.

Consent to publish: All authors agree to publish the paper in *Journal of Environmental Biology.*

References

Abboodi, S.M.T.A., E.J.A. Al-Shaibani and E.A. Alrubai: Preparation and characterization of nanosilica prepared by different precipitation methods. *Mater. Sci. Eng.,* **978**, 012031 (2020).

Adebisi, J.A., J.O. Agunsoye, I.I. Ahmed, S.A. Bello, M. Haris, M.M. Ramakokovhu and S.B. Hassan: Production of silicon nanoparticles from selected agricultural wastes. *Materials Today*: *Proceedings,* **38**, 669-674 (2021).

Adebisi, J.A., J.O. Agunsoye, S.A. Bello, I.I. Ahmed, O.A. Ojo and S.B. Hassan: Potential of producing solar grade silicon nanoparticles from selected agro-wastes: A review. *Sol. Energy,* **142**, 68-86 (2017).

Adebisi, J.A., J.O. Agunsoye, S.A. Bello, M. Haris, M.M. Ramakokovhu, M.O. Daramola and S.B. Hassan: Green production of silica nanoparticles from maize stalk. *Part. Sci. Technol.,* **38**, 661-667 (2020).

Aharoni, C., D.L. Sparks, S. Levinson and I. Ravina: Kinetics of soil chemical reactions: Relationships between empirical equations and diffusion models. *Soil Sci. Soc. Am. J.* **55**, 1307-1312 (1991).

Ananthi, A., D. Geetha and P.S. Ramesh: Preparation and characterization of silica material from rice husk ash–an economically viable method. *Chem. Mater. Res.,* **8**, 1-7 (2016).

Anuar, M.F., Y.W. Fen, M.H.M. Zaid, K.A. Matori and R.E.M. Khaidir: Synthesis and structural properties of coconut husk as potential silica source. *Res. Phys.,* **11**, 1-4 (2018).

AOAC.: International A: Official Methods of Analysis of the AOAC International. The Association: Arlington County, VA, USA (2000).

Assefi, M., F. Davar and H. Hadadzadeh: Green synthesis of nanosilica by thermal decomposition of pine cones and pine needles. *Adv. Powder Technol.,* **26**, 1583-1589 (2015)

Chandrasekhar, S., P.N. Pramada and J. Majeed: Effect of calcination temperature and heating rate on the optical properties and reactivity of rice husk ash. *J. Mater. Sci.,* **41**, 7926-7933 (2006).

Chindaprasirt, P. and U. Rattanasak: Eco-production of silica from sugarcane bagasse ash for use as a photochromic pigment. *Filler. Sci. Rep.,* **10**, 1-8 (2020).

Doke., D. Suhas, C.M. Patel and V.N. Lad: Improving performance of the synthesis of silica nanoparticles by surfactant-incorporated wet attrition milling. *Silicon,* **21**, 1-10 (2021).

Epstein, E.: Silicon: its manifold roles in plants. *Ann. Appl. Biol.,* **155**, 155-160 (2009).

Fruhstorfer, A.: Testing Granular Fertilizers for Hardness. Paper No. LE/61/58, The International Superphosphate Manufacturers' Association, Wiesbaden, Germany (1961).

Gu, S., J. Zhou, C. Yu, Z. Luo, Q. Wang and Z. Shi: A novel two-staged thermal synthesis method of generating nanosilica from rice husk via pre-pyrolysis combined with calcination. *Indus. Crops. Prod.,* **65**, 1-6 (2015).

Haynes, R.J. and Y.F. Zhou: Silicate sorption and desorption by a Si-deficient soil–Effects of pH and period of contact. *Geoderma,* **365**, 114204 (2020).

Ho, Y. S. and G. McKay: Pseudo-second order model for sorption processes. *Proc. Biochem.*, **34**, 451-465 (1999).

Imoisili, P.E and T.C. Jen: Facile extraction and characterization of silica nanoparticles from corn stalk by sol-gel hydrothermal methods. *Mater. Sci. Eng.,* **1107**, 012030 (2021)

Jackson, M.: Soil Chemical Analysis, Advanced Course. Dept. Soil Science UnivWisc, Madison, Wisconsin (1973).

Karande, S.D., S.A. Jadhav, H.B. Garud, V.A. Kalantre, S.H. Burungale and P.S. Patil: Green and sustainable synthesis of silica nanoparticles. *Nanotechnol. Environ. Eng.,* **6**, 29 (2021)

Kavaz, D. and A. Vaseashta: Synthesizing nano silica nanoparticles from barley grain waste: Effect of temperature on mechanical properties. *Pol. J. Environ. Stud.,* **28**, 1-9 (2019).

Korndorfer, G., G. Snyder, M. Ulloa, G. Powell and L. Datnoff: Calibration of soil and plant silicon analysis for rice production. *J. Plant Nutr.,* **24**, 1071-1084 (2001).

Liang, R.L.M. and L. Wu: Controlled release NPK compound fertilizer with the function of water retention. *React. Funct. Polym.,* **67**, 769–779 (2007).

Liou, T.H. and C.C. Yang: Synthesis and surface characteristics of nanosilica produced from alkali-extracted rice husk ash. *Mater. Sci. Eng. B.,* **176**, 521-529 (2011).

Mohd, N.K., N.N.A.N. Wee and A.A. Azmi: Green synthesis of silica nanoparticles using sugarcane bagasse. *J. Clean. Prod.,* **1885**, 21-29 (2017).

Mor, S., C.K. Manchanda, S.K. Kansal and K. Ravindra: Nanosilica extraction from processed agricultural residue using green technology. *J. Clean. Prod.,* **21**, 43-50 (2016).

Morales-Paredes, C.A., R.I. Linzán, M.D. Saquete, R. Luque, S.M. Osman, N. Botella and R.D.J. Manuel: Silica-derived materials from agro-industrial waste biomass: Characterization and comparative studies. *Envi. Res.,* **231**, 116002 (2023).

Morris, J.C. and W.J. Weber Jr: Equilibria and capacities for adsorption on carbon. *J. Sanit. Eng. Div.,* **90**, 79-108 (1964).

Naik, B.S.: Nanoparticles from endophytic fungi and their efficacy in biological control. In: Nanotechnology for Food, Agriculture, and Environment (Ed.: D. Thangadurai). Springer, Switzerland, pp 161-179 (2020).

Nayak, P.P. and A.K. Datta: An entropy-based TOPSIS approach for selecting best suitable rice husk for potential energy applications: pyrolysis kinetics and characterization of rice husk and rice husk ash. *Biomass Convers. Biorefin.,* **25**, 1-8 (2022).

Nayak, P.P. and A.K. Datta: Comparative assessment of chemical treatments on extraction potential of commercial grade silica from rice husk. *Eng. Rep.,* **1**, 12035 (2019).

Nayak, P.P., S. Nandi, K. Bhunia and A.K. Datta: Modelling the extraction process parameters of amorphous silica-rich rice husk ash using hybrid RSM−BPANN−MOGA optimization technique. *Mater. Chem. Phys.,* **293**, 126944 (2023).

Nie, N.H., C.H. Hull, J.G. Jenkins, K. Steinbrenner and D.H. Bent: SPSS: Statistical Package for the Social Sciences. McGraw-Hill, New York (1975).

Rafiee, E., S. Shahebrahimi, M. Feyzi and M. Shaterzadeh: Optimization of synthesis and characterization of nanosilica produced from rice husk. *Int. Nano Lett.,* **2**, 1-8 (2012).

Rao, G.R., A.R.K. Sastry and P.K. Rohatgi: Nature and reactivity of silica available in rice husk and its ashes. *Bull. Mater. Sci.,* **12**, 469-475 (1989).

Sankar, S., N. Kaur, S. Lee and D.Y. Kim: Rapid sonochemical synthesis of spherical silica nanoparticles derived from brown rice husk. *Ceram. Int.,* **44**, 8720-8724 (2018).

Santos, B.R., G.G.F. Guimaraes, V. Roncato, D.F.D. Cruz, W.L. Polito and C. Ribeiro: Biodegradable oil-based polymeric coatings on urea fertilizer: N release kinetic transformations of urea in soil. *Sci. Agric.,* **77**, 1–9 (2019).

Sarkar, J., D. Mridha, J.T. Orasugh, B. Gangopadhyay, D. Chattopadhyay, T. Roychowdhury and K. Acharya: Synthesis of nanosilica from agricultural wastes and its multifaceted applications: A review. *Biocatal. Agric. Biotechnol.,* **37**, 102175 (2021).

Setyawan, N., B. Hoerudin and A. Wulanawati: Simple extraction of silica nanoparticles from rice husk using technical grade solvent: Effect of volume and concentration. *Environ. Earth Sci.,* **309**, 012032 (2019).

Song, S., H.B. Cho and H.T. Kim: Surfactant-free synthesis of high surface area silica nanoparticles derived from rice husks by employing the Taguchi approach. *J. Ind. Eng. Chem.,* **61**, 281-287 (2019).

Sparks, D.L.: Kinetics and mechanisms of chemical reactions at the soil mineral/water interface. In: Soil Physical Chemistry. 2nd Edn., CRC press, pp. 135-192 (2018).

Uda, M.N.A., C. Subash, B. Gopinath, H. Uda, N.H. Halim, N.A. Parmin, M.N. Uda and A. Periasamy: Production and characterization of silica nanoparticles from fly ash: conversion of agro-waste into resource. *Prep. Biochem. Biotechnol.,* **51**, 86-95 (2020).

Varsha, V and T. Chitdeshwari: Screening maize hybrids for silicon efficiency to improve the growth and yield on silicon deficient soils. *Silicon,* **14**, 9711–9720 (2022).

Zaky, R., M. Hessien, A.A. El-Midany, M.H. Khedr, E.A. Abdel-Aal and K.A. Arawy: Preparation of silica nanoparticles from semi burned rice straw ash. *Pow. Technol.,* **185**, 31-42 (2008).