

Spectroscopic Studies of Different Kind of Rice Husk Samples Grown in North of Iran and the Extracted Silica by Using XRD, XRF, IR, AA and NMR Techniques

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Abstract

In this study rice husk ashes (RHAs) were obtained from different rice growing in the North of Iran. X-ray diffraction (XRD) and X-ray fluorescence (XRF) spectrometry and IR were applied for determination of crystallinity and analysis of mineral content and chemical bonding in extracted silica respectively. Our results showed that concentration of silica in Fajr rice husk is higher compared to other kind of rice husk samples. The effect of calcinations at different temperatures 600, 700, 800 and 900 C on extracted silica was also considered. In the process of silica extraction, increasing the temperature led to great porous volume in silica network.

Keywords: Rice husk; rice husk ash; microwave heating; SEM; XRD; XRF; NMR

1. Introduction

Rice Husk (RH) is one of the major agricultural wastes, a fibrous material containing 70 to 85 % organic matters and inorganic reminders containing of silica.[1-3] Dry Rice Husk Ash (RHA) contains more than 90 % SiO₂ which is abundantly available in rice-producing areas. The annual world rice production amount is approximately 400 million tons [1], in which more than 10 percent is husk. The RHA may be obtained from complete uncontrolled burning of rice husk and usually consists of crystalline silica in a mixture of tridymite and cristoballite and occasionally quartz phase if the burning is prolonged [4].

Synthesis of zeolite has been reported in several papers and patents [5,6]. Commercial zeolites are produced from commercial silica sources in the form of sol gels and amorphous fumed silica. However, waste material with high silica content such as RHA and fly ash are potential silica sources for zeolite synthesis.

Different instrumental methods are available for the analysis of major, minor and trace elements in extracted silica from RHA, and the zeolites. Although some techniques can be used for solid materials, but in most of the methods the sample needs to be placed in solution [7]. Since a large number of elements are routinely analyzed, a multi-element technique, capable of determining elements in a solid sample is preferable. One such a technique is X-ray fluorescence (XRF) spectrometry. There are two main approaches to the analytical use of XRF: wavelength dispersive and energy dispersive XRF. The former is in general more sensitive and requires more expensive equipments. However, X-ray diffraction (XRD) and X-ray fluorescence (XRF) spectrometry and IR are applied for determination of crystallinity and analysis of mineral content and chemical bonding in extracted silica respectively.

Previous studies have shown that it was possible to use crystalline ash to produce pure zeolite beta and ZSM-5 [8]. In this study the extracted silica with high purity from RHA are applied for synthesis of zeolite and is not discussed here. Attempt was made to use RHA from the uncontrolled burning of the rice husk in the synthesis of zeolites. The effect of calcinations at different temperatures 600, 700, 800 and 900 C on extracted silica was also considered by XRD and NMR methods. In addition, this study aims at finding the correct combination of the oxides in the RHA obtained from different rice husk.

2. Experimental

Different Rice Husk (RH) samples were collected from the same area in the north of Iran (Mazandaran, Babolsar). At first the rice husk (RH) samples were cleaned, and washed with water and doubly-distilled water thoroughly to remove adhering soil and dust. The washed husk was dried at ca. 105 C for 24 hours, cooled in desiccator, then ground and sieved to the diameter of lower than 0.075 mm, and stored in the desiccator. Rice Husk Ash (RHA) was prepared from the uncontrolled burning of the (RH) with further treatment. Kalapathy et al. [9] method was used for extracting silica from RHA. This method involved dissolving silica with alkali solution at 100 C to form sodium silicate and subsequently forming silica aqua gel by adding hydrochloric acid to lower the pH to 7.0. The silica aqua gel was washed twice and dried at 80 C for 20-24 h to produce silica xerogel. The silica xerogel produced by this method had sodium contaminant and required an additional washing/drying step to reduce the sodium concentration to below 0.1%.

For producing pure and active silica from RHA a thermal treatment at several temperatures 600, 700, 800 and 900 C were used and held at these temperatures for 6 h separately. The aim of this calcinations step is to increase the relative amount of silicon oxide by reduction of carbonaceous materials present in the sample as well as to burn out other

undesirable component. Heating cycles were carried out in an electric oven with a heating rate of 10°C/min. The samples were cooled down inside the oven then silica was extracted adopting the method of Kalapathy and Proctor [9]. At lower pH, or if salts are present, to neutralise the charge on the growing particles, aggregation of particles occurs, with the formation of chains and ultimately, three-dimensional gel networks. Control of this process by adjustment of pH and addition of coagulants is the basis of the technology for formation of amorphous silica [10].

A XRF analyzer (Philips Pw2404 wavelength dispersive spectrometer equipped with an Rh X-ray tube target) was used for analysis of each different RHA samples of different RH. A vacuum was used as the medium of analysis to avoid interaction of X-rays with air particles, each sample milled until 200 mesh, and 1 gram of each sample mixed with 1.5 gr Norrish Spectroflux no. 105 to start the melting process then heated for 6 h at 850°C and it was again heated at 1000°C for another 6 h. Then it was shaped into tablet form with thickness of 40 mm. The obtained disk was now ready for analysis by XRF.

IR spectra of the samples were recorded on a Bruker-Vector 22, IR spectrometer, in the range between 500 and 4000 cm⁻¹. For this purpose approximately 15 mg of the extracted silica and 1 gr of KBr were mixed, milled and ground until a fine smooth powder was obtained.

The effect of calcinations at different temperatures 600, 700, 800 and 900 C on extracted silica was also considered by XRD and NMR. Solid state ²⁹Si NMR spectra of the RHA samples were recorded on a Varian/Chemagnetics Infinity Plus 500 MHz.

3. Results and discussion:

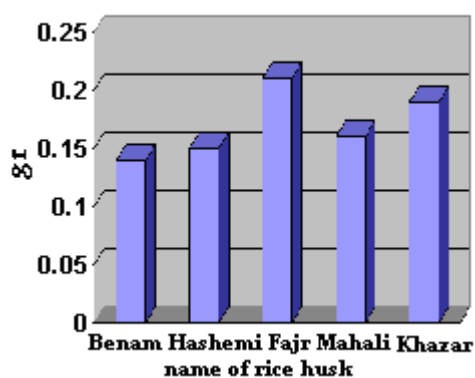
Different RHA samples obtained from different rice husks were analyzed with XRF to determine differences in concentration of components. Table I shows the XRF data obtained from different RHA samples of the different kinds of rice husk samples which were collected from the north of Iran (Mazandaran, Babolsar). The RH samples were obtained from different kinds of rice named Hashemi, Fajr, Beenam, Khazar and Mahali in Iran (the name of the samples are local area names). Fig. 1 shows the amounts of silica in different kinds of rice husk. It is found that the sample of Fajr rice husk has shown higher concentration of silica in comparison with the other four samples. Therefore the Fajr rice husk was used for the synthesis of zeolites in the present work.

Table 1. XRF chemical analysis of RHA, in weight (%) for different kinds of rice husk samples grown in North of Iran.

Sample Compounds	Fajr	Hashemi	Benam	Khazar	Mahali
SiO ₂	96.08	94.08	94.60	95.92	95.30
Al ₂ O ₃	0.21	0.39	0.41	0.37	0.38
Fe ₂ O ₃	0.14	0.21	0.26	0.25	0.24
CaO	0.24	0.40	0.41	0.45	0.32
Na ₂ O	0.20	0.43	0.33	0.19	0.41
K ₂ O	0.51	0.52	0.61	0.45	0.52
MnO	0.16	0.28	0.38	0.31	0.25
TiO ₂	0.01	0.02	0.03	0.01	0.02
MgO	0.48	0.88	0.91	0.76	0.90
P ₂ O ₅	0.33	0.71	0.54	0.46	0.66
LOI*	1.64	1.36	1.52	0.83	1.00

3.1. Loss of ignition

The structural analyses of extracted silica were obtained from XRD and IR spectroscopy methods. The amorphous nature of the extracted silica is typically shown by XRD pattern in Fig. 2, in which the broad peak centred at 2θ angle of 22° is typical for amorphous silica. Therefore, this pattern clearly illustrates that, the samples of the extracted silica xerogel by adapting the method of Kalapathy and Proctor [9] from the prepared RHA samples of the uncontrolled burning of the (RH) with further treatment as discussed in the experimental part are in amorphous form and confirm the absence of any ordered crystalline structure.

**Fig. 1.** Amounts of silica in 1 gr of different rice husk

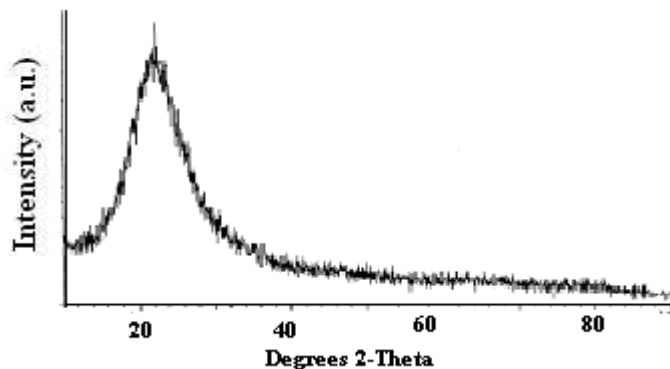


Fig. 2. XRD pattern of extracted silica from rice husk

IR spectra in Fig. 3 shows the major chemical groups present in extracted silica. The broad band between 2850 and 3700 cm^{-1} was due to absorbed water OH and silanol OH groups. The predominant absorbance peaks were obtained at 1300 to 1330 cm^{-1} from siloxane bonds (Si-O-Si). The vibration modes of the gel network also appeared in spectrum between 700 to 1200 cm^{-1} .

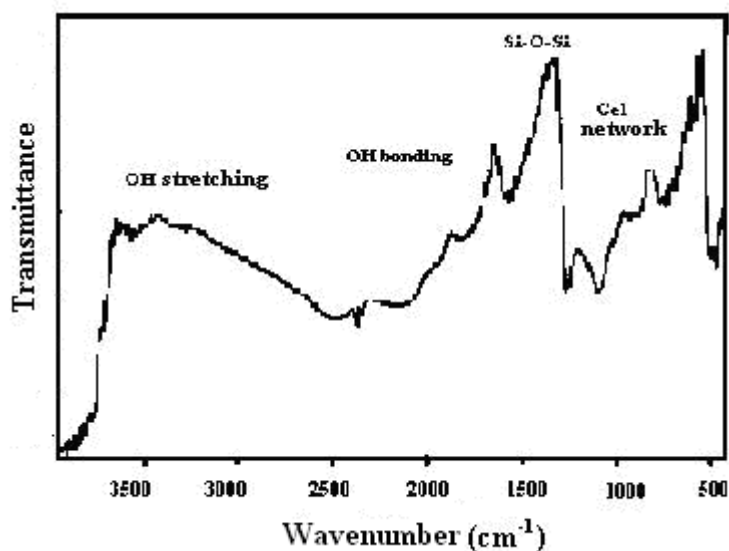


Fig. 3. Infrared spectra of extracted silica from rice husk

More interesting is the sharp signals which arise on calcinated silica xerogel XRD spectra. The XRD pattern obtained from the extracted silica xerogel using hydrochloric acid and heating at temperature 600 C is shown in lower trace in figure 4. A broad peak centred at 2θ angle of 22° confirmed the amorphous nature of silica. Also, two small and sharper peaks in these patterns appear which are due to the presence of sodium chloride impurity that was formed during the silica extraction using hydrochloric acid, the method of extraction was the same as the Kalapathy et al. [9]. Some attempts to find better understanding on these sharp peaks have been carried out. For example, we used citric acid instead of HCl in silica xerogel

extraction; these sharp peaks in the XRD pattern completely disappeared. Moreover, to find the effect of temperature or calcinations on these sharp peaks, we changed the heating temperature from 600, 700, 800 and 900 C. The XRD spectra show that the intensities of these sharp peaks are increased with increasing the temperature. Also three peaks appear instead of two peaks at higher temperature (see figure 4). The knowledge on this effect i.e. increasing the temperature increasing the intensities of these peaks is poor, and might be not observed and discussed anywhere. But, in general it could be said: firstly, these signals obviously arise from the NaCl crystal lattice because our observation shows the obtained XRD pattern of pure NaCl also showed these signals in the same degrees on XRD spectra of extracted xerogel silica. Secondly increase in the intensity by increasing the calcination temperatures could be due to two reasons: one it might be that there was bare and hydrated ions i.e. Na^+ and $\text{Na}(\text{H}_2\text{O})_n$ and also two Cl^- and $\text{Cl}(\text{H}_2\text{O})_n$ in the prepared silica which were confirmed with NMR studies, since, interchange of Na^+ between bare and hydrated sites occurs on the time scale of the experiment. Also there was free diffusion of water molecules in the pores of silica, but, not all Na^+ ions can be hydrated. Therefore silica containing ionic and hydrated Na and Cl ions and cluster are there in the external and internal surface of SiO_2 . A small amount of information is available on the mobility of the absorbed waters and the cations or the anions. Moreover, remaining structural hydroxyl groups and atoms of silica lattice in different temperatures are also important. Therefore varying the temperature causes the change on the amount of bare or hydrated ions and the structural hydroxyl groups and the silica lattice. Increasing the temperature might be increasing or changing the volume of porous in silica network and the formation of crystal lattice of NaCl. Also further test have been used in this respect. Firstly, the reason examined by XRD patterns of pure NaCl heated to the above temperatures, these peaks appeared at the same degrees and the intensities of peaks changed very slowly by increasing the heating temperature. Secondly, several samples with different mole ratios of NaCl/SiO_2 were investigated with XRD. The XRD patterns in this step showed different peak intensities; this observation showed that varying the temperature led to great porous volume in silica network and the NaCl or hydrated lattice of this salt could be formed both inside and also outside of porous silica which made different peaks in XRD patterns in different intensities at different temperatures, since, perturbations in the framework structure, crystal morphology, extra framework material, phase purity, crystallite size, and the setting and occupation of cation sites, and cation types can produce differences in the XRD spectra.

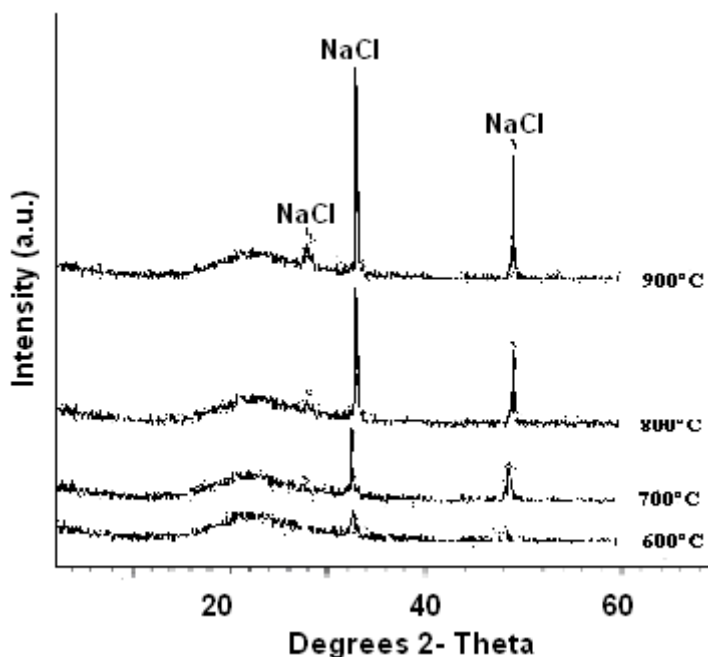


Fig.4. The XRD patterns of extracted silica at different temperatures

In order to account the effect of heating on rice husk ash silica, we obtained the solid state NMR of RHA samples. The spectrum of rice husk ash sample which burnt in air, and that of the sample which after burning, was heated at 1000 °C for 6 h, are shown in Figure 5. The earlier one showing a signal at -109.64 ppm, which obviously implies silica, is essentially the only environment present (Q^4). But the spectrum of the heated sample at 1000 °C is odd, because direct polarisation NMR spectrum (B) shows a signal at -61.62 ppm which is incomprehensible, plus a broad one, which might contain a background signal. On the base of our knowledge the peak of the monomeric silicate anion Q^0 appears at the low-field side of the spectrum (-71.3 ppm), followed in a regular sequence by the Q^1 to Q^4 units shifted by about 10 ppm to high field for each newly formed SiOSi bond [11]. Moreover, the cross polarization ^{29}Si NMR gives no signal at all. Our knowledge on this part is still poor and we believe it needs more work to clarify some detail.

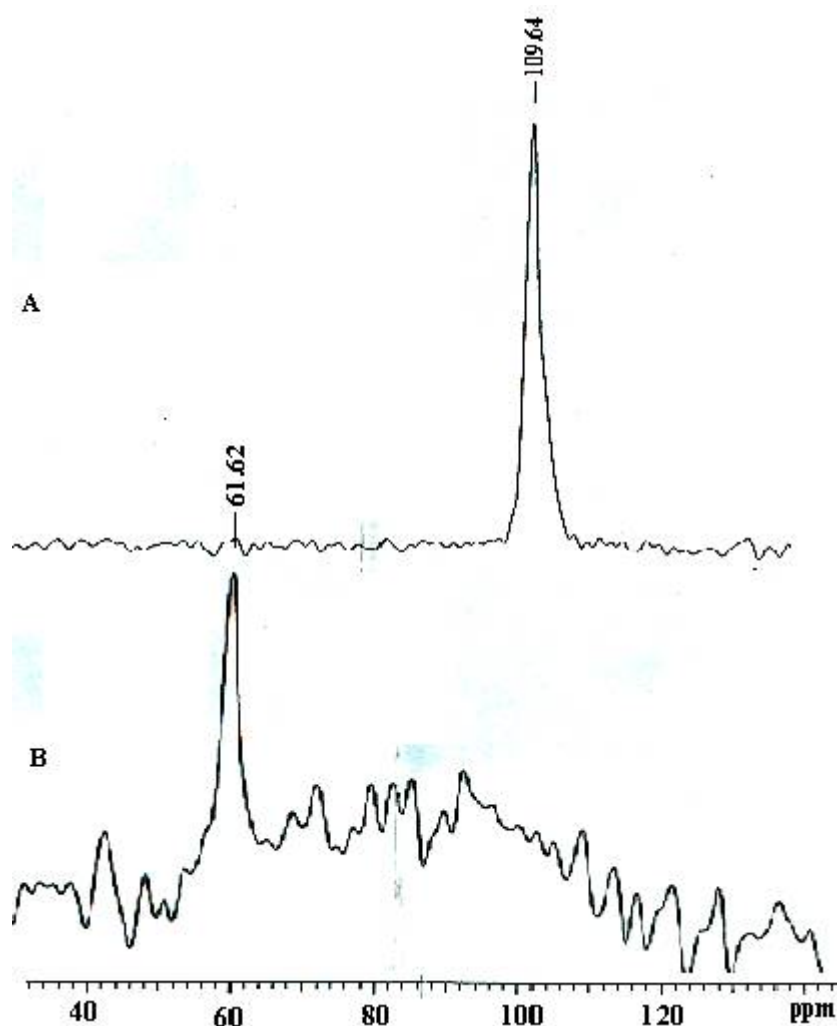


Fig. 5. Direct polarization solid state ^{29}Si NMR spectra at 59.58 MHz and ambient temperature of RHA samples: (A) burnt in air and (B) heated at 1000 °C. Both spectra were recorded with a Spectrum condition: Spectral width 30007.5 Hz. Acquisition time 10.0 ms, Relaxation delay 120.0 s, Pulse angle 90 degrees. Number of repetitions 32

4. Conclusions

This study revealed that silica with ca. 96% purity can be obtained from rice husk and the sample of Fajr rice husk has shown higher concentration of silica in comparison with the other four kinds of rice samples. In the process of silica extraction, increasing the temperature led to great porous volume in silica network.

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