

Silica Gel from Rice Hull Ash: Preparation and Characterization

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ABSTRACT

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Rice hulls, a waste coproduct of the rice industry, is composed of 20% silica. The objectives of this study were to develop a method to recover silica from rice hull ash and produce silica gel, and to determine the physical and chemical properties of the rice hull silica gel (RHSG) relative to Trisyl 300, a commercial silica gel. Rice hull ash consisting of 61% silica and 36% carbon was dispersed in sodium hydroxide to dissolve the silica and produce a sodium silicate solution. The latter was titrated to pH 7 with 1M sulfuric acid to obtain a gel at neutral pH. The RHSG was aged, washed, and dried under specific conditions to get a final product that was slightly basic and had a moisture content >65%. Energy dispersive X-ray spectrometry indicated that silicon was the most abundant element present in RHSG and Trisyl 300. Elemental analyses by inductively coupled plasma emission spectroscopy indicated a greater concentration of sodium and sulfur in RHSG relative to that in Trisyl

300. RHSG surface area was 258 m²/g, which was slightly more than half that of Trisyl 300 particles; the particle pore diameter was 121 Å, which was more than twice that of Trisyl 300. Fourier transform infrared spectroscopy showed similarities in chemical structures for both the silica gel samples with respect to siloxane bonds, surface silanol groups, and adsorbed water. X-ray diffraction patterns for both the samples showed a broad peak between 15 and 35° 2θ diffraction angle indicating their amorphous nature. Scanning electron micrographs revealed that RHSG particles ranged in sizes from <5 to >40 μm, whereas Trisyl 300 particles were smaller, ranging in sizes from <5 to 25 μm and had a more uniform appearance. Silica gel production from rice hull ash alleviates the rice hull waste disposal problem and creates a commercially viable value-added product. RHSG has wide-ranging applications in a variety of industries, such as vegetable oil refining, pharmaceuticals, cosmetics, and paints.

Annual rice production in the United States was estimated to be in excess of 171 million cwt in 1996. Arkansas produced ≈72 million cwt of rice, making it the largest rice producing state in the United States (National Agricultural Statistics Service, USDA, Washington DC, 1996). Rice hulls, a coproduct of the rice industry comprises ≈20% of the rice grain and poses a significant waste disposal problem. Traditionally, rice hulls have been disposed in landfills but environmental regulations have limited this, resulting in a need for increased utilization. Rice hull is mainly composed of cellulose, hemicellulose, lignin, and silica (Juliano 1985, Juliano et al 1987). Rice hull has been used as a source of microbial nutrients for single-cell protein production (Hussein et al 1992), for reducing sugar production (Singh et al 1984), and as a raw product for manufacturing ethanol and furfural (Singh et al 1984). Rice hull silica is amorphous and is ≈20% of the rice hull. The silica has been recovered by various methods. Chakraverty and Kaleemullah (1991) used an acid leaching process to remove silica. Luan and Chou (1990) recovered silica by the gasification of rice hull with a pilot flame in a modified fluidized bed. The rice industry has optimized a technology to burn rice hull as an energy source and produce an ash which has ≈60% silica.

Rice hull silica could be used to produce silica gel by a chemical process, but this has not been done commercially or been reported in the literature. Silica gel is widely used in a range of pharmaceutical, cosmetics, paint, and speciality chemical applications that could increase the use of rice hulls (Iler 1979). The cost effectiveness of producing silica gel from rice hull ash would be considerable in that, conventional silica gel production requires smelting of sand in a furnace to produce sodium silicate. This high-energy, expensive process could be eliminated by producing sodium silicate through alkali solubilization of the silica present in rice hull ash and subsequent acid treatment at relatively modest temperatures.

The objectives of this study were to develop a prototype silica gel from rice hull ash and to examine the structure and composition of the rice hull silica gel relative to that of commercial silica gel.

MATERIALS AND METHODS

The silica materials used were: rice hull ash (RHA) which consisted of 61% silica and 36% carbon (Producers Rice Mill, Stuttgart, AR) and Trisyl 300, a commercial silica gel (Grace Davison, Baltimore, MD).

Preparation of Silica Gel from Rice Hull Ash

Rice hull ash (30 g) and 1 L of 1M NaOH were boiled in a covered Erlenmeyer flask for 1 hr with constant stirring. The solution was filtered through Whatman No. 3 filter paper and the carbon residue was washed with 500 mL of boiling water. The filtrate, which is the sodium silicate solution, was cooled to room temperature and titrated with 1M H₂SO₄ very slowly and with constant stirring. The pH of the solution was monitored and titration stopped at pH 7. A soft gel was formed and aged for ≈18 hr. After aging, the gel was gently broken and the slurry was centrifuged for 10 min at 2,500 rpm (model CRU-5000, International Equipment Co., Needham Heights, MA). The clear supernatant solution was discarded. Distilled water (400 mL) was added to the gel, gently swirled, and centrifuged as described. The clear supernatant solution was discarded. The washing step was repeated. The gel was spread on a 9 1/4 × 10 1/2 × 5/8 in. tray and dried in a vacuum oven (Precision, Chicago, IL) at 80°C and 17–19 in. of Hg for 11–13 hr. The dried rice hull silica gel (RHSG) was ground (Swift model TSK-928) and stored in an air-tight plastic bag.

Characterization of RHSG

Chemical and physical analyses were done in triplicate throughout the study.

Moisture content was determined by weighing 2 g of RHSG and Trisyl 300 samples in a tared aluminum moisture dish and heating at 130 ± 3°C for 1 hr in an air oven (Blue M Electric Co., Blue Island, IL). The samples were cooled in a desiccator and weighed. Loss in weight was recorded as the moisture content of the samples.

A rough estimate of the silicon content was made using an energy dispersive X-ray spectrometer (EDX) (Kevex Instruments, Valencia, CA) and its relative abundance compared to other elements. The EDX data was obtained from the samples prepared for scanning electron microscopic analysis. The RHSG and Trisyl 300 samples were analyzed for Na, S, K, Ca, P, and Mg contents by nitric acid digestion (Campbell and Plank 1992) and subsequent measurement by a sequential inductively coupled plasma (ICP) emission spectrometer (model D, Spectro Analytical Instruments, Fitchburg, MA).

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The pH values were determined after adding 2 g of each sample to 50 mL of water, stirring for 15 min and filtering. The pH values of the filtrate were determined by a Corning pH meter 340 (Corning Incorporated, Corning, NY).

An accelerated surface area and porosity system (model 2010, Micromeritics Instrument Corp., Norcross, GA) was used to determine the BET-surface area (adsorbate: N₂ at 77 K), average pore diameter, and pore volume for the samples. Degassing of the samples was done for ≈10–12 hr using a vacuum of 100 mm Hg. The BET parameters were obtained by integration of the BET equation using ASAP-2100 software.

X-ray diffraction patterns of the samples were obtained by a dual goniometer X'pert XRD system (Philips Electronic Instruments, The Netherlands). The generator voltage was maintained at 45 kV, current at 40 mA and the 2θ diffraction angle was measured from 10 to 60° (Gnanasambandam and Proctor 1997).

The Fourier transform infrared (FTIR) spectra of both the samples were evaluated (Impact 410, Nicolet Analytical Instruments, Madison, WI). Interferograms (100) were added to obtain the final spectra (Adhikari et al 1994).

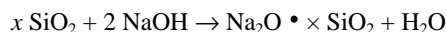
The physical morphology of the samples was determined by mounting the samples on aluminum stubs (Ted Pella, Inc., Redding, CA) with a double-sided adhesive tape, sputter-coating with gold in a Hummer JR sputter coater (Technics EMS, Inc., Springfield, VA) before examining under a scanning electron microscope (model S-2300, Hitachi, Tokyo, Japan).

RESULTS AND DISCUSSION

Preparation of Silica Gel from Rice Hull Ash

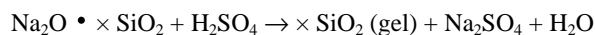
Stoichiometric quantities of RHA, sodium hydroxide, and sulfuric acid were used for RHSG preparation. The two-step process involves: alkali solubilization and acid precipitation.

For alkali solubilization, it is proposed that the silica present in the RHA dissolves in sodium hydroxide producing a sodium silicate solution:



where *x* is a variable that gives the ratio of the SiO₂ to Na₂O in the sodium silicate solution that affects its properties.

For acid precipitation, the sodium silicate solution reacts with sulfuric acid to produce silica gel:



The sodium silicate solution is acid-titrated to neutral pH. The pH curve for this titration is sigmoidal with a sharp change occurring at pH 2–9. The midpoint of the curve is pH 7 which could be the endpoint of the reaction. The final dried RHSG had twice the volume of the RHA used. Commercial silica gel manufacture

differs from the above process in that the sodium silicate solution is prepared by mixing sand (silicon dioxide) with sodium carbonate in a furnace. The acid treatment step is similar.

RHSG and Trisyl 300 contained 67.47 and 58.19% water, respectively (Table I). Silica gel is a high moisture product made up of a network of interconnected pores with a silicon dioxide core where water is entrapped and a surface consisting of silanol groups (Iler 1979). The surface silanol groups are responsible for physically adsorbing water molecules and holding them in place by hydrogen bonding. The water entrapped in the core, the silanol hydroxyl groups, and the physically adsorbed water together represent the moisture content in the silica gel samples.

Quantitative analysis of the elements identified by EDX shows Si was the most abundant element in both the samples (Fig. 1). In addition to silicon, RHSG also showed presence of Na unlike Trisyl 300. Both the samples showed the presence of gold. This is expected as both samples were coated with a thin film (≈100 Å) of gold during sample preparation for EDX and SEM evaluation.

Table I shows the elemental content of RHSG and Trisyl 300. RHSG contains significantly more Na and S than did Trisyl 300. This confirms our EDX results with respect to Na. The high concentration of Na and S in RHSG is probably due to the sodium hydroxide and sulfuric acid reagents used in its preparation that did not completely react during the process. Small amounts of sodium sulfate may also be present in the RHSG, contributing to its sodium and sulfur concentration. Minor elements present in RHSG were K, Ca, P, and Mg in decreasing order of concentrations, respectively. These elements were present in concentrations >0.1% in RHA and may have been carried over into the RHSG. The

TABLE I
Chemical (%) and Physical Properties of Rice Hull Silica Gel (RHSG) and Trisyl 300^a

Properties	RHSG	Trisyl 300
Moisture content	67.47 ± 3.38	58.19 ± 1.44
Sodium	2.037 ± 0.223	0.014 ± 0.001
Sulfur	1.261 ± 0.143	0.009 ± 0.0
Potassium	0.038 ± 0.011	0.007 ± 0.001
Calcium	0.008 ± 0.001	0.011 ± 0.0
Phosphorus	0.004 ± 0.001	0.001 ± 0.0
Magnesium	0.002 ± 0.001	0.002 ± 0.001
pH	8.8 ± 0.02	2.84 ± 0.0
Surface area (m ² /g)	258.06 ± 3.94	462.75 ± 0.274
Pore diameter (°A)	121.65 ± 11.96	50.69 ± 0.057
Pore volume (cm ³ /g)	0.7986 ± 0.04	0.625 ± 0.003

^a Mean or average of triplicate determination.

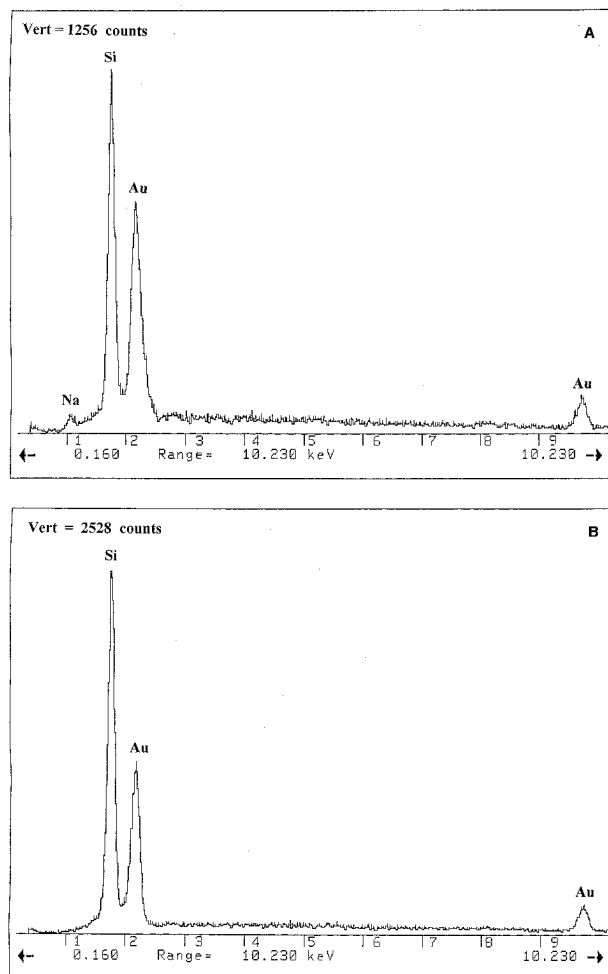


Fig. 1. Energy dispersive X-ray (EDX) spectrometry results showing silicon content of rice hull silica gel (A) and Trisyl 300 (B).

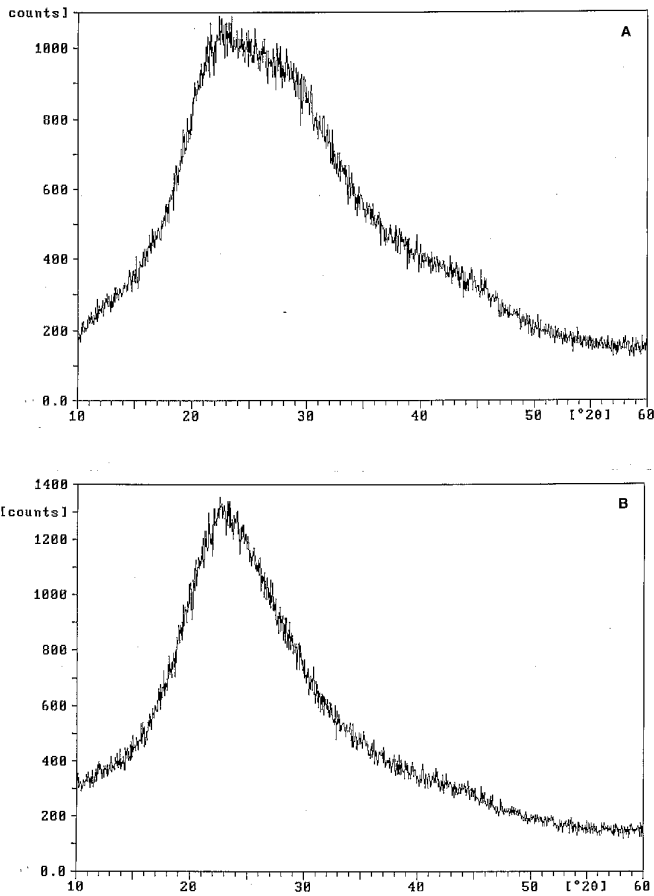


Fig. 2. X-ray diffraction patterns for rice hull silica gel (A) and Trisyl 300 (B).

minerals identified were those found in rice hulls by Banerjee and Pandey (1989), with the exception of sulfur. They reported relative concentrations as $K > Ca > Na > Mg$. Trisyl 300 also had trace amounts of these elements.

RHSG had pH 8.8, whereas Trisyl 300 had pH 2.84 (Table I). During the preparation of RHSG, the highly basic sodium silicate solution was acidified to pH 7. Incomplete neutralization or presence of residual OH^- could be responsible for the slightly basic pH of RHSG. It is also possible that some residual OH^- ions may have bonded with the silanol (Si-OH) groups of the RHSG by weak hydrogen bonds and were broken during slurry preparation releasing the OH^- ions. The concentration of the OH^- ions may have increased during the drying step of RHSG preparation. The acidic pH of Trisyl 300 is due to citric acid which is added to chelate phosphatides and metals. Our pH data for Trisyl 300 is in agreement with the manufacturer's published information.

The BET-surface area (N_2 , 77 K) of RHSG was slightly more than half that of Trisyl 300 (Table I). Although the BET method assumes that the adsorbent surface is uniform and covered with a monolayer of adsorbed molecules, it is a useful tool for comparative studies (Roberts et al 1980). The pore diameters for RHSG and Trisyl 300 were 121.65 and 50.69 Å, respectively, indicating that RHSG particles were larger than those of Trisyl 300 particles. As pore size decreased, the number of particles present in a gram of sample increased resulting in an increase in the surface area. The aging process in silica gel preparation is when the pore sizes and particle structure develop (J. Leake, unpublished). Aging and washing parameters responsible for unique physical characteristics in commercial silica gel preparation are industrial proprietary information. The pore volume for RHSG was $0.799 \text{ cm}^3/\text{g}$ and that for Trisyl 300 was $0.625 \text{ cm}^3/\text{g}$.

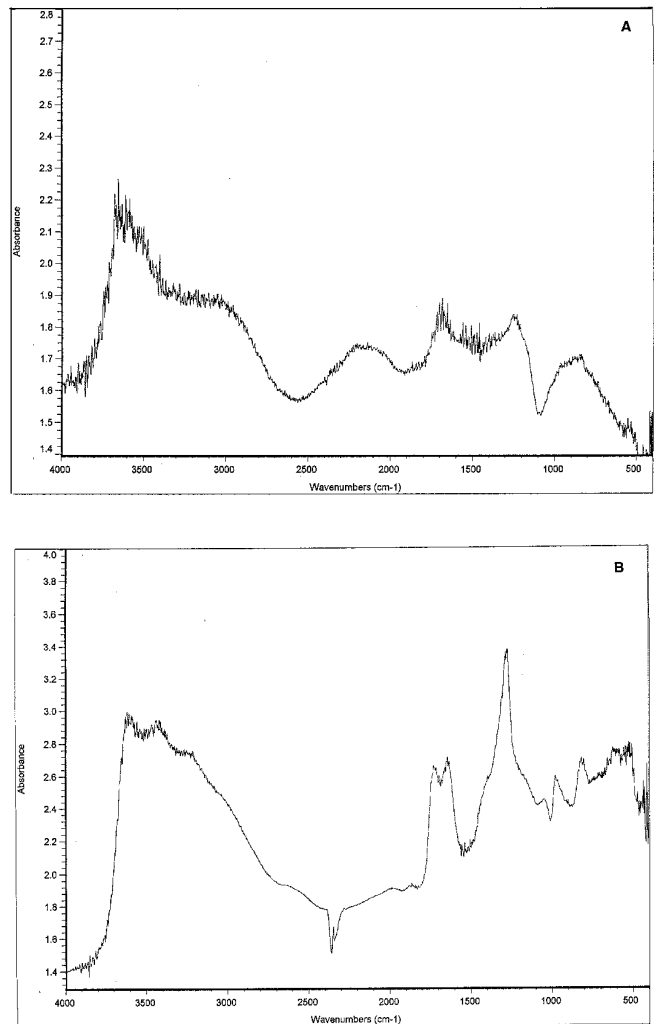


Fig. 3. Fourier transform infrared (FTIR) spectra of rice hull silica gel (A) and Trisyl 300 (B).

X-ray diffraction patterns for the RHSG and Trisyl 300 samples are shown in Fig. 2. A lack of sharp, defined peaks indicates non-crystalline or amorphous material (Chakraverty and Kaleemullah 1991). Amorphous substances display an atomic arrangement that is either random or has very short-range order (Ladd and Palmer 1993). The broad 'hump' between 15 and $35^\circ 2\theta$ diffraction angle is characteristic of amorphous substances (Gnanasambandam and Proctor 1997).

The key chemical groups present in RHSG and Trisyl 300 were identified by respective FTIR spectra (Fig. 3). In general, the FTIR spectra of Trisyl 300 was sharper, had lower noise and higher intensity when compared to that of RHSG. A broad band between $2,800$ and $3,750 \text{ cm}^{-1}$ indicates surface OH groups (Adhikari et al 1994, Yates et al 1997). This stretch is due to the silanol OH groups and the adsorbed water bound to the silica surface by hydrogen bonds. A sharper peak or shoulder at $\approx 3,700 \text{ cm}^{-1}$ in both spectra is mainly due to the isolated silanol groups that are not hydrogen-bonded to other silanols. The bending vibration peak for H-OH is shown at $1,650 \text{ cm}^{-1}$ (Proctor et al 1995) and is more pronounced in the spectra of Trisyl 300. The bands at 800 , $1,080$, and $1,220 \text{ cm}^{-1}$ which are more visible in the Trisyl 300 could be attributed to the network vibration modes indicating a highly condensed gel network. The peak between 1250 - 1400 cm^{-1} in the Trisyl 300 spectra is due to the structural siloxane bonds (Si-O-Si) and is evident to a lesser degree in the RHSG spectra.

The scanning electron micrographs for RHSG and Trisyl 300 are shown in Fig. 4. The RHSG particles range from <5 to $>40 \mu\text{m}$

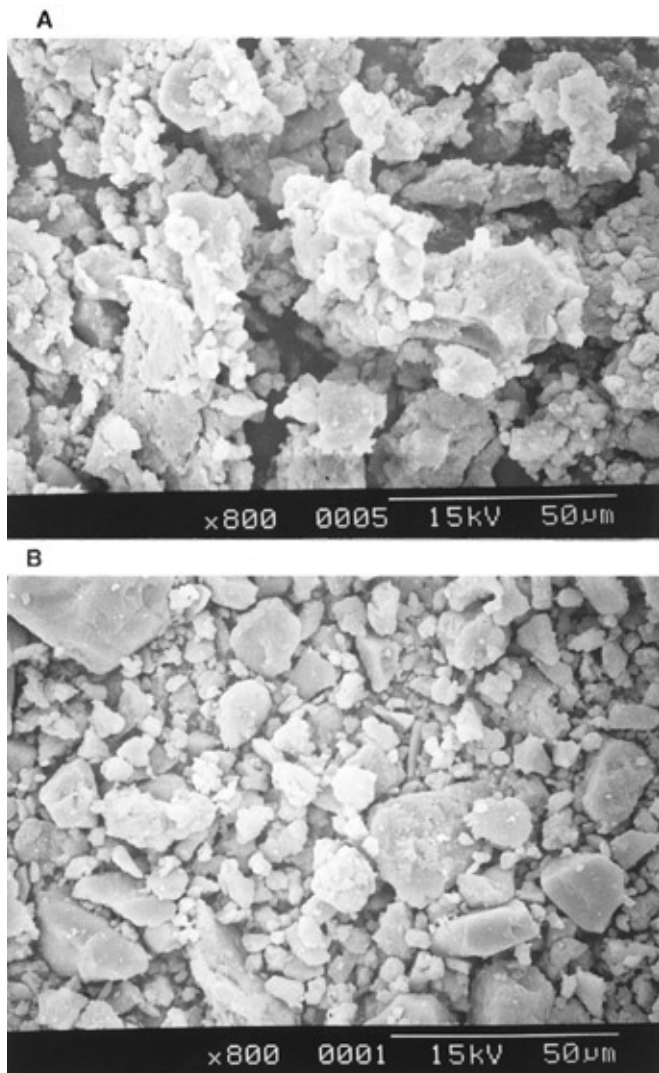


Fig. 4. Scanning electron micrographs (800 \times) for rice hull silica gel (A) and Trisyl 300 (B).

in size. Trisyl 300 particles seemed to be more uniform in appearance with sizes ranging from <5 to 25 μm . These observations are consistent with our pore diameter results wherein RHSG particles were found to be larger than Trisyl 300 particles. The lack of uniformity in the RHSG particle size is a result of the laboratory grinding process which differs from the industrial process for commercial silica gel products. Trisyl 300 undergoes a micronization step during its processing to obtain homogeneous particle properties.

The microstructure of RHSG is different from that of RHA. RHA has a "corn cob" appearance (Proctor 1990) that breaks during RHSG preparation due to the alkali leaching process releasing silica present in the rice hulls.

CONCLUSIONS

A rapid, simple, and low-energy method has been developed to produce silica gel from rice hull ash by alkali solubilization and subsequent acid treatment. The novel silica gel which has a

moisture content of >65% has certain physical and chemical properties that are similar to Trisyl 300, a commercial silica gel. The newsilica gel preparation process not only alleviates the problems associated with rice hull waste disposal but also generates a higher profit margin, value-added product creating a profitable new industry in rural America. Future studies on the rice hull silica gel will evaluate its adsorptive performance in vegetable oil refining.

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LITERATURE CITED

- Adhikari, C., Proctor, A., and Blyholder, G. D. 1994. Diffuse-reflectance fourier-transform infrared spectroscopy of vegetable oil triglyceride adsorption on silicic acid. *J. AOCS* 71:589-594.
- Banerjee, D., and Pandey, G. S. 1989. Metallic constituents in paddy husk. *Biological Wastes* 30:71-74.
- Campbell, C. R., and Plank, C. O. 1992. Sample preparation: Organic matter destruction-dry ashing. Pages 7-8 in: *Southern Cooperative Series Bull.* 368. C. O. Plank, ed. University of Georgia: Athens, GA.
- Chakraverty, A., and Kaleemullah, S. 1991. Conversion of rice husk into amorphous silica and combustible gas. *Energy Conserv. Mgmt.* 32:565-570.
- Gnanasambandam, R., and Proctor, A. 1997. Soy hull as an adsorbent source in processing soy oil. *J. AOCS* 74:685-692.
- Hussein, A. M., El-Saied, H., and Yasin, M. H. 1992. Bioconversion of hemicelluloses of rice hull black liquor into single-cell protein. *J. Chem. Tech. Biotechnol.* 53:147-152.
- Iler, R. K. 1979. Silica gels and powders. Pages 462-729 in: *The Chemistry of Silica*. R. K. Iler, ed. John Wiley and Sons: New York.
- Juliano, B. O. 1985. Rice hull and rice straw. Pages 695-698 in: *Rice: Chemistry and Technology*. B. O. Juliano, ed. Am. Assoc. Cereal Chem.: St. Paul, MN.
- Juliano, B. O., Maningat, C. C., and Pascual, C. G. 1987. Properties of fraction of rice hull. *Phytochemistry* 26:3261-3263.
- Ladd, M. F. C., and Palmer, R. A. 1993. Crystal geometry. 1. Pages 2-3 in: *Structure Determination by X-ray Crystallography*. M. F. C. Ladd, and P. A. Palmer, eds. Plenum Press: New York.
- Luan, T.-C., and Chou, T.-C. 1990. Recovery of silica from the gasification of rice husks/coal in the presence of a pilot flame in a modified fluidized bed. *Ind. Eng. Chem. Res.* 29:1922-1927.
- Proctor, A. 1990. X-ray diffraction and scanning electron microscope studies of processed rice hull silica. *J. AOCS* 67:576-584.
- Proctor, A., Adhikari, C., and Blyholder, G. D. 1995. Mode of oleic acid adsorption on rice hull ash cristobalite. *J. AOCS* 72:331-335.
- Roberts, P. V., Mackay, D. M., and Cannon, F. S. 1980. Physical characterization and preparation of activated carbon. Pages 7-17 in: *Preparation and Evaluation of Powdered Activated Carbon from Lignocellulosic Materials*. R. Dobbs, ed. U.S. EPA: Cincinnati, OH.
- Singh, A., Das, K., and Sharma, D. K. 1984. Production of xylose, furfural, fermentable sugars and ethanol from agricultural residues. *J. Chem. Tech. Biotechnol.* 34A:51-61.
- Singh, A., Das, K., and Sharma, D. K. 1984. Production of reducing sugars from bagasse and rice husk by acid hydrolysis. *Agric. Wastes* 9:131-145.
- Yates, R. A., Caldwell, J. D., and Perkins, E. G. 1997. Diffuse reflectance fourier transform infrared spectroscopy of triacylglycerol and oleic acid adsorption on synthetic magnesium silicate. *J. AOCS* 74:289-292.

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