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Production of High Purity Amorphous Silica from Rice Husk

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Abstract

Combustion of the rice husk produces rice husk ash, which consists of mainly silica. High purity silica can be produced by controlled combustion after acid treatment. In this study, leaching of rice husk with hydrochloric acid and sulfuric acid were carried out prior to combustion to obtain purer silica. It was found that pre-treatment of the rice husk with sulfuric acid had accelerated the hydrolysis and decomposition of organic components as revealed by thermogravimetry (TG) and Scanning Electron Microscopy (SEM) analyses. In a systematic study, the combustion of un-leached, hydrochloric acid-leached and sulfuric acid-leached rice husks were performed in a muffle furnace at 500, 600, 700, 800 and 900°C for 2 h. Results demonstrated that all the samples produced amorphous silica (SiO₂) and the average particle size were in the range of 0.50 to 0.70 μm. The effect of combustion at different temperatures between 500°C and 900°C on the silica production is very small, particularly at temperature above 600°C. Thus, amorphous silica with purity above 99% as confirmed by X-Ray Fluorescence (XRF) analysis can be produced by hydrochloric and sulfuric acids leaching of the rice husk, followed by controlled combustion at 600°C for 2 h. The BET surface area of the silica produced after leaching the rice husk with hydrochloric acid was higher (218 m²/g) than with sulfuric acid (209 m²/g). The silica obtained has potential application as filler in plastics and rubber compounding.

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1. Introduction

Rice husk is the outer covering of the rice grain, which is a by-product of the rice milling process. It is an agricultural waste material in all rice-producing countries. Most of the rice husk usually ends up either being dumped or burned in open spaces, thus causing damage to the land and environmental pollution. Much efforts have been made to utilize the rice husk including as an alternative fuel for energy production^{1, 2}, production of activated carbon³ and as a raw material for manufacture of industrial chemicals based on silica and silicon compounds⁴.

The major components of rice husk are organic materials such as hemicellulose, cellulose and lignin totaling about 75 – 90% and the remaining ash content of 17 – 20%⁵. The ash mainly consists of >90% silica and some metallic impurities. Combustion of rice husk under controlled conditions leads to the productions of rice husk ash containing almost pure silica. The metallic impurities such as iron (Fe), manganese (Mn), calcium (Ca), sodium (Na), potassium (K) and magnesium (Mg) that influence the purity and color of the silica could be eliminated by pre-treatments with hydrochloric acid, sulfuric acid or nitric acid prior to combustion⁶.

It has been reported that at 600 to 1000°C and depending on the time of combustion⁷, amorphous silica is formed, but at higher temperature, crystalline silica is obtained. In this systematic study, the combustion of un-leached, hydrochloric acid-leached and sulfuric acid-leached rice husks were performed in a muffle furnace at 500, 600, 700, 800 and 900°C for 2 h. The aim of the present study is to investigate the optimum conditions for obtaining high purity silica. The properties studied include functional groups determination, structure properties, SiO₂ content, Brunauer-Emmett-Teller (BET) surface area and particle size.

2. Materials and Methods

2.1. Production of silica from rice husk

Rice husk was obtained from BERNAS rice mill, Tg.Karang, Selangor, Malaysia. The rice husk was washed with sodium dodecyl sulfate solution at constant stirring for 10 min to remove dirt and water soluble impurities. Then, the rice husk was further rinsed with distilled water to remove surfactant. It was first dried at room temperature and later dried in an air-oven at 110°C for 24 h. The washed rice husk obtained is designated as un-leached rice husk. Then, the washed rice husk was separately treated with hot acid at ~60°C with hydrochloric acid or sulfuric acid at concentration of 0.5 M for 30 min with constant stirring. After the acidic solution was drained off, the rice husk was rinsed with distilled water until free from acids, filtered and air-dried. The acid-leached rice husk was then dried in an air-oven at 110°C for 24 h. The un-leached rice husk and acid-leached rice husk was placed in a muffle furnace and heated at 500, 600, 700, 800 and 900°C for 2 h to obtain un-leached rice husk ash and acid-leached rice husk ash, respectively.

2.2. Characterizations of rice husk

The thermogravimetric (TG) analysis was performed on a Perkin Elmer TGA6 instrument. Sample of 5 – 7 mg was heated at heating rates 20°C/min from 50°C to 900°C under nitrogen atmosphere with flow rate of 20 mL/min.

The Scanning Electron Microscopy (SEM) analyses of the un-leached and acid-leached rice husk were conducted on a FESEM JSM 6701F (JOEL). The sample was placed onto the specimen stub and coated with platinum evaporative coating under high vacuum. It was operated at 15kV with 15mm working distance.

2.3. Characterizations of silica

The functional groups in the sample were determined using a Thermo Scientific FTIR Nicolet 6700 equipped with attenuated total reflectance (ATR) accessory. The spectra were recorded with 32 scans at a resolution of 4 cm⁻¹ in the range of 4000-400 cm⁻¹.

The X-ray diffraction (XRD) patterns were obtained using Bruker D8 Discovery X-ray Diffractometer using CuK α operated at 40 kV and 40 mA and 2Theta between 5° to 50°. The EVA™ Software was used to record and analyze the structural pattern of sample.

About 0.05g of the sample was dispersed in 10g distilled water, vigorously mixed and sonicated for 30 min. The ultrasonic waves were used to break or minimize any particle agglomerates that may be present in the suspension. Measurements were taken using ZetaPlus Zeta Potential Analyzer (Brookhaven Instruments Corporation).

The silica content and metallic impurities in the samples were estimated by Wavelength Dispersive X-Ray Fluorescence (XRF) Spectrometer (model AxiosMAX WDXRF Spectrometer, PANalytical).

The surface area and pore volume of sample were measured by Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively according to ASTM D3663-03 using Micromeritics TriStar II Surface Area and Porosity Analyzer.

3. Results and Discussion

3.1. Thermogravimetric (TG) analysis of rice husk

TG analysis was used to determine the existence of organic components in the rice husk. The TG curves of un-leached and acid-leached rice husks are depicted in Fig.1. It can be seen that initial weight loss occurs within the range of 50 – 150°C, irrespective of acid leaching, with a weight loss of 1 - 2% corresponds to loss of water and other volatile substances.

The second stage reveals a rapid and large weight loss at temperature between 240 - 360°C. This is due to the thermal decomposition of hemicellulose and cellulose as a major organic component in the rice husk⁸. Several researchers^{9, 10} reported that hemicellulose decomposes mainly at 150 - 350°C which is the least stable component of rice husk and cellulose decomposes between 275 - 350°C. The acid-leached rice husk showed lower thermal stability compared to un-leached rice husk due to acid hydrolysis of hemicellulose and cellulose into lower molecular weights compounds that are more easily thermo-degraded.

The third stage shows a weight loss of about 26 – 31% that could be due to lignin, a thermally more stable aromatic polymer which undergoes gradual decomposition between 370 and 600°C. The residual of ash is mainly the non-combustible silica (~16%, >600°C).

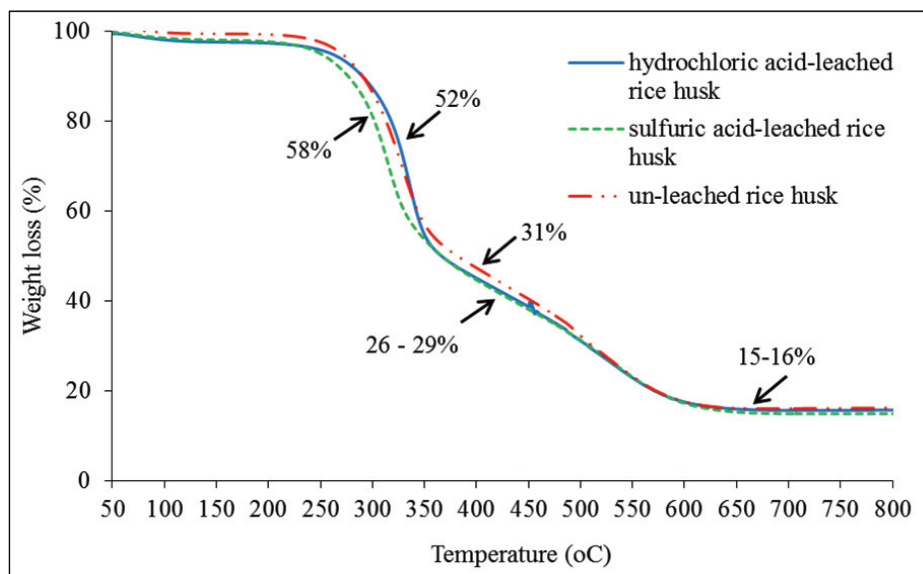


Fig.1. Thermogravimetry (TG) curves of un-leached and acid-leached rice husks (RH)

3.2. SEM analysis of rice husk

Fig. 2 shows the morphology of outer surfaces of un-leached and acid-leached rice husks. The outer surface of rice husk is uneven and highly roughened. After acid leaching, a significant change in rice husk morphology can be seen. The surfaces of un-leached rice husk showed greater degree of roughness than those that have been leached with dilute acids, presumably due to the hydrolysis of some organic components by the acids.

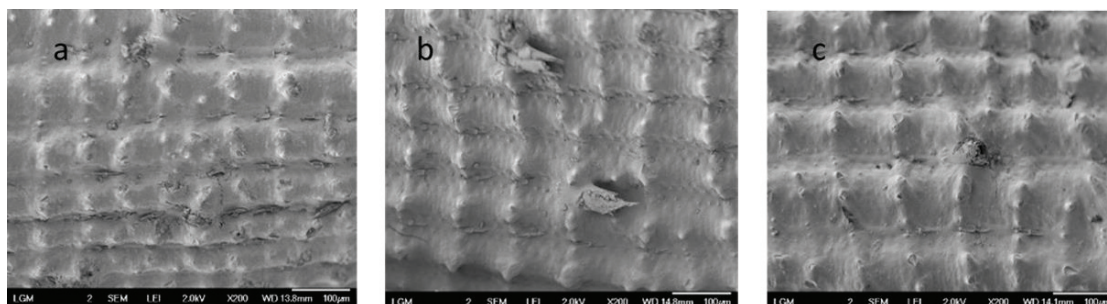


Fig. 2. Morphology of (a) un-leached; (b) hydrochloric acid-leached; (c) sulfuric acid-leached rice husks

3.3. Fourier transform infrared (FTIR) analysis of silica

The FTIR spectra of un-leached silica and acid leached-silica at 600°C are shown in Fig. 3 (combustion at 600°C is taken as an example, and the spectra of silica at other combustion temperatures were similar). The notable absorption peaks at 1044 cm^{-1} , 796 cm^{-1} and 438 cm^{-1} attributes to O-Si-O stretching and bending vibrations.

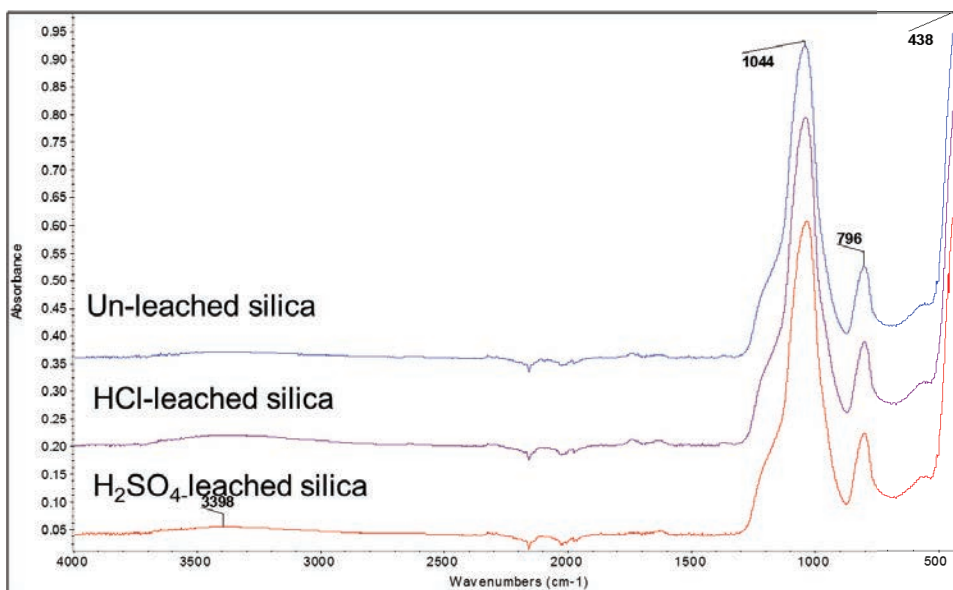


Fig. 3. FTIR spectra of un-leached, hydrochloric acid-leached and sulfuric acid-leached silica

3.4. XRD analysis

XRD patterns of the un-leached silica and sulfuric acid-leached silica at various combustion temperatures are shown in Fig. 4a and 4b, respectively. The XRD patterns of the hydrochloric acid-leached silica showed similar patterns as sulfuric acid-leached silica. The broad diffused peaks with maximum intensity at $2\theta = 22^\circ$ are observed, indicating amorphous nature of silica. However, the sharpness of this peak increases with combustion temperatures for un-leached silica shown in Fig. 4a. This indicates that the crystallization transformation of silica starts to occur at 900°C . On the other hand, acid-leached silica shows completely amorphous structures upon combustion below 900°C . This is because of the removal of alkali metals during acid-leaching which hinders eutectic reaction with silica¹¹. Thus, the optimization of combustion temperature of rice husk is necessary to hinder crystallization of silica.

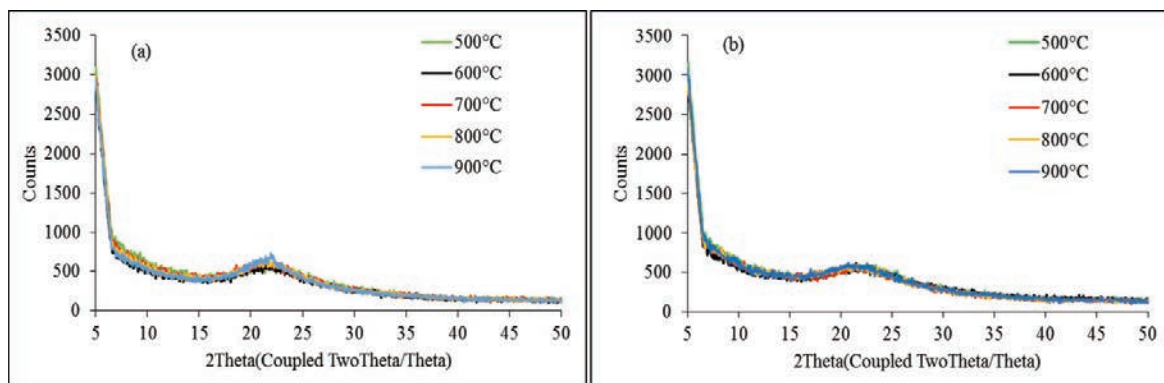


Fig. 4. XRD patterns of a) un-leached b) sulfuric acid-leached silica at various combustion temperatures

3.5. Particle size analysis

The average particle size of silica at various combustion temperatures is given in Table 1. It varies from $0.50\ \mu\text{m}$ to $0.70\ \mu\text{m}$ and has no significant change between combustion temperatures investigated.

Table 1. Average particle size of un-leached, hydrochloric acid-leached and sulfuric acid-leached silica

Sample/ $^\circ\text{C}$	500	600	700	800	900
Un-leached silica	0.59	0.53	0.64	0.59	0.60
Hydrochloric acid-leached silica	0.50	0.52	0.43	0.57	0.72
Sulfuric acid-leached silica	0.55	0.49	0.52	0.69	0.74

3.6. XRF analysis

XRF is used in identifying the chemical compositions and purity of silica produced from the rice husk. Table 2 shows that silica (SiO_2) is the major components and it also contains low amount of metallic impurities. It is noteworthy that acid leaching is effective in removal of metallic impurities in rice husks.

Table 2. Elements in un-leached and acid leached silica, in weight %

Elements, %	Un-leached silica at 600°C	Hydrochloric acid -leached silica at 600°C	Sulfuric acid - leached silica at 600°C
SiO_2	95.772	99.582	99.083

MgO	0.397	0.016	0.035
Al ₂ O ₃	0.046	0.168	0.605
P ₂ O ₅	0.459	0.106	0.130
SO ₃	0.653	0.017	0.046
K ₂ O	0.618	0.018	0.016
CaO	0.667	0.043	0.050
MnO	0.054	NA	0.014
Fe ₂ O ₃	0.050	0.025	0.017
ZnO	0.015	0.002	0.004
Cl	0.010	0.007	NA
Na ₂ O	1.259	NA	NA

NA – not available

3.7. Surface area and porosity

The surface area, pore volume and pore diameter of silica are given in Table 3. The BET surface area and pore volume of acid-leached silica are higher than un-leached silica. This indicates that acid leaching produce significant effect on the surface area as well as pore volume of silica. The increase in surface area of acid-leached silica is mainly attributed to the hydrolysis of hemicellulose and cellulose into smaller compounds which could decompose easier during combustion. Thus, high porous structure is obtained as confirms by the increase in pore volume. The average pore diameter of acid-leached silica is ~5.6 nm and un-leached silica is 7 nm, indicating the silica produced is mainly mesoporous. It is noteworthy that either hydrochloric acid or sulfuric acid has significantly increases the surface area and the pore volume, and reduces the pore diameter.

Table 3. BET surface area of un-leached, hydrochloric acid-leached and sulfuric acid-leached silica

Sample	BET surface area, m ² /g	Total pore volume, cm ³ /g	Average pore diameter (4V/A by BET), nm
Un-leached silica at 600°C	116	0.23	7.84
Hydrochloric acid-leached silica at 600°C	218	0.32	5.56
Sulfuric acid-leached silica at 600°C	208	0.31	5.68

4. Conclusion

An amorphous silica with purity above 99% were produced from rice husk by hydrochloric or sulfuric acid leaching followed by controlled combustion at 600°C for 2 h. Silica obtained under these conditions has potential application as filler in plastics and rubber compounding. The high purity amorphous silica has large BET surface area, which might be useful as an adsorbent or catalyst support in fine chemical synthesis.

Acknowledgement

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