

Effect of Experimental Variables on the Extraction of Silica from the Rice Husk Ash

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Summary: Silica was extracted from the locally obtained rice husk ash (RHA) by heating its dispersion in sodium hydroxide solution for various periods of time. Following this treatment, silica content of the dispersed RHA particles leached out into the liquid phase in the form of sodium silicate. On separation from the solid, the alkaline solution of sodium silicate was made acidified with sulfuric acid, which transformed the dissolved silicate into precipitated gelatinous silica. The yield of silica was dependent on the strength of the alkaline solution, aging time, etc. Optimum conditions were established under which maximum extraction could be made from the rice husk ash. The as-extracted silica maintained its gelatinous nature after washing with water; however, on washing with ethanol, it transformed into powder of discrete particles. On calcination at 750 °C, the water washed silica converted into powder form, comprised of ellipsoids, whereas the ethanol washed silica particles sintered together. Selected samples of the extracted materials were then subjected to characterization by various physical methods, such as SEM, EDX, XRD, and FT-IR.

Key words: Rice husk, Rice husk ash, Silica, Silicate

Introduction

Rice husk is a hard material and is composed of lignin, cellulose, traces metals, and abundant of amorphous silica [1, 2]. Since silica is used in many technological applications; therefore, rice husk is considered a cheap natural source of silica [1]. For this purpose, rice husk is converted into ash by the controlled burning process and the ash is then employed as the starting material for the extraction of silica. It was reported earlier that ash of the rice husk contains over 80 % of the amorphous silica; however, the exact amount of the extracted silica depends on the regional climates, history of the ash formation from the rice husk [3], and the extraction methods. As such, researchers have been working on establishing experimental strategies for the economical recovery of larger amount of silica from the rice husk ash. For example, Kalapathy *et al.* [4] worked on the extraction of silica from the rice husk ash (RHA). The silica was extracted in alkaline media as silicate which was precipitated in the form of silica gel by the acid addition. They heated silica gel at 80 °C for twelve hours and obtained amorphous silica xerogels. In another paper [5] the same group of researchers employed a slightly different method than used before Kalapathy *et al.* [4] for the extraction of silica from the RHA. In this method they acidified solutions of the RHA-extracted silicate with different acids. It was found that the elemental composition of the gelatinous precipitated silica was dependent upon the composition of the acid used and the subsequent washing process. Della *et al.* [1] made attempts to extract silica from the RHA. Before the

extraction process, the authors burnt out the RHA-derived carbonaceous material at various temperatures for different periods of time. It was noted that this treatment significantly affected the content of silica in the ash samples. They claimed the extraction of 95% of the silica from the RHA sample, produced at 700 °C. Yalcin *et al.* [6] worked on the extraction of relatively pure silica from the rice husk. The authors washed rice husk with acidic as well as alkaline solutions and then incinerated at 600 °C in the static air atmosphere for converting them into ash. The ash was then employed for the extraction of the silica. The silica obtained through this method was amorphous in nature and had a purity > 99%. Ahmed *et al.* [7] prepared silica compacts from RHA and worked on its possible applications for the development of material, used in the tundish lining. The authors evaluated the effect of firing temperature, and other relevant parameters on the properties of their product. Huang *et al.* [8] extracted silica from the rice husk in a fluidized bed. For this purpose they burnt the husk in fluidized bed under controlled conditions. The ash produced was subjected to purification and then used the purified ash for the extraction of silica. The quality of the silica obtained through this method was better in properties than that obtained by precipitation methods. Paya *et al.* [9] treated rice husk ash with glycerol and obtained glyceosilicate solution. This solution was then titrated against aqueous glycerol solution of Ba(OH)₂. The final product of their study was white powder which turned out to amorphous silica. Muchidzuki *et al.* [10]

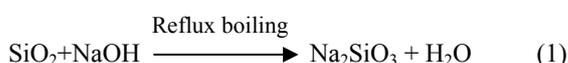
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studied the morphological properties of silica derived from the rice husk in hydrothermal and steam explosion processes. XRF and XRD techniques were employed for the analysis of their products. The authors reported that hot water treatment dissolved a small quantity of silica, affecting the particle morphology but did not affect the amorphous nature of silica obtained from the rice husk. Witoon *et al.* [11] prepared bimodal porous silica from the rice husk ash. Porosity in the finished product was found to depend upon the precipitation pH. Following the above mentioned work, It may be noted that the extraction process and the yield of the extracted silica dependent upon various factors, including variations in the region, where rice was grown. As such, it was of interest to carry out a systematic study of the extraction of silica from the rice husk ash, prepared from the husk of the locally grown rice crop.

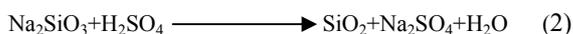
Results and discussion

Silica Extraction Process

For this purpose, known volumes of aqueous dispersions, containing 30-250 g/L of the RHA and 0.2-1.2 mol/L sodium hydroxide, were heated to boiling under reflux conditions for various periods of time (20-120 min). As a result of this treatment, silica content of the RHA leached out to the aqueous phase of the dispersion in the form of soluble sodium silicate according to the following reaction [12]:



The dispersion was filtered and the liquid was recovered. The latter was then acidified with concentrated sulfuric acid, which precipitated the dissolved silicate in the form of white gelatinous solid (SiO_2) according to the following reaction [12]:



The percent yield of the extracted silica from the RHA was estimated according to the following formula:

$$\% \text{ yield of silica} = \frac{(W_1 \times 100)}{W_2} \quad (3)$$

where,

W_1 = Weight (g) of the extracted silica and

W_2 = Weight (g) of the rice husk ash.

It was noted from the preliminary experiments that the amount of the precipitated silica was dependent upon the applied processing

parameters, such as concentration of sodium hydroxide, extraction time, solid/ solution ratio, etc. As such, these parameters were systematically varied in order to explore the optimum conditions for maximum recovery of SiO_2 from the RHA, employed in this study.

Effect of NaOH Concentration on the Extraction of Silica

Results in the Fig. 1 showed that the amount of the extracted silica was negligible at 0.4 mol/L concentration of sodium hydroxide; however, the extracted amount of silica became significant when the concentration of sodium hydroxide was increased to 0.8 mol/L. Similarly, on increasing concentration of sodium hydroxide to 1.0 mol/L, the extracted amount of silica increased by about 20 %. However, by using concentration of sodium hydroxide > 1.0 mol/L, silica recovery could not be improved under the described experimental conditions. From these findings, we explored the fact that for the RHA, employed in the present investigation, the range of sodium hydroxide concentration should preferably be 0.8-1.0 mol/L for extraction of considerable amount of silica. It is added that Kalapathy *et al.* [4] extracted 91 wt% silica from the RHA, obtained from other sources than the type employed in the study, by using 1.0 mol/L sodium hydroxide solution. This difference in the amount of the extracted silica suggested the fact that the regional variation had obvious effect on the silica content of the RHA and should be taken into consideration before using RHA for the extraction of silica on the commercial bases.

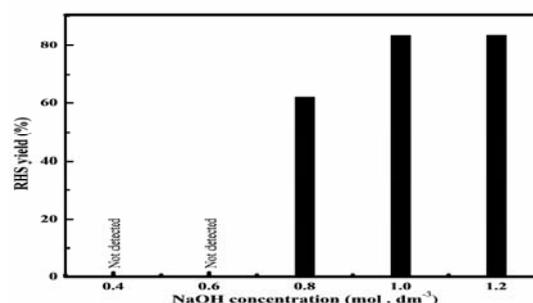


Fig. 1: Percent yield of the rice husk silica (RHS), extracted from the rice husk ash (RHA) as a function of the NaOH concentration in the reactant mixture. Volume of the reactant mixture, 60 ml; Concentration of RHA, 166.66 g/L; Extraction time, 90 min.

Effect of time on the Extraction of Silica

Following the results depicted in Fig. 1, it was of interest to study the effect of the extraction time on the extraction process of silica from the RHA.

For this purpose silica extraction experiments were performed in which the extraction time was varied from 30 to 120 min, whereas the concentration of sodium hydroxide (1 mol/L) and the amount of the dispersed RHA (166.66 g/L) were kept constant in all the reactant mixtures. The data obtained in these experiments is given in Fig. 2, which showed that the percent yield of the extracted silica increased with the increase in the extraction time up to 90 min; however, beyond this time the silica yield became almost constant. This observation clearly showed that under the applied experimental conditions, the extraction process of silica approached its limiting value in around 90 min.

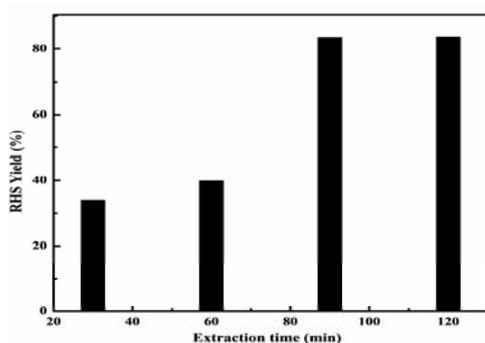


Fig. 2: Percent yield of the rice husk silica (RHS), extracted from the rice husk ash (RHA) as a function of the extraction time. Volume of the reactant mixture, 60 ml; Concentration of NaOH, 1 mol/L; Concentration of RHA, 166.66 g/L.

Effect of the Ratio (Moles of NaOH/Grams of RHA) on the Extraction of Silica

From the results presented in Fig. 1 and 2, it was noted that extraction of silica was at its maximum, when the concentration of sodium hydroxide was 1.0 mol/L, concentration of RHA was 166.66 g/L and aging time was 90 minutes. Following these results, we made attempts to explore the effect of the ratio (Moles NaOH/Grams RHA) on the extent of silica extraction. In this regards, experiments were performed in which this ratio was varied in the range of 0.03 to 0.004, while keeping the total number of moles of sodium hydroxide constant. Results are demonstrated in Fig. 3. Inspection of this figure revealed that maximum extraction of silica took place when the mentioned ratio was in the range of 0.01-0.06. We believe that these results would prove to be useful for the industry people involved in the extraction of silica from the RHA at the commercial level.

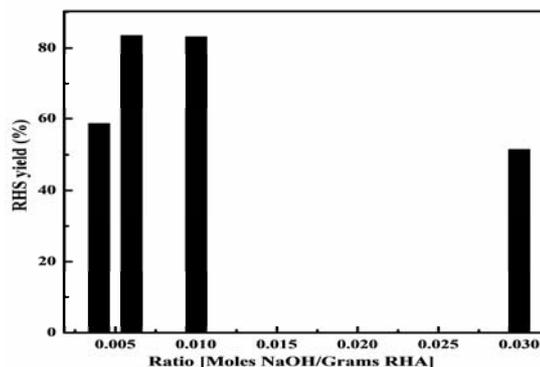


Fig. 3: Percent yield of the rice husk silica (RHS), extracted from the rice husk ash (RHA) as a function of the ratio (Moles NaOH/Grams RHA) in the reactant mixture. Volume of the reactant mixture, 60 ml; Extraction time, 90 min.

Characterization of the Extracted Silica

As-extracted Rice Husk Silica (RHS)

The RHS extracted from the RHA was either dried as such (RHS-1) or stirred in ethanol for 2 h before filtration and drying (RHS-2). It was noted that RHS-1 and RHS-2 dried in the form of solid lumps and fine powder, respectively. This observation indicated that ethanol facilitated the disruption of the gel network present in the dry RHS-1. SEM analysis showed that RHS-1 was composed of micron size aggregated crystals (Fig. 4A), whereas RHS-2 contained nanosize particles (Fig. 4B). Both these samples of the RHS were characterized by XRD, EDX and IR in order to see if ethanol treatment had any effect on the properties of the extracted RHS. The XRD patterns in Fig. 5A and Fig. 6A showed that RHS-1 contained crystalline phases, whereas RHS-2 was amorphous in nature. It was noted that the peaks in the XRD pattern for RHS-1 (Fig. 5A) were due to Na_2SO_4 , most probably inherited from the chemical treatment, involved in the extraction processes and entangled there in the precipitated gelatinous network. For instance, in the first stage of the extraction process, the RHA was treated with concentrated solution of sodium hydroxide, which extracted silica in the form of soluble silicate. After isolation from the solid phase, the liquid containing silicate and sodium ions was treated with sulfuric acid solution for the precipitation of silicate into insoluble silica. The latter thus acquired sodium sulfate from its mother liquor and existed in the dried solid in the loosely bound state. When treated with ethanol, the gelatinous network broke down, which let the associated sodium sulfate washed away with ethanol

and leaving behind the purified amorphous RHS-2. It is worth mentioning that amorphous silica was also extracted by other researchers [2, 5, 6, 9, 13] from the RHA by using other methods. However, we are of the opinion that our method could be considered a simple, time saving and economical for the recovery of amorphous silica from the as-precipitated gelatinous solids.

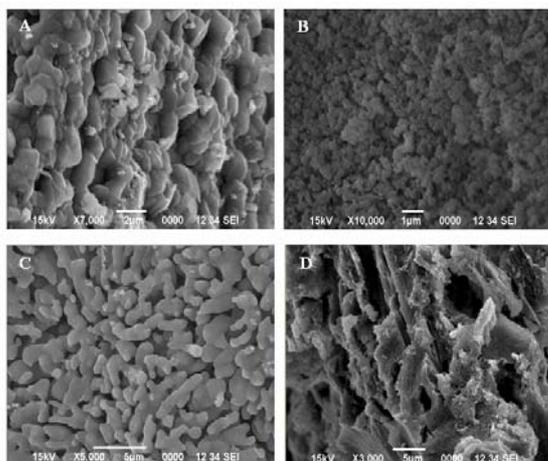


Fig. 4: Scanning Electron Micrographs (SEM) of the rice husk silica (RHS) extracted from the rice husk ash (RHA). (A), as-extracted rice husk silica (RHS-1); (B), RHS-1 agitated in ethanol for 1 h (RHS-2); (C) the solids in A heated at 750°C for 1 h; (D), the solids in B heated at 750 °C for 1 h.

The above mentioned findings were supported by the EDX analysis of RHS-1 (Fig. 7A) and RHS-2 (Fig. 7B) which demonstrated that RHS-1 contained various elements, i.e. K, O, Na, Al, Si and S, while most of these elements could not be detected in the EDX of the purified RHS-2. These results clearly revealed that ethanol treatment effectively removed the undesirable elements from the as-precipitated silica solid.

In addition, differences in the properties of RHS-1 and RHS-2 were also noted from their IR spectra. For example, the IR spectrum of the RHS-1 (Fig. 8A) was composed of prominent absorption bands, at 3000-3700 cm^{-1} , 21000 cm^{-1} , 1636 cm^{-1} , 1096 cm^{-1} , 801 cm^{-1} , 587, cm^{-1} , and 469 cm^{-1} , corresponding to the stretching vibrations of Si-OH / H-OH, Si-H stretching vibrations, H-O-H bending vibrations, Si-O-Si asymmetric stretching vibrations, Si-O-Si symmetric stretching, Al-O stretching vibrations, Si-O-Si symmetric stretching vibrations, respectively. In contrast, with the exception of the other bands, the band corresponding to Si-H shifted to 1825 cm^{-1} in the IR spectrum of RHS-2 (Fig. 8B).

Moreover, additional bands appeared at 1215 cm^{-1} and 929 cm^{-1} , which were attributed to the asymmetric vibrations of the Si-O, and Si-O-H groups, respectively [14].

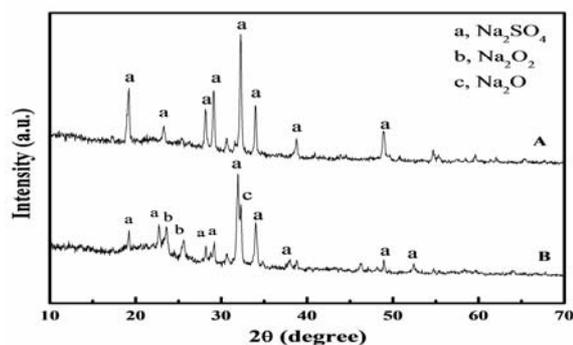


Fig. 5: X-ray diffraction (XRD) patterns of the RHS-1, (A) before and (B) after calcination at 750 °C for 1h.

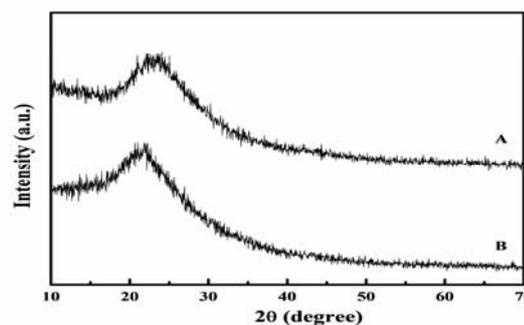


Fig. 6: X-ray diffraction (XRD) patterns of the RHS-2, (A) before and (B) after calcination at 750 °C for 1h.

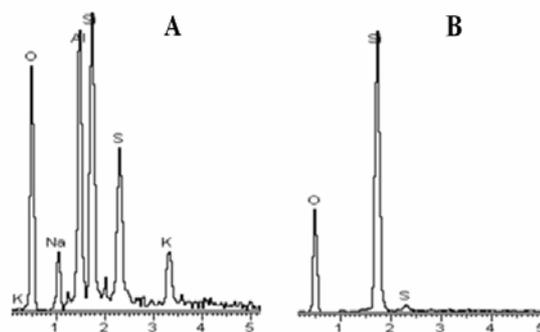


Fig. 7: Energy dispersive x-ray (EDX) analysis spectrum of the (A) as-extracted rice husk silica (RHS-1), and (B) rice husk silica (RHS-2), agitated in ethanol.

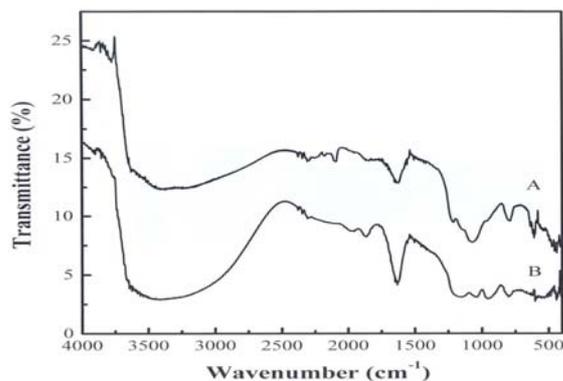


Fig. 8: Fourier Transform Infrared (FTIR) spectrum of, (A) as-extracted rice husk silica (RHS-1), and (B) rice husk silica (RHS-2) agitated in ethanol

Heat Treated RHS

Both RHS-1 and RHS-2 were heated at 750 °C for 1h in air atmosphere. SEM images of the heat-treated solids are displayed in Fig. 4C & D. As can be seen from this figure, a sort of melting of the matrix took place in RHS-1 and resulted in solids, comprised of a microstructure of uniform morphology. In contrast, the nanosize particles of RHS-2 got sintered together (SEM, Fig. 4D), possibly due to their fragile nature, and produced sintered lumps of solid. These findings suggested the fact that the presence of inherited impurities in the RHA-1 had significant effect on the microstructure of the heated solids. To our knowledge, such behavior of the RHA has never been reported before.

XRD analysis (Fig. 5B & 6B) showed that the solid shown in Fig. 4C was crystalline and composed of Na_2SO_4 , Na_2O_2 , and Na_2O , whereas the one in Fig. 4D was amorphous. These results demonstrated that the compositional variations in both the solids significantly affected the properties of the heat-treated solids.

Experimental

Materials

Husk of rice was provided by the rice processing mills, located in the vicinity of Peshawar City, Khyber Pakhtunkhwa, Pakistan. Other required chemicals, such as Sulfuric acid, sodium hydroxide, ethanol, etc were purchased from Merck. Pyrex glass vessels were used for solution storage and as reaction vessels. Doubly distilled water was used throughout for making reactant solutions.

Preparation of Rice Husk Ash (RHA)

Rice husk ash was produced by burning of the rice husk at ~ 500 °C in air atmosphere in a thermostated furnace for about 4 h. After cooling to room temperature, the obtained ash was washed with water, dried at 60 °C and then stored in a dessiccator.

Extraction of Silica from the RHA

In this case, known amounts (2-14 g) of the RHA were dispersed in 60 ml of 0.2 - 1.2 mol/L NaOH solutions and allowed it to boil for 30-120 min with constant stirring. The heating vessel was equipped with reflux condenser for maintaining volume of the dispersion constant during the reaction period. After this treatment, dispersions were cool down to room temperature, filtered through Whatman filter paper for separating solid from the liquid. The volume of filtrate was made to 100 cm^3 with water. This solution was transferred to a 250 ml titration flask and then titrated against 2 mol/L H_2SO_4 at room temperature with constant stirring till the appearance of transparent gelatinous solid in the titrant. The gelatinous solid was allowed to settle down at the bottom of the reaction vessel. The supernatant was decanted and the gel was either kept for drying or redispersed in 100 ml of ethanol. In the latter case, the dispersion was kept stirred for about 2 h which resulted in the uniform dispersion of white colloidal particles. The particles were separated from the liquid by filtration, washed with copious amount of water, and then dried at 60 °C for 24 h in oven. It was noted that in the absence of ethanol treatment, the dried solids were in the form of hard flakes which were made into fine powder (designated as RHS-1) by grinding process, whereas the ethanol washed product was in the form of white powder (designated as RHS-2). Parts of these powders were heated at 750 °C for 1 h in a tube furnace and then cool down to room temperature inside the furnace after turning it off. Both the as-prepared and heat-treated solids were characterized with SEM, XRD, and IR.

Characterization

Scanning Electron Microscopy (SEM)

The microstructures of the desired solids were imaged with scanning electron microscope (SEM: JSM-6490, JEOL). Aluminum stubs were employed as sample holders. Each sample was coated with gold in a sputtering apparatus (JFC-1600, JEOL) before examination in the SEM at the accelerating

voltage of 15 keV. Working distance of the test sample was kept at 10 mm. Similarly, metal content of the same samples were qualitatively analyzed with energy-dispersive x-ray analyzer (Oxford, Inca-200).

X-ray Diffractometry (XRD)

Desired samples were analyzed with x-ray diffractometer (XRD, JEOL JDX-3532) for the identification of the crystalline phases. The x-ray beam was comprised of CuK α radiations. All the analyses were performed by keeping operational voltage of the machine at 40 kV and current at 20 mA. Similarly, in each case, the test sample was scanned from the 2 θ 5 to 80°, while keeping the scan speed of the machine at 0.1° sec⁻¹ and step angle at 0.05°.

FT-Infrared Spectrometry (FTIR)

All the powder samples of interest were subjected to infrared spectroscopic analysis. These analyses were performed with the Fourier Transform Infrared Spectrometer (Schimadzu, IR-Prestige-21, and FTIR-8400S) in the range 400-4000 cm⁻¹. Before analysis, an estimated amount of the desired powder was thoroughly mixed with KBr and then transferred to the sample cup of the Diffuse Reflectance Accessory (DRS-800A) for scanning in the mentioned wavenumber range.

Conclusions

It was noted that rice husk ash, obtained from the locally produced rice husk, contained significant amount of silica. The latter was extracted from it in the form of silicate in alkaline solution and then the extracted silicate was converted into gelatinous silica by acidification of its alkaline solution. Undesirable impurities, associated with the precipitated silica, could not be removed by washing with water; however, washing with ethanol resulted in the purified amorphous silica. Calcination of water-washed silica at 700 °C generated a number of

crystalline phases in it, which were originated from the impurities entangled in the silica gel network. In contrast, calcination under the same conditions produced negligible change in the amorphous nature of the ethanol-washed solid, though the originally discrete particles got sintered together in the heat-treatment process.

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