Synthesis and Characterization of Mesoporous Nanosilica Derived from Rice Husk Ash

ABSTRACT

Rice husk, an abundant agricultural byproduct, has garnered attention as a potential source of natural silica, a material with a myriad of applications. Natural silica is particularly attractive due to its low cost of production and safe handling. In this study, sodium silicate derived from rice husk ash was employed to create mesoporous nanosilica (MNS) via the sol-gel process. The extraction process commenced with the utilization of rice husk as a precursor for silica, capitalizing on its silica-rich composition. Fourier-transform infrared (FTIR) analysis was performed to ascertain the presence of Si-O-Si bonds within the synthesized MNS. This critical step confirmed the successful formation of silica-based materials. Subsequently, X-ray diffraction (XRD) analysis was employed, revealing a significant peak at 22 degrees, a clear indicator of the presence of crystalline silica. Examining the morphology of the MNS, field-emission scanning electron microscopy (FESEM) results showcased a smooth surface and spherical morphology. Additionally, high-resolution transmission electron microscopy (HR-TEM) was employed, revealing the presence of nanoparticles smaller than 100 nanometers, which is indicative of the mesoporous nature of the synthesized nanosilica. Characterization techniques, including FTIR, XRD, FESEM, and HR-TEM, provided compelling evidence of successful nanosilica extraction. The findings underscore the potential of utilizing agricultural waste products for the sustainable production of valuable materials like nanosilica, which holds promise in various industrial applications. This research not only contributes to the valorization of agricultural residues but also aligns with the pursuit of eco-friendly and cost-effective materials for a wide range of applications.

KeywordsRice husk, Mesoporous nanosilica, FTIR, XRD, FESEM, HR-TEM.

1. INTRODUCTION

In recent trends, nanotechnology has gained attention as an emerging technology. Research on nanomaterials is crucial to the advancement of nanotechnology. One of the nanomaterials being developed by several researchers right now is mesoporous material. Since the successful synthesis of the mesoporous silica material MCM-41 in 1992, the researcher's interest in studying mesoporous materials has significantly expanded [1]. Rice husk (RH), a kind of agricultural waste is a possible source of natural silica resources.

Rice serves as the primary source of nutrition for more than 3 billion people and rice growing tracts produce a significant quantity of agricultural waste, including husk, straw and ash[2]. More than 120 tonnes of RH are thought to be wasted each year after being processed for milling[3]. Rice husk makes up 20% of the bulk grain weight of rice [4]. It comes from the rice milling industries as a by-product. Since the RH waste sites are often set on fire, open burning has become the preferred technique for disposing of RH[5]. Since rice milling is necessary to generate high-quality, edible rice kernels, waste management must also follow sustainable agriculture and circular economy principles[6]. Rice husk is composed of cellulose (40–50%), lignin (25–30%), and silica (15–20%)[7][8]. RH is resistant to deterioration, offers minimal nutritional content and is often used as a component of animal feed and as a cheap fuel source[9].

The Food and Drug Administration (FDA) defines nanoparticles (NPs) as inorganic materials having dimensions less than 1000 nm. They have valuable qualities like magnetic or optical properties[10]. Mesoporous silica nanoparticles are highly advantageous as they offer distinctive structural characteristics such as large surface area, high volume of pores, durable mesoporous structure, adjustable pore and particle size, as well as easy internal and exterior surface functionalization[11][12].

MNS have not yet completely fulfilled their potential in the agriculture sector. MNS porosity and tunable interior and surface characteristics, as well as their diameter and shape, enable them to function as cargo or vehicle that can load and unload proteins, nutrients, and tiny molecules or chemicals into the soil system [13].In the present study, a simple sol gel approach was used to synthesize Mesoporous nanosilica (MNS) and it was characterized with FTIR, XRD, FESEM, and HR-TEM.

2. MATERIAL AND METHODS / EXPERIMENTAL DETAILS / METHODOLOGY

2.1 Rice husk pre- processing and calcination

Mesoporous silica was produced using rice husk ash as the source, following the synthesis method outlined by Purwaningsih*et al.* [1], and Dorairaj*et al.* [14]. The rice husk was thoroughly washed with water to remove dirt, dust, sand, and other contaminants and then dried in an oven at 100 °C for 24 h. The rice husk was calcined at 700˚C for 5 hours to obtain white-colored rice husk ash.

2.2Synthesis of mesoporous silica nanoparticles (MNSs)-

The MNS was extracted from amorphous RHA according to sol–gel method with few modifications. The ash was subjected to acid leaching using a 1:15 ratio of 1 M HCl solution in a magnetic stirrer for 2 hours. Afterward, the acid-treated husk was washed with water to eliminate any excess acid from the surface and then dried in an oven overnight at 90˚C.

The dried acid leached RHA was mixed with 2 N NaOH solution at a 1:10 ratio and heated at 90°C with constant stirring for 120 minutes to extract sodium silicate from the ash. The solution was then filtered and kept aside for aging. The sodium silicate extract was titrated against 0.5 M H_2SO_4 with 4% PEG (Polyethylene glycol) to form a gel. The solid material was collected in a centrifuge tube and centrifuged at 5000 rpm four times, with alcohol used for two washings and water for the other two. The collected solid was then dried in an oven overnight at 90˚C and subsequently calcined at 500˚C for 3 hours.

2.3 Characterization of Mesoporous Nanosilica (MNS)

2.3.1 Physical characterization

Functional groups present in the synthesized MNS were identified from the spectra of Fourier transform infrared (FTIR). The spectra were collected in the range of 400–4000 cm^{-1}. X-Ray diffractometer (XRD) Analysis (Empyrean, Malvern Panalytical) is done to evaluate the structure and composition of the synthesized MNS.

2.3.2 Electron microscopic observation

The surface topology, morphology and elemental composition of the MNS were characterized using a high-resolution field emission scanning electron microscope (FESEM) (FEI, Netherlands.). The structure and particle size were examined using a high-resolution transmission electron microscope (FEI, TECHNAI G-2, Netherlands.)

3. RESULTS AND DISCUSSION

3.1 FTIR ANALYSIS

The FT-IR spectrum of MNS (Fig. 1) exhibited distinct absorption bands corresponding to the structured silica material. The broad spectral feature observed at 3340.71 cm−1 was ascribed to the stretching vibration associated with the Si–OH (silanol) groups. The absorption band observed at 1072 cm^{-1}, which exhibited broad characteristics, was assigned to the stretching vibrations of Si–O–Si (siloxane) bonds. Additionally, the absorption peaks at 964 cm^{-1}, 794 cm^{-1} and 439 cm^{-1}were associated with the bending vibrations of Si–OH bending, SiO–H symmetrical stretching, and Si–O bending respectively. Similar results are already reported by Wanyika *et al.* [15].

Singh *et al.* [16] reported that the FTIR spectra of MNS revealed the characteristics absorption bands of ordered silica at 3319.16 cm^{-1}, 2950.76 cm^{-1}, 2840.39 cm^{-1}, 1649.96 cm^{-1}, and 1016.79 cm^{-1}. The broad bands appearing at 3319 cm^{-1} 2950.76 cm^{-1} and 2840.39 cm^{-1} were attributed to the stretching vibration of the Si–OH (silanol) groups. The 1016.79 cm^{-1} broad absorption bands were ascribed to Si–O–Si (siloxane) stretching vibrations whereas the 1649.96 cm^{-1} band was attributed to Si-OH bending ions [17].

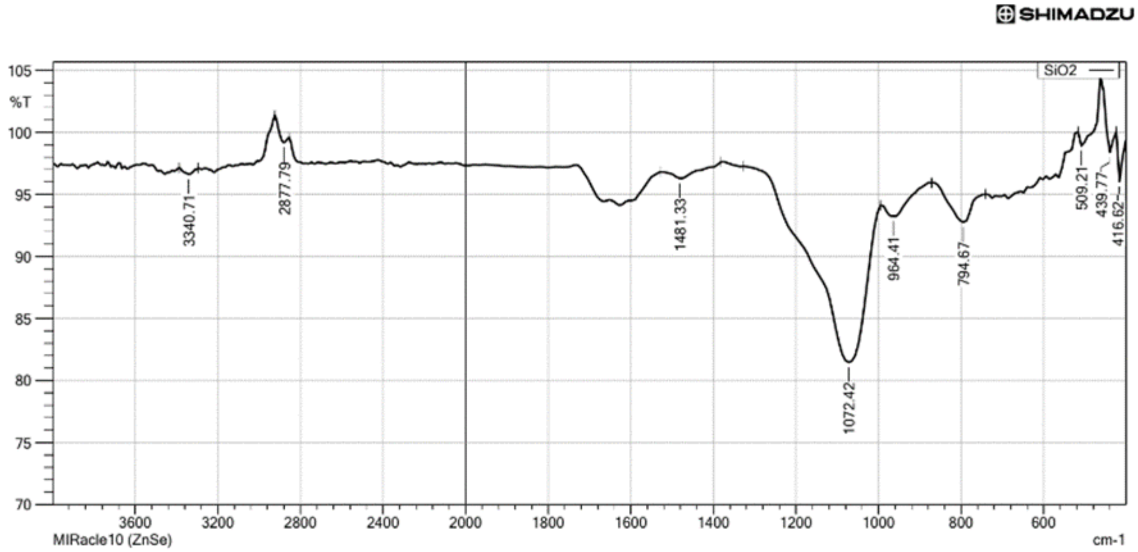

Fig. 1FTIR spectrum of Mesoporous Nano Silica (MNS)

3.2 X-RAY DIFFRACTION (XRD)

The surface area and crystalline phase of the mesoporous nanosilica were evaluated by powder X-ray diffraction (XRD) analysis. The diffractogram of mesoporous silica nanoparticle (Fig.2) indicated that the largest peak at 2θ = 22^{o}. This is attributed to silica, thus indicating the existence of silica in the nanosample. The results are in agreement with the findings of Purwasinghe*et al.*[1].

The preference for amorphous RHA over the crystalline form arises from its enhanced reactivity, non-hazardous characteristics, and ease of absorption by plants, as noted by Shen *et al*. (2017)[18]. The alteration in the structure of rice husk from crystalline to amorphous depends on the duration and temperature of incineration. Therefore, the combustion conditions are critical in producing reactive silica, as highlighted by Khan *et al.* [19] and Ilochonwu*et al.*[20].

The RH kept for calcination at 700^{o}C showed ivory color. However, there were variations in their coloration. Specifically, the RH subjected to combustion at 550°C resulted in a greyish RHA, while the RHA produced through combustion at 600°C exhibited an ivory hue, as reported by Dorairaj*et al.*[14].

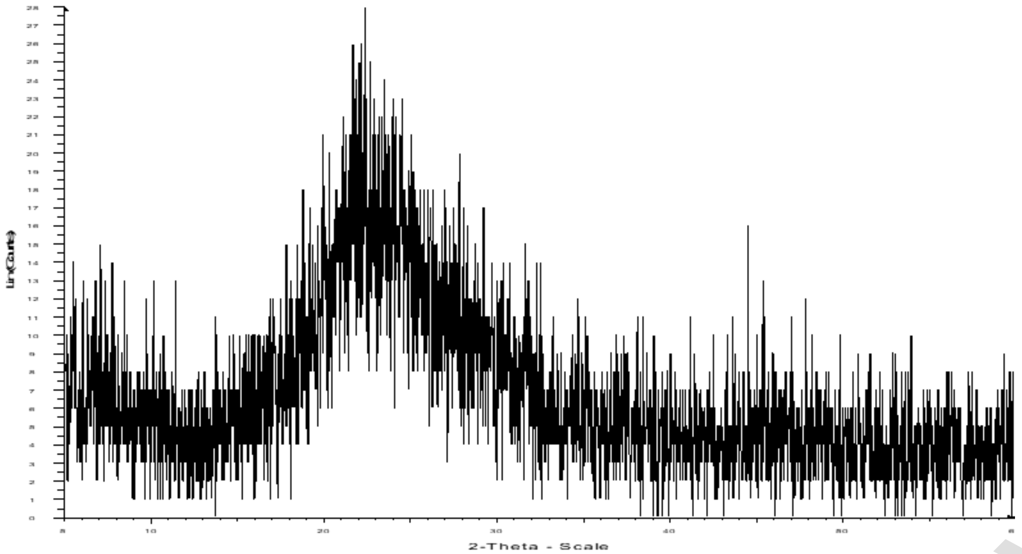

Fig. 2 XRD Characterization of Mesoporous Nano Silica (MNS)

3.3 Field Emission Scanning Electron Microscope (FESEM)

Based on FESEM imaging, the silica nanoparticles (NPs) were very homogeneous and spherical (Fig. 3). The clusters of particles imply aggregation of MNS. The presence of a somewhat diversified grain size with uneven distribution on the surface was noted. The distinction between clusters may be observed pretty clearly.

The results were in agreement with previous studies which had demonstrated that electron microscopic observation confirmed the formation of Si-NPs as aggregating clusters of uniform nanostructures. Further examination through FESEM micrographs showed that the NPs were 20–25 nm, in size [14].

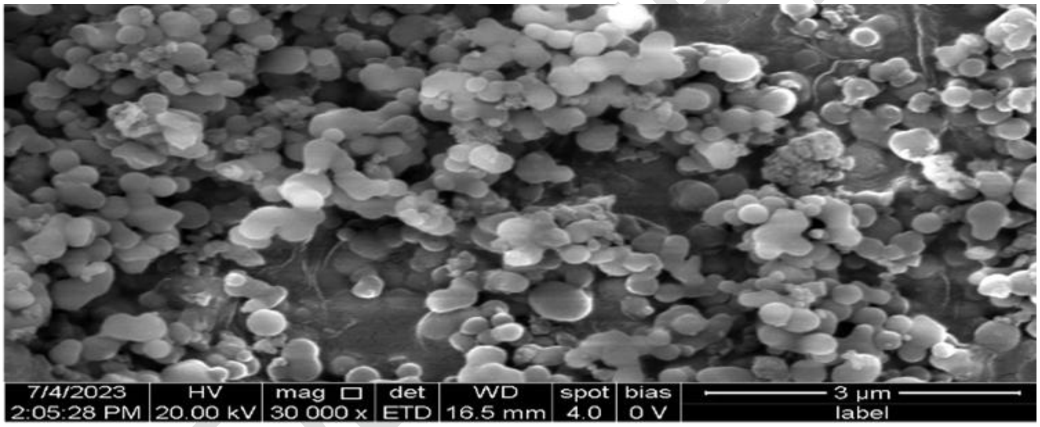

Fig 3. SEM image- Mesoporous Nano Silica (MNS)

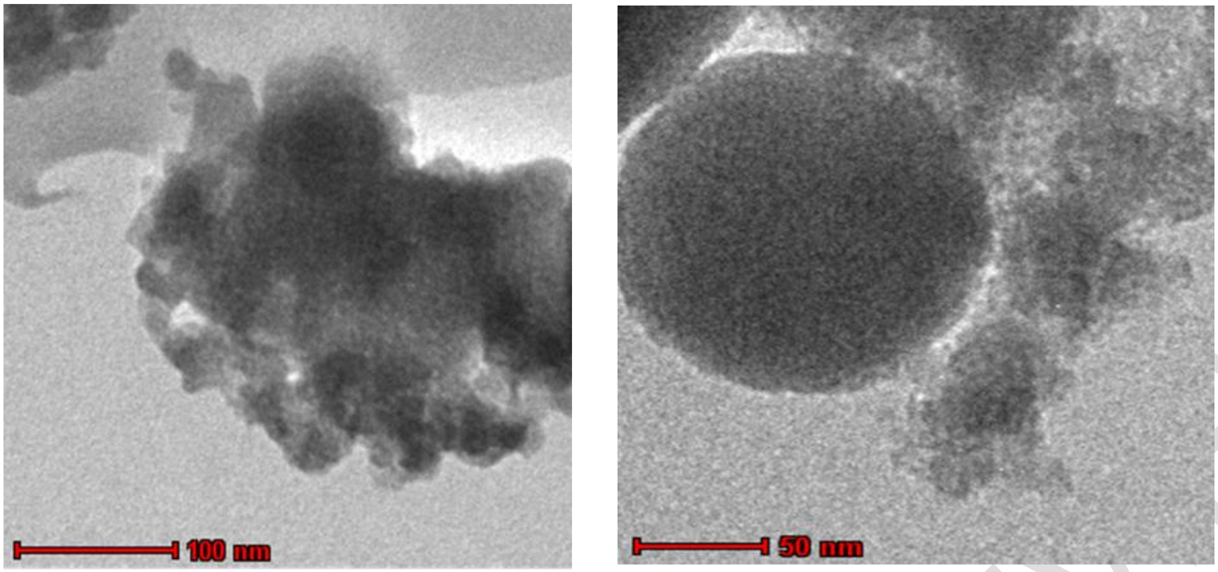

Fig 4.TEM image- Mesoporous Nano Silica (MNS)

3.4 High-Resolution Transmission Electron Microscopy (HR-TEM)

Based on the TEM imagery, the silica nanoparticle morphologies are coarse and identical shapes (Fig.4). It reveals that the silica particles agglomerates and there is no obvious border between particles. It displays the size of particles are smaller than 100nm.

Purwasingh*et al.*[1] reported that the silica nanoparticle morphologies are granular and similar shapes. TEM images of hydrothermal treatment at 100^{o}C and 115^{o}C have the most uniform particle size. The average size of particles from hydrothermal at 100^{o}C was 73.54 nm and 115^{o}C was 79.65nm.

4. CONCLUSION

From the research that has been done, it can be concluded that silica extraction (SiO2) was successfully performed by using acid-leaching and sol-gel method with rice husk ash as the source. The synthesis of mesoporous silica nanoparticles with the addition of PEG surfactant was successful. Extracted silica has an amorphous structure and a particle size of less than 100nm. The synthesis of MNS holds promising potential across various applications in agriculture.

Rice husk ash is a potential green resource. The extraction of MNS from RHA involves a relatively straight forward process that includes a pre-treatment step. The proposed method of preparing nanosilica from rice husk is simple and helps minimize waste disposal problems. Moreover, this method proves to be cost-effective since it primarily relies on readily available and inexpensive chemicals as reagents and reduces environmental impact.

REFERENCES

1. Purwaningsih, H., Pratiwi, V. M., Purwana, S. A. B., Nurdiansyah, H., Rahmawati, Y., & Susanti, D. (2018, April). Fabrication of mesoporous silica nanoparticles by sol gel method followed various hydrothermal temperature. In *AIP Conference Proceedings* (Vol. 1945, No. 1). AIP Publishing.

2. Moraes, C. A., Fernandes, I. J., Calheiro, D., Kieling, A. G., Brehm, F. A., Rigon, M. R., & Osorio, E. (2014). Review of the rice production cycle: by-products and the main applications focusing on rice husk combustion and ash recycling. *Waste Management & Research*, *32*(11), 1034-1048.

3. Bodie, A. R., Micciche, A. C., Atungulu, G. G., Rothrock Jr, M. J., & Ricke, S. C. (2019). Current trends of rice milling byproducts for agricultural applications and alternative food production systems. *Frontiers in Sustainable Food Systems*, *3*, 47.

4. Hossain, S. S., Mathur, L., & Roy, P. K. (2018). Rice husk/rice husk ash as an alternative source of silica in ceramics: A review. *Journal of Asian Ceramic Societies*, *6*(4), 299-313.

5. Goodman, B. A. (2020). Utilization of waste straw and husks from rice production: A review. *Journal of Bioresources and Bioproducts*, *5*(3), 143-162.

6. Dhankhar, P., & Hissar, T. (2014). Rice milling. *IOSR J. Eng*, *4*(5), 34-42.

7. Chindaprasirt, P., Kanchanda, P., Sathonsaowaphak, A., & Cao, H. T. (2007). Sulfate resistance of blended cements containing fly ash and rice husk ash. *Construction and Building Materials*, *21*(6), 1356-1361.

8. Singh, B. (2018). Rice husk ash. In *Waste and supplementary cementitious materials in concrete* (pp. 417-460). Woodhead Publishing.

9. Dhaneswara, D., Fatriansyah, J. F., Situmorang, F. W., &Haqoh, A. N. (2020). Synthesis of amorphous silica from rice husk ash: comparing HCl and CH3COOH acidification methods and various alkaline concentrations. *Synthesis*, *11*(1), 200-208.

10. Tang, F., Li, L., & Chen, D. (2012). Mesoporous silica nanoparticles: synthesis, biocompatibility and drug delivery. *Advanced materials*, *24*(12), 1504-1534.

11. Lv, X., Zhang, L., Xing, F., & Lin, H. (2016). Controlled synthesis of monodispersed mesoporous silica nanoparticles: Particle size tuning and formation mechanism investigation. *Microporous and Mesoporous Materials*, *225*, 238-244.

12. Hao, N., Li, L., & Tang, F. (2017). Roles of particle size, shape and surface chemistry of mesoporous silica nanomaterials on biological systems. *International Materials Reviews*, *62*(2), 57-77.

13. Hui, K. N., Lee, J. Y., Guo, W., & Hui, K. S. (2011, August). Production of MCM-41 from rice husk. In *18 th International Conference on Composite Materials, Jeju Island, Korea* (pp. 21-26).

14. Dorairaj, D., Govender, N., Zakaria, S., &Wickneswari, R. (2022). Green synthesis and characterization of UKMRC-8 rice husk-derived mesoporous silica nanoparticle for agricultural application. *Scientific Reports*, *12*(1), 20162.

15. Wanyika, H., Gatebe, E., Kioni, P., Tang, Z., & Gao, Y. (2012). Mesoporous silica nanoparticles carrier for urea: potential applications in agrochemical delivery systems. *Journal of nanoscience and nanotechnology*, *12*(3), 2221-2228.

16. Singh, K., Ram, S., Nehra, A., & Singh, K. P. (2019). Effect of magnetized water on urea-loading efficiency of mesoporous nano-silica: A seed germination study on wheat crop. *Journal of Nanoscience and Nanotechnology*, *19*(4), 2016-2026.

17. Van Phu, D., Du, B. D., Van Tam, H., & Hien, N. Q. (2017). Preparation and foliar application of oligochitosan-nanosilica on the enhancement of soybean seed yield. *International Journal of Environment, Agriculture and Biotechnology*, *2*(1), 238688.

18. Shen, Y. (2017). Rice husk silica derived nanomaterials for sustainable applications. *Renewable and sustainable energy reviews*, *80*, 453-466.

19. Khan, M. N. N., Jamil, M., Kaish, A. B. M. A., & Zain, M. F. M. (2014). An overview on manufacturing of rice husk ash as supplementary cementitious material. *Australian Journal of Basic and Applied Sciences*, *8*(19), 176-181.

20. Ilochonwu, C. E., Nwajagu, C. O., Onyenanu, I. U., &Nwonye, E. I. (2016). Effect of temperature in extraction of high purity amorphous silica from rice husk for silicon production. In *EPD Congress 2015* (pp. 219-227). Springer International Publishing.