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Eco-friendly Synthesis and Characterization of Amorphous Nanosilica from Rice Husk

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ABSTRACT

Background: A significant amount of rice production waste is rice husk. It is not humifiable and turns into a significant environmental pollutant if not properly utilized. Rice husk contains silica nanoparticles, which is a major inorganic component. High purity amorphous silica nanoparticles can thus be produced using simple thermo-chemical procedures without polluting the environment by cutting out the release of carbon dioxide during the process.

Methods: A study was carried out to extract amorphous silica nanoparticles from rice husk ash using an environmentally benign chemical process. Utilising a variety of material characterization techniques *viz*., X-ray diffraction (XRD), fourier-transform infrared spectroscopy (FT-IR), field emission scanning electron microscope (FESEM), energy dispersive X-ray spectroscopy (EDS) and Particle size analyser (PSA), the extracted nanoparticles properties were confirmed.

Result: The amorphous behaviour of the silica sample was confirmed using transmission electron microscopy-selected area electron diffraction patterns and X-ray diffraction analyses, whilst siloxane and silanol groups were primarily discovered using Fourier-transform infrared spectroscopy. Images obtained using scanning electron and transmission electron microscopy showed initial nanoparticles to be present along with secondary microparticles, possibly as a result of their agglomeration. The extracted amorphous silica has particles with an average diameter of 35 nm. This synthesized silica nanoparticles can be used in agriculture, nano-additives, microelectronics, sensors and in other fields.

Key words: Characterization, Environment, Nanosilica particles, Rice husk.

INTRODUCTION

Agro-wastes are a significant byproduct of agricultural activity. The advancement of value-added products including nanoparticles, pulp, biochar, organic fertiliser and biogas from agricultural crop leftovers may be a significant way to address the issue of the best way to dispose of agro-waste (Bhuvaneshwari *et al*., 2019). Burning crop residue or agricultural waste was seen to be a severe health peril (Nagendran, 2011). It is a significant contributor to local pollution in addition to subjecting the majority of those around to high levels of particulate matter (Bhuvaneshwari *et al*., 2019). An alarming rise in air pollution, especially in 2015 and beyond, has been attributed to the widespread burning of agricultural waste in different parts of the world, which has brought the issue of agricultural waste management to the attention of various international agencies. Cereal crops are mostly grown in East Asian nations including China, India, Pakistan and Bangladesh. China and India are the two countries with the highest global carbon emissions, respectively (FAOSTAT, 2021). Prior research stated that in-situ agricultural crop residue combustion accounted for more than 33% of all biomass combustion in Asian countries (Chen *et al*., 2019). After China, India has the second-largest agro-based economy in the world with year-round crop cultivation. According to the Indian Ministry of New and Renewable Energy (MNRE), India generates 500 Mt of crop residue annually. The remaining 92 Mt of this 500 Mt of agricultural residue is still burned in various agricultural fields throughout India, while some of it has been utilised for fodder and other uses (NPMCR, 2014). The world's top rice-producing nations, including India, have an abundance of rice husk (RH), a biomass that is discarded throughout agricultural practises. While being burnet as a fuel, RH

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produces a large volume of rice husk ash (RHA) and has a very high thermal efficiency. Rarely employed in the commercial sector, RH creates a significant amount of RHA around 20% of RH when used as fuel. According to Koteswara and Pranav (2011) and Soltani *et al.* (2015) when rice husk is burned in ambient air with twenty million tonnes per year worldwide, the by-product is rice husk ash. The handling and transportation of rice husk are difficult due to its low density and poor commercial interest, which leads to disposal issues and significant environmental hazard (Pode, 2016). Therefore, numerous efforts have been made to use RH/RHA for the manufacture of Nanosilica, which typically resides in the amorphous phase in RH/RHA. The numerous techniques for extracting silica from RH/RHA and their sustainable usage in diverse fields were compiled and addressed by Fernandes *et al.* (2017) and Shen (2017).

Environmentalists from all around the world have focused on the agriculture industry in recent years in an effort to create an effective strategy for minimising agro waste. Agro-waste can be used in a wide variety of ways for reuse and sustainable development. One such area that has tremendous potential for agro-waste prevention is nanotechnology. Naddaf *et al.* (2020) and Yuvakkumar *et al.* (2014) described the preparation of silica materials utilising a variety of extraction procedures, including solution precipitation, sol-gel processing, thermochemical redox reaction and vapour-phase reaction. Tetraethyl orthosilicate (TEOS), sodium silicate and silicon alkoxide are typically utilised as precursors to silica for manufacturing in large quantities. At high temperature (1300°C), silicon alkoxide is traditionally derived from raw silica sand via a multistep carbo thermal reaction pathway (Arunmetha *et al*., 2015), while sodium silicate is extracted by heating quartz, an earth substance, to a high temperature of 1300°C and then treating it with sodium carbonate (Mejia *et al*., 2016). Both of the aforementioned methods use a lot of energy and have environmental risks. Additionally, these technologies produce greenhouse gases like CO_2, making them unsuitable for silica production in large quantities (Ma *et al*., 2012). Furthermore, the primary raw material may become scarce if natural resources like quartz are used to produce silica. Laane (2018) reported that the synthesized amorphous silica nanoparticles with diameters in the range of 20 to 40 nm are most commonly used in foliar application in the field of agriculture. Therefore, in recent years, there has been an increase in interest among researchers in finding alternative sources of silica and ways to extract it.

Instead of sodium carbonate (Na_2CO_3), sodium hydroxide (NaOH) is preferable for the alkali-SiO_2 extraction method for producing silica from RHA because Na_2CO_3 releases a tremendous amount of CO_2 during the extraction process, making the procedure unsustainable for the environment. As a result, a few tweaks were made to the current study's process to make it more environmentally friendly. The prevailing technique involves mixing RHA directly with Na_2CO_3, which results in the production of sodium silicate and CO_2. Despite being straightforward and affordable, this practice pollutes the environment as its produces CO_2 (Sun and Gong, 2001). Therefore, in the current investigation, RHA was first dissolved in the water before Na_2CO_3 was added. As an outcome, carbonic acid, which is safe for the environment, rather than CO_2 has been produced. This is because silica rich husk ash did not completely dissolve when distributed in water since it was difficult to break the covalent structure of silica; instead, meta-silicic acid (H_2SiO_3) was produced. When this meta-silicic acid was combined with sodium carbonate, sodium silicate (Na_2SiO_3) and carbonic acid (H_2CO_3) were produced. The byproduct carbonic acid is a mild acid upon stabilization poses no threat to the environment. As a result, this method may be appropriate for producing silica in large quantities. As a result, the objective of this study was to extract pure amorphous silica nanoparticles (SiO_2-NPs) from RHA using a reusable, environmentally benign process. Energy-dispersive X-ray spectroscopy (EDS), fourier transformation infrared (FT-IR) and X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) were used to characterise the retrieved silica.

MATERIALS AND METHODS

Materials and chemicals

This study was carried out during the year 2022, in Tamil Nadu Agricultural University, Coimbatore. The study subject rice husk was collected from the Department of Food processing and engineering milling unit. Department of Agronomy, Tamil Nadu Agricultural University (TNAU) in Coimbatore provided the muffle furnace, magnetic stirrer, sonicator, centrifuge, pH metre, vacuum oven, sodium carbonate and hydrochloric acid, distilled water, a mesh with a 5 mm cell size, petri dish and a hot air oven. XRD, FT-IR, EDS and PSA from Centre for Agricultural Nano Technology, TNAU, Coimbatore and FESEM from Avinashilingam University, Coimbatore, were employed for characterization.

An *et al.* (2011) effectively synthesised amorphous SiO_2-NPs from acid treated RHA (amorphous powder) using a two-step acid-alkali reaction technique. The procedure was modified to be more environmentally friendly. The rice husk was washed twice with running tap water and distilled water, then leached for 30 minutes with one normal hydrochloric acid at a ratio of 1:5, followed by a second two-washing process with double-distilled water to remove any remaining acid, flour, dust, or contaminants. The cleaned rice husk was removed from the liquid using a filter mess with a cell size of five millimetres and the remaining rice husk was shade dried at room temperature for a day before being collected in a clean glass petriplate and dried uniformly in a hot air oven at 105°C.

Rice husk was first leached with 1 N HCl and then RHA was produced by calcining RH at 700°C for six hours. Ten grams of RHA were dissolved in 100 ml of double-distilled water at a ratio of 1:10. For proper mixing, the mixture was placed on a magnetic stirrer for 30 minutes at 500 rpm at room temperature. After that, the mixture was ultrasonically treated using an ultrasonic probe for 15 minutes at a frequency of 24 kHz to ensure that the RHA particles were evenly distributed throughout the water, which is represented in equation (Eq 1) below:

$$SiO_2\ (RHA) + H_2O \rightarrow H_2SiO_3 \qquad .....Eq\ (1)$$

It was then combined with an equivalent volume of one normal sodium carbonate and heated for two hours at 90 °C while being stirred occasionally, given below in (Eq 2).

$$H_2SiO_3 + Na_2CO_3 \rightarrow Na_2SiO_3 + H_2CO3_3 \qquad .....Eq\ (2)$$

The obtained solution was then cooled to ambient temperature and centrifuged three times at 5000 rpm for 10 min each, discarding the carbonic acid supernatant (H_2CO_3). To the remnant Sodium silicate (Na_2SiO_3) with one drop of one normal hydrochloric acid (HCl) at a time, the residue was brought to neutral pH shown in equation (Eq 3).

$$Na_2SiO_3 + 2HCl \rightarrow SiO_{2\ (aq)} + 2NaCL + H_2O \quad .....Eq\ (3)$$

The sample was then left to aged for 24 hours before being repeatedly cleaned with double-distilled water to remove the impurities. The sample was then dried in a vacuum oven that operated for two hours at 650 mm Hg pressure in order to remove water. Utilising Eq 4, silica recovery from RHA was computed.

$$\text{Silica recovery \%} = \frac{\text{Mass of the silica obtained}}{\text{mass of RHA}} \times 100 \qquad .....Eq\ (4)$$

Characterization

The FT-IR approach was used to analyse the SiO_2 nanoparticles' functional groups. In an agate mortar, spectral-grade KBr powder was combined with Nanosilica at a weight ratio of 2 mg SiO_2:200 mg KBr. The powder combination was formed into pellets with a thickness of 0.5 mm and a diameter of 13 mm. FT-IR 6800 type A spectroscopy was used to measure the infrared (IR) spectra of Nanosilica over the 4000 to 400 cm wavenumber range.

The RIGAKU's ULTIMATE-IV X-ray diffractometer was used to identify the amorphous phase of Nanosilica. Cu Kα was used as a radiation source (λ = 1.5405) operating at a constant voltage and current of 30 mA at 40 kV with a diffraction angle (2θ) scan range of 5 to 80° to get the XRD pattern.

Tescan Mira3 FESEM was used to evaluate the morphology and particle size of the Nanosilica. 'Image J' software was used to compute the size of the silica particles from the image obtained from FEGSEM. An examination of Nanosilica's dynamic light scattering was also carried out utilising a PSA (HORIBA, LB550). Using a JEOL 6610 LA and energy dispersive X-ray spectroscopy (EDS), the chemical makeup of Nanosilica was evaluated.

RESULTS AND DISCUSSION

The aforementioned process was used to make silica nanoparticles from RHA. The silica sample percentage recovery was found to be 92.20. This outcome is comparable to the silica recovery reported by Nayak *et al.* (2019) using rice husk ash and sodium carbonate. The following section provided a description of RHA-Silica characteristics. RHA-Silica's XRD pattern is illustrated in Fig 1. For the silica sample, a broad hump at a 2θ angle of 22.56 degree was noticed, demonstrating the sample amorphous nature. Ma *et al.* (2012) Yalc and Sevinc (2001) also found similar results when they isolated silica nanoparticles from rice husk and reported a large peak oriented at a 2θ angle of 22°. Other scanning angles from 10° to 80° showed no sharp peaks, indicating no evidence of any sort of specified structure in the crystalline form. On top of that, the Bragg diffraction peaks' Gaussian peak fitting was carried out. Broader de-convoluted peaks were produced after the entire Bragg diffraction peak set was fitted with Gaussian functions (Fig 1). This finding demonstrates that the sample contained the typical amorphous constituents despite the lack of any organised phases of crystalline nature. Sampath *et al.* (2012) used the Gaussian function for an X-ray diffraction analysis of amorphous and nanocrystalline structures and they found that a wider Gaussian peak denotes the presence of an amorphous constituent. In Fig 2, the FTIR spectrograph was depicted. Hossain *et al.* (2019) stated that between the bands 1700 and 2750 cm^{-1}, silanol (Si-O-H) and siloxane (Si-O-Si) groups predominate in RHA-Silica. While the band position at 1635.03 cm^{-1} for the silica sample is attributed to the bending vibration of the H_2O molecule in the Si-OH group, the band at 3495.14 cm^{-1} for RHA-Silica was attributed to the stretching vibration of the O-H group. Si-O-Si is described as having an asymmetric stretching vibration in the band at 1054.72 cm^{-1}. The Si-O bond's symmetric stretching vibration generated the wavenumber at 800.97 cm^{-1}, while the Si-O bending of the siloxane group for RHA-Silica is designated for the band at 450.13 cm^{-1} (Costa and Paranhos, 2018). Silanol groups are produced by solubilizing sodium silicate with hydrochloric acid, whereas siloxane groups are produced by condensation (Azat *et al*., 2019).

Fig 3, depicts the FESEM pictures of SNPs sample using FESEM micrograph, by using FESEM with high enlargement, the spongy structure of synthesised Nanosilica was demonstrated, the particle size and shape of synthesised silica were studied. SNPs can be depicted to have a circular form and have particles that range in size from 19.79 to 36.51 nm. In RHA-Silica, agglomeration and spherical SiO_2-NPs were witnessed. Hossain *et al.* (2019) reported that instead of gravitational force, strong cohesive intramolecular forces may be the dominant force in the aggregation process. The results of the elemental composition analysis of the extracted sample from rice husk using the EDS study are shown in Table 1, which was supported through graphical representation by EDS peaks

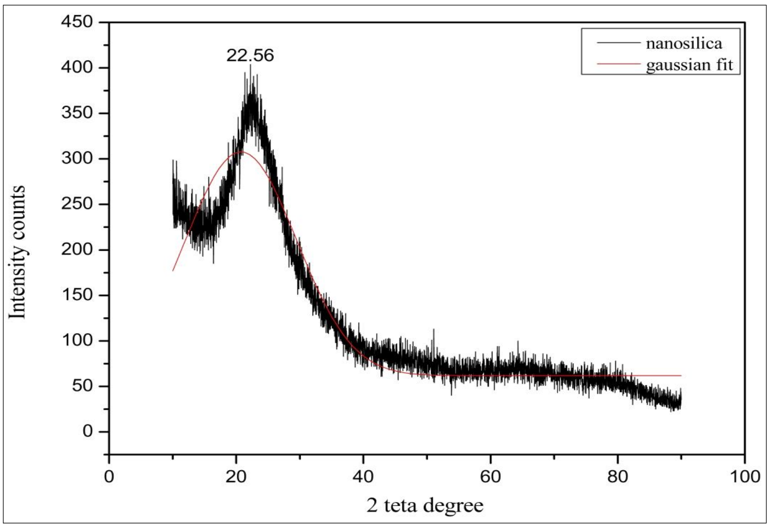

Fig 1: XRD spectra.

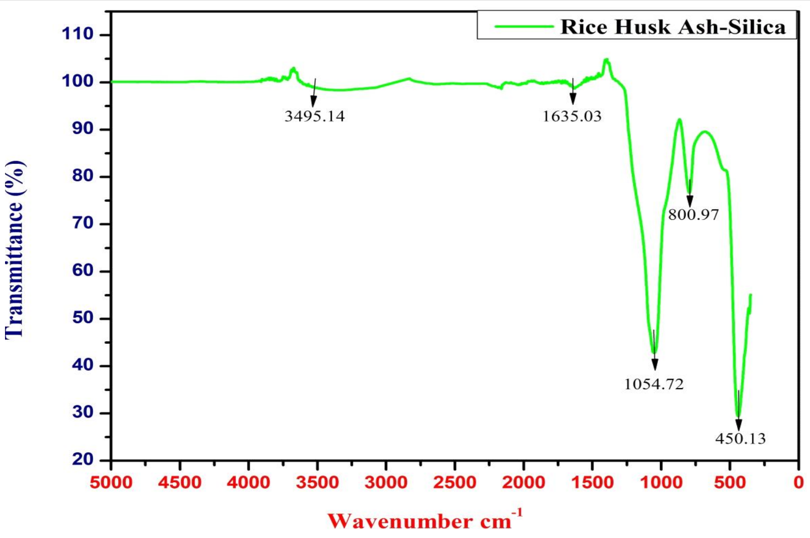

Fig 2: FT-IR spectra.

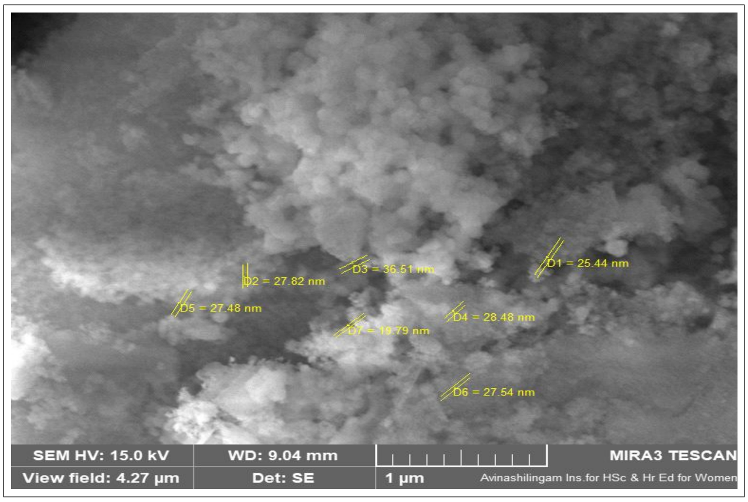

Fig 3: FESEM image.

Table 1: Elemental composition of silica sample extracted from RH obtained through EDS analysis.

Element	Weight (%)	Atomic (%)
O K	47.75	61.84
Na K	0.73	0.66
Mg K	0.68	0.58
Si K	49.12	36.24
K K	0.29	0.15
Fe K	1.43	0.53
Total	100	100

in Fig 4. It was found that the RHA-Silica sample only had two strong peaks of O K and Si K and minuscule peaks of Na K, Mg K and Fe K.

The extracted silica sample is 96.87 (weight percent) and 98.08 (atomic per cent) pure, according to the EDS investigation. The outcomes are consistent with those of Mourhly *et al.* (2019), who investigated mesoporous nano-silica. It is important to note here, though, that a few secondary micro-particles that were also found could be the result of the agglomeration effect. After sonication particle size distribution histogram was obtained (Fig 5) using

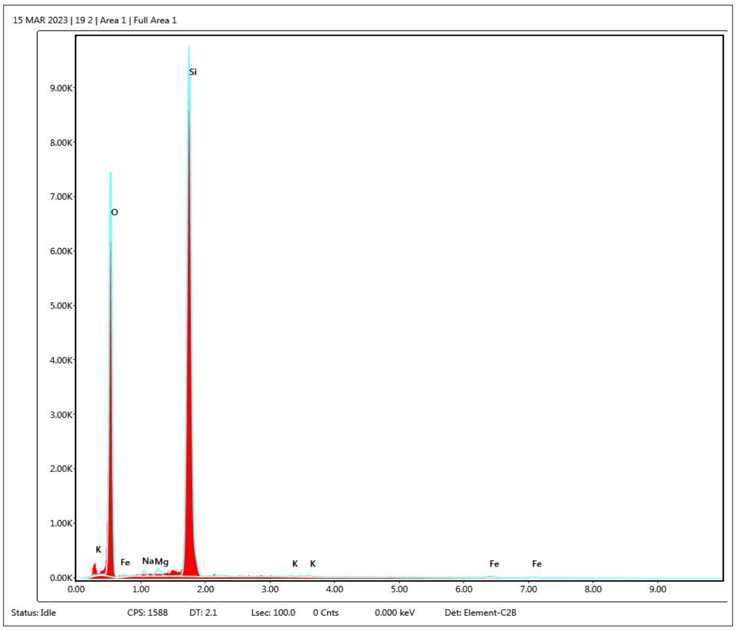

Fig 4: EDS graph.

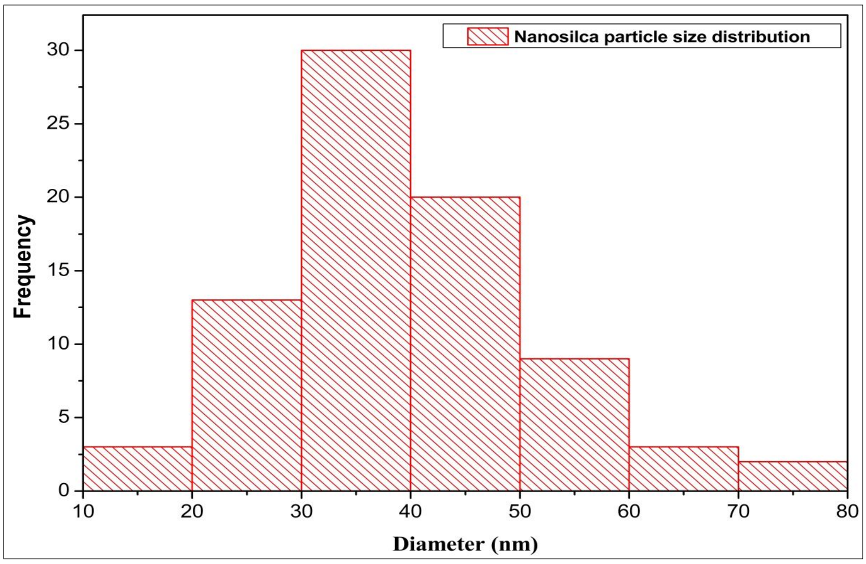

Fig 5: Particle size histogram.

Particle Size Analyser revealed the SiO_2-NPs isolated from RHA had an average particle size of 35 nm.

CONCLUSION

Rice Husk, an inevitable byproduct of agriculture, can be processed to provide a lucrative product with a variety of industrial uses. To research its utilisation, it is crucial for analysts to determine the precise quantity and grade of silica. In the current investigation, RHA was used to extract silica nanoparticles (SiO_2-NPs) with a yield of 92.20%. This process does not release CO_2 or any other dangerous molecule into the environment, in contrast to other methods described in the older literature. Due to the utilisation of inexpensive Na_2CO_3, this process is also more affordable for mass manufacturing than the other stated methods. The recovered SiO_2-NPs from RH were found to be amorphous in form and have an average particle size of 35 nm based on the characterisation analysis. The produced Nanosilica can be used in many different industries and aids in reducing worries about the disposal of rice husk and its ash.

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Conflict of interest: None.

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