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RICE HUSK – AGRICULTURE WASTE AS RAW MATERIAL FOR SBA-15 MESOPOROUS SILICA

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Abstract:

The obtaining of molecular sieves using alternative sources of silica represents a promising approach for replacing the conventional expensive silica sources, such as tetraethyl orthosilicate. These new raw materials with low costs can be agriculture wastes, such as barley husks, rice husks, wheat straws, or wheat husks. Therefore, the synthesis of silica nanomaterials using rice husk ash has been the focus of various studies, considering also the ecological, economic, and environmental issues. SBA-15 is a mesoporous silica sieve having uniform hexagonal pores with narrow pore size distribution and tuneable pore diameter, between 5 and 15 nm. Typical SBA-15 presents high surface area, increased thermal and mechanical stability, and is not harmful to the environment. Consequently, it represents well-suited material for different applications, such as adsorption and separation, support material for catalysts, or template to produce ordered mesoporous carbon. Considering all the above-mentioned details, this study reports the preparation of SBA-15 type mesoporous silica using rice husk ash as silica source, followed by a hydrothermal method. The morpho-structural properties of mesoporous silica were elucidated using various techniques, proving that the resulted mesoporous silica had typical features of SBA-15 molecular sieve, but with lower specific area (around 140 m^2/g) and pore volume (0.240 cm^3/g) than the one obtained from commercial sources.

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1. INTRODUCTION

Huge quantities of agricultural wastes containing valuable bioactive compounds are worldwide discarded [A. Capanoglu et al., 2022]. To minimize environmental problems, the first option must be the valorisation of food wastes and their byproducts. The Food Waste Index Report stated that, in 2019, approximately 931 million tons of food wastes (17% of

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total food available) were dumped into the waste bins of households, retailers, restaurants, or other food services [U.N. Environment, 2021].

The second most consumed food item is the rice (*Oryza sativa*). The rice mill industry disposes rice husk (RH) that represents around 20-25%. The RH is mainly disposed by burning, the resulted smoke being toxic, having a negative impact on environmental health [H. H. A. Matin et al., 2023].

Paddy rice worldwide production in 2022 is presented in figure 1. China and India were the main producers, with more than 55% of the global production [Top paddy rice producers worldwide, 2022].

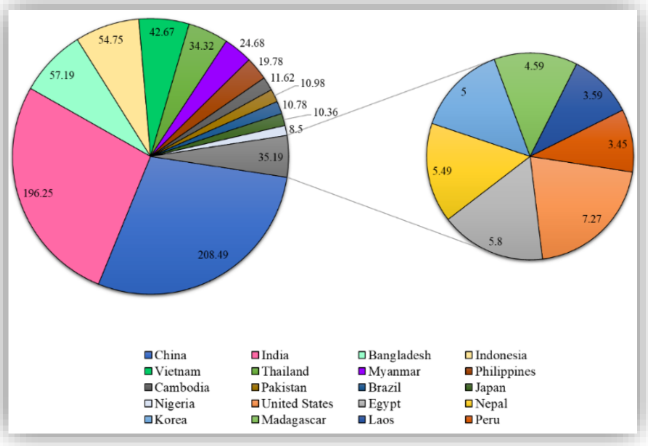

Figure 1. Paddy rice worldwide production in 2022 (in million metric tons)

Rice husk is an interesting agriculture waste, containing organic compounds (around 80%) and mineral components, such as silica or trace elements (around 20%) [V. C.Niculescu and S. M. Raboaca, 2021; S. Pimprom et al., 2015]. SiO_2 content determined in husk varies from 8.5% up to 20% [Ding T. P. et al., 2005]. The SiO_2 exists within rice husk as hydrated amorphous state [M. Z. Asuncion et al., 2005]. As a consequence, the resulted rice husk ash (RHA) can be applied in different domains, including ceramics, chemicals, construction, or electronics [Hossain S. K. S. et al., 2018]. It was demonstrated that rice husk ash is more appropriate to be applied as raw material than rice husk itself [Y. Shen, 2017]. Rice husk burning generates rice husk ash which have high content of silica and can be considered an economically valuable raw material for biogenic natural silica. Various studies have investigated this ash to obtain different zeolites and mesoporous silica (ZSM-5, ZSM-11, MCM-41, or MCM-48) [V. C. Niculescu and S. M. Raboaca, 2021; S. Pimprom et al., 2015].

Among them, SBA-15 mesoporous silica proved to be an interesting material, with highly ordered mesopores and high surface area, being intensively applied as absorbents, catalyst support, drug delivery system, etc [S. M. Parmegiani Marcucci et al., 2022].

In this study, the obtaining of SBA-15-type mesoporous silica with high specific surface area was achieved by using sodium silicate solution resulted from RHA leaching as silica source through a simple temperature-controlled method. The obtaining route demonstrated to be simple, cost-effective, and environmentally friendly.

2. MATERIALS AND METHODS

Rice husk ash (defined as RHA) resulted from the rice husk (RH) heat-treatment at 550°C for 6 h in a muffle furnace (Nabertherm GmbH - Lilienthal, Germany). SBA-15 mesoporous silica was synthesized by modifying a previously described hydrothermal method [D. Zhao et al., 1998; J. J. Rodrigues et al., 2018]: 2.2 g triblock copolymer Pluronic P123 [poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol)] (Sigma Aldrich, Steinheim, Germany) were dispersed in 6.5 mL ultrapure water. Then, 76 mL HCl 2M (Sigma Aldrich, Steinheim, Germany) were added under magnetic stirring at 35°C. Subsequently, 4.5 g RHA were added as silica source, leading to formation of a reactive gel composition. This was stirred at 35°C for 24 hours and then it was transferred to a Teflon autoclave and conditioned for 48 hours at 100°C. The resulted material was washed with ultrapure water, dried at 60°C/24 hours. A white powder, denoted as SBA-15, resulted after calcination in a muffle furnace at 550°C/6 hours.

The specific surface area and pores distribution were estimated by Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) approaches, using a Quantachrome Autosorb-IQ porosity analyser, the sample previously being degassed at 120°C [A. Marinoiu et al., 2019]. The mesoporous silica was structurally characterized by scanning electron microscopy, using a Carl Zeiss - Variable Pressure Field Emission Scanning Electron Microscope - FESEM VP (resolution: 0.8 nm at 30 kV/2.5 nm at 30 kV in VP mode). Thermogravimetric analysis was performed using a SDT Q600 equipment (TA Instruments, New Castle, DE, USA), estimating the weight loss under gaseous nitrogen (100 mL/min) and a heating rate of 10°C/min. Functional groups of SBA-15 were identified by Fourier-transform infrared spectroscopy (FTIR) (Agilent Cary 630 ATR-FTIR spectrophotometer - Agilent Technologies, Santa Clara, CA, USA). The sample were conditioned and then subjected to analysis using a previously developed FTIR method [F. Bucura et al., 2023].

Furthermore, an Energy Dispersive X-ray Fluorescence (EDXRF) analysis using a MiniPal 2 Energy Dispersive PW4025 EDXRF spectrometer (Philips Analytical, Almelo, Netherlands), and elemental analysis (combustion and pyrolysis methods coupled with gas chromatography - Flash EA2000, Thermo Scientific, Waltham, MA, U.S.) [M. Constantinescu et al., 2019] were performed.

3. RESULTS AND DISSCUSION

The strategy to obtain SBA-15 was based on the hydrothermal treatment of the porous SiO_2 produced from RH, which behaved not only as the skeleton matrix, but also as the raw material. Figure 2 displays a detailed flow chart for the SBA-15 from rice husk.

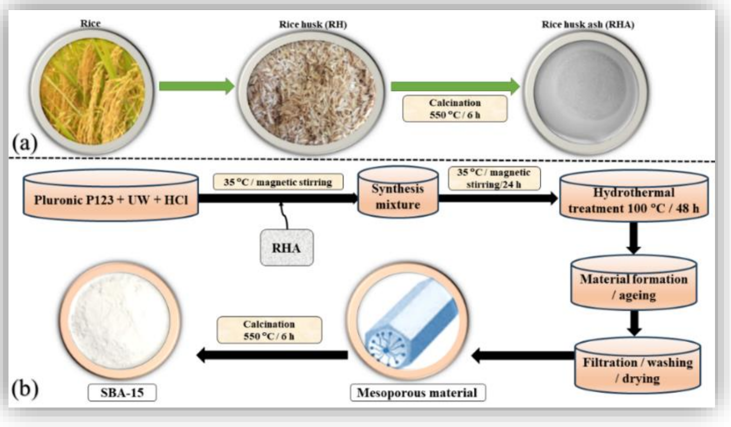

Figure 2. (a) Flow chart showing RHA obtaining from rice. (b) Detailed flow chart of the SBA-15 synthesis from RHA

Elemental analysis, EDXRF and EDS revealed a content of 14% by weight Si for the raw material (RH) and 61% by weight Si for the resulting SBA-15 (table 1).

Table 1. Elemental analysis, EDXRF and EDS

Sample	**C (%)**	**H(%)**	**O (%)**	**N (%)**	**S (%)**	**Other minerals (%)**	**Si (%)**
RH	40.41	5.03	34.92	0.61	0.23	4.48	14.32
RHA	0.59	0.66	48.29	0.36	0.21	14.27	35.62
SBA-15	0.15	0.68	37.28	0.40	0.31	1.42	61.30

The SEM images (figure 3) indicated that the rice husk ash containing silica obtained from the treatments has elongated particles and twisted leaves (figure 3). Fluttering of the outer epidermis in denser areas was also visible [J. J. Rodrigues et al., 2018]. In the inner regions, the formation of a porous cellular structure known as the silica skeleton occurred, resulting from the removal of lignin and cellulose during combustion [J. James and M. S. Rao, 1986]. The concentration of silica tended to be higher in the outer part due to the removal of organic compounds from the shell structure.

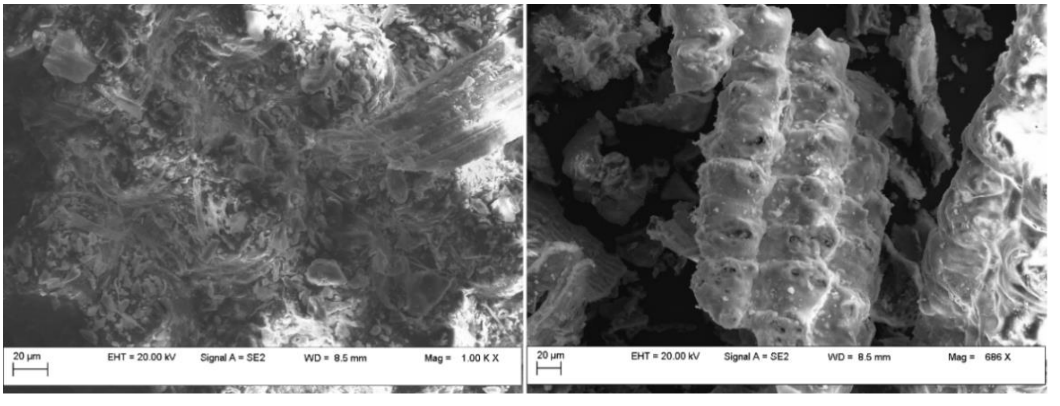

Figure 3. SEM images for RH (left) and RHA (right)

Figure 4 presents the SEM image for SBA-15 synthesized from rice husk ash.

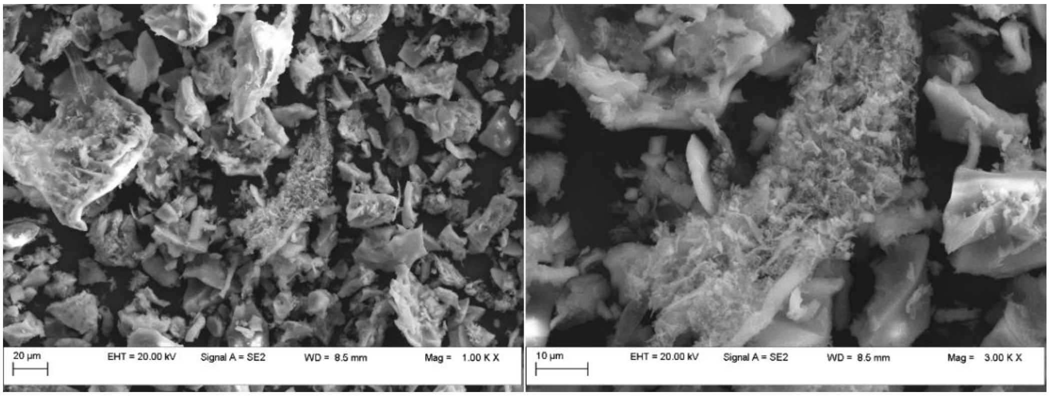

Figure 4. SEM images for SBA-15

When SBA-15 was obtained, SEM images (figure 4) indicated the formation of silica nodules in micrometric sizes, joined together by smaller particles that form interlocking collars, typical for this type of molecular sieve. Atypical formations for SBA-15 were also observed. The fibrous exoskeleton, characteristic of the interior of the epidermis of rice husk ash, formed around SBA-15 micrometric nodules, indicating the presence of primary silica morphology [J. J. Rodrigues et al., 2018]. These particles hinder the molecular sieve formation, due to the fact that their structures do not "frame" the organic driver, potentially reducing the silica fraction in the form of SBA-15 sieve [J. J. Rodrigues et al., 2018].

Brunauer-Emmett-Teller (BET) surface area and average pore diameters were determined from the N_2 adsorption-desorption isotherms. The BET surface area and mesopore volume of rice husk silica were lower (table 2 and figure 5) than those of classically synthesized SBA-15 [S. M. Parmegiani Marcucci et al., 2022]. However, the adsorption isotherm was type IV (figure 5), showing that the obtained material belongs to SBA-15 mesoporous materials. Furthermore, H1-type hysteresis is characteristic for mesoporous materials with cylindrical pores and uniform pore size [Q. N. Khanh Nguyen et al., 2020].

Table 2. Textural properties

Sample	S_{BET} (m^2/g)	D_{pBJH} (nm)	V_p (cm^3/g)
RH	1.474	9.310	0.003
RHA	31.328	8.966	0.232
SBA-15	140.039	3.716	0.240

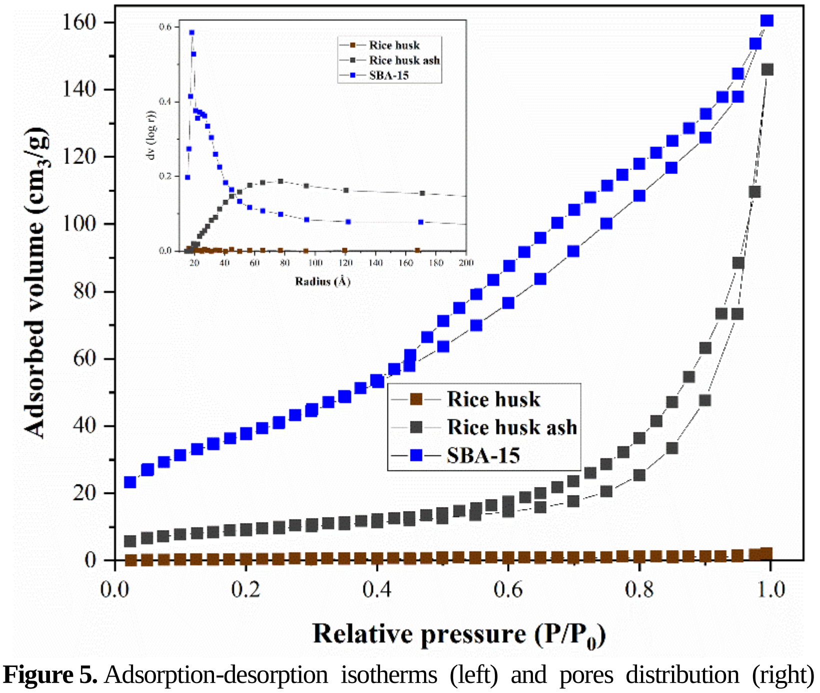

Figure 5. Adsorption-desorption isotherms (left) and pores distribution (right)

The infrared spectra of the rice husks (RH), the resulting ash (RHA) and the final product (SBA-15) are shown in figure 6.

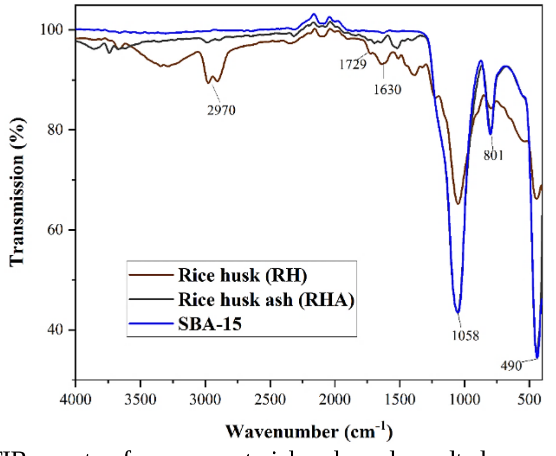

Figure 6. FTIR spectra for raw material, ash and resulted mesoporous silica

The appearance of an absorption band at about 1729 cm^{-1} and the decrease in intensity of the bands at 1630 and 2970 cm^{-1} indicated the progress of decomposition of organic matter in the shells [S. Steven et al., 2022]. Their disappearance is an indication of the completion of the decomposition of organic constituents. The peak at 1729 cm^{-1} was attributed to the C=O bond and the band at 1630 cm^{-1} could be attributed to either the C=C vibration or the O-H elongation of adsorbed water. The ash obtained at 550°C had a spectrum like that of fumed silica. It can be concluded that with isothermal heating, a minimum of 500°C was required for the complete destruction of organic matter in rice husks and the release of silica [J. James and M. S. Rao, 1986].

In the FTIR spectrum of SBA-15, the characteristic peak of siloxane (-Si-O-Si-) appeared at 1058 cm^{-1}. The stretching vibration of the Si-OH bond was observed at 801 cm^{-1} and the rocking vibration of the Si-O bond can be seen at 490 cm^{-1} [S. M. Parmegiani Marcucci et al., 2022; Q. N. Khanh Nguyen et al., 2020].

Thermogravimetric analysis (figure 7) revealed two distinct regions of weight loss.

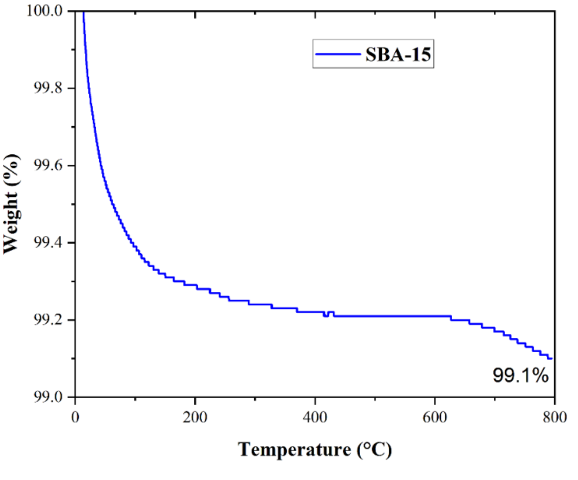

Figure 7. Thermogravimetric analysis curve for SBA-15

The first region of mass loss, (about 0.75%) appeared in the temperature range between 0 and 200°C, which could be attributed to the thermos-desorption of water physically adsorbed on the silica surface [L. B. de O. Freitas et al., 2016]. In the second region, in the temperature range from 200 to 800°C, the weight loss curve was relatively flat. The loss in this second region was almost negligible (0.19%) and corresponded to silanol condensation [L. B. de O. Freitas et al., 2016]. As a result, SBA-15 type silica exhibited stability in the investigated temperature range.

4. CONCLUSIONS

Agricultural wastes, particularly rice husks, proved high potential as a precursor to prepare value-added silica materials such as mesoporous silica. The benefits of using rice husk include, but are not limited to, environmental protection, sustainability, and diversity. This study provided both an insight into techniques for extracting biogenic silica from rice husk, as well as its use for the preparation of morphology-controlled mesoporous silica for potential applications in catalysis, drug delivery, energy, adsorption, and environmental remediation.

SBA-15 was synthesized by the hydrothermal sol-gel process using rice husk ash as the silica source and Pluronic P123 triblock copolymer [poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol)] as surfactant.

The material obtained by the hydrothermal method using rice husk ash as a silica source showed characteristics typical to the SBA-15 molecular sieve, but with a lower specific surface area than the material obtained from commercial sources.

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