

Production of High Purity silica from Rice Husk

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Abstract

High purity amorphous silica has several industrial applications. The conventional methods of its production are chemical and energy intensive, and they also generate carbon dioxide. This study was undertaken to investigate the production of this vital material from rice husk using a low cost and green process route. Rice husk was pretreated using sodium dodecyl sulphate solution, citric acid and hydrogen peroxide. The pretreated rice husk was dried in an oven dryer at 110°C. The dried pretreated husk was combusted at process setting conditions which were designed using Design Expert software. The optimum process conditions were determined using response surface methodology (RSM). The amorphous silica produced under these optimum conditions were analysed. The composition, phase and surface area of the silica were investigated using X-ray diffraction, X-ray fluorescence, scanning electron microscopy and BET surface analyser. A high purity silica (99.97%) was obtained. The silica has a specific surface area of 229 m²g⁻¹ with pronounced porosity. The silica will find useful application in photovoltaic industry for the manufacture of solar cells

Keywords: High purity, Silica, rice husk, surface area, response surface methodology.

Introduction

Silica is the most abundant compound on earth. It is applied in a wide range of industries. Its usefulness to specific industry depends on the grade of silica which is defined as the amount of silica content. Photovoltaic silica is 99.9 percent silica with impurities less than 1ppb. For various applications, silica must be in the amorphous form or non-crystalline form. The conventional methods of producing amorphous silica are very energy and chemical intensive, and they produce a lot of carbon dioxide. Biomass resources have been proven as alternative feedstock for low energy, and green process for the production of silica [Johan et al. (2016)]. Rice husk contain about 20% silica. The production of silica from biomass has recently attracted great research interest Gosh and Bharathacherjee (2013) prepared silica using acid and alkali sodium hydroxide. Their study indicated that various grades of silica can be prepared from rice husk. Umeda and Kondoh (2008) reported on the production of high quality amorphous silica from rice husk using citric acid pretreatment. They established that the metallic impurities in hush can be removed by the chelate reaction between the carboxyl group and the metal elements. Johan, E. et al. produced silica of more than 99% purity from rice husk using citric acid treatment before heating the husk at 700 to 1000°C. They converted the silica into ZSM-5 catalyst. Ngoc N.N. et al. (2018) prepared amorphous silica from rice husk using two methods. They characterized the silica using XRD, EDX, SEM and BET techniques. The silica powder 50 nm sized and had 186 m²/g specific surface area. Dizagi et al. (2019) prepared biogenic silica with purity up to 99 % from rice husk using hydrochloric acid leaching. Azat, S. et al. (2019) extracted high purity silica from rice husk using Hydrochloric acid leaching before calcining at 600°C They utilized the silica for the production high value silica based materials. ASkaruly, K. et al. (2020) obtained high purity silica from rice husk using pretreatment with hydrochloric acid These investigations are limited to narrow and isolated process conditions and lack data on optimized process. These short comings have provided the motivation for further research on the subject matter. This paper reports on the production of high quality silica from readily available rice husk in Nigeria.

Methodology

Rice husk was obtained from Anambra Rice Mill and washed with sodium dodecyl sulphate solution at a concentration of 1M at constant stirring for 30 minutes to remove dirt and water soluble impurities. The husk was further rinsed with distilled water to remove any surfactant. The washed husk was treated with hot 0.5 M citric acid at 60°C for 30 minutes with constant stirring. This process ensured the removal of elemental metals and metallic oxides that influences the purity, structure and colour of silica. The acidic solution was drained. The rice husk was rinsed with distilled water until it was free of acid.

The pretreated sample was mixed in a 2M hydrogen peroxide solution in a beaker. The solution was stirred for 30 minutes at 60°C. The pretreated husk was filtered, air dried, and later dried in an air oven dryer at 110°C for 12 hours. The husk was then combusted at 800°C for 2 hours in a muffle furnace. This served as a control experiment. An experimental design (DOE) was carried out using Design Expert software. The pretreated husk was then roasted at the resultant experimental settings. The responses from the experiments were analysed for models, ANOVA, diagnostics and model graphs. The model was showed in response surface and contour 3D plots. The maximization of purity of silica was carried out at the range of the variables. The optimized values of the factor settings were then used to repeat the experiment in triplicates. The silica produced was characterised with XRF equipment.

The rice husk ash (RHA) and the silica were characterised for surface area, particle morphologies, structure and content using Coulbler 5A 3000 analyser, FESEMJSM 670 scanning electron microscope, Bruke D8 Discovery X-Ray Diffractometer with Xpert graphics software package and X-Ray Fluorescence (XRF) Spectrometer respectively.

The Coulter 5A 300 Analyzer, together with BET calculation model was used to determine the surface area. 2 g of the silica was weighed into the glass tube sample holder of the instrument and the free space was measured using helium gas. The sample tube and contents were then out gassed with the system's in-built vacuum pump. A known dose of Nitrogen (adsorbate gas) was introduced into the previously evacuated tube containing the sample. The glass tube was maintained at constant temperature by immersion into a Dewar of Nitrogen. When the pressure in the tube was equilibrated, the resulting pressure reading was recorded and then used to compute the volume of gas adsorbed on the surface and pores of the sample.

The scanning electron microscope was used to characterize the particle morphologies of the samples. Sample specimens with diameter of 12 mm each were gold plated in a gold sputter coater for 90 seconds and at 15 mA current output. The gold coating was necessary to ensure a conducting sample was obtained for electron bombardment and characterization. The scanning electron microscope was operated at 15KV and a working distance of 15 mm selected area was focused and the micrograms were taken.

The X-ray diffractometer with XPERT graphic software package was employed to analyze the structure of the silica samples. An aluminum glass composite sample holder with a rectangular slot measuring 2 cm x 1 cm x 0.2 cm was filled with powdered sample using the front loading method. The samples were analyzed using the CuK ($\lambda = 1.54056\text{\AA}$) with Nickel filter. Bragg's angle (2 theta) range of 10 – 50° and scan speed of 0.72 degree per minutes with the step size of 0.015° was used. The diffractometer was operated at 15 KV and 15 mA. The structural pattern was recorded and analyzed by the XPERT software.

The silica content and metallic impurities in the samples were determined with Dispersion X- Ray Fluorescence (XRF) Spectrometer model Axioms AWDXRF pan analytical..

Results

The results from the experiments are presented in the subsections below.

Chemical composition

The chemical composition of the as received rice husk ash (RHA) is given in Table 1.

Oxides Present	As Received RHA	RHA Lit. Values (Houston et al. 1972)
SiO ₂	93.6	86.9
MnO	0.06	Not available
Al ₂ O ₃	0.51	Not available
Fe ₂ O ₃	0.41	0.54
Na ₂ O	0.90	0.0 – 1.25
K ₂ O	2.14	0.58 – 2.5
CaO	0.07	0.2 – 1.5
MgO	0.40	0.12 – 1.96
P ₂ O ₃	0.35	0.2 – 2.85

The content of silica in the as received RHA is high but not enough for several application. This justifies the need for further treatment of the rice husk ash (RHA). The value is higher than the established value in literature. Geneieva et al. (2008) reported similar data and pointed out that compositional differences in RHA may be influenced by geographical and climate factors, soil chemistry and fertiliser employed in cultivating the rice. Azat S. et al. (2019) also established that the pretreatment of rice husk in dilute hydrochloric acid before combustion reduced the total content of impurities in the produced RHA.

Percentage Weight Loss

The percentage weight losses of the pretreated and as received rice husk were plotted against temperature as shown in Figure 1. The initial weight loss between 50 and 100°C corresponds to the loss of water and other volatile substances present in the husk. The second stage weight loss in the temperature interval 250 and 400°C was rapid and large. This corresponds to the thermal decomposition of the cellulose and hemicellulose. This phenomenon is supported by literature data [Shafizadeh et al. (1976) and Antal et al. (1983)]. The third stage shows a weight loss of about 23 to 35 percent which could be due to lignin. Lignin is thermally more stable aromatic polymer which undergoes gradual decomposition between 550 to 800°C. The residual ash is mainly the non- combustible highly unreactive silica.

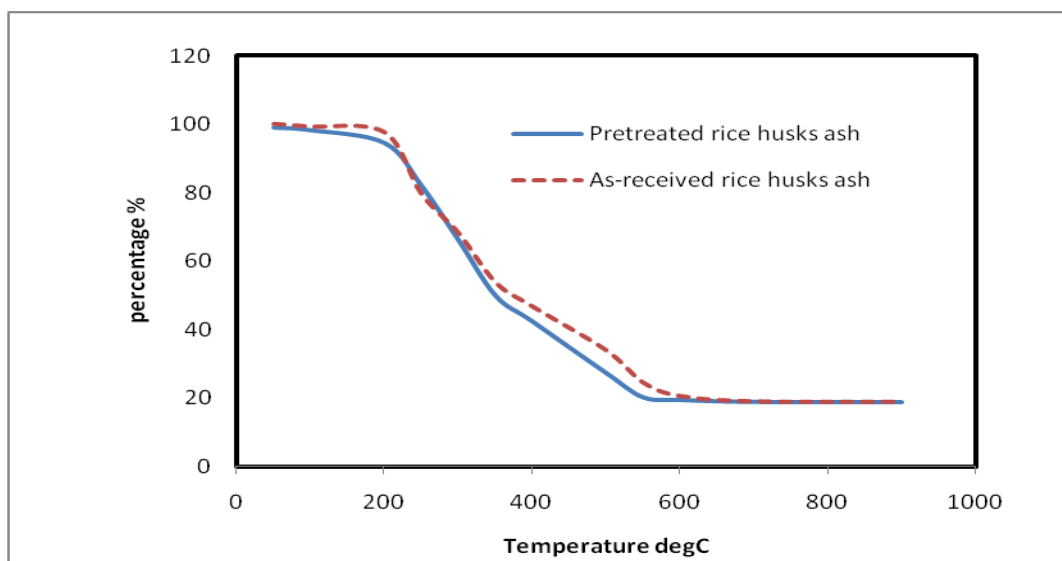


Figure 1: Weight Loss Rice Husk Versus Temperature

The pretreatment of the rice husk was carried out in four basic steps. The overall effect of these unit operations resulted in the high purity level of the silica.

Regression Model Equation

The experimental results from the full factorial central composite design were fitted with a polynomial equation:

$$\text{Percent Purity} = 99.35 + 1.92 A + 1.79 B - 0.28 AB - 1.02 A^2 - 0.93 B^2 - 0.17 A^2B - 0.76 AB^2$$

In the model, A represents the combustion temperature and B represents the combustion time. The model indicates the main effects, the interactive effects and the quadratic effects of both variables. The model is characterised with F value of 1049.7, regression square coefficient of 0.999. This value of R^2 indicates that 99.93 percent of any data within the experimental region can be explained and analysed using the model.

The response surface and contour plots of these data are shown in in Figure 2. The plots revealed the optimum process variables of 870°C and 132 minutes are needed to achieve 99.95 % silica. Experimental runs at these optimum conditions in the muffle furnace yielded silica of 99.975 % purity from the XRF analysis. This result is similar and better than the 99.95 silica content reported by Ngoc, N. N. et al. (2018). This improvement shows the effectiveness of the pretreatment carried out on the rice husk before the controlled combustion process.

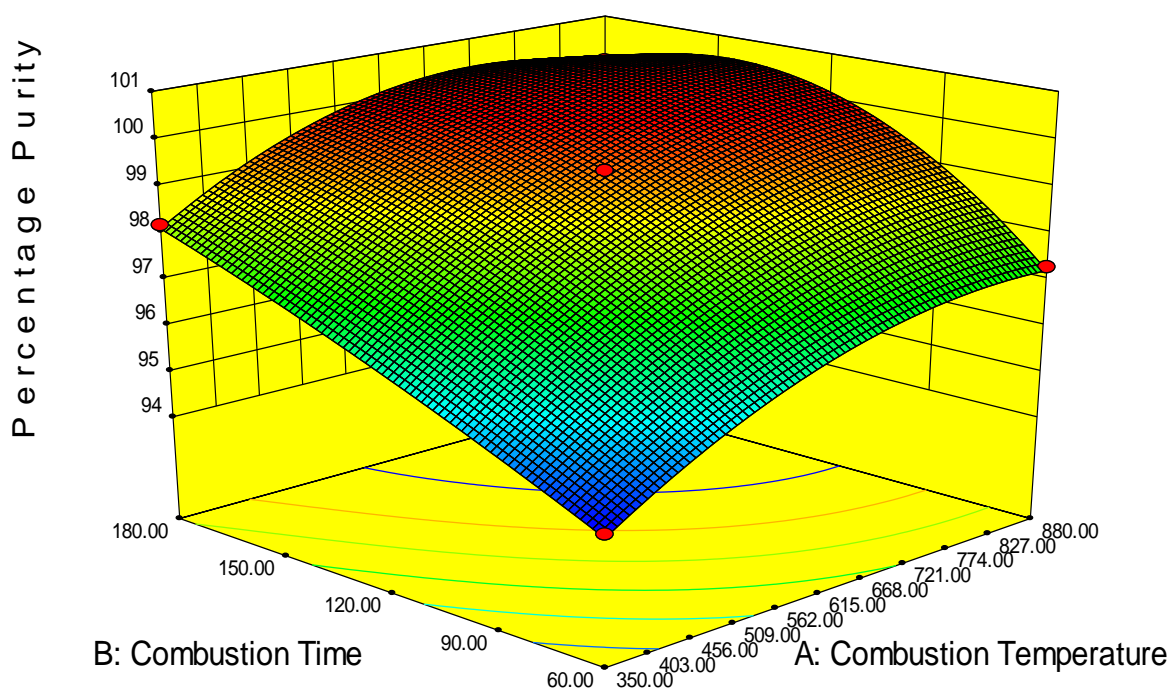


Figure 2: Response Surface and Contour 3D Plots

Figure 4 shows the BET isotherm plot of the as received RHA. It shows an initial concave shape towards the pressure axis at low relative pressure which corresponds to the uptake of nitrogen into the micro pores (<20Å) in the sample, followed by a linear segment representing the multilayer adsorption of nitrogen on the surface of the sample. The convex shape with respect to the pressure axis corresponds to the filling of the meso pores (20 - 500Å) and macro pores (>500Å) [Brunauer et al. (1938)]. The linear region of the adsorption isotherm plot was employed in the calculation of the surface area. The surface area of the as received RHA and the pretreated rice

husk were 39.2 and 229.09 m²/g respectively. There is great improvement of 197 m²/g of the rice husk silica surface as a result of the pretreatment.

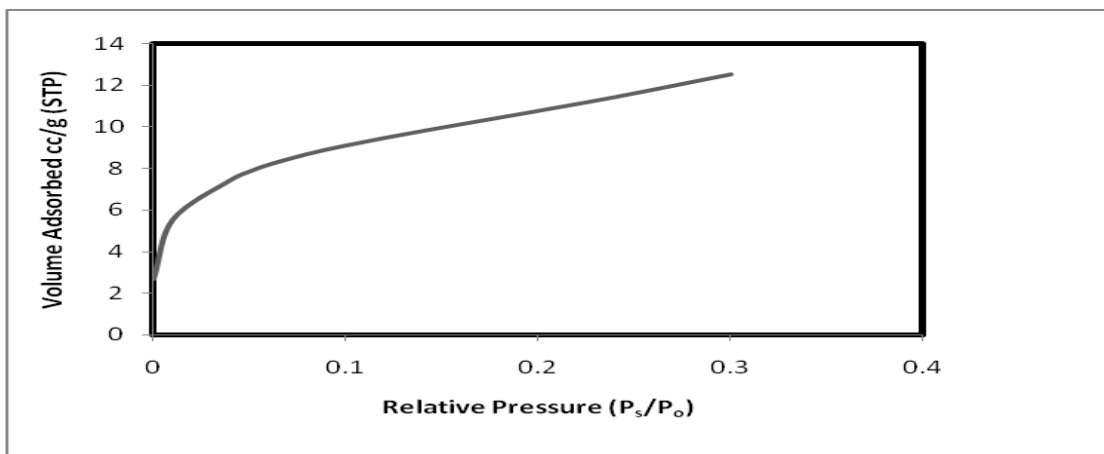


Figure 3: BET Isotherm For As Received RHA

Figure 5 shows the SEM of the silica produced at the optimum process conditions. It shows a good porosity and surface smoothness. It also demonstrates great improvements when compared with that of silica produced by an earlier investigator [Azat et al. (2019)]. Figure 6 shows the XRD pattern of the produced rice husk silica. It does not reflect sharp peaks which are clear characteristics of amorphous silica. The amorphous silica is reactive with no harmful health effects. A proposed process flow sheet for the production of high purity amorphous silica from Nigerian rice husk is given in Figure 6 below.



Figure 4: SEM of Silica Produced

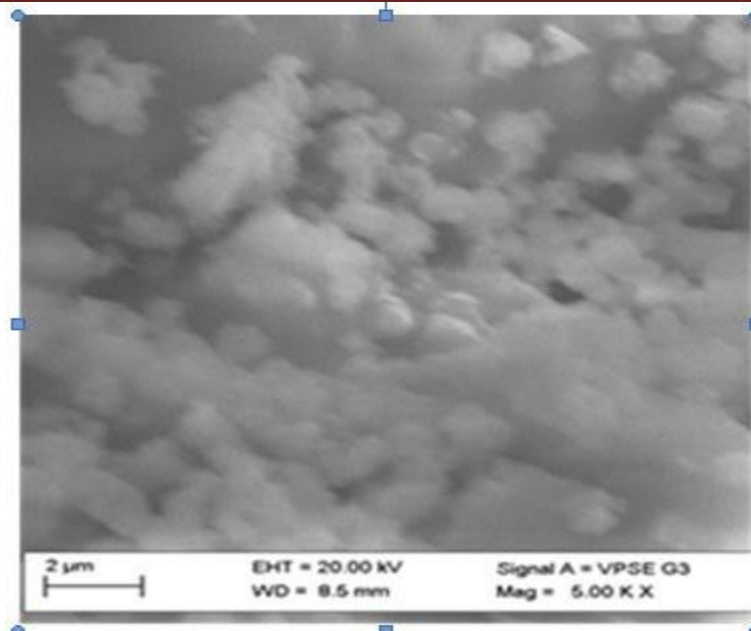


Figure 5: SEM of Silica Produced at 870°C

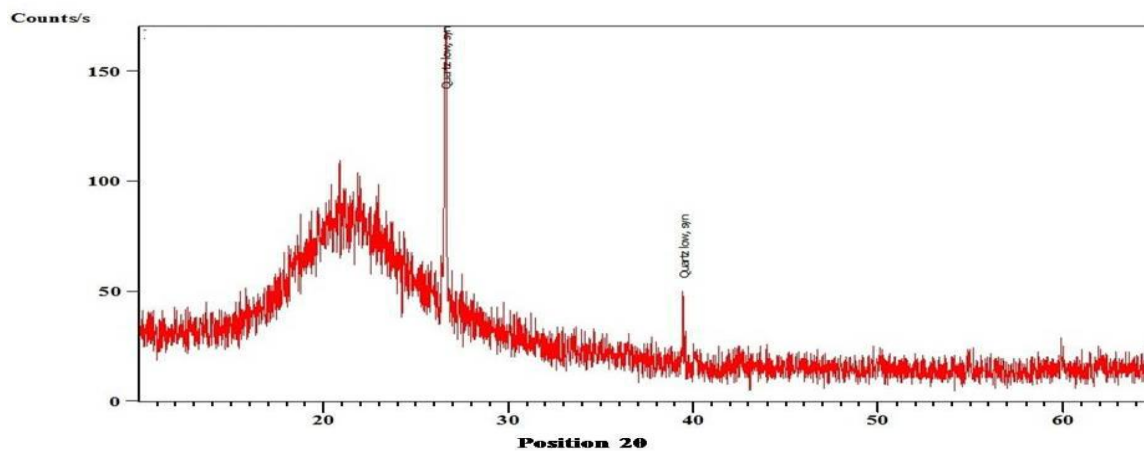


Figure 6: XRD Pattern of Pretreated RHA.

Conclusion

The production of high purity (99.97%) amorphous silica from rice husk has been successfully carried out in a laboratory scale. The optimum process parameters have been established using the response surface methodology. The yield of the high purity silica has been modeled as a function of combustion temperature and time. The produced silica has been analysed and found to have particle size of 50 nm and specific surface area of 229 m²/g. These qualities satisfy the requirements for their promising engineering and industrial applications. A process route has been developed for the low cost production of this valuable material. Several industries will benefit from the results of this research effort. The industries include the photovoltaic solar cells manufacturers, electronic industries, oil and gas companies, pharmaceutical, fertilizer and the structural construction companies.

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Profile of the First Author

Engr. Dr. Jimoh.O. Sumaila earned his Msc. in Metallurgical Engineering from Russia in 1990, M.phil and PhD in Extractive Metallurgy and materials processing from Ural Federal University, Ekalerinburg, Russia respectively.

Dr. Jimoh. O. Sumaila is currently a senior Lecturer and the Acting Head of Department of Industrial and Production Engineering, Ambrose Alli University, Ekpoma, Edo State, Nigeria with over 25 years of International experience independent and collaboration research in drivers areas of Extractive Metallurgy and materials processing with over 30 Journal publications including books and peer reviewed papers in both journals and conference proceedings. He is a member of the following Professional bodies COREN, NSE, NMS, NSE/MME.

Dr. Jimoh is resourceful energetic committed to excellence, highly motivated to achieve outstanding (positive result with little or no supervision and quick at learning).

He possessed strong analytical interpersonal and communication skills with the drive to solving problems and contribute immensely to any organization and the world at large, also to contribute his quota to attaining organizational goals, with the Zeal to conveying Philosophies for creating more relationship and success in the workplace and the strive to implanting them through academics and industrials.

Dr. Jimoh. O. S. takes pride in unleashing the creativity, talent and energy of the Vast majority of the WORKFOCE, Whose jobs neither require nor reward such resources. He follows "inner voice" free from all needs and gives selfless service to others and experience no resistance but to earn the appreciation of honest critics and endure to Learn in becoming a better person.