



ACID LEACHING AS EFFICIENT CHEMICAL TREATMENT FOR RICE HUSK IN PRODUCTION OF AMORPHOUS SILICA NANOPARTICLES

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ABSTRACT

High purity, high surface area silica nanoparticles could be produced from rice husk through chemical pre-treatment and combustion process. Acid leaching as efficient method of removing metallic impurities was employed during the chemical pre-treatment of rice husk prior to the burning process. In this paper, nano silica was generated from rice husk through citric and hydrochloric acids leaching by reflux boiling at 373K for 7200s so as to eliminate inorganic impurities and induce the hydrolysis of organic substances followed by burning at 973K of the residual solid husks from the leached husk. The generated silica nanoparticles were characterized to be of high purity (greater than 99%) by X-ray Fluorescence (XRF) analysis in all the two acids treated husks. X-ray Photoelectron Spectroscopy (XPS) and Energy Dispersive Spectroscopy (EDS) confirmed this percentage purity as detection of negligible impurities. Brunauer Emmett Teller (BET) surface area of 234.6m²/g and 215.8m²/g with a pore diameter of 5.3nm and 5.5nm were obtained for hydrochloric and citric acids treated husks respectively, which proved the generated silica nanoparticles to be of high surface area. Danger is less with citric acid as compared to hydrochloric acid and with proven efficiency in removal of metallic impurities in rice husk and production of high purity silica, citric acid may be the best alternative.

Keywords: rice husk, silica nanoparticles, acid leaching.

INTRODUCTION

Asia cultivates and consumes almost 90% of the entire rice farm produce. The world production of rice husk reached about 120 x 10⁶ tons annually [1] but with valueless profit which results in disposal problems linked to the solid waste management. Adequate handling should be arranged to avoid enticement of disease-carrying animals, fire risk, landfill sites full occupation, or even release of greenhouse gas (methane) during the decomposition of the husks disposed into the riverside.

Embodiment of silica in rice husk started in 1938 [2]. The silica originates from soil in form of silicic acid which is taken by the rice plant and collected around cellulose micro-compartments [1]. In addition, the silica naturally happened to be of nanoparticle size within the rice husk, thus providing a promising alternative source of amorphous silica nanoparticle since silica obtained in plants is basically amorphous and more reactive compared to crystalline silica.

Accessibility, cost and eco-friendliness made natural resources based silica to gain high relevance in the biomedical and materials science fields. This environmental concern put together with the economic values and the continuous need for porous silica nanoparticles (less than 100 nanometers in at least one dimension) in new applications suggests alternative synthesis approach that is more sustainable.

Different methods were employed in synthesizing silica nanoparticles. These include combustion synthesis [3], flame synthesis [4], microwave hydrothermal processes [5], and sol-gel processes [6, 7]. Most of the synthesis methods consumed a lot of time with less pure silica been generated. Sol-gel synthesis depends on hydrolysis at low temperature and precursors molecular condensation [8]. As indicated by [9], very pure

homogeneous silica nanoparticles may be obtained from sol - gel method though the processing route which consumed a lot of time. Rice husk was processed to very pure amorphous silica (99.5wt% – 99.77wt%) through polysaccharide hydrolysis and air combustion [10]. As mentioned in [11], purity enhancement to 99.92% of amorphous nano silica obtained from rice husk was achieved by pre-soaking process. Similarly, combustion (calcination) method proved to be a more cost-efficient process of synthesizing silica nanoparticles from rice husk due to its simplicity and stability.

Many researchers focused on studies of rice husk with some findings been patented. Production of highly pure silica from rice husk was proven efficient with a preliminary leaching of rice husk by boiling in strong acid solutions (conventionally sulfuric acid (H₂SO₄), hydrochloric acid (HCL) and nitric acid (HNO₃) which are dangerous to the people and the environment) [12] under pressure before burning process, thereby removing the metallic impurities contained within the husk. Formation of metallic sulphates, which may be insoluble in water, were normally possible with the use of H₂SO₄ during the acid pretreatment of the husk. Also, HNO₃ is not as cheap and efficient as HCL. For no drastic drop of silica melting point from 1713 °C to 789 °C, removal of some alkali metal impurities from the husk becomes necessary due to eutectic reaction with silica. Use of strong acid would warrant usage of more special disposal treatment and expensive materials that resist corrosion to strong acids. Mild acid solutions like citric acid (C₆H₈O₇) were seldom used during the leaching process.

The inorganic compounds contained within the rice husk reached about 20%wt of the dry husk with silica occupying 94%wt of the total while Potassium oxides



(K₂O), calcium oxides (CaO), Magnesium oxides (MgO), Aluminum oxides (Al₂O₃), and Phosphorous oxides (P₂O₅) constituting the remaining 6% in descending order of concentrations. Cellulose and lignin which are the main organic components take more than 75% of the total dry weight of the husk while the remaining percentage as oils, proteins, etc. The percentage composition varies with soil type, climatic conditions, crop type, plantation year and fertilizers.

High purity silica finds numerous applications as raw material in various industries such as electronics material, ceramic material, building material, and polymer material. Particles size made ultrafine silica particles useful for engineering applications as thixotropic agents, thermal insulators, composite fillers etc. Manufacture of insulating or refractory materials from rice husk ash provides an additional value to the residue as well as alternative for environmental subjects.

In this paper, effect of citric acid solution as compared to that of hydrochloric acid in removal of organics and metallic impurities from rice husk during acid pre-treatment stage would be investigated in terms of the percentage purity of the generated silica particles as well as their specific surface area. The silica purity would be ascertained by XRF, XPS, and EDS analyses while BET would be used in specifying the surface area.

EXPERIMENTAL SETUP

The rice husks employed as raw material during the leaching process were harvested in Perak area of Malaysia and processed by Beras Bernas, KBB Changkat Lada, Kampong Gajah. Two different types of acid solutions were used for this investigation namely citric and hydrochloric. The citric acid was anhydrous while the Hydrochloric acid was 37%, and were all analytical reagent-grade supplied by R & M Marketing, Essex, UK. Distilled water was used in preparing the citric acid solution (10% w/v) and diluting the HCL acid to 10% concentration solution. Milli-Q water was used in rinsing the acid treated husks after the leaching process.

Dirt-free husks were obtained by first soaking the husks in clean water at room temperature and rinsing followed by drying in an oven at 383K for 1 day. Almost 10g of the dried husks was subjected to reflux heating at 373K under constant stirring in 150ml of the two different acid solutions for 2 hours. This invoked the acid leaching of the metallic oxides and partial hydrolyzation of the organic content of the rice husks. The residue from the leached husk was collected by filtration and rinsed repeatedly with milli-Q water many times till the pH value diminished to neutral. The treated husks were then dried at 383K in an air oven for 1 day for further processing. The treated husks were then weighed on Mettler Balance and subsequently pulverized in a Muffle furnace at 973K for 2 hours with a ramp rate of 283K/min. This eliminates the organic substances in the husk and silica formation is evident with the change in color of the treated husk into whitish amorphous particles. As indicated by International Agency for Research on Cancer (IARC), an organ of

World Health Organization (WHO), crystalline silica belongs to Group 1 carcinogenic risk to humans [13], hence more undesirable as compared to amorphous silica when processed from rice husk. This was the basis for choosing the pulverizing temperature of 973K as transformation from amorphous to crystalline structure occurred only at very high temperature.

The synthesized nanoparticles silica was assessed for specific surface area and average pore size by using Brunauer Emette Teller. Chemical compositions of the generated silica nanoparticles were analyzed by collecting EDS spectra from the investigated silica in scanning electron microscope coupled to an EDS as well as the established elemental profile of the silica nanoparticles from XPS spectra. The quantitative chemical values of the impurities within the synthesized silica nanoparticles were assessed by XRF.

RESULTS AND DISCUSSION

The researcher previously reported the production of silica nanoparticles from rice husk by HCL acid leaching and thermal combustion at 973K [14] with a view of employing it in the development of POC-Silica composite for bone fracture plate application. The synthesized silica nanoparticles obtained from the two different acids leached husks composed of porous and agglomerate structure.

Table1 shows the result of BET analysis. A higher specific surface area was attainable with the silica nanoparticles obtained through HCL acid leaching process. This may be ascribed to the cross-linking network of the porous silica particulate which made particle size determination very hard due to the irregular shape of the particles.

Table-1. BET result of the silica nanoparticles obtained via HCL and citric acids leaching.

Sample	Specific surface area (m ² /g)	Single Point total pore vol. (cm ³ /g)	Average pore diameter (nm)
Silica*	234.6	0.3126	5.3
Silica**	215.8	0.2976	5.5

* - HCL acid leached

** - citric acid leached

Nitrogen (N₂) adsorption/desorption isotherms analysis confirmed the surface area of the two different type generated silica nanoparticles to be 235 m²/g and 215.8 m²/g with corresponding average pore size of 53nm and 55nm respectively with the increase in surface area corresponding to decrease in particle size.

Table-2 shows the EDX analysis. The silica elements, Oxygen (O) and silicon (Si), were seen present as revealed by the observed peaks in both the two different generated silica nanoparticles.

**Table-2.** EDS result of the generated silica nanoparticles via HCL and citric acids leaching.

Elements	Average weight %	
	HCL acid leached	citric acid leached
Si	45.6	61.9
O	54.4	38.1
Total	100	100

This confirmed the high percentage purity of each of the two different silica nanoparticles that were synthesized as no trace of other elements was seen as peaks as indicated in Figure-1. Formation of siloxane bonds (Si-O-Si) and silanol groups (Si-OH) made Silicon and Oxygen to be present.



(a) Silica from HCL acid leached husk
(Si: 45.6wt% and O: 54.4wt%)



(b) Silica from citric acid leached husk
(Si: 61.9wt% and O: 38.1wt%)

Figure-1. EDS elemental profile for the synthesized silica nanoparticles.

The quantitative analysis in terms of chemical composition of the silica and impurities was as contained in Table-3. Both the two generated silica nanoparticles were found to be of high purity with remarkable reduction in the metallic impurities which varies with the type of acid solution used for the pretreatment of the rice husk.

Table-3. XRF chemical compound values of the generated silica nanoparticles via HCL and citric acids leaching.

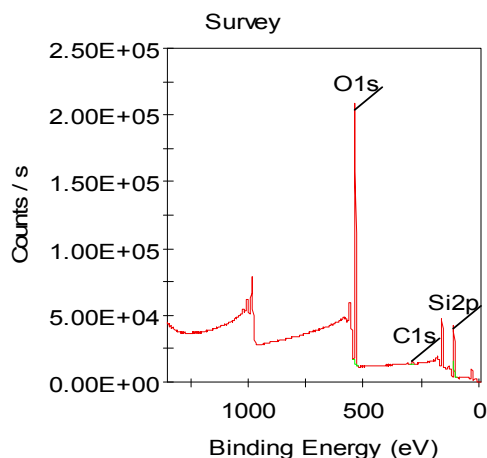
Oxides Formula	Concentration %	
	HCL	citric
SiO ₂	99.761	99.769
Al ₂ O ₃	0.088	0.071
P ₂ O ₅	0.049	0.047
SO ₃	0.014	-
Cl	0.015	-
K ₂ O	0.009	0.033
CaO	0.034	0.034
Fe ₂ O ₃	0.029	0.029
CuO	-	0.009
ZnO	-	0.008

Table-4 shows the XPS result obtained for elemental composition of each of the two generated silica nanoparticles. Carbon trace was noticed here unlike the case with EDS analysis where the obtainable peaks were depicting only silica elements (Si and O).

Table-4. XPS chemical composition for the synthesized silica nanoparticles via HCL and citric acids leaching.

Elements	Average weight %	
	HCL	citric
O	67.2	73.25
Si	30.26	24.5
C	2.54	2.25
Total	100	100

This may be attributed to the system via which the XPS spectra were collected as shown in Figure-2(a) and 2(b) or to the eutectic reaction between the silica elements and alkali metals when burning, thereby causing carbon to remain in the melt silica.

**Figure-2(a).** XPS spectra for elemental composition for the HCL acid leached synthesized silica nanoparticles.

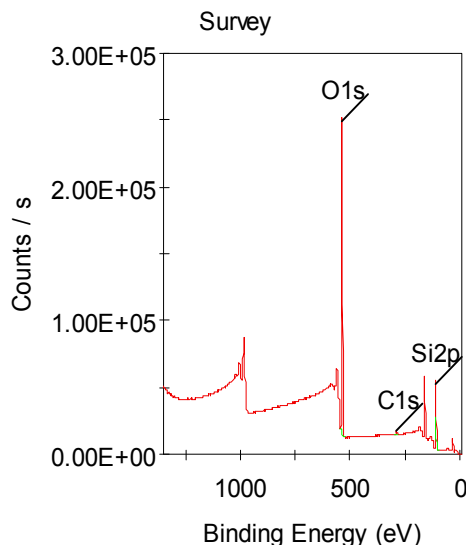


Figure-2(b). XPS spectra for elemental composition for the citric acid leached synthesized silica nanoparticles

CONCLUSIONS

Successful and simple generation of silica nanoparticles was achieved through acid leaching and pulverization of natural bio precursor agricultural waste; rice husk. The leaching carried out under HCL and citric acids pretreatment, via reflux boiling at constant stirring, resulted in two different kind of amorphous silica nanoparticles. The difference in purity of the synthesized silica was so insignificant as proved by XRF analysis. This was evident with the EDS elemental profile investigation and XPS chemical composition analysis. The result obtained from BET indicated that both the two synthesized silica are of high surface area. Although higher values are obtainable with the silica generated from the HCL treated husk, the difference may not be seen significant considering the fact that the danger associated to the citric acid is less as compared to the hydrochloric acid. Hence, citric acid pretreatment of rice husk during amorphous silica synthesis may be an optimum alternative to HCL acid pretreatment. The high purity percentage achieved in the two generated samples of amorphous silica nanoparticles indicates the efficiency of acid leaching in dissolving the impurities contained within the rice husk.

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