A simple method for production of pure silica from rice hull ash

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Abstract

Rice hull ash (RHA), a waste product of the rice industry is rich in silica. A simple method based on alkaline extraction followed by acid precipitation was developed to produce pure silica xerogels from RHA, with minimal mineral contaminants. The silica gels produced were heated to 80°C for 12 h to obtain xerogels. Silica and mineral contents of xerogels were determined by energy dispersive X-ray (EDX) and inductively-coupled plasma (ICP) emission spectrometers, respectively. Xerogels produced from RHA had 93% silica and 2.6% moisture. The major impurities of silica produced from RHA at an extraction yield of 91% were Na, K, and Ca. Acid washing prior to extraction resulted in silica with a lower concentration of Ca (<200 ppm). However, final water washing of the xerogel was more effective in producing silica with lower overall mineral content (Na < 200 ppm and K < 400 ppm). X-ray diffraction patterns revealed the amorphous nature of silica xerogel. Fourier transform infrared (FTIR) data indicated the presence of siloxane and silanol groups. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Rice hull ash; Silica xerogels; Minerals

1. Introduction

Burning rice hull as fuel to generate energy results in the waste product, rice hull ash (RHA). RHA is rich in silica (about 60%) and can be an economically viable raw material for production of silica gels and powders (Kamath and Proctor, 1998; Chakraverty and Kaleemullah, 1991). RHA has been evaluated as an adsorbent of minor vegetable oil components (Proctor et al., 1995; Proctor and Palaniappan, 1990). Although various uses for rice hull and RHA have been suggested in the literature, their disposal or utilization remains a major concern.

Soluble siliculates produced from silica are widely used in the glass, ceramics, and cement as a major component and in pharmaceuticals, cosmetics, and detergents industries as a bonding and adhesive agents (Anon., 1997; Laxamana, 1982). Silica also has been used as a major precursor for a variety of inorganic and organometallic materials which have applications in synthetic chemistry as catalysts, and in thin films or coatings for electronic and optical materials (Lender and Ruiter, 1990; Brinker and Scherer, 1990). Mizuki et al. (1993) and Krishnaro and Godkhindi (1992) have investigated the formation of silicon carbide from rice hulls at high temperatures and Maeda and Komatsu (1996) studied the semiconductor properties of silicon carbide produced from rice hull. Semiconductor industries require pure silica, currently produced by smelting quartz in a high temperature furnace, to produce ultrapure polycrystalline silicon and silicon hydride. Development of a simple low energy chemical method for producing pure silica should lead to a variety of industrial applications for RHA.

Acid leaching (Chakraverty and Kaleemullah, 1991) and gasification (Luan and Chou, 1990) methods have been investigated for recovering silica from rice hull. Amorphous silica from RHA can be extracted using low temperature alkali extraction; the solubility of amorphous silica is very low at pH < 10 and increases sharply above pH > 10. This unique solubility behavior enables silica to be extracted in pure form from RHA by solubilizing under alkaline conditions and subsequently precipitating at a lower pH (Iler, 1979; Kamath and Proctor, 1998). This low energy method based on alkaline solubilization of amorphous silica could be more cost effective compared to the current smelting method.

Silica gel is a rigid three-dimensional network of colloidal silica, and is classified as aquagel (pores are...
filled with water), xerogel (aqueous phase in the pores is removed by evaporation) or aerogel (solvent is removed by supercritical extraction) depending on how they were made. Xerogels are mainly used to prepare dense ceramics. Further, their high porosity and surface area leads to applications such as catalytic substrates, ultrafilters, and chromatography column packing materials (Brinker and Scherer, 1990). Since impurities present in silica gels can affect their surface adsorption properties, purity of the silica is very important in characterizing rice hull silica adsorption.

In previous work, silica gel produced from RHA using an alkali extraction method had over 65% moisture, 2% of sodium, 0.04% of potassium, 0.01% of calcium and traces (<0.01%) of other elements (Kamath and Proctor, 1998). On the basis of dry material, Na, K, and Ca concentrations in this gel would be 6%, 0.12%, and 0.03%, respectively. Concentrations of Na and K in this gel were relatively high compared to Na, and K concentrations in commercial silica. Hence, an effective mineral leaching step is necessary to produce xerogels with reduced Na and K concentrations from RHA.

The objective of this study was to investigate the effectiveness of: (1) washing RHA with acid prior to alkali extraction, and (2) washing dried silica gel (xerogel) with water, in reducing the mineral content of silica produced by the alkali extraction method developed in our laboratory.

2. Methods

2.1. Acid washing

An acid washing step was used to remove the small quantities of minerals prior to silica extraction from RHA in the following manner. Ten grams of RHA samples were dispersed in 60 ml of distilled water, and the pH was adjusted to 1, 3, 5 or 7 using 6 N and 1 N HCl. These dispersions were stirred for 2 h, filtered through Whatman No. 41 ashless filter paper and then the RHA residues were washed with 100 ml of water. The residues were used for silica extraction. The filtrate and washings at each pH were collected and dried in an evaporating dish. These dried filtrates containing soluble minerals were re-dissolved to determine Na, K, Ca, Mg, Fe, and Mn contents by inductively-coupled plasma (ICP) emission spectrometer (Spectro Analytical Instruments, Fitchburg, MA).

2.2. Silica extraction

Silica was extracted from RHA adapting the method of Kamath and Proctor (1998). Sixty ml portions of 1N NaOH were added to the washed and unwashed RHA samples and boiled in covered 250 ml Erlenmeyer flasks for 1 h with constant stirring to dissolve the silica and produce a sodium silicate solution. The solutions were filtered through Whatman No. 41 ashless filter paper, and the carbon residues were washed with 100 ml of boiling water. The filtrates and washings were allowed to cool to room temperature and were titrated with 1N HCl with constant stirring to pH 7. Silica gels started to precipitate when the pH decreased to <10. The silica gels formed were aged for 18 h. Deionized water (100 ml) was added to gels and then the gels were broken to make a slurry. Slurries were then centrifuged for 15 min at 2500 rpm, the clear supernatants were discarded and the washing step was repeated. The gels were transferred into a beaker and dried at 80°C for 12 h to produce xerogels. Selected silica xerogel samples were ground and subjected to additional washing with water. All the samples were stored in airtight plastic bottles. Major modifications in the present method relative to that of Kamath and Proctor (1998) were incorporation of: (1) an initial acid washing, (2) longer drying time to produce the xerogel, and (3) final washing of the xerogel. A flow diagram of the procedure is shown in Fig. 1.

2.3. Moisture content of silica gels

Moisture content of the silica gels was determined using an air oven method (AOAC, 1990). About 1 g of each sample was heated in aluminum moisture pans at 130°C for 1 h. The samples were cooled in a desiccator and weighed. The weight loss (%) was recorded as the moisture content of samples.

2.4. Chemical analyses of silica gels

The silicon content of the samples was estimated using energy dispersive X-ray (EDX) spectroscopy (Kevex Instruments, Valencia, CA). Mineral content of the xerogels was determined by nitric acid digestion followed by atomic emission measurements using ICP emission spectroscopy (Spectro Analytical Instruments, Fitchburg, MA).

X-ray diffraction patterns were obtained by a dual gonimeter X’pert XRD system (Philips Electronic Instruments, The Netherlands) using an acceleration voltage of 40 kV and current of 45 mA. The diffraction angle was scanned from 10° to 90° 2θ, at a rate of 5°/min. Fourier transform infrared (FTIR) data were obtained by adding 100 interferograms using a Impact 410 Nicolet instrument (Analytical Instruments, Madison, WI).

2.5. Experimental design and statistical analyses

Silica was prepared from unwashed and acid washed RHA, with and without final washing of xerogel with water, to investigate the effect of acid washing of RHA
and washing xerogel with water on the purity of silica. Silica was also prepared from RHA washed at pH 7, as an additional treatment control to establish the effect of acid washing. All the treatments were performed in triplicate in a completely randomized design. Data were analyzed by ANOVA and means were separated by the least significant difference when significant F (P < 0.05) values were observed (SAS, JMP IN Version 3.2.1. SAS Institute, Cary, NC, 1997).

3. Results and discussion

3.1. Silica extract composition

EDX elemental spectra of xerogel produced from unwashed RHA showed major element silicon and impurities Na and Cl (Fig. 2). Silica content of the xerogels was estimated from the EDX data based on the assumption that all of the silicon was in the form of silica. The silica and moisture contents of xerogels produced from unwashed RHA were 93% and 2.7%, respectively. Compositions of minerals leached from RHA by acid washing at pH 1, 3, 5, and 7 are shown in Table 1. Since acid leaching at a pH of 1 was found to be more effective in removing Ca, Fe, and Mn from RHA, a washing step at pH 1 was used in all subsequent acid leaching treatments. Unwashed RHA, and RHA washed at pH 7 were used as controls to evaluate the effectiveness of acid washing on the purity of the xerogel. The effect of acid leaching and final washing of xerogel on the mineral content of RHA silica is shown in Table 2. Trace metal ions such as polyvalent iron and manganese with 3+ and 4+ charges, respectively, might have been strongly adsorbed onto silica surface and subsequently trapped inside the silica network during gel formation from silicate solution (Iler, 1979). As a result of this, Fe and Mn might not be completely solubilized during the nitric acid digestion for ICP measurements. The Fe and Mn concentrations in the silica would be affected by the factors such as surface area, porosity, and particle size.

Table 1

<table>
<thead>
<tr>
<th>Minerals</th>
<th>Acid leaching treatment</th>
<th>pH 1</th>
<th>pH 3</th>
<th>pH 5</th>
<th>pH 7</th>
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<tr>
<td>Sodium (%)</td>
<td>2.42&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.97&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.81&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.90&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
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<tr>
<td>Potassium (%)</td>
<td>29.5&lt;sup&gt;a&lt;/sup&gt;</td>
<td>31.7&lt;sup&gt;a&lt;/sup&gt;</td>
<td>39.4&lt;sup&gt;a&lt;/sup&gt;</td>
<td>37.5&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>Calcium (%)</td>
<td>8.14&lt;sup&gt;b&lt;/sup&gt;</td>
<td>7.03&lt;sup&gt;c&lt;/sup&gt;</td>
<td>2.77&lt;sup&gt;b&lt;/sup&gt;</td>
<td>3.93&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>Magnesium (%)</td>
<td>2.57&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2.85&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2.05&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2.41&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>Iron (ppm)</td>
<td>3204&lt;sup&gt;a&lt;/sup&gt;</td>
<td>539&lt;sup&gt;a&lt;/sup&gt;</td>
<td>20&lt;sup&gt;a&lt;/sup&gt;</td>
<td>17&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>Manganese (ppm)</td>
<td>19745&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1557&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2228&lt;sup&gt;c&lt;/sup&gt;</td>
<td>5823&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
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</table>

<sup>a</sup> Values are means of triplicate analyses. In each row, values with different superscripts are significantly (P < 0.05) different from each other. Average standard deviations of Na, K, Ca, Mg, Fe, and Mn measurements were 0.2%, 3%, 0.6%, 0.3%, 20 ppm and 120 ppm, respectively.

Fig. 2. EDX spectrometric data of silica produced from RHA.

![Flow diagram of the procedure used to extract silica from RHA.](image)
of the silica. Hence, the following discussion will be focused on the effect of washing on the major impurities Na, K, and Ca. The initial acid washing did not improve the purity of silica when compared to the purity of silica obtained from unwashed RHA and RHA washed at pH 7. Incorporation of an additional washing step after drying the extracted silica, resulted in a silica product with even lower mineral (Na, and K) content. Washing the dried silica (xerogel) with deionized water is more effective than washing the silica gel (aquagel) prior to drying, in removing minerals from the silica. This could be due to entrapment of metal ions in the silica gel network, which may not be leached out by water washing. Drying silica gel to a very low moisture level might result in disruption of the silica gel network structure and would free the trapped mineral ions (Na, and K). Sodium and potassium ions might be easily leached out by washing the dried gel with water. The Ca content was comparatively lower for silica prepared from acid washed RHA. This may be due to the fact that, Ca being the major divalent cation in RHA, will require lower pH washing as it is strongly adsorbed on the silica surface at pH > 5 (Iler, 1979). Therefore, to keep the Ca content in silica at a lower concentration, an initial acid washing might be required. Further, it should be noticed that the silica extraction yields were similar for unwashed RHA, RHA washed at pH 7 and acid washed RHA. These data indicate that final washing of xerogel is necessary to keep the overall mineral content at a lower concentration. However, if a very low concentration of Ca is required, acid pre-wash of RHA can be used without any adverse effect on silica yield.

3.2. Silica extraction yield

EDX analysis of RHA non-carbon materials showed that silica content of RHA (assuming that all of the Si is in the form of silica) was about 54% (Fig. 3). Carbon content of RHA was 39% (determined by ashing at 660°C for 8 h). Since silica is insoluble at pH < 10, highly alkaline conditions were necessary for efficient extraction of silica from RHA. Yields of silica extracted from 10 g of RHA using 0.1, 0.25, 0.5 and 1.0 N NaOH are shown in Table 3. The pH of dispersion of RHA in 0.1, 0.25, 0.5 and 1.0 N NaOH were 12.0, 12.4, 12.6, and 12.9, respectively. During the course of extraction, the pH of these dispersions decreased to 9.8, 10.8, 11.0, and 11.4, respectively at the end of the 1 h extraction period. Silica yield from RHA for 1 N NaOH extraction was 91% (see Table 4). Extraction with more concentrated NaOH did not improve the silica yield. Therefore, 1 N NaOH was used to extract silica from RHA in this study.

3.3. Structural features of RHA silica

As shown in Fig. 4, the broad X-ray diffraction pattern of RHA silica, which is typical for amorphous solids (Kamath and Proctor, 1998), confirmed the ab-
sence of any ordered crystalline structure. In a previous investigation, X-ray diffraction studies of raw and heated RHA, indicated relatively high disordered structure of silica. Although heating RHA to temperatures over 500°C could convert a less ordered structure to a more highly ordered structure, the absence of a highly ordered structure in RHA was attributed to the thermal insulation properties of the ash (Proctor, 1990).

The major chemical groups present in silica are identified by the FTIR spectra shown in Fig. 5. The broad band between 2800 and 3750 cm\(^{-1}\) was due to silanol OH groups and adsorbed water. The predominant absorbance peak at 1320 cm\(^{-1}\) was due to siloxane bonds (Si–O–Si). The peaks between 1200 and 700 cm\(^{-1}\) are attributed to vibration modes of the gel network (Kamath and Proctor, 1998).

### 4. Conclusions

This study revealed that silica xerogels with 93% silica content and minimal mineral contaminants can be produced from RHA using a simple low energy chemical method. The silica extraction yield from RHA was 91%. The initial acid washing of RHA resulted in a lower Ca content in the silica xerogel. The final washing of the xerogel led to a silica product with lower Na, and K contents. Incorporation of initial acid washing of RHA and final washing of the xerogel resulted in a pure silica with total Na, K, and Ca contents of <0.1%.

### Acknowledgements

We wish to thank Producers Rice Mill (Stuttgart, AR) for providing RHA; and Bruce Cottingham, (Tyson Foods, Springdale, AR) for his assistance during this study.

### References


<table>
<thead>
<tr>
<th>Table 3</th>
<th>Effect of concentration of sodium hydroxide used for silica extraction on the yield of silica*</th>
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</thead>
<tbody>
<tr>
<td>Extraction</td>
<td>Yield of silica (%)</td>
</tr>
<tr>
<td>0.1 NaOH</td>
<td>Not extracted</td>
</tr>
<tr>
<td>0.25 N NaOH</td>
<td>17c</td>
</tr>
<tr>
<td>0.5 N NaOH</td>
<td>35b</td>
</tr>
<tr>
<td>1.0 N NaOH</td>
<td>91a</td>
</tr>
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</table>

*Values are means of triplicate measurements. Values with different superscripts are significantly (P<0.05) different from each other. Average standard deviation of silica yield was 2.3%.

<table>
<thead>
<tr>
<th>Table 4</th>
<th>Yield and moisture content of silica from washed and unwashed rice hull ash (RHA)*</th>
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</thead>
<tbody>
<tr>
<td>RHA</td>
<td>Yield of silica (%)</td>
</tr>
<tr>
<td>Acid washed</td>
<td>91a</td>
</tr>
<tr>
<td>Washed at pH 7</td>
<td>91a</td>
</tr>
<tr>
<td>Unwashed</td>
<td>89a</td>
</tr>
</tbody>
</table>

*Values are means of triplicate measurements. In each column, values with similar superscripts are not significantly (P<0.05) different from each other. Average standard deviations of silica yield (%) and moisture contents (%) were 4 and 0.5, respectively.