



PROCESSING OF RICE HUSK TO BIO-SILICA NANOPARTICLES THROUGH THERMAL COMBUSTION

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ABSTRACT

High silica content makes rice husk an important non-metallic precursor for silica nano particle production that worth researchers attraction. Moreover, rice husk is considered to be cost-effective and widely available agro waste bioresource. In this investigation, bio-silica nanoparticles were produced using rice husk as precursor. Under reflux heating, the husks were acid pretreated to remove inorganic impurities and induce the hydrolysis of organic substances. Residual solid husks from the acid pretreatment were then calcined at 973K. Morphology and non-crystal structure of the bio-silica nanoparticles was analysed by TEM and XRD. An aggregate of primary particles having amorphous structure was seen with detection of negligible impurities. This was confirmed by the EDX elemental profile of Si and O as the observed peaks which indicate high purity of the generated silica nanoparticles. This also corroborated the XRF result of 99.761% SiO₂. BET surface area of 234.6380 m²/g with a pore diameter of 5.3304 nm were obtained from the analysis. This characterized the silica nanoparticles to be of high surface area.

Keywords: rice husk, nanoparticles, bio-silica.

INTRODUCTION

Rice husk, a fibrous material, is a major agricultural waste being produced worldwide with main constituents (cellulose, lignin and ash) varying with the crop type, plantation year, climatic and geographical conditions, as well as in the composition of silica and organic content of the rice husk as presented in many researches. Chandrasekhar (2003) reported the extensively reviewed data provided by Govindarao on the chemical composition of rice husk from various countries including western world and Asia. The data presented an average composition on dry basis as ash 20%, lignin 22%, cellulose 38%, pentosans 18% and other organic matter 2%.

Huge amount of rice husk (about 120 x 10⁶ tons) is being generated annually (Nian Liu 2013) but with no commercial value and extremely underutilized due to low nutritive potentials, resistance to degradation and high ash content. Thus, it is been stacked on farmland or dumped in an open heap near the mill site to be burnt later to ash. This disposal problem constitutes environmental pollution via air pollution, greenhouse gas emission, occupancy of landfill space, as well as energy wastage (Johar, Ahmad *et al.* 2012, Gu, Zhou *et al.* 2015). However, burning rice husk to ashes in an air would make the organic matter to decompose with relatively pure silica as the greater remnant amounting to ~20% of the dry weight rice husks. Various researches highlighted that rice husk could be an excellent source of high grade amorphous silica with pure silica been obtained through simple acid leaching procedure. High purity white amorphous silica may be prepared from rice husk by either thermal treatment or chemical treatment with (HCl, H₂SO₄, HNO₃, NaOH, NH₄OH) before and after combustion at 773K to 1673K for different intervals of time.

Silicon source typically silicon tetraethoxysilane have been used as silica precursor for synthesizing porous

silica and nano silica through various approach. Despite effectiveness of such methods of synthesizing different silica with controlled particle size, morphology, and porosity, the associated cost and sustainability issues remain great disadvantage. Silicon tetraethoxysilane (silicon alkoxides) are usually synthesized by carbothermal reduction of sand (raw silica) through a multistep reaction route which is energy intensive and associated with high temperature, high pressure, and strong acidity, and hence eco-hazardous (Wang, Martin *et al.* 2012). Moreover, emission of large quantity of CO₂ to the environment makes the process hazardous (Ma, Zhou *et al.* 2012).

Natural resources based silica has currently acquired significant concern in the field of materials science and biomedicine because of the accessibility, cost efficiency and eco-friendliness of the materials. Matching the economic and environmental issues with continuous need for porous and nano silica (that contain nanoparticles smaller than 100 nanometres in at least one dimension) in new applications may require an alternative synthesis approach that is more sustainable.

Extraction of silica nanoparticles was conducted through various methods that comprise flame synthesis (Chang, Park *et al.* 2008), sol-gel processes (Du, Hamilton *et al.* 2009, Van Hai Le 2013), combustion synthesis (M. S. WOOLDRIDGE 2002), and microwave hydrothermal processes (Corradi, Bondioli *et al.* 2006). Low purity silica is usually generated through most of the silica production processes with high time consumption. Low temperature hydrolysis and the condensation of molecular precursors was the basis of sol-gel process (Samantha Pinheiro Buás de Lima 2011). High purity and homogeneous nanosilica could be produced through this method as reported by (Zulkifli, Ab Rahman *et al.* 2013) despite high time consumption of the processing route. High purity amorphous silica (99.5-



99.77 wt%) was produced from rice husk through polysaccharide hydrolysis and air combustion (Umeda and Kondoh 2010). Purity of silica nanoparticles obtained from rice husk was improved to 99.92% by pre-soaking method (Gu, Zhou *et al.* 2013). In contrast, the combustion (calcination) synthesis is a more cost-effective means of processing rice husk to silica nanoparticles due to the simplicity and stability of the process.

Existence of silica in rice husk has been known since 1938 (S. Chandrasekhar 2003). Silica in the form of silicic acid is being absorbed from soil by the rice plant and accumulates around cellulose micro-compartments (Nian Liu 2013). Furthermore, the silica within the ricehusk naturally occurs in the form of nanoparticles, hence rice husk may be a natural reservoir and promising precursor material for amorphous nanosilica production.

Chandrasekhar (2003) reported that most of the metallic ingredients are removed from rice husk by leaching with diluted HCl (1N) without any effect on the amorphousness of the silica as revealed by Chakraverti *et al.* Patent by Huang, (1988) shows how rice husk is processed to amorphous superfine silica powder (with >92% silica and average diameter 0.04–0.05 μm). Likewise, white amorphous pure silica (98.5%) was obtained from rice husk by pre-treatment with HNO_3 and calcination at 873K as illustrated in Figure-1. High purity nano structured silica (>99% SiO_2 and surface area $\geq 250 \text{ m}^2/\text{g}$) has also been prepared from rice husk as reported in (S. Chandrasekhar, 2003).

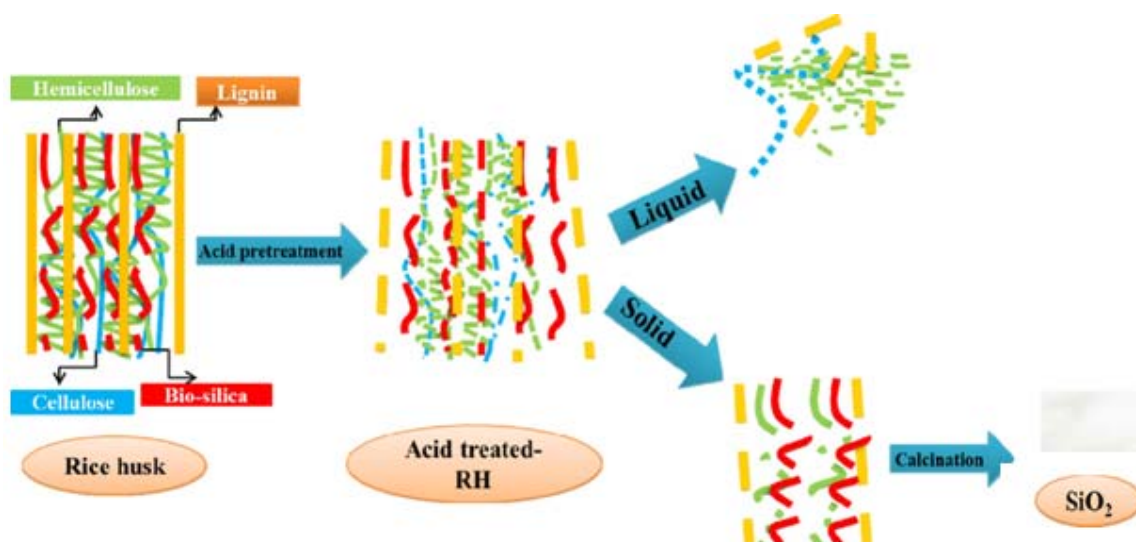


Figure-1. Formation mechanism for silica nano particles (Athinarayanan, 2015).

Unlike bulk Si, smaller size nature and porosity made the recovered nano-Si to be highly functional which rendered it electrochemically excellent without any further coating or modification (Nian Liu, 2013).

Excitingly, biocompatibility and bioactivity of silica-based nanoparticles provide a versatile framework for biomedical applications (Bhakta, Sharma *et al.* 2011, Bitar, Ahmad *et al.* 2012, Jaganathan and Godin 2012). Good understanding of the biocompatibility aspect of silica nanoparticles extracted from rice husk would promote its subsequent application in human therapeutics. Silica nanoparticles may be characterized by in vitro induction of osteoblast differentiation and mineralization as well as osteoclast differentiation inhibition (Beck Jr, Ha *et al.* 2012). Imaging, targeting and treatment of cancer has been accomplished by trifunctionalized meso-porous SiO_2 nanoparticles. The presence of silica in various biological system has been well-known and investigated as reported by (Wang, 2012).

Comprehensive exploration of the silica nano particles obtained from rice husk by the combustion

(calcination) synthesis have been done by many researchers with regard to the effects of pretreatment reagents (Ang, Ngoh *et al.* 2013), calcination parameters (Shen, Liu *et al.* 2011), as well as the kinetics of extraction and characterization of silica nano particles from rice husk (Carmona, Oliveira *et al.* 2013). Purity of the generated rice husk silica was the main focus of the past works, such crucial parameters like the specific surface area and pore structure were not generally given attention. As reported by (Lazaro, van de Griend *et al.* 2013) these parameters confer upon nanosilica particles special properties and applications, such as use as in medical, dental, cosmetic, or catalytic materials.

The essence of this paper is the production of bio-silica nanoparticles from rice husk and structural properties analysis of the generated silica nanoparticles for used in bone plate bioresorbable composite.



EXPERIMENTAL SET UP

Materials and reagents

The rice husks were sourced from Beras Bernas, KBB Changkat Lada, Kg Gajah, Perak, Malaysia. Analytical reagent-grade hydrochloric acid, HCl, (Fuming 37%) was obtained from R and M Marketing, Essex, UK. Three different types of water, clean, distilled, and deionized were used throughout the process. The analytical reagent-grade hydrochloric acid was used after dilution with distilled water to 10% concentration.

Generation of bio-silica nanoparticles

The husks were soaked in clean water at 25 °C and rinsed to clean the husks from dirt. The cleaned husks were dried for 24 hours at 105 °C in an oven. The dried husks were subjected to acid leaching by reflux heating in 10% diluted HCl acid at 100 °C for 2 hours at a ratio of 10g husk/150ml. This was to remove the metallic oxides contained within the rice husk. The residual solid husks were collected by filtration and rinsed with deionised water several times till the acidity diminished to neutral pH of 7. The washed husks were then dried at 105 °C in an air oven for 24 hours for further processing.

The acid pretreated husks were measured with Mettler Balance and put inside porcelain crucibles for subsequent calcination in a Muffle furnace which was preheated to 700 °C with a ramp rate of 5°C/min and maintained for 2 hours.

Characterization of bio-silica nanoparticles

The generated bio-silica nanoparticle were characterized in terms of structural property. X-Ray Diffractometry was carried out to analyse the crystallinity of the nanosilica particles via collection of diffraction patterns over the 2 θ scan range from 15° to 80°. Elemental composition profile of the silica nanoparticles were assessed by EDX.

Transmission electron microscopy (TEM) was conducted to examine the morphology and particle size of the nanosilica particles. The particles were ultrasonically dispersed in isopropanol for 15 min prior to imaging.

The percentage quantity of the silica (SiO₂) was analysed by X-ray fluorescence (XRF).

Brunauer Emmett Teller (BET) analysis was then conducted for the evaluation of specific surface area of the silica nanoparticles as well as the average pore diameter.

RESULT AND DISCUSSIONS

Formation of bio-silica nanoparticles

Acid pretreatment of rice husk, an inexpensive agricultural waste, followed by calcination under controlled condition generated a nanosilica particles of high surface area. The formation of the nanosilica is as a result of elimination of metal ion impurities by hydrochloric acid and hydrolysis of the cellulose, hemicellulose and lignin of the rice husk. Upon burning

the pretreated residues, organic substances decomposed with relatively pure nanosilica as the remnant (Figure-1).

Characteristic of nanosilica particles

The XRD pattern (Figure-2) of the generated silica nanoparticles depicts a broad peak at 2 θ = 21.8° which is an indication of X-ray amorphous. This conformed to the earlier investigations (Umeda and Kondoh 2010, Wang, Martin *et al.* 2012) that have proven the amorphous nature of nanosilica particles obtained from rice husk. Absorbance of any crystalline structure can be seen by lack of sharp peaks confirming detection of no other impurities.

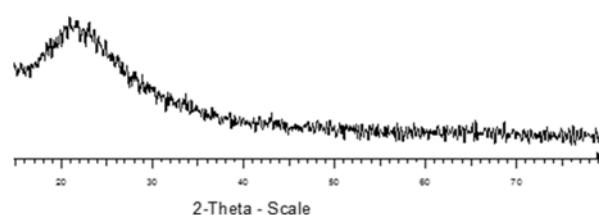


Figure-2. XRD Pattern of silica nanoparticles.

Display of the elemental profile of the silica nanoparticles is done by EDX. Figure-3 revealed Si and O as the observed peaks with presence of no other element. This is an indication of high purity of the generated silica nanoparticles.

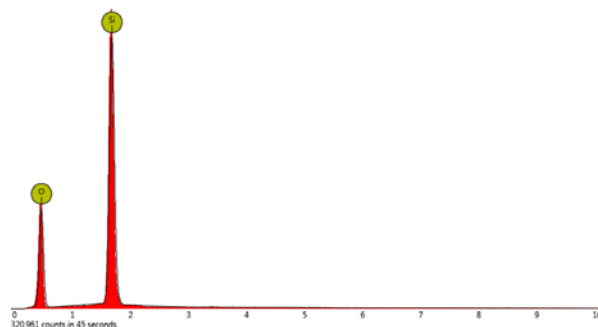


Figure-3. EDX Elemental Peaks for silica nanoparticles (Si: 45.6wt% and O: 54.4wt%).

Transmission electron microscopy (TEM) micrograph showed that the silica nanoparticles composed of cluster of primary particles that overlapped and stuck to each other. The primary particles are spherical and having a diameter about 7nm and aggregating with amorphous structure (Figure-4). This might be attributed to the inherent tendency of the nanoparticles to aggregate.

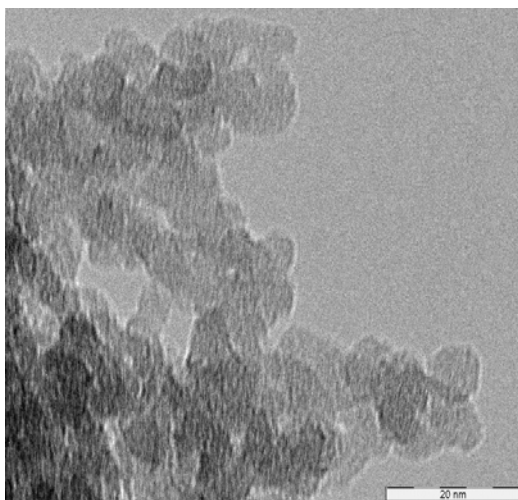


Figure-4. TEM micrograph of the silica nanoparticles.

As reported by (Lazaro, van de Griend *et al.* 2013) materials with high surface area possess a high surface energy and are thermodynamically unstable. As such specific surface area and pore volume plays significant role in nanomaterials. Tailoring the specific surface area and pore volume of nanosilica to the requirements of different application is very essential because the distribution of the pore volume can directly reflect the degree of shrinkage of primary particles and the spatial physical structure of aggregation in nanomaterials. The BET surface area characterization shows that the silica nanoparticles possessed surface area of $234.6380\text{m}^2/\text{g}$ with a pore diameter of 5.3304nm .

X-ray fluorescence (XRF) gives the silica content together with the metallic oxides impurities as indicated in the table below with the silica content reaching 99.761%.

Table-1. Quantitative chemical values of the generated silica and metallic oxide impurities.

Compound	Value (%)
SiO_2	99.761
Al_2O_3	0.088
P_2O_5	0.049
SO_3	0.014
Cl	0.015
K_2O	0.009
CaO	0.034
Fe_2O_3	0.029

CONCLUSIONS

Bio-silica nanoparticles were successfully produced from natural agro-waste precursor through acid pretreatment and thermal combustion. The silica may be characterized by high purity (99.761%), high surface area ($234.6380\text{m}^2/\text{g}$), and high reactivity with amorphous structure. Considering the worldwide availability of rice

husk, the economic technology may be harnessed through this eco-friendly route of bio-silica nanoparticles preparation. This may provide an alternative for various forms of synthetic silica that could lead to the production of more functional nanosilica materials for industrial applications and low cost precursor for other silica based products.

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