

Research Article

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Comparison of adsorption properties of commercial silica and rice husk ash (RHA) silica: A study by NIR spectroscopy

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Abstract: Adsorption properties of Silica gel (commercial silica), rice husk ash (RHA) silica, and their hydrothermally treated products towards water molecules were studied in this work. RHA silica was prepared by heating rice husk to 650°C for 4 h after pretreatment with hydrochloric acid. Portions of the samples of silica were evacuated at 200°C and then allowed to adsorb water molecules from the surrounding air at either 42 or 50% humidity. The near infrared spectra of these samples were measured at different time intervals during their adsorption of water molecules. The evolved near infrared spectra were analyzed using second derivative techniques. Adsorption properties of these samples were further studied by gravimetric analysis. Surface functionalities and adsorption evolution of water molecules on silica samples studied showed that the adsorption of water molecules on commercial silica gel sample and RHA silica Samples takes place readily with hydrogen-bonded silanol groups on the surfaces of the samples. This adsorption arising from the OH stretching and bending vibrations of these water molecules gives rise to a band at 5,270 cm⁻¹ in the near infrared region. The adsorbed water molecules then continue at the free silanol groups which is indicated by the absorption around 5,314 cm⁻¹. The results clearly show that the silica made from rice husk adsorb water in the same manner as the commercial silica, but the quantity of water molecules adsorbed is less compared to commercial silica

used in this experiment. However, the study clearly shows that the rice husk silica can replace the commercial silica as a substitute for desiccant purposes in industry.

Keywords: adsorption, commercial silica gel, rice husk ash silica gel, near infrared spectroscopy, gravimetry, thermal treatment

1 Introduction

Silica gel is produced by condensation polymerization of silicic acid (Si(OH)₄). Silica gel produced by this method contains porous particles with cross-linked siloxane (Si–O–Si) structure in the bulk and silanol groups on the surface. Dry silica gel adsorbs water molecules when exposed to air. This quality of silica gel found its use in electronic industry as a desiccant. The surface of silica gel particles contains free and hydrogen-bonded silanol groups [1–3]. The hydrogen atoms in the silanol groups are acidic and can be replaced by different functional groups to yield several different new materials that are useful in the fields such as separation science, catalysis, polymer science, etc. [4]. The adsorbed water molecules can be removed by heating under vacuum at 200°C. The surface of silica can be manipulated by using high temperatures over 700°C to remove hydrogen-bonded silanol groups or hydrothermally treated to open the siloxane bondings to yield new silanol groups to facilitate extended hydrogen bonding with the free and hydrogen-bonded silanol groups already found on the surface.

Silica in several different materials and forms has been successfully characterized by Near infrared spectroscopy. Christy [5] has studied several silica gel and silica gel-based samples and their water adsorption evolutions using gravimetry and near infrared reflectance spectroscopy with the help of second and fourth derivative techniques and showed that the hydrogen-bonded silanol groups adsorb water readily compared to free silanol groups. The second derivative technique enhances the

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sharp bands in a peak relative to the broad band in the absorption spectrum of a sample. The technique resolves and reveals the hidden bands buried in a broad peak. The fourth derivative resolves the bands in a broad second derivative profile. In quantitative analysis, second derivative technique improves the accuracy of quantification by eliminating base line shift and scattering in the spectra. The derivative spectra (all the derivatives) follow Beer's law and therefore can be used in quantitative determination by calibration using intensities of the bands in the second derivative spectra [4,6].

A completely dry silica gel sample gives a simple near infrared spectrum in the region 11,000–4,000 cm^{-1} . The near infrared band assignments of amorphous silica are given in Table 1 [4,5].

Utilization and recycling wastes in environmental applications have become priority of some of the research workers during the past several years. Rice is one of the major food products in the world and its production generates waste, namely rice husk (RH). This is just a portion of the toxic, hazardous, crop, animal wastes found in the environment [7]. Rice husk (RH) is a cheap agriculture waste of the rice milling industry [8] and contains 70% of biopolymers and 20% amorphous silica [9]. The organic content of the rice husk enables it to be used as a source of energy by burning. However, the burning process generates a new waste, namely, Rice Husk Ash (RHA) and creates disposal problem in the environment. The RHA produced by burning at 650°C for 4 h yields RHA ash with approximately 80% of amorphous silica.

The aim of this work is to compare the water adsorption properties of silica produced from rice husk and commercial silica. The study would provide an opportunity to evaluate the suitability of RHA silica as a possible desiccant in industry. Furthermore, the work also looks at the water adsorption properties of hydrothermally treated rice husk silica and hydrothermally treated commercial

silica to understand the mechanism of adsorption. In addition, gravimetry was also used for comparison of the mass of water adsorbed by these samples.

2 Experimental

2.1 Commercial silica gel sample, preparation of rice husk silica and hydrothermal treatment

The commercial silica gel sample (60 μm – 60 F_{254}) was bought from Sigma-Aldrich. The rice husk was purchased from a local vender (Bryggselev) dealing with supplies for beer brewing. A portion of the RH (10 grams) was warmed with 100 mL 1 M HCl for 90 min at 90°C to remove metallic impurities. The content was cooled to room temperature and washed with distilled water several times to remove the remaining HCl acid until the filtrate showed a neutral pH. The filtered sample was then dried in an electric oven at 90°C for 24 h. The treated rice husk was heated in a Carbolite TM CWF chamber furnace at 650°C for 4 h. The high temperature burns out the organic matter in the RH and the resulting product is a white powder with silica as the major component.

Hydrothermal experiments were carried out in steel bombs of 25 cm long and 1 cm internal diameter [10]. One gram of dry sample (commercial and RH silica) and 0.4 mL of distilled water were added to the bomb and sealed. The bomb was then placed in a chromatographic oven set at 160°C and left for 2 h. The hydrothermally treated sample was then removed and evacuated at 200°C to remove the physically adsorbed water from the surface. The same procedure was followed for the RHA silica sample.

Table 1: Near infrared band assignments [4,5]

Peak (cm^{-1})	Band assignment
7,316	Overtone –OH stretching Free silanol groups
7,225	Vicinal silanol groups
7,121, 6,861	Water molecules hydrogen bonded to silanol group; water molecules hydrogen bonded to other water molecules
5,311	Combination band OH stretching and bending water molecules hydrogen bonded to free silanol groups
5,270	Water molecules hydrogen bonded to vicinal groups
5,119	Water molecules hydrogen bonded to silanol group
4,579	Combination band OH stretching free silanol and siloxane (Si–O–Si)
4,518, 4,422	Combination band silanol OH stretching (hydrogen bonded to water molecules) and siloxane (Si–O–Si) bending

2.2 Sample drying and spectroscopic measurements

The commercial and RHA silica samples as well as the hydrothermally treated samples were heated and evacuated again in separate glass vials using a ceramic heater (BA electric Bunsen from Electrothermal, UK) controlled by an external power supply. Digital thermometer with a K type thermocouple (Clasohlson, UK) was used to measure the temperature of the sample. The glass vials containing the samples were evacuated at 200°C for 1 h and 20 min using a powerful vacuum pump (Edwards, UK) (Figure 1). Then each of the vials containing the sample was cooled and placed on the ZnSe crystal of the transreflectance accessory mounted in the spectrum one NTS FT-NIR (Perkin Elmer Ltd.) spectrometer (Figure 1). The transreflectance accessory uses reflectance technique where the NIR radiation can penetrate the sample and reflected back in the instrument. The reflected light that reaches the detector will contain information about the sample. The cap containing the glass tube and the stopper was removed and exposed to absorb water molecules from a humidity-controlled atmosphere. A glycerol/water system was used to control the relative humidity during the water adsorption experiments and near infrared measurements [11] (Figure 1). The adsorption experiments and Infrared measurements were carried out at two different relative humidities, namely 42 and 52%. The reflectance spectra of the samples were measured in the region 10,000–4,000 cm^{-1} at a resolution of 16 cm^{-1} . A total of 32 scans were made each time and the average spectra were converted to $\log(1/R)$ format and saved. The near infrared measurements continued until the absorption peak at 5,314 cm^{-1} arising from the adsorption of water molecules showed no change. The spectra of the samples in $(1/R)$ format were derivated twice and saved for further analysis. When the second derivative profiles

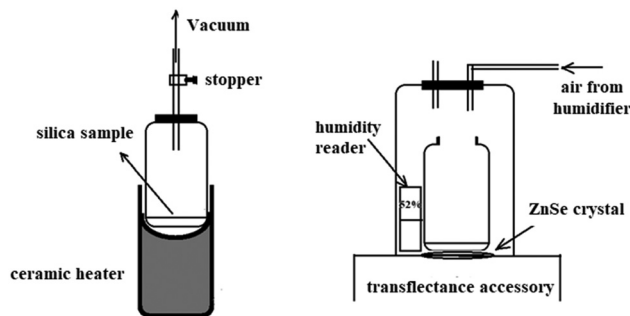


Figure 1: Sketch showing the setup for sample drying and spectral measurements in humidity.

had overlapping bands, the second derivative profiles were further derivated twice to yield the fourth derivative profiles of the NIR spectra.

2.3 Gravimetric measurements

A portion of the evacuated Silica gel sample was placed in a Near Infrared sample cup and placed on an analytical balance that can record a weight change of nearly 0.0001 g. The weight of the sample was recorded continuously over a period of 1 h and 30 min. The measurements were carried out separately at 42 and 52% relative humidity. Procedure followed for the commercial silica gel was repeated with the RHA silica and hydrothermally treated samples.

Ethical approval: The conducted research is not related to either human or animal use.

3 Results and discussion

The near infrared spectra of the commercial silica and RHA silica from the bottles before and after drying under vacuum are shown in Figure 2. The changes in the spectra after drying under vacuum are very clear. The broad peak in the region 7,500–6,000 cm^{-1} is due to the OH overtone of the free and vicinal silanol groups as well as water adsorbed free and vicinal silanol groups. The spectra measured after evacuating show that the RH silica contains free (sharp peak at 7,316 cm^{-1}) and vicinal silanol groups (broad peak overlapping with the peak at 7,316 cm^{-1}). The RHA silica preparation involves high temperature treatment and some of the hydrogen-bonded vicinal groups are eliminated as water molecules. In contrast, the broadness of the peak at 7,316 cm^{-1} of commercial silica is due to the presence of higher concentration of hydrogen-bonded silanol groups compared to RHA silica. The peaks in the region 5,300–5,100 cm^{-1} purely arise from the absorption of the combination frequencies (OH stretching and bending) of the water molecules adsorbed by the silica samples.

The peaks that arise in the region 5,300–5,100 cm^{-1} are purely from the absorptions of the combination of OH stretching and bending vibrations of water molecules adsorbed on the silica surface. The types of silanol groups adsorbing the water molecules are revealed by the second and fourth derivatives of the spectral profiles in this region. Therefore, the discussion on the types of silanol

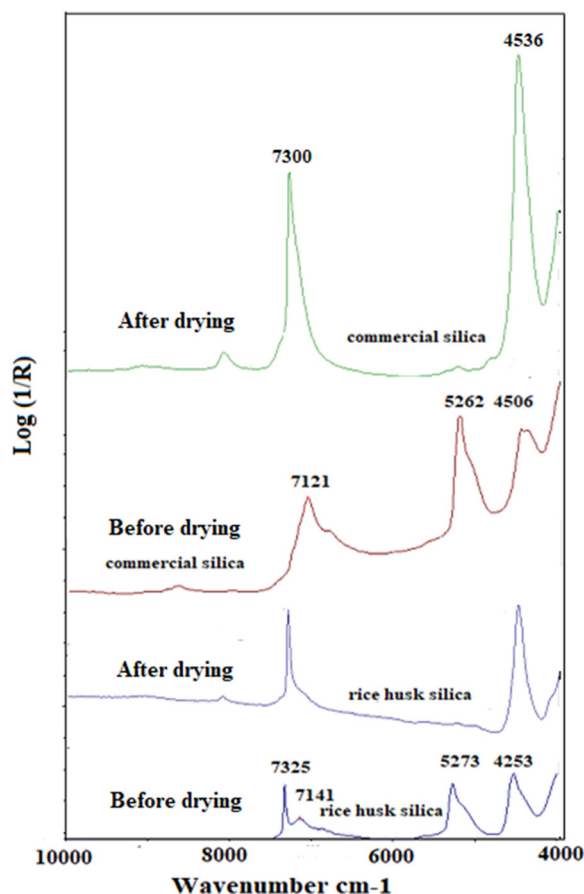


Figure 2: Near infrared spectra of silica samples before and after drying.

groups on the silica samples surfaces will be solely based on the spectral profiles and their second and fourth derivatives in this region.

The second derivatives of the spectral profiles of the absorptions arising during the water adsorption evolution on the silica surfaces at 52 and 42% relative humidity over a period of 2 h and 30 min are shown in Figures 3 and 4. The differences are very clear. There is clear difference in the derivative profiles of the spectra acquired at 52% relative humidity. The commercial silica sample shows two different absorptions starting with an absorption at $5,270\text{ cm}^{-1}$ due to the water molecules adsorbed to the vicinal hydrogen of the silanol groups on the silica surface and an absorption at $5,314\text{ cm}^{-1}$ due to the water molecules adsorbed to the hydrogen of the free silanol groups. The latter peak starts appearing after 1 h of exposure. This feature is different in the RHA silica and here the adsorption seems purely from the vicinal hydrogen of the silanol groups. The fourth derivative profiles of the spectra of the samples after 2 h and 30 min exposure are shown in Figure 5. The fourth derivative profiles show the

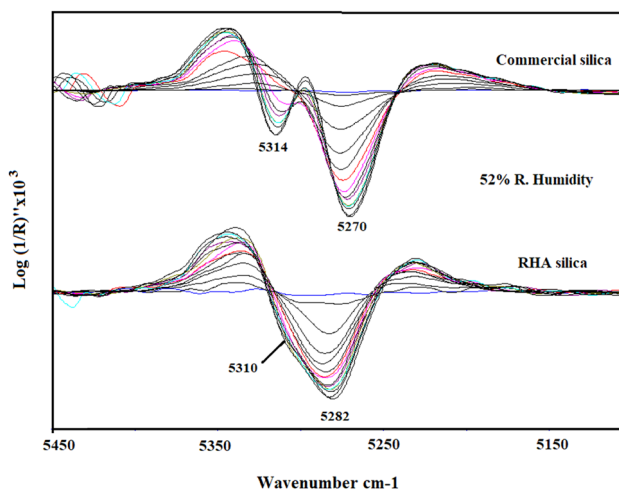


Figure 3: Second derivative profiles of the spectra evolved during the exposure of silica samples for 2 h and 30 min at 52% humidity in the region $5,450\text{--}5,100\text{ cm}^{-1}$.

presence of water molecules adsorbed on both free and vicinal silanol groups on the samples. There is another interesting thing revealed in the fourth derivative which is that the absorption arising due to the water molecules adsorbed onto the vicinal silanol groups experiences a blue shift in the absorption ($5,277\text{--}5,282\text{ cm}^{-1}$). This may indicate that the vicinal groups on the RHA silica are more acidic than the vicinal group hydrogen on the commercial silica (Figure 6). However, we are unable to confirm this in our present study. The second derivative profiles of the spectra of water adsorbed at 42% humidity show the adsorption of water molecules at only vicinal

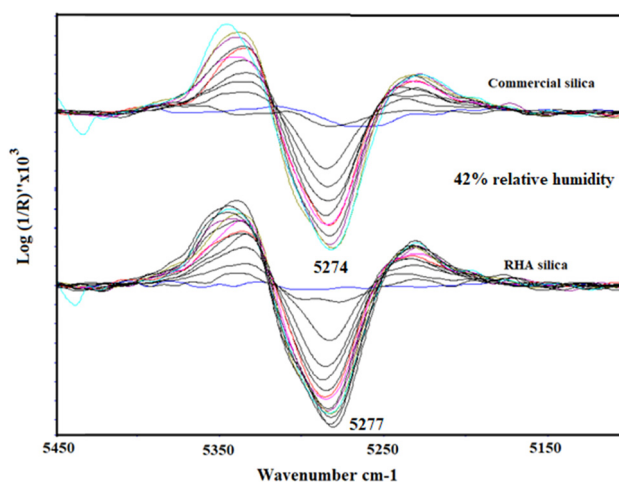


Figure 4: Second derivative profiles of the spectra evolved during the exposure of silica samples for 2 h and 30 min at 42% humidity in the region $5,450\text{--}5,100\text{ cm}^{-1}$.

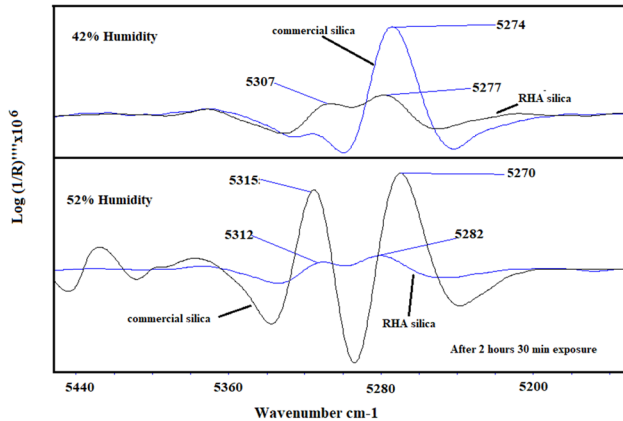


Figure 5: Fourth derivative spectral profiles of the spectra of commercial and RHA silica after 2 h and 30 min exposure in the region 5,450–5,150 cm⁻¹.

silanol groups (Figure 5). This is expected because of comparatively fewer water molecules available in the environment at 42% relative humidity.

The free silanol groups on silica surface play an important role in the water molecular adsorption. Water molecules form a network connecting the free and vicinal silanol groups. When there are equal number of free and vicinal hydrogen on the surface, effective adsorption of water molecules takes place [4]. RHA silica contains few acidic vicinal groups and free silanol groups; the adsorption of water is not effective because of the lack of free silanol groups. The effect can be seen in Figure 7, showing the adsorption of water molecules on hydrothermally treated silica surfaces. Here, the absorptions are clearly by the vicinal silanol groups which is indicated by the NIR absorption at 5,270 cm⁻¹. The silica loses its effectivity in adsorbing water molecules because of the deficiency of free silanol groups to sustain the network of water molecules [4].

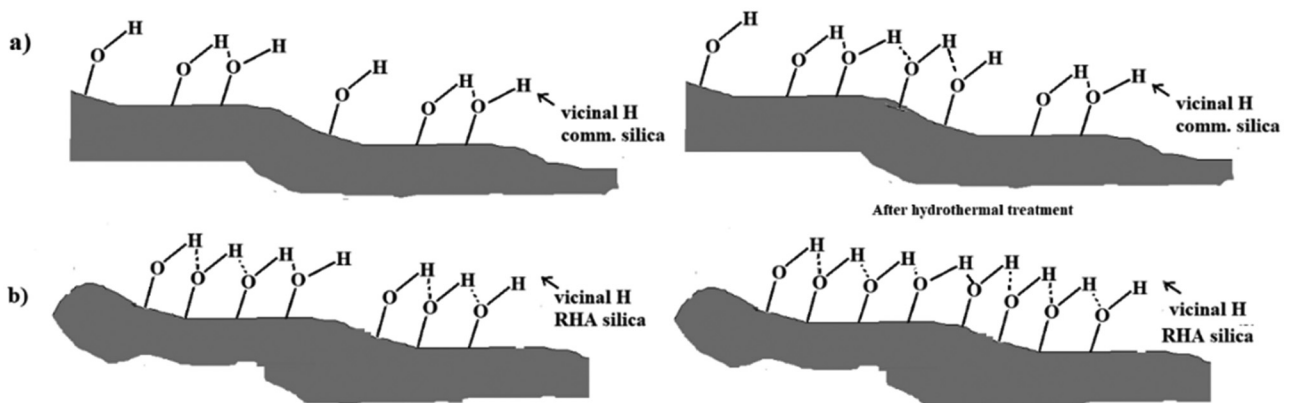


Figure 6: Models showing the differences in acidities of the vicinal hydrogen from the hydrothermally treated samples. (a) Commercial silica and (b) RH silica.

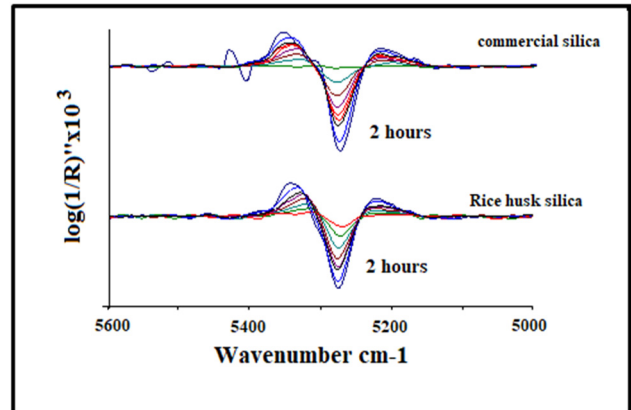


Figure 7: Second derivative spectral profiles of hydrothermally treated silica samples acquired during the adsorption evolution of water molecules at 42% humidity.

The amount of water adsorbed by both silica samples over a period of 1 h and 40 min is given in Figure 8. The graph shows clearly that the commercial silica sample adsorbs more than twice the amount of water at 52% humidity. The adsorption at 42% humidity is 0.03 g/g for commercial silica and 0.025 g/g for RHA silica. The difference in water adsorption by the RHA silica can also be attributed to the silica content of RHA. The RH ash contains around 80% of silica and the reduction in the amount of water adsorbed compared to commercial silica is partly due to this silica content.

4 Conclusion

Near infrared reflectance accessory provides an easy sampling technique that requires almost no sample preparation.

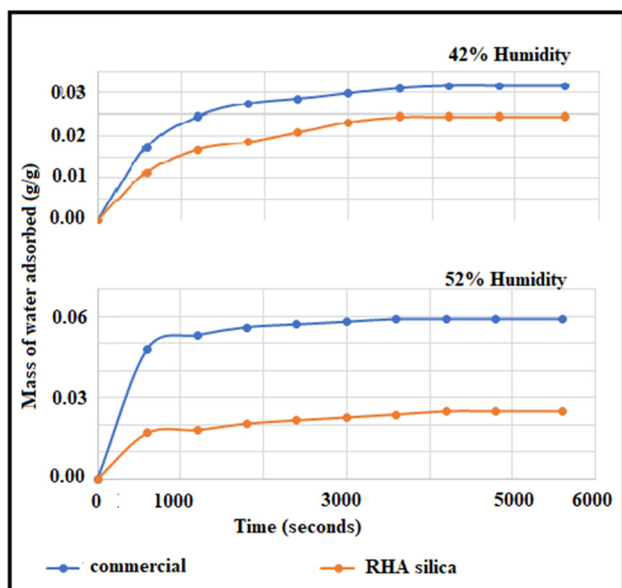


Figure 8: Mass of water adsorbed by the silica samples.

The bands present in the near infrared spectra of silica samples were easily identified by second and fourth derivative techniques. The analysis of the derivated profiles of the absorption spectra of the samples provides clear insight into the chemistry of water adsorption and the types of silanol groups found on the surfaces of commercial and RHA silica samples.

The chemistry of the adsorption of water molecules by commercial silica and RHA silica is the same. The difference in the amount of water adsorbed by the sample can be attributed to the concentration of vicinal silanol groups and free silanol groups on the surfaces of the samples. A part of the reduction in the amount of water also comes from the reduced concentration of silica in RHA (80%).

Gravimetric analysis reveals the amount of water adsorbed by these two silica samples. Even though the amount of water adsorbed by RHA silica is less compared to commercial silica, the RHA silica functions in the same manner as commercial silica and can be used as a desiccant instead of silica. The amount of RHA silica can be increased in proportion to compensate for the adsorption reduction characteristics of RHA. The use of RHA silica instead of commercial silica for desiccant purposes can find a use for an environmental waste from rice producing Asian countries and thus avoid using an environmental unfriendly commercial silica.

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Data availability statement: The spectra measured and data generated are used in the article.

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