

## **A Simple Method for Production of Humidity Indicating Silica Gel from Rice Husk Ash**

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### **Abstract**

The objective of the present work is to develop a procedure for obtaining and characterizing active blue silica from rice husk ash. About 25 wt.% silica powder (from total mass of rice husk) of 95% pure silica could be produced after heat-treating at 700°C for 6 hours. A simple method based on alkaline extraction followed by acid precipitation was developed to produce pure silica hydrogel from RHA. A well-defined very minimum amount CoCl<sub>2</sub>-containing blue silica gel was prepared by impregnation of the aqueous solution of the salt to silica hydrogel, ageing and drying method. The sharp colour changing from blue to pink of the dried blue silica gel of amorphous characteristics was obtained at 3% moisture adsorption, and total moisture adsorption capacity was 39.5% at 80% RH. The gel was characterized using X-ray diffraction (XRD), Scanning Electron Microscope (SEM), energy dispersive X-ray (EDX), FT-infrared spectroscopy (FT-IR), thermal analysis (DSC/TG) and UV-vis reflectance spectroscopy (UV-vis) techniques. The results show that this novel preparation procedure provides an easy pathway to produce blue silica gel from rice husk according to specification.

**Key words:** Rice husk ash, Amorphous, Silica, Humidity, Silica gel

### **Introduction**

Rice husk is an agricultural waste material abundantly available in rice-producing countries. They are the natural sheaths that form on rice grains during their growth.<sup>(1)</sup> Removed during the refining of rice, this husk is sold as cheaper material than its value. World rice production in 2007 was approximately 645 million tons, of which more than 10% is husk. Asian farmers produce rice about 90% of total production of 100,000 tons or more, with two countries, China and India, growing more than half the total crop.<sup>(1, 2)</sup> When disposed of, rice husk occupies large areas, where it can self-burn, spreading the ashes and causing damages to the environment. Nowadays, the rice-producing countries are challenged by the problem of rice husk, and have been trying to use it in an economical manner.<sup>(3)</sup>

The major constituents of rice husk are cellulose, lignin and ash.<sup>(4, 5, 6)</sup> The organic materials in rice husk consist of celluloses (55–60 wt.%, including cellulose and hemicellulose) and lignin (22 wt.%). Approximately 25wt.% of ash is obtained

on burning rice husk in air. The ash contains 98-99% silica by mass with minor amounts of metallic elements.<sup>(4, 7)</sup> This rice husk ash (RHA) can be an economically viable raw material for the production of silicates and silica. Sodium silicate can be produced very cheaply from the RHA by simply boiling it with refluxed sodium hydroxide solution for 1 hour whereas this sodium silicate, the precursor for silica production, is currently manufactured by melting quartz sand with sodium carbonate at 1300°C.<sup>(8)</sup>

Silica gel has been used as a desiccant for many years to protect sensitive materials from damage due to excess humidity. As the gel is normally white or colourless, and shows no obvious change in colour during use, it is difficult to tell when it has become saturated with moisture and needs to be regenerated by heating, or replaced. There is therefore a need for a visible indication when the gel is saturated. Traditionally this has been achieved by immersing it with a cobalt salt, usually the chloride. This produces a deep blue colour for the dry gel, which turns to a light pink as the gel absorbs moisture. Cobalt

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chloride has recently been classified as a Category 2 carcinogen with the result that silica gel containing it will require much tighter control.<sup>(9,10)</sup> But due to sharp changing of colour it can be used preferably for special industrial applications except the food industry.

The aim of this work is to prepare low cost humidity indicating silica gel with using rice husk ash (RHA). The gel has been studied using X-Ray diffraction (XRD), Scanning Electron Microscopy (SEM), Fourier Transform Infra-Red Spectroscopy (FTIR), Humidity Adsorption/Desorption Kinetics, DSC/TG, UV-vis spectroscopy techniques.

## Materials and Experimental Procedures

### Experimental

Rice husk ash, Sodium Hydroxide pellets (99%, Loba), hydrochloric acid (35%, Loba) and  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (reagent grade, Loba) were used for this purpose. Rice husk (RH) was collected from a rice mill in Rorkela, India. The RH was washed with water and dried. The dried husk was heated at  $700^\circ\text{C}$  for 6 hours for complete combustion. The ash obtained was used for silica extraction. 5.0 g of the ash was added to 100 ml of 1.0 M NaOH solution in a covered 250 ml Erlenmeyer flask, and stirred under boiling condition for 1 hour to extract the silica as sodium silicate. The solution was filtered to get cleared solution. The extracted sodium silicate solution was added at a slow rate into 1N HCl solution with constant stirring to obtain the solution pH 6.0. The titration was continued until the solution pH reached 6.0. Within a few minutes the solution turned into gel. The gel was broken and added with water to turn into hydrogel (HG). The silica HG was washed with water to remove the sodium ions. The HG immersed and aged with aqueous solution of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  having  $2.1 \times 10^{-3}$  mol.dm<sup>-3</sup> concentrations for 1 week. The equilibrium pH of the solution was 6.35. Co(II) immersed silica hydrogel was dried at  $100^\circ\text{C}$  until constant weight was obtained. Ageing in 92% relative humidity (RH) for 1 day and re-drying at  $150^\circ\text{C}$  was carried out in order to obtain homogeneous distribution of the salt on the surface of the silica gel.

### Characterization of the Humidity Indicating Silica Gel

The powder X-ray diffraction patterns of the samples were obtained using (Philips PW1830 Holland) X-ray diffractometer. The microstructures

of the unwashed and washed blue silica gels were studied by SEM (JSM-6480LV). FTIR spectra of the as-dried powder of pure and blue silica gels were observed in a Perkin Elmer FTIR spectrophotometer (Spectrum RX-1). The spectrum was taken in the KBr pellet mode in the wave number range  $4400 - 400\text{cm}^{-1}$ . The humidity adsorption rate of pure and blue silica gels were measured at a constant temperature and relative humidity. The weight loss Endothermic peak was performed using thermal gravitational analysis (DSC/TG, Netsch STA 449 C Jupiter), from room temperature up to  $1000^\circ\text{C}$  under inert gas,  $\text{N}_2$  with  $10^\circ\text{C}/\text{minute}$ . All UV-visible spectra were collected in Perkin Elmer UV-visible spectrophotometer (Lambda 35) measuring the UV-visible absorbance at each wavelength between 400 and 700 nm. Both the dried and humidified blue silica gel samples were loaded in a 0.5-ml quartz cuvette. The pure white dried silica gel was taken for the base line correction purpose and spectra were recorded at  $25^\circ\text{C}$ .

## Results and Discussion

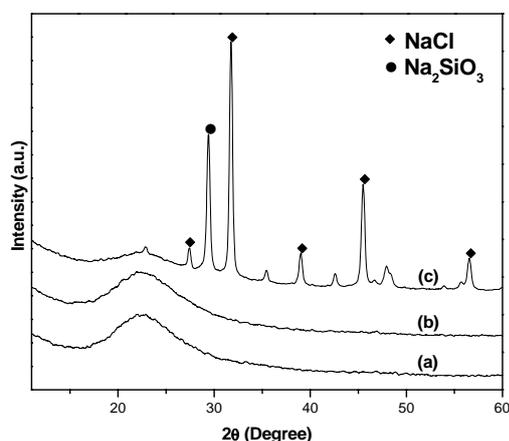
$\text{CoCl}_2$  impregnated colour indicating silica gel samples were obtained from RHA as described in experimental part and are shown in Figure 1 (a) dried blue silica gel and (b) humidified blue silica gel. By addition of  $\text{CoCl}_2$  solution with HG, protons were transferred from HG to solution, and Co(II) ions vice versa. Due to water evaporation during drying, the concentration of Co(II) increases in the aqueous phase, hence Co(II) ions moved along with the water and migrated to the external surface of the gel. Silica gel with a homogeneous blue colour was obtained with the evaporation of the adsorbed water from the samples at  $150^\circ\text{C}$ . On the other hand, upon taking moisture the blue colour changes to pink up to the point of saturation.



**Figure 1.** (a) dried blue silica gel and (b) humidified blue silica gel

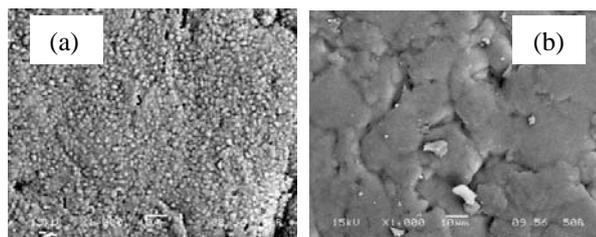
X-ray diffraction patterns of pure,  $\text{CoCl}_2$  impregnated and unwashed silica gel are shown in Figure 2. Both washed pure silica gel and cobalt

salt impregnated silica gel are exhibit amorphous characteristics; whereas, sharp crystalline peaks are found in case of unwashed silica gel. Without washing the gel with de-ionized water, the sodium ion in the form of sodium chloride or in sodium silicate remains inside the gel which shows the crystallinity of its nature.



**Figure 2.** X-ray diffraction patterns for (a) Washed pure silica gel and (b) Blue silica gel impregnated with  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  ( $2.1 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ ) and (c) Unwashed Silica gel.

Figure 3 shows the microstructure morphology of unwashed and washed blue silica gel obtained by using RHA. The particulate distribution of Na element may be in the form of NaCl compound present on the surface of the unwashed blue silica gel, clearly visible in white grain form as shown in Figure 3 (a). On the other hand, there is no such kind of white grains found on the surface of washed blue silica gel as shown in Figure 3 (b). This characteristic has exhibited only when drying the gel without washing. At that point, the Na element preheated the surface of the gel and dominated the Co (II). After washing the hydrogel repeatedly with de-ionized water, the sodium portion has completely removed from it. Only due to the presence of Co(II), the dried gel displayed pure and transparent blue colour.



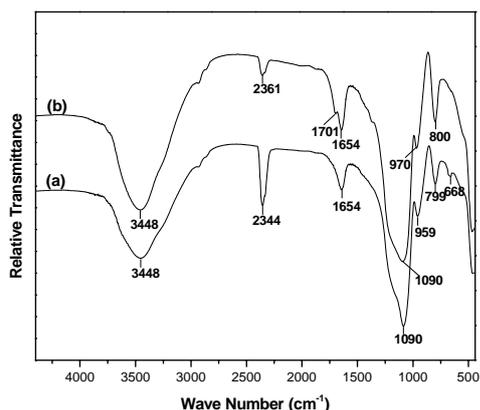
**Figure 3.** SEM photographs of (a) Unwashed blue silica gel and (b) Washed blue silica gel

The EDX analysis of unwashed and washed blue silica gel represents the percentage of Na element present in the gel as mentioned in Table 1. In case of unwashed blue silica gel, the percentage of the Na element was found in the range of about 35% (wt.) whereas in washed blue silica gel, the percentage is zero. The EDX analysis corroborates well with the SEM data in that  $\text{Na}^+$  element in any compound form will not be present in silica gel after washing.

**Table 1.** EDX analysis of unwashed and washed blue silica gel

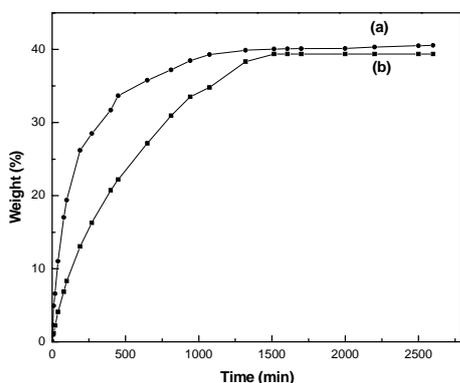
	Unwashed blue silica gel	Washed blue silica gel
Elements	Weight (%)	Weight (%)
O	0.93	57.04
Na	35.09	0.00
Si	0.05	42.34
Cl	63.93	0.38
Co	0.00	0.51
Total	100.00	100.00

The FT-IR spectra of pure and blue dried silica gel samples are shown in Figure 4. Si-O peaks were obtained in the range  $3700\text{-}3200 \text{ cm}^{-1}$  of Si-OH compound due to the reaction of Silica with sodium hydroxide. There is a probability of formation of Silane, i.e. Si-H bond, as shown in FTIR spectroscopy in the range of about  $2200$  to  $2400 \text{ cm}^{-1}$  due to stretching vibration and  $800$  to  $980 \text{ cm}^{-1}$  due to bending vibration. The peak range  $700$  to  $800 \text{ cm}^{-1}$  shows the formation of Si-Cl bond due to the reaction with HCl. The Si-O bond in Si-O-Si shows IR peak in the range of  $1000$  to  $1100 \text{ cm}^{-1}$ . The peak range  $1600$  to  $1650 \text{ cm}^{-1}$  indicates that there is a formation of double bond between Si-O due to the donation of a lone pair of electrons to the vacant d-orbital of silicon atom. As  $\text{CoCl}_2$  is added in the silica gel there is no broad change in the IR peak, but there is a slight shifting in the peak value, which can be explained as there is a probability of donating a lone pair of electrons from oxygen or silicon atom in silica gel to the vacant d-orbital of cobalt atom, in place of chloride. Hence it can be concluded that due to the presence of  $\text{CoCl}_2$  no major change in the IR spectrum of blue silica gel could be observed.<sup>(11)</sup>



**Figure 4.** FTIR spectra of 150°C-dried (a) Pure silica gel (b) Blue silica gel impregnated with  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  ( $2.1 \times 10^{-3} \text{ mol dm}^{-3}$ )

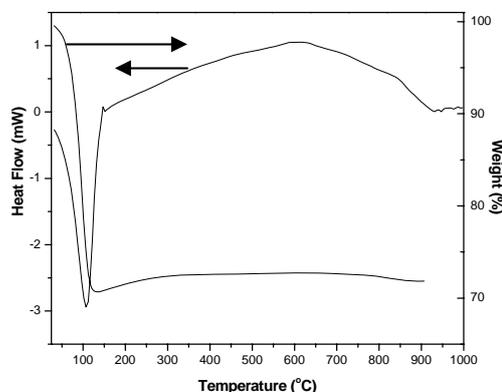
The colour inversion of blue silica gel is controlled by the transfer of  $\text{H}_2\text{O}$  from vapour phase to the solid surface and into the pores of the gel. At 80% relative humidity (RH) and 25°C, the water adsorption kinetics of pure and blue silica gel is shown in Figure 5. Pure silica gel adsorbed around 41% of moisture/water, whereas blue silica gel adsorbed about 39.5% of moisture. Thus the presence of  $\text{CoCl}_2$  lowered the adsorption capacity of the silica gel; because the pores of silica gel are filled by the  $\text{CoCl}_2$  in some extent depending upon the concentration. The higher the concentration of  $\text{CoCl}_2$  in silica gel, the greater the chance of filling more pores. Hence a lower amount  $\text{CoCl}_2$  impregnation in silica gel is advantageous for colour inversion and also for safety purpose. We have also observed that  $2.1 \times 10^{-3} \text{ mol dm}^{-3} \text{ CoCl}_2 \cdot 6\text{H}_2\text{O}$  impregnated silica gel is capable of changing the colour from blue to pink when it adsorbed about 3% of moisture.



**Figure 5.** Water Adsorption kinetics of (a) Pure silica gel (b) Blue silica gel at 25°C and 80% RH

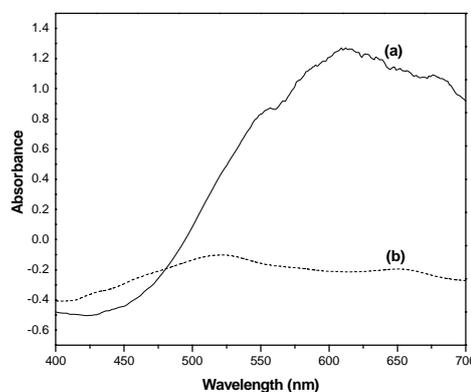
Water desorption starts from humidified blue silica gel at around 35°C as seen in TG curve

(Figure 6). At approximately 150°C, water desorption from the blue silica gel occurs, resulting in a sharp and drastic decrease in weight of approximately 31% by taking the heat of in the range  $5.5\text{--}72.5 \text{ Jg}^{-1}$  as shown in DSC curve.



**Figure 6.** DSC/TG of Humidified Blue Silica Gel

The deep blue colour of the dried  $\text{CoCl}_2$  containing silica gel is due to presence of  $\text{CoCl}_2$ . The strong interactions between the  $\text{Co(II)}$  and surface oxygen is the cause of the blue colour of the gel. The visible spectra of the  $\text{CoCl}_2$  containing silica gel shown in Figure 7. It indicates that the gel has absorbed in the red region of the spectrum, thus it appeared blue. Silica gel with  $2.1 \times 10^{-3} \text{ mol dm}^{-3} \text{ CoCl}_2$  in dried form has adsorption maxima at 615 and 680 nm. The change of  $\text{CoCl}_2$  containing silica gel spectrum with the adsorption of moisture is at lower absorbance i.e. 520 nm. The gel in moist form is pink absorbing in blue region. The colour inversion ability from blue to pink of the  $\text{CoCl}_2$  containing silica gel is originated by the presence of  $\text{Co(II)}$ . A change of colour in reverse direction is possible upon moisture adsorption. Higher absorbance values or the darker colour of the blue form allow easy differentiation of the dry and the moist gel by human eye.



**Figure 7.** Visible spectra of (a) dry and (b) moist  $\text{CoCl}_2$  containing blue silica gel.

## Conclusions

This study showed that RHA prepared from agricultural waste rice husk can be evaluated as a high purity reactive silica replacement material in the synthesis of humidity indicating silica gel with employing a simple low cost pre-treatment step including impregnation of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ . From investigation the washed blue silica gel indicated amorphously and porosity in nature.  $\text{NaCl}$  is the dominant compound over  $\text{CoCl}_2$  in case of unwashed gel. The functional group in silica gel makes the same vibration motions whether  $\text{CoCl}_2$  is present or not. But there is a slight shift in value of peaks due to the donation of a lone pair of electrons from oxygen or silicon atom to cobalt atom of chloride. Active blue silica gel which was capable of adsorbing 39% of moisture in 80% RH shows colour inversion from blue to pink when humidified with 3% moisture. Pink gel emit all of its adsorbed surface water at nearly  $150^\circ\text{C}$  by absorbing a quantity of heat in the range  $5.5\text{--}72.5 \text{ Jg}^{-1}$  and turn into pure blue. The blue silica gel has an almost indefinite shelf life if stored under airtight conditions. It can be regenerated and reused if required. Gently heating silica gel will drive off the adsorbed moisture and leave it ready for reuse. It is a very inert material, it will not normally attack or corrode other materials and with the exception of strong alkalis and hydrofluoric acid is itself resistant to attack.

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