

Extraction of high-purity silica from rice husk via hydrochloric acid leaching treatment

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Abstract: The present paper aimed at the investigation of the effect of preliminary acid treatment on the structure and purity of extracted silica. In this study, the acid leaching of rice husk (RH) in 2 M hydrochloric acid solution before the calcination process at 600 °C was proposed to achieve completely white silica with high specific surface area and low content of impurities. RH, selected from the Almaty Region, Kyzylorda Region, and Turkestan Region was used as the main silica source. The results confirmed that the highest purity (98.2%–99.7%) amorphous silica with a specific surface area between 120 and 980 m² g⁻¹ could be extracted during acid treatment and controlled calcination. The structure is amorphous, porosity diameter decreased from 26.4 nm to 0.9 nm, and specific pore volume increased from 0.5 to 1.2 cm³ g⁻¹.

Key words: Rice husk, rice husk ash, silica, hydrochloric acid leaching

1. Introduction

Rice husk (RH) is a widely known waste product left during paddy rice processing in the agricultural industry [1]. The rice growing of Kazakhstan is concentrated mostly in the Kyzylorda Region and approximately 64,000 t of RH are produced per year, causing the problem of its disposal. RH does not disintegrate in the ground and when it is burned various form of toxic gases and fine particles are released [2]. However, burning in open air is still practiced, especially in poor and developing countries, causing environmental and health problems [3]. Therefore, at this time, special attention is being paid to the recycling and utilization of this agricultural residue and its processing to obtain valuable products.

RH has been applied as a raw material for different industrial applications such as an additive for cement or concrete fabrication [4], fuel for power generation [5] and the synthesis of carbon materials [6,7], an organic fertilizer in agriculture [8], an adsorbent for the removal of toxic metals from wastewater [9], an adsorbent for biomedical use [10], and in the production of bioethanol [11]. Furthermore, the higher silica content in RH makes it an ideal potential source for the preparation of value-added silicon-based materials, including silicon carbide, silicon nitride, silicon tetrachloride, zeolite, and silicates [12].

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RH consists of organic components, mainly 50% cellulose, 25%–30% lignin, and 15%–20% silica [13]. Silica is the major mineral component of RH ash, which also contains potassium, sodium, magnesium, calcium, iron, and phosphorus and much smaller quantities of other elements [14,15]. Silicon dioxide in RH differs from other popular types of silicon-containing raw materials (quartz, cristobalite, etc.). Its amorphous state contains less metal impurities and is more chemically active. Because of this, the process of obtaining silica from RH requires less energy. By contrast, obtaining it from other sources of raw materials consists of a complex process, including crushing, grinding, and enrichment followed by purification from impurities.

Researchers have focused on numerous techniques for the extraction of silica by controlling conditions such as burning temperature and time. The structure and properties of the produced silica can be different from amorphous to crystalline phase depending on the selected temperature or chemical treatment. The convenient, template-free method of chemical treatment with hydrochloric acid was used in the present study to prepare silica of ultrafine size, high reactivity, and high purity. The purpose of acid pretreatment is to improve purity and give a high surface area to the silica product during its precipitation [16]. It proves to be an effective way for substantially removing most of the metallic and carbonaceous impurities and producing silica completely white in color [17–19]. The obtained XRF results confirm this finding in that the content of oxides of potassium, calcium, iron, and magnesium was observed in all of the untreated ash samples irrespective of the temperature and conditions of burning. Leaching of raw RH with 2 M hydrochloric acid and calcination at 600 °C was found to give an ash product almost white in color with purity index in the range of 98.2%–99.7%. The results indicated that HCl leaching treatment was more effective in removing metal ions than H_3PO_4 or H_2SO_4 . Silica produced from RH at a temperature of 500 to 650 °C with a calcination time of 2.5 to 6 h is predominantly amorphous, while crystallinity is achieved when the calcination temperature rises above 700 °C.

The objectives of the current study are to demonstrate 1) the experimental verification of the feasibility of amorphous silica production from RH; 2) that the RH could be burned to extract amorphous silica with high purity and high surface area; and 3) that a convenient acid treatment method is one of the optimal solutions for RH utilization in the rice-producing regions of Kazakhstan.

2. Results and discussion

Preliminary acid treatment affects the chemical composition of RH-derived products but not their structure, whether crystalline or amorphous. The structure of silica depends on the temperature and duration of calcination and above 700–900 °C crystalline forms are produced. The composition variation of the RH is caused by several factors, such as agricultural practices (amount and type of fertilizers used) and climatic or geographical factors [20]. The main chemical elements in the samples of obtained RH ash (RHA) and silica are listed in Table 1. The chemical compositions of the RHA indicate that SiO_2 is the main component of the siliceous precipitate and the content of metal impurities is low.

The samples of RHA without acid pretreatment contain from 73.9% to 84.4% SiO_2 . After treatment with hydrochloric acid, the content increased to 99.7%. This proved that the application of the preliminary treatment method is useful for removing metallic impurities and improving the purity of silica. However, as shown in Table 1, after treatments with H_3PO_4 and H_2SO_4 , the silica content increases only to 73.4% and 97.4%. The major impurities of untreated RH ash are potassium oxide, calcium oxide, and iron oxide with 18.5%, 8.3%, and 2.5% contents, respectively. Oxides of potassium and calcium have been almost completely removed from the RH ash after pretreatment with HCl, while iron oxide could be better removed with H_3PO_4 and H_2SO_4 . All chemical treatments showed that the effective removal of oxides varies depending on the nature of the reagent used in treatment of RH ash.

Table 1. Results of X-ray fluorescent analysis of RH ash and silica samples.

Elemental composition	RH ash (untreated)			RH ash (after treatment with HCl)			Pure SiO ₂ sample				
	RHA* ¹	RHA* ²	RHA* ³	RHA* ¹	RHA* ²	RHA* ³	HCl* ¹	HCl* ²	HCl* ³	H ₃ PO ₄	H ₂ SO ₄
SiO ₂	83.8	73.9	84.4	97.2	89.6	93.0	98.2	99.1	99.7	73.4	97.4
Na ₂ O	–	–	–	–	–	–	–	–	–	7.0	0.5
MgO	–	–	–	–	–	–	–	–	–	–	–
Al ₂ O ₃	–	–	–	–	–	–	–	–	–	0.03	–
SO ₃	–	–	–	–	–	–	–	–	–	–	2.0
Cl	–	3.1	–	0.9	6.1	2.8	1.8	0.8	–	–	–
K ₂ O	8.6	18.5	4.8	0.3	–	0.5	–	–	0.1	0.03	–
CaO	6.7	2.8	8.3	–	–	1.2	–	–	0.2	–	0.02
MnO	0.2	0.6	–	–	0.2	–	–	–	–	–	–
Fe ₂ O ₃	0.6	0.6	2.5	1.2	3.7	2.2	–	0.02	–	–	–
CuO	–	–	–	0.3	0.3	0.1	–	–	–	–	–
ZnO	0.2	0.5	–	–	–	0.1	–	0.1	0.04	0.01	–
Cr ₂ O ₃	–	–	–	–	0.01	–	–	–	–	–	–
PtO ₂	–	–	–	–	–	–	–	–	–	0.01	–
P ₂ O ₅	–	–	–	–	–	–	–	–	–	19.4	0.01
NiO	–	–	–	–	–	–	–	–	–	0.2	–

*¹Almaty Region, *²Kyzylorda Region, *³Turkestan Region.

Figure 1 shows the XRD pattern of SiO₂ obtained from RH after pretreatment with HCl and calcination at 600 °C for 4 h.

The presented corresponding broad peak at 2θ equal to 22° in the XRD pattern was identified as the amorphous structure and depended on the calcination temperature and the impurity level in the RH [21,22]. The nonappearance of the sharp peak of any well-ordered crystalline peaks confirms the amorphous nature of the sample [23]. The result is in agreement with other studies [24,25].

The functional group changes of the samples were investigated by analyzing FTIR spectra (Figures 2 and 3). The absorption peaks located at 1055 cm⁻¹ and 1058 cm⁻¹ are related to C–OH and siloxane (Si–O–Si) stretching bands that were found in the FTIR spectra of untreated RH samples. The peak at 2921 cm⁻¹ indicates the presence of the symmetric and asymmetric stretching vibrations of the aliphatic C–H bonds in –CH₃ and CH₂ groups in the structures of cellulose, hemicellulose, and lignin, respectively. The FTIR spectra of extracted silica [26,27] after the preliminary acid washing in Figure 3 showed the same absorption peak at 1055 cm⁻¹ as the raw RH, since the pretreatment method did not significantly change the surface properties of silica.

Figures 4 and 5 present the TG curves obtained from the thermal decomposition of treated and untreated RH samples from 50 °C to 850 °C. The obtained curves depict that RH undergoes decomposition in three different stages. The first stage is weight loss associated with moisture and primary volatile substances' evaporation that occurs within the range of 50-150 °C [25]. The second stage shows a relatively rapid and considerable loss in weight at temperatures ranging from 210 to 360 °C. DTG curves show a peak in the range of 330-360 °C associated with the thermal decomposition of hemicellulose and glycoside bonds of cellulose [28,29]. The endothermic DTA peak at 345 °C is observed when the cellulose powders are heated under argon

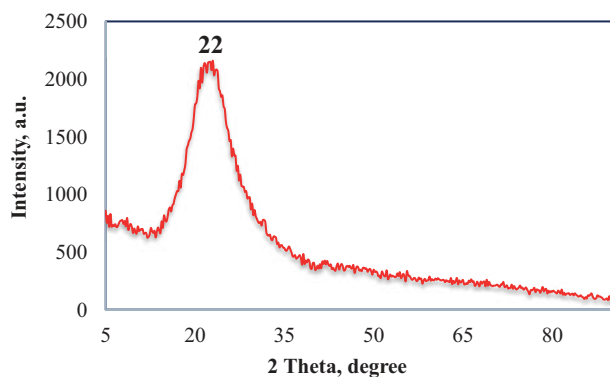


Figure 1. The X-ray diffraction pattern of SiO₂ extracted by pretreatment acid leaching.

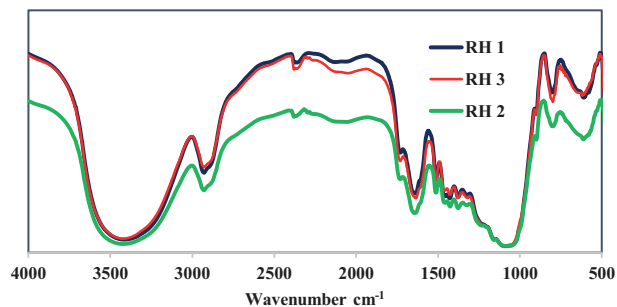


Figure 2. FTIR spectra for RHs (RH 1 – Almaty rice husk, RH 2 – Kyzylorda rice husk, RH 3 – Turkestan rice husk).

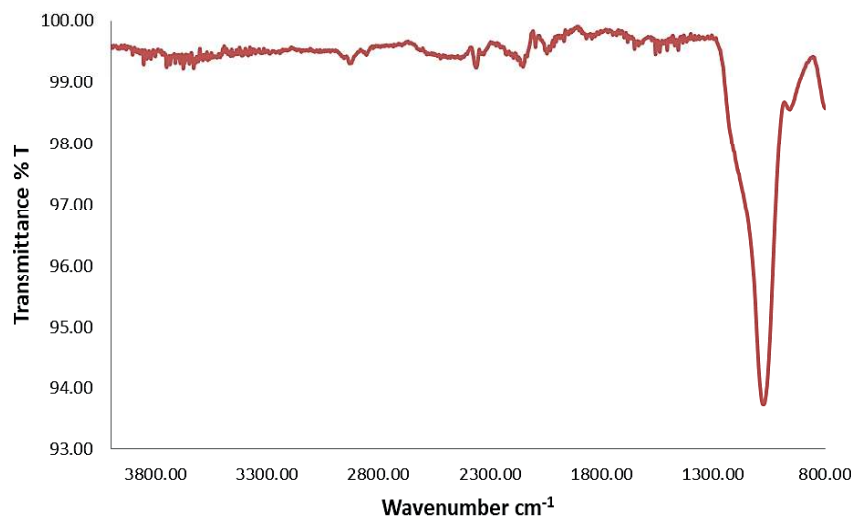


Figure 3. FTIR spectra for silica from RH.

atmosphere, and this is due to its carbonization without combustion [30]. The third stage of decomposition shows a weight loss of about 30 wt.% in a total weight loss that starts at 380 °C. At this stage, the thermal decomposition of lignin compounds is indicated in all samples from 380 to 600 °C, for RH_2 terminating at about 800 °C [30]. The thermal profiles of RH_1 and RH_3 are similar, and the weight of the samples is stabilized at temperatures of 560 °C and above. Differences in the thermal profile of RH_2 are explained by differences in rice varieties and climatic zone of growth. Stabilization of mass loss for samples RH_1 and RH_3 at 560 °C indicates a complete burnout of volatile components and suggests a temperature of about 600 °C in the air atmosphere for calcination of the samples. The residual masses of samples are 15.3 wt.% (RH_2), 17.0 wt.% (RH_1), and 19.1 wt.% for RH_3.

TGA curves for RH_1 and RH_HCl_1 are shown in Figures 4 and 5, respectively. The first weight loss in sample RH_HCl_1 occurred near 100 °C, which is associated with evaporation of water. Hemicellulose and cellulose thermal decomposition started at 220 °C and lignin decomposition occurred beyond 400 °C. The result showed less than 3% difference in total weight loss between acid-treated RH and untreated RH. This reveals the influence of acid treatment on the thermal stability of RH.

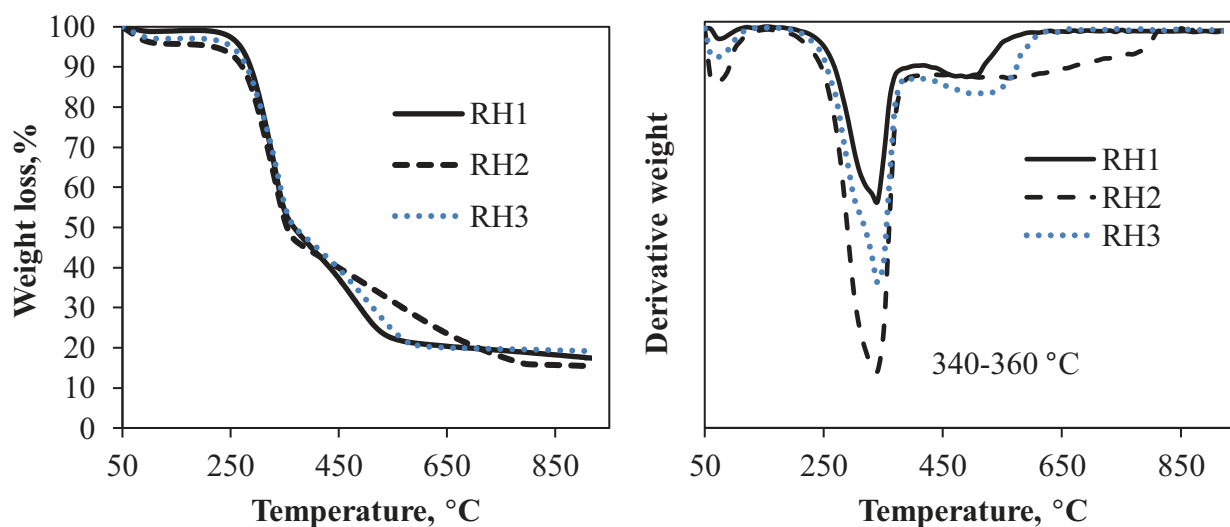


Figure 4. TGA curves for RH_1, RH_2, and RH_3 and corresponding DTG curves for RH_1, RH_2, and RH_3.

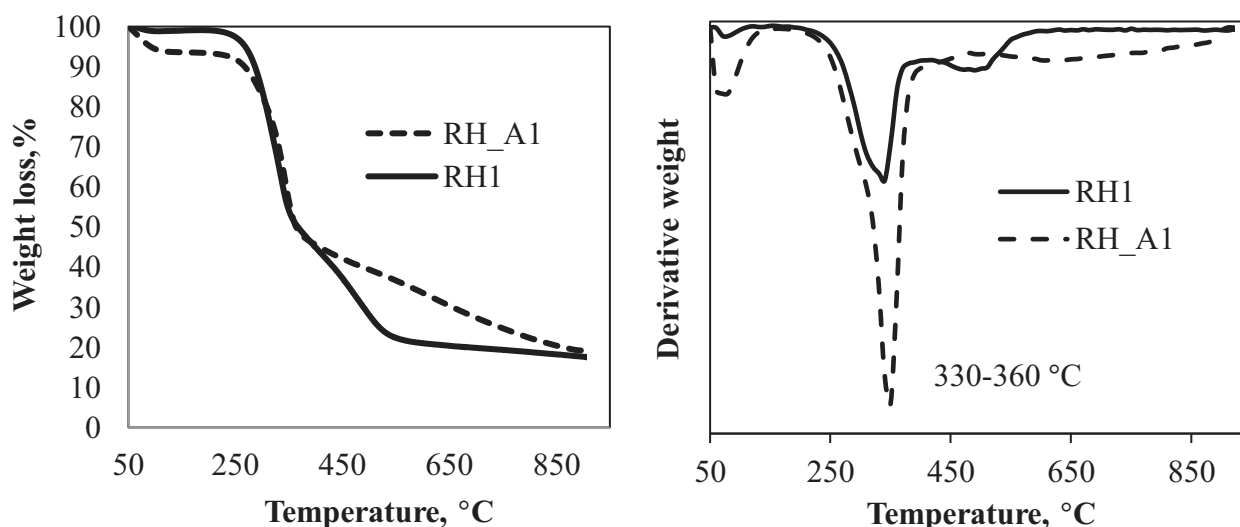


Figure 5. TGA curves for comparison of TGA of RH_1 and RH_HCl.1 and comparative DTG graph of RH_1 and RH_HCl.1 samples.

Figure 6 illustrates the scanning electron micrographs of the surfaces of untreated RH and treated RH. The results showed that the untreated RH had a rough and undulating surface texture (Figure 6a). After treatment in HCl solutions, a significant destruction in the morphology of RH and the almost complete removal of asperities from its surface were observed (Figure 6b). The morphology of the silica prepared from pretreated RH is shown in Figure 6c. The SEM image exhibits full transformation of pretreated RH into amorphous nanomaterial with a particle size of about 50 nm.

The surface area and the pore characteristics of the silica samples were determined by the Brunauer–Emmett–Teller (BET) and density functional theory (DFT) methods. The specific surface area of the silica samples was observed to be 120, 150, and 980 $\text{m}^2 \text{g}^{-1}$, respectively. Compared to the surface area of the

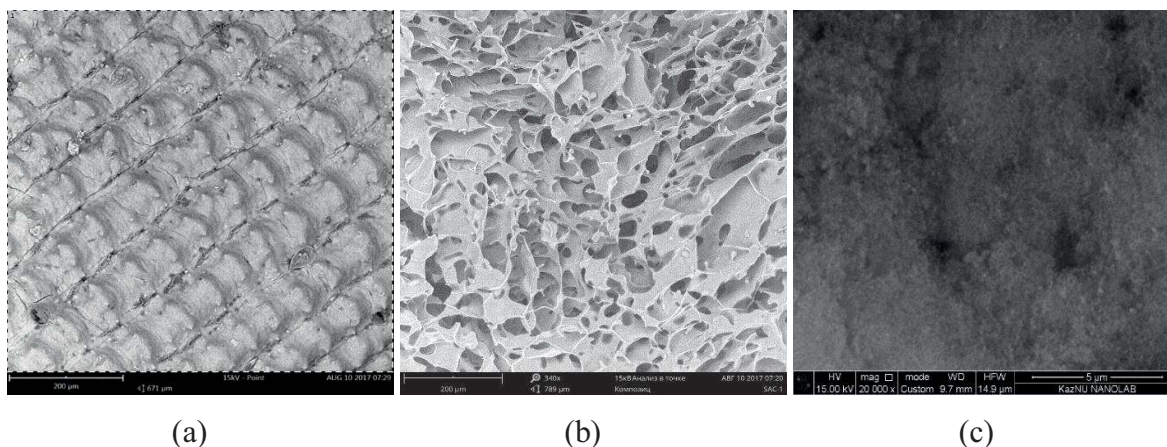


Figure 6. SEM images of untreated RH (a), acid treated RH (b), and SiO₂ (c).

samples derived from RH₁ and RH₂, the surface area of the SiO₂-HCl₂ was indicated to be the largest specific surface area (980 m² g⁻¹) due to the smallest pore size of the extracted SiO₂ sample. The pore volume of the SiO₂-HCl₁, SiO₂-HCl₂, and SiO₂-HCl₃ silica samples was increased from 0.5 to 1.2 cm³ g⁻¹ and the average pore diameter decreased from 26.4 nm to 0.9 nm. The specific surface areas, pore diameters, and pore volumes of the three silica samples are summarized in Table 2.

Table 2. The surface area and pore characteristics of the silica samples.

Sample	BET surface area, m ² g ⁻¹	Pore characteristics (DFT method)	
		Pore volume, cm ³ g ⁻¹	Pore size, nm
SiO ₂ -HCl ₁	120	0.5	26.4
SiO ₂ -HCl ₂	980	1.2	0.9
SiO ₂ -HCl ₃	150	0.8	18.4

Figures 7 and 8 demonstrate the nitrogen adsorption-desorption isotherms and pore size distribution of the silica samples. The isotherms of the SiO₂-HCl₁ and SiO₂-HCl₃ samples are closer to type III with a weak hysteresis loop and curvature in low pressures indicating mesoporous-macroporous materials. The isotherm of the SiO₂-HCl₂ sample is closer to type II with a more intense hysteresis loop and curvature in low pressures indicating a mesoporous-macroporous material with some microporosity. These conclusions are confirmed by the pore volume and average pore size (Table 2) and the pore size distribution of samples (Figure 8). Thus, it seems that the samples obtained from RH₂ demonstrate significant differences in the structure of pores compared to samples obtained from RH₁ and RH₃.

2.1. Comparison of results of silica samples extracted from RH by hydrochloric acid leaching with other studies

Comparison of the previous investigations in Table 3 indicates that the chemical procedure and the combustion process could be effectively combined with the utilization of RH or RHA by converting them into silica nanoparticles. Some of them used different temperature ranges in thermal treatment (500, 600, 700, 800, 900, and 1000 °C) or mineral acids such sulfuric, acetic, nitric, and hydrochloric acids in various concentrations to identify the best conditions for extraction among them.

Table 3. Comparison of the extracted silica with the previously reported silica obtained from RH by hydrochloric acid leaching.

Rice variety	Conditions of extraction	Surface area, average particle size	Purity index (XRF/EDX analysis)	Reference
RH from Bernas rice mill, Selangor, Malaysia	Preacid treatment: C (HCl) = 0.5 M τ (leaching) = 30 min Thermal treatment: muffle furnace, t = 600 °, τ = 2 h	218 m ² g ⁻¹ , 50 nm	99.6%	[14]
RH from Malaysia	Preacid treatment: C (HCl) = 1 M τ (leaching) = 2 h t = 70 ° Thermal treatment: electric furnace m (RH) = 5 g 1) t = 500 °, τ = 1 h 2) t = 800 °, τ = 2 h	–	97.6%	[31]
RH from Kastamonu Province, Turkey	Preacid treatment: m (RH) = 5; 10 g C (HCl) = 2 M V (HCl) = 100 mL Thermal treatment: electric muffle furnace t = 700 °, τ = 2 h	–	98.5%	[32]
RH from Dong Nai Province, Vietnam	Preacid treatment: m (RHA) = 5 g C (HCl) = 1 N V (HCl) = 30 mL τ (leaching) = 2 h t = 80 ° Thermal treatment: programmable furnace t = 700 °, τ = 2 h	45.5 nm	40.0%	[33]
RH from a poultry farm in the city of Balikesir, Turkey	Preacid treatment: m (RH) = 20 g C (HCl) = 0.1 M V (HCl) = 300 mL τ (leaching) = 5 h t = 85 ° Thermal treatment: fixed bed reactor t = 500 °, v (N ₂) = 150 cm ³ min ⁻¹	247.6 m ² g ⁻¹ , 2.2 nm	98.0%	[34]
RH from Heilongjiang Province, China	Preacid treatment: m (RH) = 30 g V (HCl) = 500 mL τ (leaching) = 1 h t = 20-25 ° Thermal treatment: muffle furnace t = 600 °C; 700 °C; 800 °C; 900 °C τ = 30 min	207.8 m ² g ⁻¹ , 0.8 nm	98.4%	[35]

Table 3. Continued.

Rice variety	Conditions of extraction	Surface area, average particle size	Purity index (XRF/EDX analysis)	Reference
RH from Ilam Province rice farms, Iran	Preacid treatment: C (HCl) = 1 N Thermal treatment: electric furnace t = 600 °, τ = 6 h	272.9 m ² g ⁻¹ , 200 ± 20 nm	95.6%	[36]
RH from Perak area, Malaysia	Preacid treatment: m (RH) = 10 g V (HCl) = 150 mL τ (leaching) = 2 h T = 373 K Thermal treatment: muffle furnace T = 973 K, τ = 2 h v (ramp) = 283 K min ⁻¹	234.6 m ² g ⁻¹ , 5.3 nm	99.8%	[37]
RH from a rice mill in the north of Iran	Preacid treatment: C (HCl) = 0.01; 0.1; 1 M τ (leaching) = 90 min Thermal treatment: programmable furnace t = 500 °C; 700 °C; 1000 °C v (ramp) = 2 °C; 5 °C; 10 °C min ⁻¹	623 m ² g ⁻¹ , 6 nm	98.8%	[38]
Regul	Preacid treatment: C (HCl) = 2 M Thermal treatment: muffle furnace	120 m ² g ⁻¹ , 26.4 nm	98.2%	Current work
Lider	V (HCl) = 500 mL τ (leaching) = 2 h t = 90 °	980 m ² g ⁻¹ , 0.9 nm	99.1%	
42	m (RH) = 50 g t = 600 °, τ = 4 h	150 m ² g ⁻¹ , 18.4 nm	99.7%	

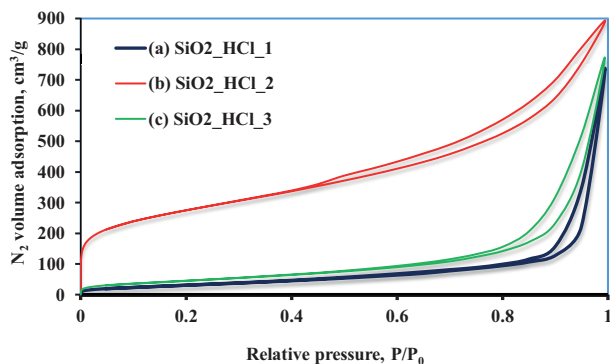
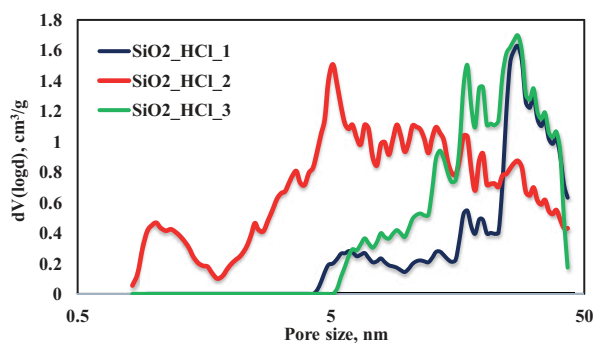


Figure 7. Low-temperature nitrogen adsorption-desorption isotherms of silica samples.

Figure 8. Pore size distribution of SiO₂-HCl.1, SiO₂-HCl.2, and SiO₂-HCl.3.

Bakar et al. [14] researched the optimal conditions for obtaining high purity amorphous silica from RH. The goal of this approach was achieved using pretreatment with hydrochloric acid and combustion at 600 °C for 2 h. The experimental results indicated that a lower amount of silica was produced especially at temperatures higher than 600 °C. As shown in Table 3, the highest purity of produced silica was described in approaches

from Malaysia [14,31,37]. It can be assumed that due to the low level of impurities in the composition of the used RH, samples were extracted with purities of 99.6% [14], 97.6% [31], and 99.8% [37]. As is known, the level of impurities in the composition of the RH depends on the geographical location and used fertilizer. The Malaysian government encourages the use of organic fertilizers, which is important for the recycling of agricultural waste and for improving soil quality. The highest results of surface area (623 and 980 m² g⁻¹) of silica were demonstrated in a paper from Iran [38] and in the current research work. Compared with our extraction procedure, Rafiee et al. [38] treated RH with various chemicals in varied conditions, which gives the opportunity to produce highly purified nanosilica. Extracted nanosilica can be applied as a support for catalysts due to containing a large number of acidic sites.

Researchers have used various chemical and thermal treatment methods, but it has been reported that acid leaching treatment and controlled combustion of RH produced the samples with the highest silica content and surface area. Most studies investigated the production of silica directly from RH, not from its ash. Among the described studies, Tuan et al. [33] used RHA as a source of silica, which was burned in an open environment.

2.2. Conclusions

Highly purified amorphous silica samples (98%–99%) with a surface area in the range of 120 to 980 m² g⁻¹ were successfully synthesized using RH from different regions of Kazakhstan. Leaching under HCl pretreatment and controlled calcination at 600 °C for 4 h revealed a decrease in the metal oxide content in the RH composition. The purity of the synthesized silica was proved by XRF analysis. The current approach was compared with other studies that also aimed to produce silica samples from RH. The comparison was carried out to show the importance of parameters such as duration and temperature of thermal treatment, rice variety, geographical location, and concentration of used acid.

This research work shows the possibility of using the described simple chemical method in the production of large amounts of silica with lower costs in rice-producing countries, which also solves the problem of the effect of open air RH burning on the environment.

3. Experimental

3.1. Raw materials and chemicals

Three different rice varieties were chosen for this research work: Regul, Lider, and 42. The RHs were collected from rice farms in the Almaty, Kyzylorda, and Turkestan regions of Kazakhstan. All obtained RHs were previously treated with deionized water and dried in a bench oven (Carbolite, PF 300, Keison, UK) at 105 °C for 8 h. Hydrochloric acid (37%, Sigma Aldrich, Germany) and sodium hydroxide (98%, Sigma Aldrich, Sweden), which were purchased from Sigma Aldrich, were used in extraction procedures without further purification.

3.2. Sample characterization and analysis

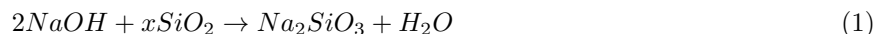
The inorganic chemical compositions of RH ash and extracted silica were analyzed using an Axios mAX X-ray fluorescence spectrometer (PANalytical, Inc., USA). The phase composition and microstructure were observed by SmartLab X-ray diffractometer (Rigaku Corporation, USA) with Cu K α radiation source ($\lambda = 1.540056 \text{ \AA}$) at a scan rate of 0.02° s⁻¹ in the 2 θ range of 10–90°. A Nicolet 6700 FTIR spectrometer (Thermo Scientific, USA) was used to collect the FTIR spectra. Thermal analysis was carried out with a Simultaneous Thermal Analyzer (STA) 6000 (PerkinElmer, Inc., USA) with a heating rate of 10 °C min⁻¹ in a temperature range

from 50 to 950 °C under nitrogen atmosphere. The surface structure and morphology of the obtained RH and RH silica were represented using a scanning electron microscope (Quanta 200i 3D, FEI Company, USA). The surface area and pore size results were obtained using the Brunauer–Emmett–Teller method (Autosorb-1, Quantachrome, UK) from nitrogen adsorption and desorption isotherms. The pore volume was taken at five points of P/P_0 .

3.3. Extraction procedure

About 50 g of each variety of RH was treated with the 500 mL of 2 M hydrochloric acid solution and dried at 90 °C for 2 h. All the prepared samples were continuously washed with deionized water until pH 7 and separated from the solution via filtration. RH was then dried at 105 °C overnight.

The calcination was performed in a muffle furnace (Carbolite, CWF 1200, Keison, UK) at 600 °C for 4 h. Based on the thermogravimetric analysis data, it was identified that the optimum calcination temperature to form reactive ash is 600 °C. All organic compounds in the RH were burned completely and eventually the ash of white RH was formed. After that, collected RHA was mixed with 100 mL of 2 M NaOH at 90 °C under continuous vigorous stirring for 2 h to convert the solid silica into water-soluble sodium silicate. The sodium silicate solution was filtered via cellulose membrane filter (Millipore, 0.45 μm) to eliminate insoluble residues and carbonizates. Then sodium silicate was transformed into insoluble silicic acid by titration with 2 M HCl under continuous stirring. The consequences of the procedure can be represented by the following chemical reactions:



The reaction of hydrochloric acid with sodium silicate promotes silanol group (R_3Si-OH) formation and condensation, which leads to the formation of an extended 3D Si–O–Si network. The final product was washed with hot deionized water to remove NaCl residue. Then it was dried at 105 °C for 4 h.

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