

Original Research Article

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Biosynthesis and Characterization of Silica Nanoparticles from Rice (*Oryza sativa* L.) Husk

Nita Babaso Patil^{1*}, H. Sharanagouda¹, S.R. Doddagoudar²,
C.T. Ramachandra³ and K.T. Ramappa¹

¹Department of Processing and Food Engineering, ²Department of Seed Science and
Technology, University of Agricultural Sciences, Raichur- 584104 (Karnataka), India

³Department of Agricultural Engineering, College of Agriculture, GKVK,
Bengaluru-560065 (Karnataka), India

*Corresponding author

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Silica nanoparticles were synthesized efficiently and effectively from rice husk and characterized by various analytical techniques. The highest percentage (89.28 ± 0.03 %) yield of silica synthesized from rice husk ash burnt at 700 °C for 2 h. Dynamic light scattering analysis data of silica nanoparticles (SNPs) showed that the average particles diameter 93.14 nm with hydrophilic nature. The UV-Visible spectrum Si-O-Si bond confirming the presence of silica nanoparticles the presence of silica nanoparticles. FT-IR data revealed the presence of hydrogen bonded silanol and siloxane groups in SNPs, XRD pattern revealed amorphous form. SEM analysis data showed that uniformly distributed silica nanoparticles were in the agglomerated form with spherical shape. The use of rice husk as source of SNPs has both positive environmental and economic impact through the use of an abundant low-value agricultural by-product that can alleviate waste disposal problems.

Introduction

Agriculture is the backbone of India, with more than 60 per cent of the population relies on it for their livelihood. Science and technology played major role in increasing agricultural productivity. Among the latest line of technological innovations in the field of agriculture, nanotechnology occupies a distinguished position in remodelling agriculture and food production to fulfil the demands in an efficient and cost effective

way. Nanotechnology in the field of agriculture focuses currently on target farming that involves the use of nanoparticles with unique properties to boost crop productivity. The aim of the use of nanomaterials in the field of agriculture is to improve the efficiency and sustainability of agricultural practices by putting less input and generating less waste than conventional products and approaches (Mousavi and Rezaei, 2011). The increased surfaces of nanoparticles are responsible for their different chemical, optical, mechanical,

magnetic properties as compared to bulk materials (Mazur, 2004). Physical and chemical methods of synthesis of nanoparticles (NPs) are expensive, time consuming, labour intensive and also requires more energy. These methods are potentially hazardous to the environment and living organisms due to use of toxic reducing and stabilizing agents (Mittal *et al.*, 2013). Therefore, there is a need to develop cost effective, non-toxic and eco-friendly method for synthesis of nanoparticles. Biosynthesis involves using an environment friendly green chemistry based approach that employs unicellular and multicellular biological entities such as actinomycetes, bacteria, fungi, plants, viruses and yeast (Vithiya and Sen, 2011). Mahgoub and Samaras (2014) reported that bio-waste materials such as cow dung ash, corn cob ash, mango stone ash, lemon peel, pomegranate peel, orange peel and rice husk ash are eco-friendly to produce typical nanoparticles with well defined chemical composition, size, and morphology.

Globally, approximately 600 million tonnes of paddy are produced each year. India stands second with a production of 120 million tonnes of paddy every year. An average 20 per cent paddy gives around 24 million tonnes of rice husk and 4.4 million tonnes of rice husk ash (Manore *et al.*, 2016), which is great source of silica. With such a large availability of rice husk, it becomes economical to use as a source for more commercial applications. Presently, no commercial value in RH itself, usually it ends up being burned in open spaces, thus causing environmental hazards and disposal problems (Rafiee *et al.*, 2012).

Silica nanoparticles (SNPs) have gained a greater attention because of its highly reactive surface area to volume ratio, chemical and physical stability, low toxicity and straight forward surface chemistry (Ghorbani *et al.*, 2015). It is frequently used in industrial

manufacturing, packaging, ceramic and synthesis of high molecule composites material, drug delivery, cancer therapy, disease labelling, biosensor, food and agriculture (Kasaai, 2015). Therefore, it is need of hour to develop an economically viable method to synthesize the silica nanoparticles from rice husk.

The characterization of nanoparticles is significant to appreciate and control nanoparticles synthesis and their applications. It is executed using a range of diverse techniques like scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), dynamic light scattering (DLS), X-ray diffractometry (XRD) and UV-visible spectroscopy (UV-Vis). These techniques are helpful to resolve diverse parameters such as morphology, particle size, shape, crystallinity and surface area (Ingale and Chaudhari, 2013). The use of rice husk as source of SNPs has both positive environmental and economic impact through the use of an abundant low-value agricultural by-product that can alleviate waste disposal problems.

Materials and Methods

Washing, acid treatment and thermal treatment of rice husk

Rice husk was washed thoroughly with potable water to remove the soluble particles, dust and other contaminants. The cleaned rice husk was dried in a hot air oven (Kadavil Electro Mechanical Industries, KOMS. 6FD, India) at 110°C for 24 h. The dried rice husk was refluxed with an acidic solution of 1N HCl at 85 °C. The sample was cooled at room temperature and kept intact for about 24 h. Then the sample was decanted and thoroughly washed with warm distilled water until the rinse became free from acid. The wet refluxed rice husk was subsequently dried in hot air

oven at 110 °C for 24 h. The dried rice husk was subjected to heat treatment in muffle furnace (Macro Scientific Works Pvt. Ltd., MSW-251, India) at 700 °C for 2 h to obtain the ash.

Extraction of silica

A sample of 20 g ash was stirred in a 160 ml of 2.5 M NaOH solution. The solution was heated in a covered beaker at 90 °C for 3 h by stirring constantly and filtered through filter paper. The obtained viscous, transparent and colourless filtrate solution was allowed to cool at room temperature and 10 M of H₂SO₄ was then added under constant stirring at controlled conditions until it reached to pH 2, then NH₄OH was used to adjust pH level up to 8.5 and was allowed to stand at room temperature for 3 h. White silica participate was washed repeatedly with the distilled water until the filtrate was completely free from alkali (Rafiee *et al.*, 2012). The silica was dried in hot air oven at 105 °C temperature at for 24 h.

Preparation of nanosilica powder

Silica nanoparticles were prepared by using refluxing technique of the above extracted silica with 6 M of HCl at 85 °C for 4 h and washed repeatedly using distilled water to make it acid free. Then it was dissolved in 2.5 M of NaOH by continuous stirring and sulphuric acid (H₂SO₄) was added until it reached to pH 8. The precipitated silica was washed repeatedly with warm distilled water to make it alkali free and then dried in the hot air oven at 50 °C for 48 h (Rafiee *et al.*, 2012).

Characterization of biosynthesized silica nanoparticles

Biosynthesized silica nanoparticles were subjected to characterization for identification of its size, morphology and functional group.

Particle size analysis using Zetasizer

Zetasizer (Malvern, ZETA Sizer, nano383 issue 5.0, England) was used (dynamic light scattering) to study the average particle diameter (nm) of SNPs. SNPs and ethanol suspension solution was sonicated at 25 °C using the digital ultrasonication bath (Labman Scientific Instruments, LMUC-2.8L, India) for 15 min. After sonication, the sample was centrifuged using high speed centrifuge (MPW Med. Instruments, MPW-350R, Poland) at 10000 rpm for 10 min. The prepared sample of SNPs suspension filled in disposable cuvette up to $\frac{3}{4}$ th of volume and cuvette was placed in dynamic light scattering chamber. The average particle diameter (nm) was recorded from size distribution by intensity graph (Das *et al.*, 2014).

Absorbance analysis using UV-Visible spectrophotometer

Silica nanoparticles were characterized by using UV- Visible spectrophotometer (Perkin Elmer, Lamda 35, Germany). The sample was prepared by diluting of 30 mg of silica nanoparticles into 5 ml ethanol and ethanol was used as reference in quartz cuvette (1 cm path length). The absorbance of the sample recorded in wavelength ranged between 300-650 nm (Djangang *et al.*, 2015). The amount of the radiation absorbed at each wavelength was recorded. The absorbance was plotted against wavelength to obtain the spectrum. From the graph, the wavelength (λ_{max}) was recorded at maximum absorbance.

Functional groups analysis using Fourier Transform Infrared Spectroscopy (FT-IR)

Fourier transform infrared (Shimadzu, FTIR-8400S, Japan) spectra was obtained on a Vertex 70 spectrometer equipped with a digital detector *via* the conventional potassium bromide (KBr) pellet method. The sample of

0.1 % was mixed with 250 mg of potassium bromide powder. The material was finally ground using pestle and mortar. The ground sample was put into pellet forming die to form pellet size of 13 mm. Then the pellet was placed on sample holder and subjected to scan in transmission mode with 4 cm^{-1} resolution at the range of $4000\text{--}450\text{ cm}^{-1}$ (Mourhly *et al.*, 2015).

Phase identification using X-Ray Diffraction (XRD)

X-ray diffraction (Theta-theta type X-ray diffractometer, Rigaku corporation, Japan) pattern of silica nanoparticles was recorded in the high angle of 2 theta range ($5\text{--}70^\circ$). Silica nanoparticles ($\sim 1\text{ g}$) were placed uniformly spread on glass sample holder and placed in scanner chamber. The set scan speed and step size $0.3^\circ/\text{min}$ and 0.001 s , respectively were fixed (Djangang *et al.*, 2015).

Surface morphology analysis using Scanning Electron Microscope (SEM)

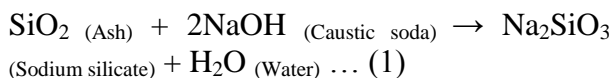
The morphological features of silica nanoparticles were studied by using SEM (Carl Zeiss Microscopy, EVO 10, Germany). The aluminium stub ($\sim 1\text{ cm}$ dia.) was employed on sample holder and cleaned to remove surface oils or dirt by using acetone and blowing with compressed gas. The double coated conductive carbon tape was used as adhesives and pasted on stub. Thin layer of dried sample ($\sim 0.2\text{ mg}$) placed on adhesive surface, then it was coated with palladium to make the samples conductive using sputter coater (Quorum technologies, OM-SC7620, United Kingdom) for about 90 s. Sample holder was removed from the sputter coater and placed in vacuum chamber of SEM and magnification was (1 to 30,000 times) carried out to get clear morphology of silica nanoparticles at the accelerating voltage of 1 to 30 kV with working distance of the sample at 10 mm (Haq *et al.*, 2014).

Results and Discussion

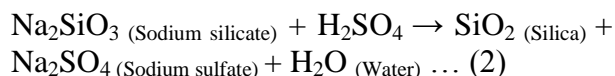
Biosynthesis of silica nanoparticles

In order to obtain maximum recovery of silica from the RHA, silica was synthesized at optimized conditions as per past research. Washing of rice husk (RH) with potable water results clean RH with removal of the soluble particles, dust and other contaminants present, whereby the heavy impurities such as sand and dirt also removed. During refluxing of dried RH with 1 N HCl, the original yellow colour of RH was changed to brown colour on increasing the time of digestion. The metallic ingredients have a substantial effect on the quality of silica from RH, which is mainly potassium that causes surface melting and accelerates the crystallization of amorphous silica and carbon fixation in rice husk ash. Also, a strong interaction occurs between the metallic ions and silica which leads to a considerable decrease in the surface area. Therefore, it is preferable to treat RH with an optimized acidic solution such as 1 N of HCl to effectively diminish impurities and to obtain highly purified silica powder (Carneiro *et al.*, 2015; Ghorbani *et al.*, 2015). The change in colour during digestion is also remarkable. The original yellowish and light yellow colour of the rice husk changed to brown colour on increasing the time of digestion this happens probably due to chemical reaction between acid and metals.

The white colour amorphous rice husk ash (RHA) was obtained from burning of dried refluxed RH in muffle furnace at 700°C for 2 h, it contains less quantity of unburned carbon residues. At the dissolution stage sodium hydroxide reacts with silica and formed sodium silicate Eq. (1). The obtained filtrate of sodium silicate solution was transparent, colourless and viscous.



The silica particles were generated from the solution by adding sulphuric acid as catalyst. The acidic condition of pH 2 indicates, approximately the complete precipitation of silica from sodium silicate by the following reaction.



RHA sample after being extracted by 2.5 N of sodium hydroxide (NaOH) recorded the silica yield 89.28 ± 0.03 %. The metallic impurities of extracted silica were removed by refluxing using 6 M HCl and dissolved in 2.5 N NaOH while continuously stirring with magnetic stirrer and H₂SO₄ used for predicated nano-silica. Finally the amorphous pure white nanosilica was obtained by drying in the hot air oven at 50 °C for 48 h. Haq *et al.*, (2014) reported that, the amount of precipitated silica was dependent upon the applied processing parameters, such as concentration of sodium hydroxide, extraction time, solid to solution ratio, etc. The present finding is in good conformity with the results of Thuadaj and Nuntiya (2008) and Indhumathi *et al.*, (2011) who reported that the concentration of NaOH had strong effect on the dissolution, particle size and surface area of silica and also remove

some impurities which were not dissolved from the main product. Highest percent yield of silica (90.3 %) were extracted using 2.5 N of NaOH treatments. Also, Yuvakkumar *et al.*, (2014) found that 2.5 N of NaOH treatment was best suited for the synthesis of high purity nanosilica powders with a low synthesis technique.

According to Rafiee *et al.*, (2012) pH plays an important role during silica synthesis, a low silicate concentration (pH less than 8), Si(OH)₄ is the dominant species in its aqueous solution. At higher concentrations (pH greater than 8), the silanols, Si(OH) groups, spontaneously polymerize to yield higher oligomers linked by a disiloxo bond. This reaction is most favourable when one of the silanols is deprotonated to a Si-O group. These oligomers grow into colloid sized silica particles in which larger particles grow at the expense of smaller ones. At a higher pH (greater than 8), however, the much more concentrated silicate solution is stable. This is because disiloxo bonds undergo nucleophilic attacks by OH via a five coordinated intermediate. The magnetic stirring of 3 h, during dissolution of 2.5 M of NaOH and silica, reduce the size of extracted silica, which converts into silica nanoparticles.

Fig.1 Average particle diameter of silica nanoparticles

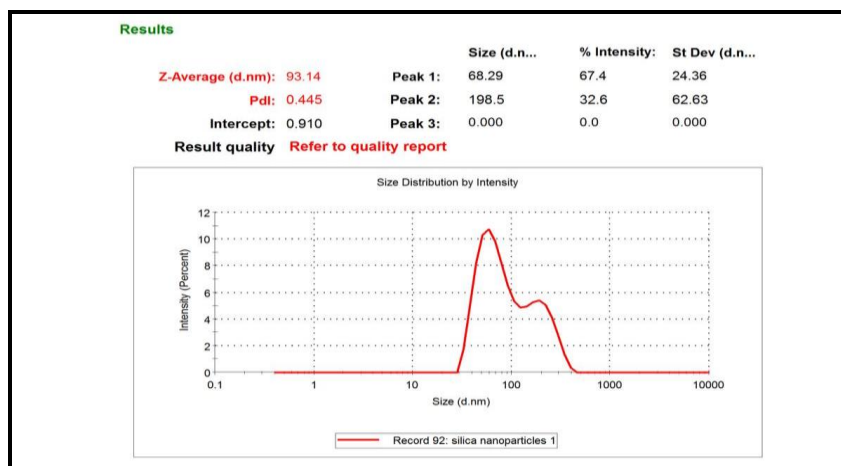


Fig.2 UV-Visible spectrum of silica nanoparticles

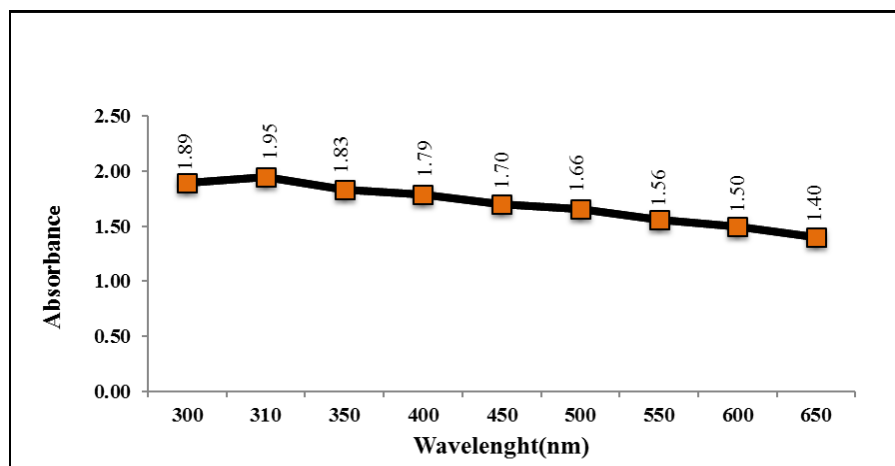


Fig.3 FT-IR spectra of silica nanoparticles

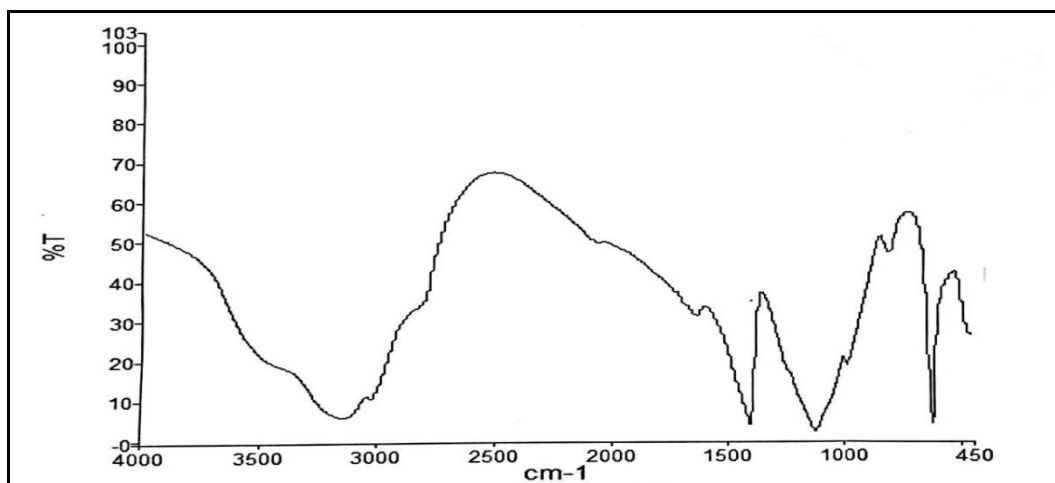


Fig.4 XRD pattern of silica nanoparticles

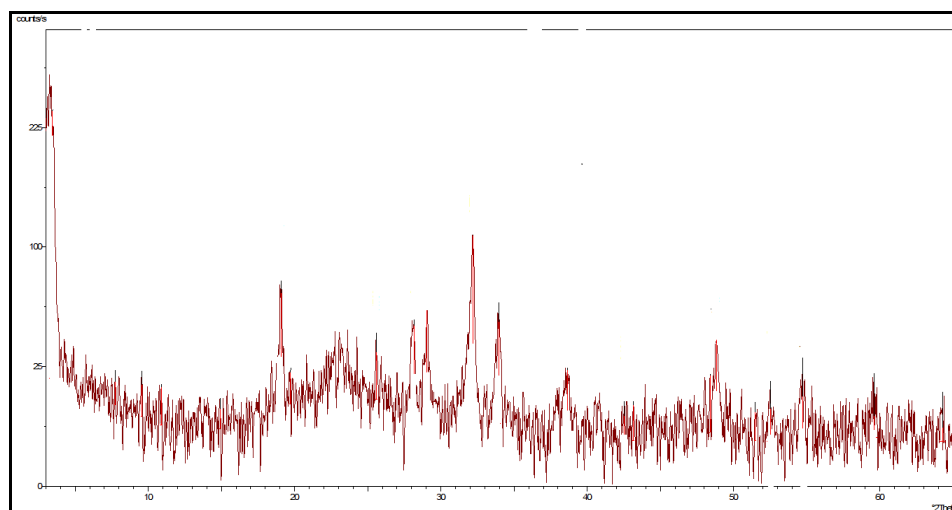
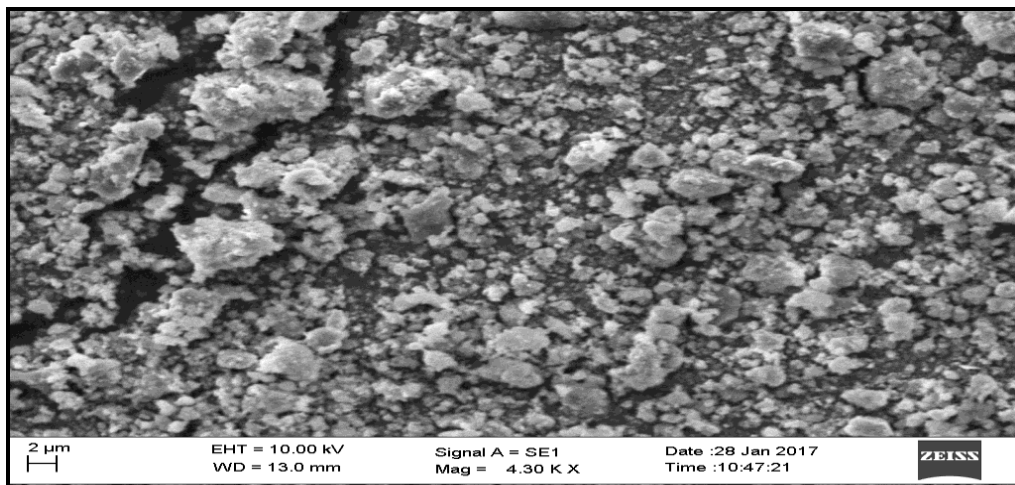


Fig.5 SEM image of silica nanoparticles



Characterization of biosynthesized silica nanoparticles

The results of Zetasizer reevaluated that average particle diameter of silica nanoparticles was 93.14 nm as shown in Figure 1.

The UV-Visible spectrum of SNPs recorded maximum absorption band edge of 310 nm in 1.95 absorbance as shown in Figure 2. These optical features are similar to those obtained in previous reports and attributed to Si-O-Si bond confirming the presence of silica nanoparticles (Vaccaro *et al.*, 2013; Djangang *et al.*, 2015).

FT-IR spectra of SNPs as shown Figure 3 revealed that, the broad band between 2800 and 3750 cm^{-1} was due to silanol OH groups and adsorbed water and 2100 to 2300 m^{-1} was due to silane group Si-H. The predominant absorbance peak at 1320 cm^{-1} was due to siloxane bonds (Si-OSi), the peaks between 1200 and 700 cm^{-1} were attributed to vibration modes of the gel network. IR spectrum was clearly shown the pure silica. Results are in good agreement with findings of Indhumathi *et al.*, (2011) and Balamurugan and Saravanan (2012).

X-ray powder diffraction pattern of the biosynthesized silica nanoparticles showed broad halo at of absorption about $2\theta = 15-25$ region, which confirms the amorphous structure of silica nanoparticles in the sample. Figure 4 shows that, the X-ray diffraction pattern of silica nanoparticles which is characterized by a broad halo band of absorbance at about $2\theta = 15-25^\circ$ region which confirms the amorphous structure of silica nanoparticles, similar results were recorded by Djangang *et al.*, (2015) who reported amorphous nature of silica nanoparticles from rice husk.

SEM analysis data as shown in Figure 5 showed that uniformly distributed silica nanoparticles were in the agglomerated form with spherical shape.

In conclusion, biosynthesis of silica nanoparticles from rice husk involves as an environment friendly green synthesis approach. The use of rice husk as source of SNPs has both positive environmental and economic impact through the use of an abundant low-value agricultural by-product that can alleviate waste disposal problems. Biosynthesized silica nanoparticles can be used in various purposes in industry and agriculture.

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