



Facile methods for the preparation of micro- and mesoporous amorphous silica from rice husk

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Abstract

Silica was obtained from rice husk (RH) by five different methods. (1) Burning RH as received in muffle at 850 °C for 2 h, (2) RH was firstly burned at 450 °C to reduce its volume. The obtained ash was refluxed with 1N HCl; after washing and drying, ash was burned at 700 °C for 3 h. (3) Un-grinded (or grinded (method 4)) RH was firstly soaked in water, treated with 1N HCl, and burned at 700 °C. (5) To utilize cellulosic fiber, RH was autoclaved with 15% NaOH, and silica was precipitated from the residual liquor. Silica hydrogel was prepared from the obtained ashes by reflux with 2.5 N NaOH followed by neutralization with 1N HCl to form silica gel. The silica gel was filtered, washed, and freeze-dried. XRF analysis confirmed the excellent removal of metal oxide impurities from RHs by acid leaching treatment. Silica precipitated from black liquor shows the most homogeneous particle size. Mesoporous silica with purity over 99% and with a homogeneous particle of average size 41.3–71.3 nm was synthesized using CTAB surfactant as the structure-directing template and RH ash as the silica source.

Keywords Mesoporous silica · Amorphous silica · Rice husk · Silica hydrogel

1 Statement of novelty

Silica was obtained from rice husk by five different simple methods. Silica hydrogel was prepared from the obtained ashes and used successfully to prepare micro- and mesoporous amorphous silica. Mesoporous silica with purity over 99% was synthesized using CTAB surfactant (as a structure-directing template) and rice husk ash (as a silica source).

2 Introduction

Amorphous silica has an excellent recognized performance, due to its application in different industries and electronics for being a good semiconductor [1]. Also, it has diverse properties such as nontoxicity; large surface area; chemically, physically, and thermally stable; compatible with various materials; largely available; and relatively inexpensive [2]. Mesoporous silica has

particles with pore sizes in the range of 2–50 nm. Due to their high surface area, controllable narrow pore size distribution, and ability of surface chemistry functionalization, mesoporous silica has received great attention for numerous applications in adsorption, separation, catalysis, wastewater treatment, and drug delivery [3, 4]. However, the large-scale manufacture of mesoporous silica is difficult due to the high cost and toxicities of both the templates and the silica source. Mesoporous silica is produced via poly-condensation of silica species (like tetraethyl- (TEOS) or tetramethyl- (TMOS) orthosilicate) in the presence of surfactants (e.g., hexadecyltrimethylammonium bromide (CTAB)) as structure-directing agents. But, these raw materials, particularly the TEOS, are expensive for large-scale production [5]. Thus, many attempts are done to find alternative silica sources to synthesize mesoporous silica. Using rice husk (RH) waste as a source of potential silica is valuable and economic in the industrial production of efficient mesoporous materials.

RH is an abundantly available waste product from the agriculture industries, comprising about 22% of 760 million tons of world rice production [6]. In general, RH is composed of 35% cellulose, 25% hemicellulose, 20% lignin, 17% ash, and 3% moisture by weight [7]. Silica represents about 94% of the total rice husk ash (RHA) while the remaining 6% are trace amounts of other elements oxides such as potassium, magnesium, calcium, and sodium [8].

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Annually production of a huge amount of RH creates the disposal problem. A significant amount of RH is discarded as waste at landfills. Small bulk density and high silica content of RH residues cause severe pollution for water and earth and consequent health-related troubles [9]. Due to its high calorific value, RH was used as a fuel in boilers for power production in rice mills, which generates RHA in huge amounts. The discharge of RHA in the open environment causes many problems to human health, for instance, respiratory disorders, fatigue, silicosis disorder, loss of appetite, and even death [2]. Utilization of RHA as fillers in cement or polymers, fertilizers, catalyst carriers, and silica production will have a benefit of preserving the environment and adding value to the RHA waste [10]. RHA could be used as an efficient adsorbent for wastewater treatment [11]. Rice husk amorphous silica nanocomposites were successfully used for heavy metal ions adsorption from aqueous solutions [12, 13]. Silica manufactures from disregarded RH protects human health and environment and provides an additional advantage of RH waste [14].

Previous results on extracting pure silica nanoparticle from RH, using acid-leaching by both sulfuric and nitric acid, demonstrate the significant effect of the acid during leaching and neutralization steps on the yield, purity, and crystallite size of the prepared silica nanoparticles. Also, the pH value at which silica gel precipitates and calcination temperature were found to have a vital role in the synthesis of pure silica nanoparticles [15]. Pre-treatment of RH with mineral acids before its burning at lower temperatures (around 500–600 °C) is an effective technique to remove most of the metallic impurities, accelerate the hydrolysis of cellulose and hemicelluloses in RH, and produce wholly white amorphous silica with a high specific surface area [16]. This method is an eco-friendly and cost-effective substitute for the high energy processing of silicon dioxide. This study aims to investigate and compare various simple methods to prepare amorphous mesoporous silica by cost-effective methods without consumption of high energy or using hazardous chemicals from RH wastes.

3 Experimental

3.1 Materials

Acetic acid, hydrochloric acid, sodium hydroxide, cetyltrimethylammonium bromide (CTAB), and other chemicals were of pure analytical reagent-grade and used as received without further purification.

3.1.1 Raw materials

RH was obtained from a local rice mill in Egypt. It was first washed with tap water to remove dirt and aqueous soluble substances, and dried in a sunny place for 72 h.

3.1.2 Extraction of silica from RH

Five different methods were investigated in this study to extract silica from RH.

1 Ash of blank RH waste without purifications

In this method, silica was obtained by burning RH as received in muffle at 850 °C for 2 h. The obtained ash was refluxed with 2.5 N NaOH in liquor ratio 1:10 for 3 h followed by neutralization with 1N HCl to form silica gel, as shown in Scheme 1. Slow titration was performed under vigorous stirring to prevent the formation of large aggregates. The silica gel was filtered, washed, and freeze-dried to remove water. The freeze-dried silica appeared as fine white powders at a yield of 93% from the ash. This method was simple and fast but has the disadvantage of possibility for forming undesired crystalline silica and it may contain some impurities; also it requires a relatively higher temperature.

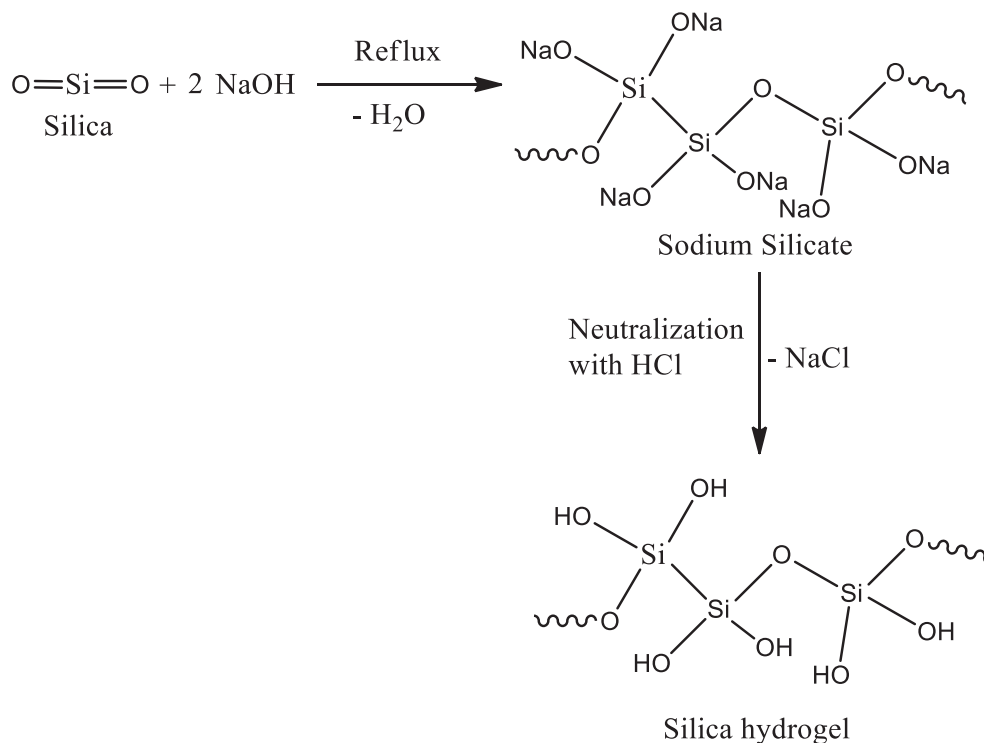
2. Ash of un-grinded RH which burned at 450 °C then refluxed with HCl

In this method, bulky RH was firstly burned at 450 °C to attain ash of less than one-tenth volume compared to RH; the reduced volume ash is easy to handle and requires lower chemicals for treatment. The obtained ash was refluxed with 1N HCl (liquor ratio 1:7) at 130 °C for 3 h. After washing and drying, ash was burned at 700 °C for 3 h. It was reported that the burning of RH treated with acid at 700 °C for 2 h can efficiently eliminate the organic components in RH to obtain highly pure silica. The lower temperature during burning will result in partial degradation of organic components, leaving carbon residues in silica [16]. The obtained ash was refluxed with 2.5 N NaOH in liquor ratio 1:10 for 3 h followed by neutralization with 1N HCl to form silica gel.

3. Ash of un-grinded RH which soaked in water and treated with HCl

In this method, RH was firstly soaked in water at room temperature for 48 h. After washing with distilled water, it was treated with 1N HCl (liquor ratio 1:7) at 130 °C for 3 h. After washing and drying, it was burned at 700 °C for 3 h. The obtained ash was refluxed with 2.5 N NaOH in liquor ratio 1:10 for 3 h followed by neutralization with 1N HCl to form silica gel.

4. Ash of grinded RH which soaked in water and treated with HCl

Scheme 1 Silica hydrogel preparation from RHA

To study the effect of grinding on the quality of obtained silica, method number 3 was repeated typically by using grinded RH instead of un-grinded RH. RH was grinded and screened through an ASTM standard sieve to approximately 40-mesh.

5. Ash of black liquor silica gel

In this method, the RH was firstly treated in an autoclave with 15% NaOH (liquor ratio 1:6) at 140 for 2 h. The raw RH material was pulped in a 15 L batch reactor heated by an outer jacket containing electrical wires. The reactor contents were stirred by rotating the reaction vessel via a motor connected through a rotary axle to a control unit including the required instruments for measurement and control of pressure and temperature (the pulping process was carried out in the central lab. at Rakta company, Egypt). Cellulosic fibers were separated from the pulping liquor for further use. The residual liquor (black liquor) contains the dissolved lignin, carbohydrates, and silica, which precipitated upon neutralization with 1N HCl. This precipitate was washed, dried, and burned at 700 °C for 3 h to eliminate organics substances. The obtained ash was refluxed with 2.5 N NaOH in liquor ratio 1:10 for 3 h followed by neutralization with 1N HCl to form silica gel.

3.1.3 Silica hydrogel preparation

Silica hydrogel was prepared from RHA by refluxing with 2.5 N NaOH in liquor ratio 1:10 for 3 h followed by neutralization with 1N HCl according to the following Scheme [17]:

3.1.4 Preparation of mesoporous silica

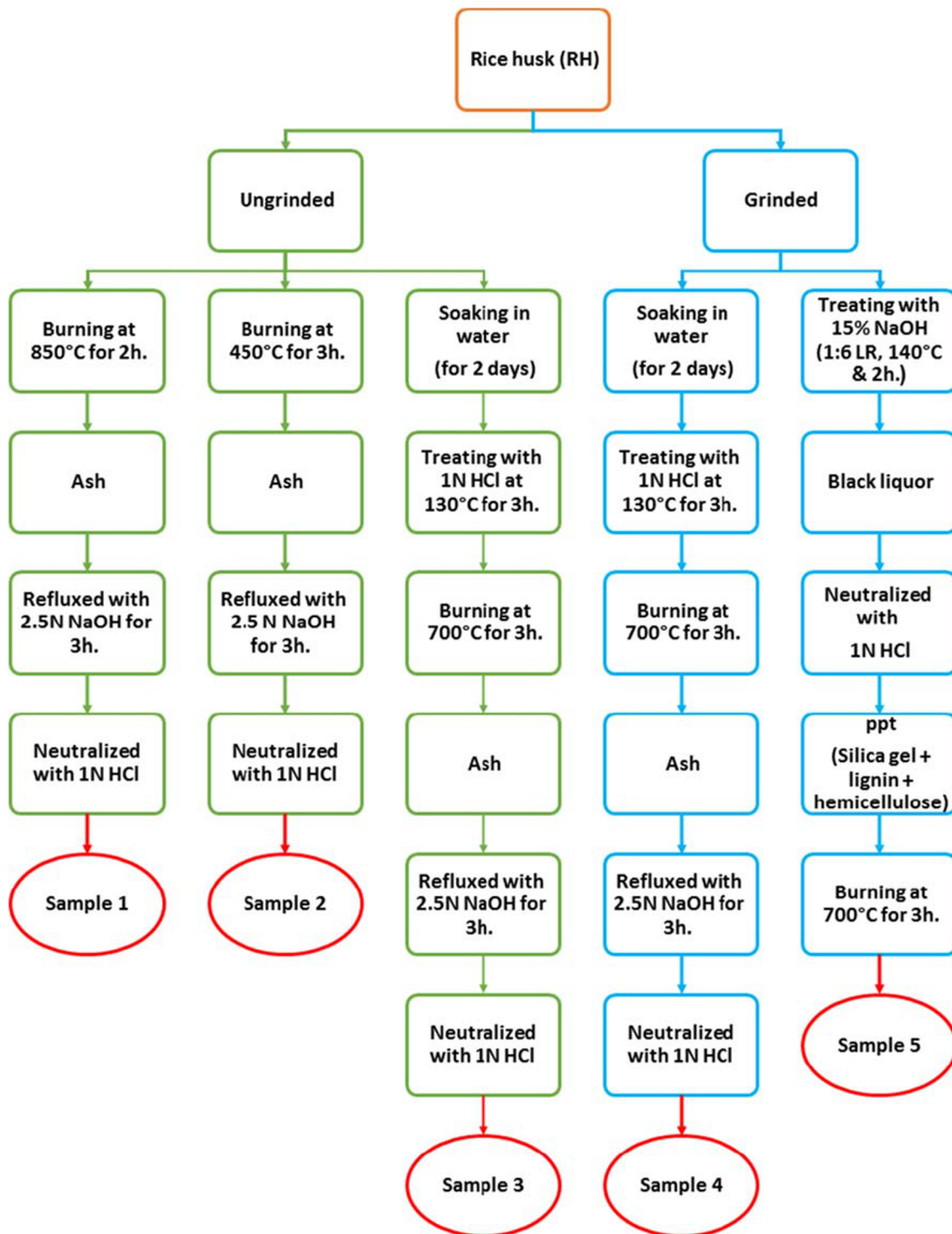
Mesoporous silica was synthesized by a modified procedure according to the literature [18]. Namely, 6 g RH silica was dissolved into 100 mL of 2 M NaOH. It was then filtered to separate the un-dissolved residues from the solution, and then heated at 80 °C in an oil bath for 24 h to produce sodium silicate (Na_2SiO_3). Two percent CTAB was dissolved in 100 mL distilled water then stirred for 30 min at room temperature. CTAB solution was added to the Na_2SiO_3 solution slowly under stirring conditions. Stirring for 30 minutes was to make the solution homogeneous. After that, the solution was titrated with 5 M CH_3COOH to pH 10 and stirred for 6 h at room temperature to obtain a gel, followed by hydrothermal treatment at 100 °C for 24 h. The gel was aged for 24 h at pH = 10, filtered, and washed using a mixture of distilled water and 96% ethanol, continued with drying at 27 °C for 12 h. To remove CTAB, we applied the reflux process into a mixture of 9 mL of 37% HCl and 160 mL of methanol for 12 h followed by centrifuging to separate the solid material from the solution. The precipitate was washed with distilled water and dried, followed by calcination in air at 550 °C for 5 h to completely remove the surfactant template.

3.2 Characterization

The content of each metallic oxide impurity and chemical composition of the ashes was measured using energy dispersive X-ray fluorescence spectroscopy (Axios 2005,

PANalytical, Netherlands). Scanning electron microscopy (SEM) was done on Model Quanta 200 scanning electron microscope, (FEI CompanyBV, Netherlands), with an accelerating voltage of 20 kV. Transmission electron microscope images were carried out by JEOL JEM-1400 TEM, USA. Particle size was measured using version Particle Sizing

Systems, Inc., Santa Barbara, California, USA. Fourier transform infrared (FTIR) was carried out for different RH samples by using spectrum (Perkin-Elmer 2000), with a wavenumber range of 4000–400 cm^{-1} . X-ray diffraction (XRD) patterns were recorded with an Empryan Powder Diffractometer with a monochromatic CuK radiation source ($\lambda = 0.154 \text{ nm}$) at



Scheme 2 Representations for the silica extraction steps from RH

Table 1 XRF analysis for different ashes samples

Method no.	SiO ₂ %	Metal oxides	LOI ^a
Raw material	13.91	2.96	83.13
2	91.29	1.06	7.65
3	85.5	0.77	13.73
4	84.93	1.31	13.76
5	87.63	2.07	10.30
CTAB	99.4	0.6	0

^a LOI loss weight on ignition

45 kV and 45 mA, in step-scan mode with a 2° angle ranging from 5 to 70° with a step size of 0.01°s⁻¹. TG analysis was

applied to the prepared amorphous silica powder by using the Setaram TGA instrument (Setaram, France).

4 Results and discussion

4.1 Silica extraction

Five different methods were investigated in this study to extract silica from RH. Scheme 2 summarizes the experimental steps used for each method. The yield of ash from RH was 17 ± 0.5% for the various studied methods. The combustion temperature at 700 °C or more was reported to be enough for complete thermal degradation of all carbohydrates founded

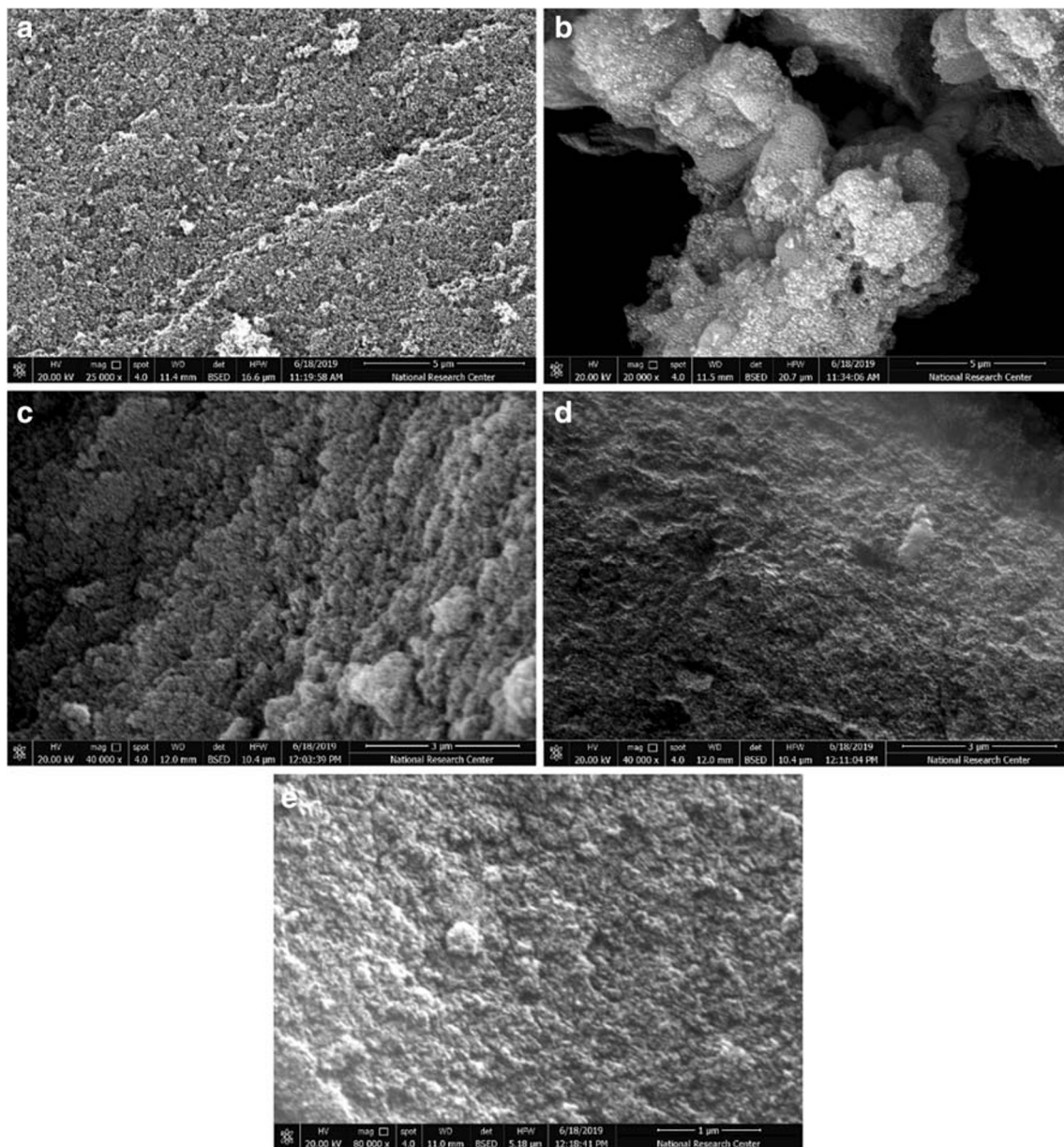


Fig. 1 Scanning electron microscopy (SEM) for different ashes samples

in RHs and resulted in very few carbon contents [19]. By using the proper conditions for acid leaching and air combusting processes, amorphous silica materials could be produced with higher purity from RH [12, 20].

4.1.1 Ash of blank RH waste without purifications

In this method, the calculated ash yield from RH raw material was 12.63%. The obtained ash was white without any carbon residues, but it is known that the ignition of RHs over 700 °C causes the crystallization of amorphous silica to the undesired cristobalite and/or tridymite inactive crystal, especially when no acid leaching treatment for raw RHs was used [21]. Anyhow, this pure ash was used as a silica source to prepare the sodium silicate solution required for mesoporous silica synthesis.

4.1.2 Ash of un-grinded RH which burned at 450 °C then refluxed with HCl

The aim of burning at 450 °C was to overcome the bulky problem of RH. Black ash was attained in about one-tenth volume compared to RH raw material. This ash is easy to handle and requires lower liquor during leaching with acids, and consequentially lower chemicals. The obtained ash was refluxed with 1N HCl. Leaching of RH with HCl before thermal treatment is an efficient technique to raise the hydrolysis rate of cellulose in RH as it eliminates the majority of the metallic contaminations and produces high purity white silica [16]. After washing and drying, leached black ash was burned at 700 °C for 3 h, to give 17% yield (to RH raw material). The obtained ash was faint grey and contains 7.65% lose weight on ignition (LOI). The upper layer of ash on the crucible was entire white on color but the lower layers were gray. It may require a longer time or higher temperature during ignition, but this could lead to a formation of crystalline silica. In the current study, the alkali method is used for silica extraction after the thermal treatment of RH followed by acid precipitation. During refluxing with NaOH hydroxide to form sodium silicate, insoluble carbon

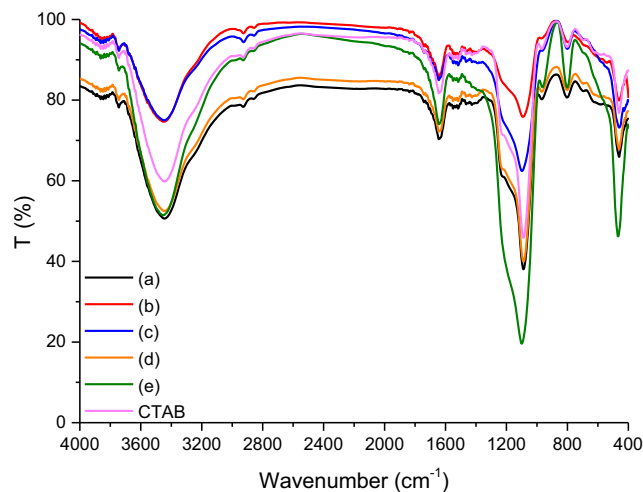


Fig. 2 FTIR for **a** sample 1, **b** sample 2, **c** sample 3, **d** sample 4, **e** sample 5, and CTAB silica

residues could be eliminated by filtration leaving a clear and transparent sodium silicate solution.

4.1.3 Ash of un-grinded RH which soaked in water and treated with HCl

In this method, RH was firstly soaked in water at room temperature. The soaking pre-treatment aimed to remove most of the alkali metals from RH to make the subsequent hydrolysis process more efficient. After washing with distilled water, it was treated with 1 N HCl. The preliminary acid pretreatment process before heat treatment is an efficient technique to remove metal ion impurities and partially hydrolyzed the carbohydrates constitutes of the RH. The treatment method using 1 N HCl was proved as the optimum method for extraction of silica from rice husk [22]. The incineration of RH (even over 700 °C) after acid pretreatment generated pure white silica nanoparticles with amorphous morphology [20]. After washing, drying, and burning at 700 °C for 3 h, grey ash with 13.73% LOI was obtained. The proposed method does not involve the use of high pressure and temperature.

Table 2 Particle size measurement for different ashes samples

Method no.	Mean diameter nm	St. deviation nm	25% ≤ nm	50% ≤ nm	75% ≤ nm	90% ≤ nm	99% ≤ nm
1	1065	1103	354	669	1304	2391	6355
2	1663	1365	699	1202	2080	3411	7892
3	1765	1861	577	1097	2157	3990	10688
4	1687	1842	534	1025	2052	3861	10501
5	1290	973	590	976	1619	2555	5573
CTAB	908	359	643	840	1096	1393	1171

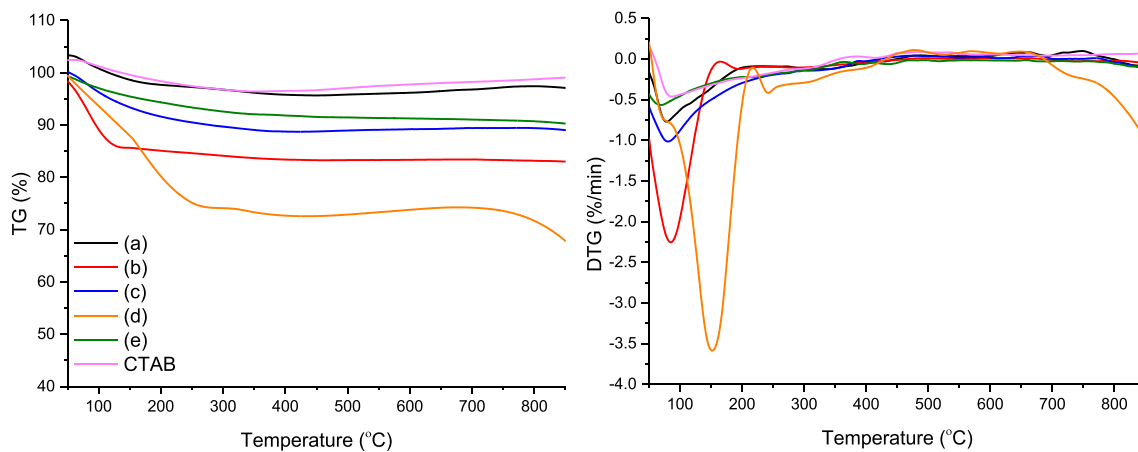


Fig. 3 TGA and DTG thermograms for **a** sample 1, **b** sample 2, **c** sample 3, **d** sample 4, **e** sample 5, and CTAB silica

4.1.4 Ash of grinded RH which soaked in water and treated with HCl

The effect of RH grinding on the silica extraction was investigated in comparison with un-grinded RH (method number 3). In this study, comparable results were obtained for both grinded/ un-grinded RH concerning yield and purity (LOI%). So, it recommended using un-grinded RH to save time and energy.

4.1.5 Ash of black liquor silica gel

In the first 4 methods to attain silica, the valuable cellulosic fibers in RH were burned without any use. To save valuable cellulosic fibers for further use, RH was primary pulped using 15% NaOH. Cellulosic fibers (suitable for paper, board making, or saccharification) were separated from the pulping liquor in a yield of 53%. After neutralization of the black liquor, dissolved lignin, carbohydrates, and silica were precipitated. Silica was extracted in a yield of 12% (to RH raw material) from this precipitate by burning at 700 °C for 3 h to eliminate organics substances.

4.1.6 Preparation of mesoporous silica

Amorphous mesoporous silica nano-disks have great potential to be utilized as molecular sieves, catalyst supports, absorbents, etc. Mesoporous amorphous silica particles were obtained throughout the simple green method as was described in the preceding section. The mesoporous silica was synthesized successfully from clear sodium silicate solution obtained by using different RHA as the silica source, in the presence of cationic–neutral surfactant CTAB, as the structure-directing template [22]. X-ray fluorescence (XRF) and XRD prove the formation of amorphous silica with purity over 99%. The estimated cost production of commercial mesoporous silica

from RH shows the process to be economical and environmentally sound.

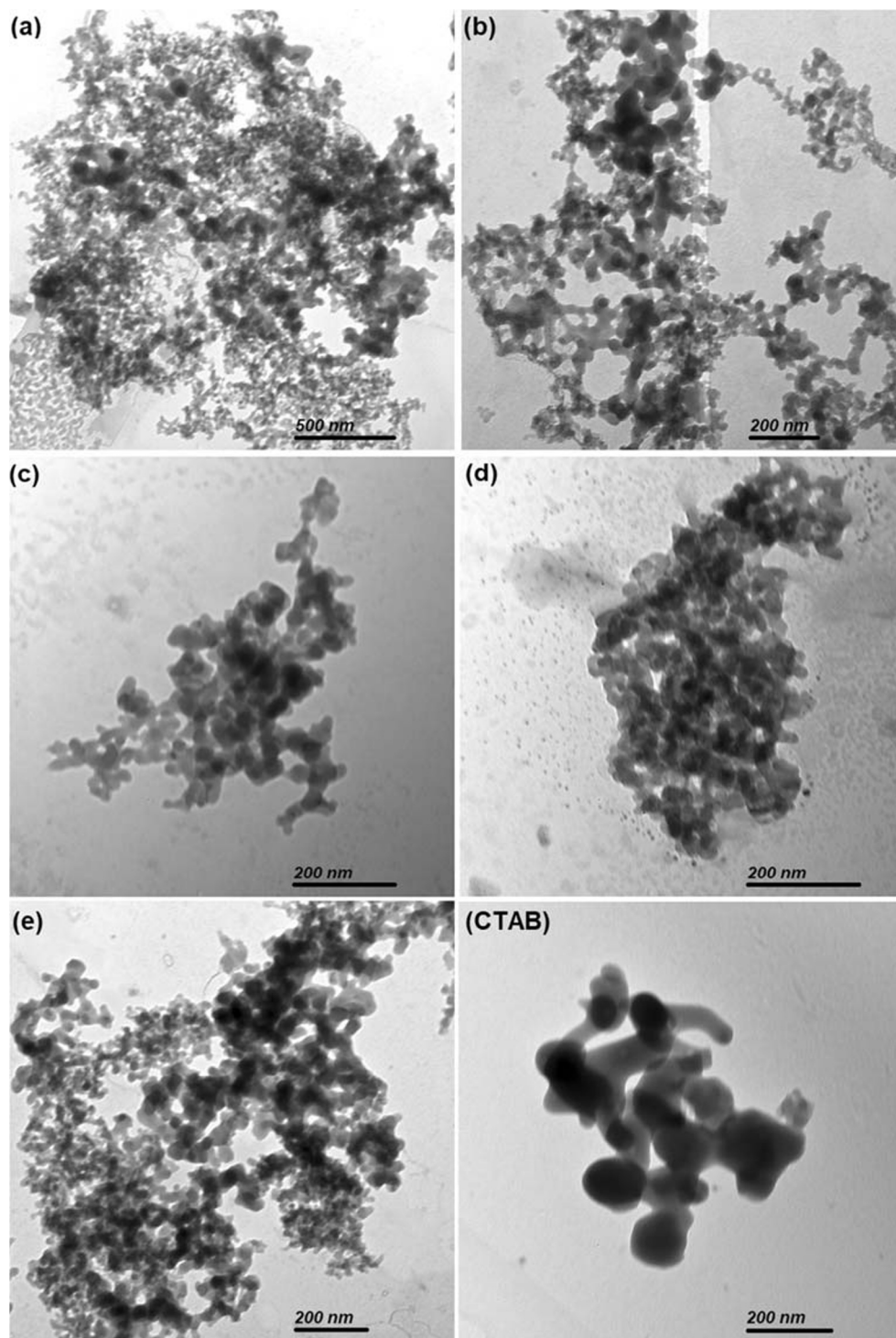
4.2 Characterization

4.2.1 X-ray fluorescence spectroscopy

Metallic oxide impurities and chemical composition of RH and different obtained ashes were measured using energy dispersive X-ray fluorescence spectroscopy. XRF analysis revealed the presence of silicon and oxygen elements together as the main constituent for ashes. Table 1 shows that RH raw material contains 13.91% silica, 2.96% K, Ca, Al, Na, Fe, Mg, S, and P metal oxides, besides Cl and Zn, Sr, and Zr oxides in traces amount. Loss weight on ignition (LOI) is high (83.1%) due to its main constituent of cellulose, hemicellulose, and lignin. Refluxing with HCl removes 56–74% from metal oxides (samples 2, 3, and 4).

Alkaline treatment as seen in Table 1 (sample 5) seems to reduce metal oxides by only 30%, but this is a false impression because details of metal oxides concentrations show a 50–80% decrease for different metal oxides, while NaO% increased to some extent. XRF analysis confirmed the excellent removal of metal oxide impurities from RHs by acid leaching treatment. K, Na, and Ca were greatly (nearly completely) removed by acid leaching, especially for samples 3 and 4, which proves the benefits of the water soaking step. Removing these alkali metal impurities is important to avoid the eutectic phenomenon by its reaction with SiO₂ which forms crystalline silica. CTAB ash sample is composed of 99.7% SiO₂ without any LOI%. As mentioned above, the upper layer of ash on the crucible was white on color but the lower layers were gray. This is the reason for the high LOI for different samples. The optimization of the operating parameters and air combustion of RHs was essential to attain pure amorphous silica.

Fig. 4 TEM micrographs for **a** sample 1, **b** sample 2, **c** sample 3, **d** sample 4, **e** sample 5, and CTAB silica



4.2.2 SEM analysis

Scanning electron microscopy (SEM) for different ashes samples were introduced in Fig. 1. SEM micrographs revealed the surface morphology of uniform porous spheroid shaped silica particles with a little agglomeration of varying size in the micron range. The absence of a regular geometry verifies the amorphous nature of the silica.

4.2.3 Particle size measurement

Table 2 shows the particle size measurement for different ashes samples. From RH waste, silica particles with finite micron dimensions were successfully synthesized using simple extraction methods. Samples 3 and 4 (grinding effect) show a comparable particle size measurement. Lower particle dimensions were recorded for sample 1 (higher ignition

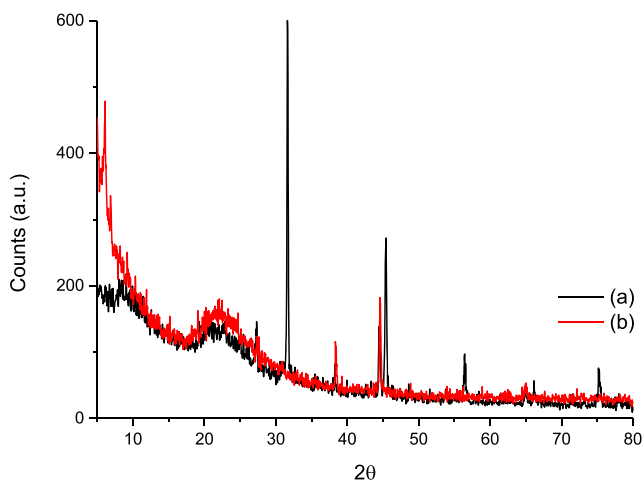


Fig. 5 XRD analysis for (a); RHA and (b); CTAB silica

temperature). Silica precipitated from black liquor shows the most homogeneous particle size as obvious from its lower standard deviation value and the lower particle size dimension for the 99% of the sample. Using CTAB surfactant as the structure-directing template reduces about 50% of the particle size and produces homogeneous particle size and the lowest standard deviation value.

Simplicity and variety of methods, low-cost raw material, utilization of biomass waste, template-free synthesis, makes the proposed methods more sustainable and greener.

4.2.4 Fourier transform infrared spectroscopy for silica

The most important chemical groups of silica powder were studied by FTIR spectroscopy over the range of 4000 to 400 cm^{-1} (Fig. 2). FT-IR spectrum contains several absorption bands, which indicated the presence of individual structural groups, such as the weak bands at 3744 cm^{-1} which were assigned to the original Si-OH groups in different silica samples [23], and to the physical absorption of water molecules [12]. Broadband was observed at about 3440–3455 cm^{-1} corresponding to the asymmetry stretching vibrations of the bonding surface silanol groups (Si-OH), while the weak band at 965 cm^{-1} was assigned to the symmetric stretching vibration of the Si-OH groups [20]. A weak band at 2926 cm^{-1} observed for samples 1, 2, and 3 was attributed to CH₂ stretch vibrations of residual carbon ashes in these samples, while sample 5 and CTAB ash have no polysaccharides signals [20]. The disappearance of peaks between the frequency of 1700 and 2900 cm^{-1} indicates the absence of any other organic matter in the studied silica [24]. The broad absorption band between 3440 and 3455 cm^{-1} and little absorption band at 1644 cm^{-1} could attribute to H-O-H stretching and bending vibration of water molecules absorbed on the silica surface [25, 26]. FTIR spectrum also exhibits bands around 1098, 798, and 465 cm^{-1} characteristic of the asymmetric stretching,

symmetric stretching, and bending vibrations of Si-O-Si, respectively [12, 16]. A sharp and smooth band at 1098 cm^{-1} indicates the polymerization of the Si-O bond due to intermolecular dehydration to form the Si-O-Si chains [27].

4.2.5 TGA and DTG analyses

TG analysis was used to make sure that organic components have been removed from RH. Thus from the thermal analysis curves of silica powder, TG, and DTG thermograms in Fig. 3, it is clear that the decomposition stage occurred in the range between 50 and 200 °C, which attributed to the evaporation of moisture and remaining volatile organic impurities that might present in small proportions. The weight loss at this decomposition stage of silica powder samples ranged between 2.30 and 25.10%. These results agreed well with those obtained from XRF analysis. Also, according to the works previously done on water confined in porous silica, this degradation step represents both surface physisorbed and hydrogen-bonded chemisorbed water molecules [28].

4.2.6 TEM analysis

The TEM analysis of silica powders was used to investigate their surface morphology. The shape of silica is almost spherical with slight agglomerations. Samples from 1 to 5 show a broad range of particle size distribution of about 6.78–65.9 nm (Fig. 4a–e). On contrary, CTAB-templated silica was uniform with an average homogeneous particle size distribution of approximately 41.3–71.3 nm.

4.2.7 XRD analysis

The crystallization phase of the silica powder was detected by the XRD spectrum. As is shown in Fig. 5, a broad peak at around 22.5° (2θ) was observed, which confirms the amorphous structure of silica and indicates the non-appearance of orderly crystalline structure. Some additional peaks were observed for RHA due to the residual carbon char ash in silica, while the CTAB silica pattern proves the formation of pure silica.

5 Conclusions

Five different processes were described for the preparation of silica from RH. The effect of temperature, soaking on water, acid leaching, and grinding were considered in addition to precipitation of silica from pulped RH black liquor. XRF analysis revealed the presence of silicon and oxygen elements together as the main constituent for ashes. XRF analysis confirmed the excellent removal of metal oxide impurities from RHs by acid leaching treatment; HCl removes 56–74% from

metal oxides. SEM micrographs revealed the surface morphology of uniform porous spheroid shaped silica particles with a little agglomeration of varying size in the micron range. Silica precipitated from black liquor shows the most homogeneous particle size. The mesoporous silica was synthesized from a clear sodium silicate solution obtained by using different RHA, successfully throughout a simple green method. TG analysis proved the thermal stability of silica powder produced by the different methods.

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