

Production of Silica Nanoparticles from Rice Husk as Agricultural Waste by Environmental Friendly Technique

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ABSTRACT

Extensive application of silica nanoparticles (SNPs) in various industrial products has led to the development of silica extraction methodologies out of various waste products. Rice husk is an agricultural waste with a high content of amorphous silica. However, the presence of metal ion impurities and unburned carbon in the rice husk content may present an adverse effect on product color and purity. The purpose of the present study is to optimize silica extraction procedure and improve its purity and eventually produce high quality SNPs from rice husk as agricultural waste by environmental friendly technique. In this regard, nitric, sulfuric and hydrochloric acids were applied to evaluate the effect of different rice husk pretreatments. Silica extraction process was carried out under controlled calcination conditions in an electric furnace at 600 °C. The results of XRF and XRD analyses reveal that hydrochloric acid treatment exhibited the highest performance among the other acid treatments. A purity of 95.55% amorphous silica with major impurities of K₂O, CaO and P₂O₅ were obtained indicating a relatively significant portion of it removed by acid treatment. This product was then subjected to chemical precipitation followed by slow gelation to obtain SNPs. The BET specific surface area of 409 m².g⁻¹, the average particle size of 200±20 nm, the spherical particle shape and purity of 97% indicate the successful production of silica nanoparticles.

1 INTRODUCTION

Silica nanoparticles (SNPs) are frequently used nanomaterials in a variety of technological applications such as industrial manufacturing,

packaging, composite and ceramics materials, drug delivery, adsorption, bio sensing and catalytic applications. The great interest shown

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to SNPs is attributed to their large surface area to volume ratio, low toxicity, high chemical and physical stability, and straightforward surface chemistry, which allows them to be combined or functionalized with a variety of functional species or molecules. Sodium silicate applied as a silicon source in industrial production of silica. However, sodium silicate produced by smelting quartz sand and sodium carbonate at 1300°C not only requires a large quantity of energy, but also further purification (Affandi, Setyawan et al. 2009) and also it can be cause of widespread environmental pollution. In contrast, low temperature extraction of amorphous silica from plant biomass yields high quality, environmental friendly and cost effective product as opposed to the high energy processing of the inorganics (Liou and Yang 2011). It is well known that certain plants, including Equisetaceae, Graminae, Cyperaceae and Poaceae, contain high levels of biogenic silica in the form of hydrated silica ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) deposited in the tissue (Kaufman, Dayanandan et al. 1985, Ghorbani, Habibollah et al. 2013). Plant species containing high levels of silica accumulated in silica-accumulator plants in the range of 5 to 20% of dry weight in their tissues (Agarie, Agata. et al. 1996). In this regard, several studies were conducted in relation to silica distribution, precipitation, physiology and extraction from many plants such as rice, wheat, bamboo and sugar beet pulp (bagasse) (Motomura, Fujii et al. 2000, An Dongmin., Guo Yupeng. et al. 2010, Chen, Wang et al. 2010, Ghorbani, Habibollah et al. 2013). Rice husk is an agricultural waste containing high content of silica, distributed in high-volume worldwide. According to the FAO report, rice production in 2011 was about 475 million tons. In Iran, the average output of the country is about 3.2 million tons per year (FAO

2011). The annual generation of rice husk is estimated to be about one-fifth of the annual gross rice production throughout the world (Chakraborty, Chowdhury et al. 2011). The majority of rice husk applied as feed for livestock in Iran. However, the rice husk has limited applicability in stock-breeding, because it contains more than 70% of lignin-cellulose material and more than 20% of amorphous SiO_2 (Angelova, Uzunov et al. 2011). Therefore, the best application of rice husk appears as a good source of silica. Rice husk upon burning yields 14–20% ash, which contains 80–95% silica in the crystalline form together with trace amounts of metallic impurities (Chandrasekhar, Pramada et al. 2005). By pretreatment methods and controlling the burning conditions like temperature and time, amorphous silica by high purity and ultrafine particle size can be produced. The combustion temperature and time are two important factors to define whether the silica in the rice husk ash (RHA) remains amorphous or becomes crystalline (Della, Kühn et al. 2002). Some studies have been performed to confirm an appropriate temperature for preparing the amorphous silica from the plant biomass. Our previous work (Ghorbani Farshid., Habibollah Younesi. et al. 2013) revealed that 600 °C is the optimum temperature for producing amorphous silica. Also, Rozainee *et al.* (Rozainee, Ngo et al. 2008) found that the RHA remains amorphous upon calcination at 700 °C for 6 h. Shen *et al.* (Shen, Liu et al. 2011) found that the silica phase of the RHA is sensitive to both combustion temperature and time. Evidently, many authors have concluded that preliminary leaching of agricultural byproducts with a solution of HCl, HNO_3 , H_2SO_4 , NaOH and NH_4OH , can be effective in substantially removing most of the metallic

impurities (Chakraverty, Mishra et al. 1988, Real, Alcalá et al. 1996, An, Guo et al. 2011, Ghorbani Farshid., Habibollah Younesi. et al. 2013). However, few studies have considered the effects of pretreatment of the rice husk with mineral acids followed by controlled calcination on specific surface area and purity of amorphous silica (Carmona, Oliveira et al. 2013). On the other hand, SNPs was produced by various techniques including Stobër technique (Gholami, Salavati-Niasari et al. 2013), sol-gel methods (Le, Thuc et al. 2013), and water-in-oil nanoemulsion system (Park, Oh et al. 2003). However, few studies have been carried out using slow gelation technique and freeze-drying methods (Lu and Hsieh 2012).

In the present study, we have focused our effort on preparing highly pure amorphous silica particles from RHA followed by production of stable SNPs using the slow gelation technique. Towards this aim, two different procedures for silica extraction were used. First, pretreatment of the rice husk with mineral acids (1N of hydrochloric, nitric and sulfuric acids) followed by controlled combustion. Second, extraction without any pretreatment under controlled combustion. A slow gelation and freeze-drying processes were applied to produce the SNPs. The structural features of the products were thoroughly characterized by various techniques including XRD, XRF, N₂ sorption-desorption, FT-IR and SEM analysis.

2 MATERIALS AND METHODS

2.1 Chemicals

Analytical grade hydrochloric acid (37%), nitric acid (90%), sulfuric acid (95%-98%) and sodium hydroxide (NaOH) were all purchased from Aldrich and used without further

purification. Deionized distilled water was used in the preparation of all solutions. Rice husks were collected from Ilam province rice farms, West of Iran.

2.2 Silica extraction

The collected rice husks were first washed with tap water to remove dirt and impurities and then dried in the oven at 60°C for 24 h. Two methods of silica extraction were examined including: a) pretreatment by acid leaching and then combustion, b) combustion without any treatment. In the first method, three treatment solutions of 1N acid, i.e. hydrochloric, nitric and sulfuric were used for assessing leaching process performance. The combustion process was conducted in an electric furnace at 600°C for 6 h.

2.3 Silica nanoparticle production

Silica extracted from rice husk (5 g) was dispersed in 500 mL of 0.5M NaOH aqueous solution and heated at 100 °C for 4 h under vigorous stirring to dissolve silica and produce sodium silicate. The solution obtained was filtered to remove the nonreactive impurities. The transparent filtrate of sodium silicate solution was allowed to cool to room temperature and titrated with 10% H₂SO₄ to pH 7 under vigorous stirring. Sodium silicate has shown to be neutralized with diluted sulfuric acid to precipitate silica (Lu and Hsieh 2012). Hereafter, the solution was first stirred for 24 h and then aged for 48 h to allow the silica gel to slowly precipitate. The formed gel was fragmented, filtered, and washed with water to remove the sulfate salt. The clean silica gel was freeze-dried overnight to remove water. The

SNPs product was stored in a vacuum desiccator for further characterization.

2.4 Characterization

The chemical analysis of the silica produced was performed by X-ray fluorescence (XRF) using a Philips PW 1480 spectrometer. The crystalline structure of produced silica was examined by X-ray diffraction (XRD) using GBC-Difftech MMA diffractometer. The nickel filtered Cu Ka ($\lambda = 1.54 \text{ \AA}$) radiation was used at an acceleration voltage of 35 kV and current of 34.2 mA. The diffraction angle was scanned from 5° to 60° [20]. Fourier transform infrared spectrometry (FT-IR) analyses were carried out on FTIR1650 spectrophotometer (Shimadzu, Japan) in the range of $400\text{--}4000 \text{ cm}^{-1}$ employing the KBr pellet method. The structure and morphology of silica and SNPs were examined by electron scanning microscopy (SEM) using MIRA 3 TESCAN (Czech Republic). In order to determine the textural properties, the nitrogen sorption–desorption isotherms were run using a BEL sorp-mini II volumetric adsorption analyzer. All the samples were degassed at 100°C under an argon gas flow for 3 h before analysis. The specific surface area of the SNPs was evaluated using the BET method, and the pore size distribution was calculated by the BJH method.

3 RESULTS AND DISCUSSIONS

Table 1

Physical properties of extracted silica with different acid treatment methods

Treatment methods	Ash product (%)	BET ($\text{m}^2\cdot\text{g}^{-1}$)
Leaching by HCl	24.58	272.96
Leaching by H_2SO_4	22.93	299.04
Leaching by HNO_3	30.92	277.52
No leaching	16.60	19.57

3.1 The structural features of the produced silica

The ash contents and BET surface areas of the extracted silica using different treatment methods are presented in Table 1. The minimum ash content of 16.60 % obtained after combustion of rice husk refers to the sample with no leaching. Evidently, the maximum ash content of 30.92 % is associated with the sample pretreated by nitric acid. The results in Table 1 reveal that although the ash contents based on the reference sample increased in a moderate manner, the specific surface areas exhibited a tremendous change upon leaching. Despite small differences in the resultant ash contents and BET surface areas, among the three different acid treatment techniques, HNO_3 leaching yielded the best results. The unburned carbon can be removed from the ash by further heat treatment at high temperatures, but this usually leads to the crystallization of the amorphous silica to cristobalite and/or tridymite (Shinohara and Kohyama 2004). Such crystallization is a disadvantage towards preparing silicon based materials, because silica is rendered inactive in its crystalline form (Payá, Monzó et al. 2001). In our previous study, temperature optimization for silica extraction from plant biomass yielded the best condition for silica extraction at 600°C for 6 hours (Ghorbani Farshid., Habibollah Younesi. et al. 2013).

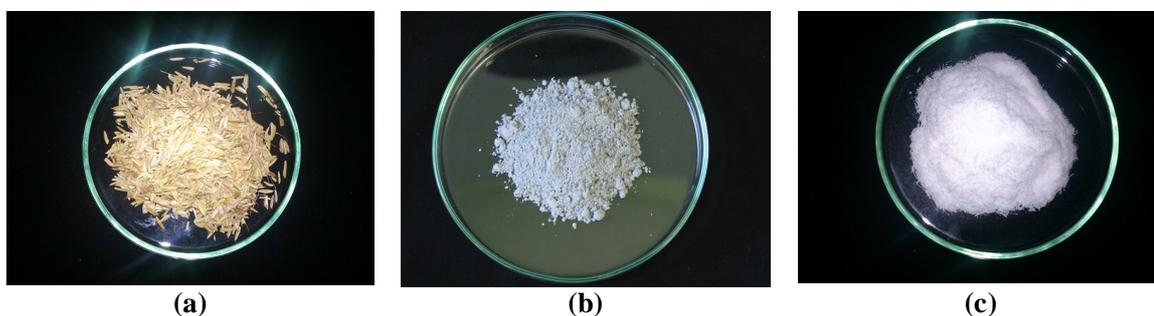


Fig. 1. Appearance of raw rice husk and extracted silica by different treatment schemes: a) raw rice husk, b) extracted silica by combustion of untreated rice husk at 600 °C, and c) extracted silica from treated rice husk in 1 N HCl acid followed by combustion at 600 °C.

Hence, in the present study the combustion temperature was kept for 6 hours at 600°C.

On the other hand, the silica produced by combustion of raw rice husk (Fig. 1.a) at low-temperature (600 °C) was found to contain unburned carbon indicative of gray color (Fig. 1.b). However, pretreatment of rice husk by acid before combustion, as shown in Fig. 1.c solved the problem completely. Fig. 1.c illustrates that leaching of rice husk by 1N hydrochloric acid has led to the production of pure white silica. It should be noted that no significant difference was observed by silica samples produced out of sulfuric and nitric acids treatments.

Several authors reported that preliminary leaching of plant biomass with a solution of HCl, HNO₃, H₂SO₄, and NH₄OH before heat

treatment is an effective way in substantially removing most of the metallic impurities and producing silica completely white in color (James and Rao 1986, Patel, Karera et al. 1987, Chakraverty, Mishra et al. 1988). Our results confirm this finding in that gray color was observed in all of the untreated ash samples irrespective of the temperature and conditions of burning (Fig. 1b). However, leaching of raw rice husk with 1 N hydrochloric acid followed by heat treatment was found to give an ash product almost white in color (Fig. 1c). Table 2 presents the chemical constituents of the ash samples with and without leaching and their calcination at 600°C. Therefore, the main effect of acid leaching is to remove metal oxides, especially potassium, calcium and phosphate oxides.

Table 2

Mineral content of RHA with or without acid treatment (some compounds with trace levels were not included).

Treatment	Compound (% by wt.)									
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	K ₂ O	P ₂ O ₅	MnO	LOI*	TOTAL
Leaching by H ₂ SO ₄	92.89	0.08	0.02	0.13	1.14	0.02	0.37	-	5.23	99.88
Leaching by HNO ₃	94.79	0.06	0.02	0.11	0.49	0.11	0.72	0.01	3.17	99.47
Leaching by HCl	95.55	0.13	0.03	0.09	0.56	0.05	0.45	-	2.75	99.63
No treatment	85.15	0.29	0.19	0.92	1.31	4.95	2.50	0.25	3.04	98.86

* Loss on Ignition

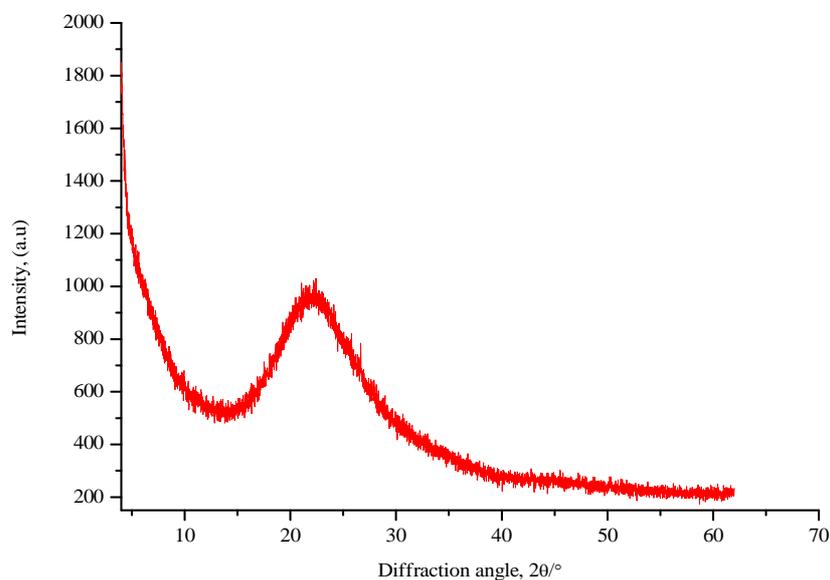


Fig. 2. X-ray diffraction pattern of extracted silica from treated rice husk in 1 N HCl acid followed by combustion at 600 °C.

Ghorbani and coworkers (Ghorbani Farshid., Habibollah Younesi. et al. 2013), found similar results and showed that application of hydrochloric acid was remarkably effective in reducing the content of alkali metal oxides (Na_2O and K_2O) in the sedge ash.

The obtained results revealed that the silica content of the ash samples after leaching by 1 N hydrochloric, nitric and sulfuric acids increased from 85.15% to 95.55%, 94.79 and 92.89, respectively. Hence, the highest purity of 95.55% amorphous silica was obtained by applying HCl pretreatment to the rice husk. Real and coworkers (Real, Alcalá et al. 1996) have shown that the preliminary leaching of rice husk with a solution of HCl before combustion at 600°C could result in a relatively pure silica of approximately 99.5%. X-ray diffraction pattern

of silica produced by combustion of treated rice husk in 1 N HCl acid is presented in Fig. 2. Hill like peak in the range of $[2\theta] = 15^\circ$ to 30° , indicated the absence of any ordered crystalline structure and highly disordered structure of silica.

3.2 The structural features of silica nanoparticles

Silica in RHA was solubilized by reacting with a strong base, to form water soluble sodium silicate (Na_2SiO_3). The filtered sodium silicate solution was clear and transparent, while the residue impurities left on the filter might be the unburned products remained upon heating at 600 °C. Sodium silicate solution was then slowly neutralized with 10% sulfuric acid solution to pH 7 to precipitate silica ($\text{SiO}_2 \cdot \text{H}_2\text{O}$). This slow

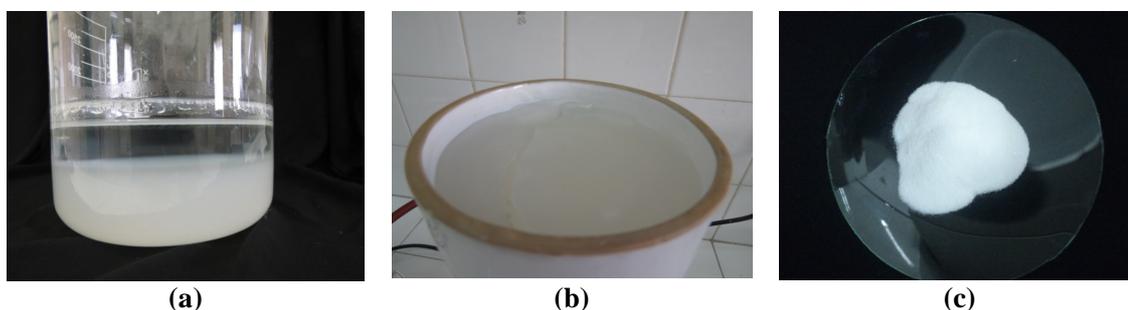


Fig. 3. Silica nanoparticle production process: a) precipitated silica gel b) filtered silica gel c) silica nanoparticles.

Table 3

Textural properties of silica nanoparticles.

Product	S_{BET} ($m^2 \cdot g^{-1}$)	Microporous surface area, ($m^2 \cdot g^{-1}$)	D_{BJH} (nm)	V_{Total} ($cm^3 \cdot g^{-1}$)
Silica nanoparticles	409.69	0.00	10.89	0.95

titration was performed under vigorous stirring to allow diffusion of sodium sulfate and prevent formation of large aggregates. Upon reaching pH 7, silica was gradually precipitated and leads to gel formation over a period of 72 h (Fig. 3a). The resultant silica gel was fragmented and washed repetitively with plenty of water until no sodium sulfate was detected in the wash water. The silica gel was filtered (Fig. 3b) and quickly frozen with freeze-drier to remove water. The freeze-dried silica appeared as fine and white powder with purity of 97% (Fig. 3c).

FTIR spectroscopy was used to detect the presence of binding groups in the SNPs (Fig. 4). The vibration signals around 1075, 780 and 665 cm^{-1} are typical of Si–O–Si bands attributed to the asymmetric stretching, symmetric stretching and bending, respectively (Ghorbani Farshid., Habibollah Younesi. et al. 2013). These three peaks are the main indices of the silica materials, which represent the successful production of SNPs. The absorption band for H–O–H bending vibration in water is at around 1650 cm^{-1} (An

Dongmin., Guo Yupeng. et al. 2010). The spectra show a broad band around 2850–3700 cm^{-1} , which is due to adsorbed water molecules (Kalapathy, Proctor et al. 2000). Physical parameters of sorption-desorption of N_2 for the Barret-Joyner-Halenda average pore diameter (D_{BJH}), the Brunauer-Emmett-Teller surface area (S_{BET}) and the total pore volumes (V_{Total}) of the produced SNPs are summarized in Table 3. The results revealed that S_{BET} was 409.69 $m^2 \cdot g^{-1}$

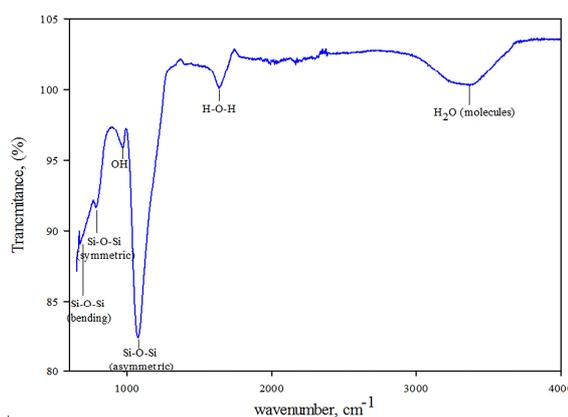


Fig. 4. FT-IR spectra of silica nanoparticles.

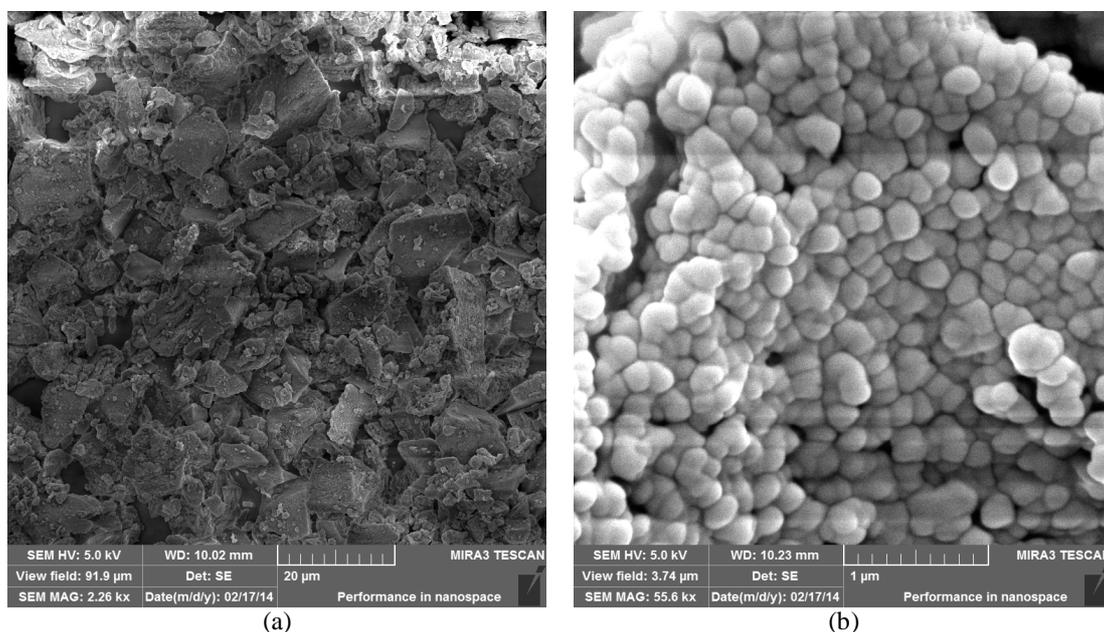


Fig. 5. Scanning electron micrograph (SEM) of: a) RHA produced by leaching process and combustion at 600°C (20 μm), b) Final silica nanoparticles (1 μm).

indicating a significant increase in the surface area in comparison to the silica produced in Table 1. The total pore volumes of SNPs was $0.95 \text{ cm}^3 \cdot \text{g}^{-1}$ which show that the produced material can be classified as porous material (the porous material should have porosity between $0.2\text{-}0.95 \text{ cm}^3 \cdot \text{g}^{-1}$). The average pore size distribution (ADS) of the SNPs according to BJH methods was equal to 10.89 nm.

3.3 Morphology of silica nanoparticles

Fig. 5 illustrates the SEM images of RHA and SNPs samples. RHA sample produced upon by pretreatment with 1N HCl and combusted at 600°C is presented in Fig. 5a at a magnification of more than 2000 times. It is clear that silica particles exhibit non spherical and irregular fiber-like structures. This is in agreement with

the previous studies (Kordatos, Gavela et al. 2008). Fig. 5b presented the image of silica nanoparticles (SNPs) at a magnification of 55600X. It can be observed that SNPs have a circular shape with average particle size of $200 \pm 20 \text{ nm}$. Due to the nonconductive nature of silica, the charges quickly accumulated on the powder surfaces even after gold sputtering caused agglomeration of particles (Lu and Hsieh 2012).

4 CONCLUSIONS

The following salient points have been achieved out of this investigation:

- a) High purity amorphous silica (95.55%) was extracted from RHA as agricultural waste. Leaching of RHA with 1 N hydrochloric acid

followed by heat treatment (600° C) produced an ash powder completely white in color.

b) SNPs produced out of this silica extract by slow gelation technique exhibited a spherical shape with an average particle size of 200 ± 20 nm and purity of 97%. In addition, relatively high surface areas up to about $409 \text{ m}^2 \cdot \text{g}^{-1}$ and total pore volume of $0.95 \text{ cm}^3 \cdot \text{g}^{-1}$ with the

average pore sizes of about 10.89 nm indicated a successful yield of nanoparticles.

c) Production of SNPs from agricultural byproducts, as opposed to that of quartz, provided an environmentally friendly solution with technically acceptable and economically attractive value added product.

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