Preparation and Characterization of Silica Material from Rice Husk Ash – An Economically Viable Method

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Abstract

Rice husk is a form of agricultural biomass that provides an abundant silicon source. Rice husks are widely burnt in agricultural fields in India because it is difficult to find other uses for them. Farmers burn rice hulls usually under incomplete combustion conditions to avoid accidental fires. The objective of this study was to develop a new method of amorphous silica was prepared from rice husk ash by sol - gel method. Initially received from Rice husk ash was calcined at 400^0C, 500^0C, 600^0C and 700^0C for 5 hrs to remove the volatiles in the sample and determine the amorphous structure of SiO_2. Next, the thermally treated *RHA was mixed with alkali solution to produce sodium silicate solution and precipitated silica was produced by the neutralization of sodium silicate solution. Rice Husks soaked in nitric acid produced the maximum amount of the sodium silicate solution and precipitated silica. Sodium oxide (Na_2O) content and silica (SiO_2) content in the sodium silicate solution were also determined. Extracted precipitated silica particles were characterized by Fourier transform infrared (FTIR), X-Ray diffraction and Optical microscopy techniques.* The chemical composition of silica was confirmed by FTIR and SEM with EDX.. Highly pure amorphous silica was derived from rice husk ash was confirmed by XRD pattern. The morphology of the obtained materials was analyzed by SEM. At optimized conditions, a nano sized highly pure silica was produced with a high reactivity and 99.9% amorphous in form. This economic technology as applied to waste material also provides many benefits to the local agro industry. Thus this paper may be providing a low cost and simple method to prepare functional materials.

Keywords: Rice husk ash, Silica gel, Minerals, Amorphous material, Agricultural bio-waste

1. INTRODUCTION

Rice culture stands by the production and refined area, playing a strategic role in the world frugality (1). The agricultural by product include rice straw, rice husk and plant materials etc., of all these by products, rice husk (RH) may be considered as suitable energy and silica a contrivance is Asian countries. The main purpose for chosen rice husk is due to its granular structure, chemical stability and its local availability at very low cost (2-3). The chemical composition of rice husk varies from sample to sample connected to the type of paddy, year, crop, change of climate and geographical condition (4). In terms of properities they have a very nature, low bulk density (below $150Kg/m^3$), low water and moisture permeability, low value of equilibrium moisture content (below 10% at an air relative humidity (RH) of 60%), low value of the coefficient of the temperature conductivity (below 0.036 $W.m^{-1}.k^{-1}$), high resistance to the action of harmful fungi, good anticorrosion properties of steel, aluminium and copper. Many methods have been developed to produce pure silica from rice husk ash in low cost. By heating higher temperatures, the unburned carbon can be removed from the ash but this leads to the crystallization of the ash from amorphous silica into tridymite or cristobalite. At lower temperatures, the amorphous nature of rice husk ash (RHA) silica will be happened. Under the complete combustion, the colour of the ash is grey/white but in partially burning condition a black colour ash is occurred. In some areas, a huge amount of rice husk ash is used as waste and disposed land fill site, which leads to air and water pollution. The air bone particles have been related to respiratory disease in humans. If not only avoids environment pollution combustion of rice husk, but also produces enormous economic benefits (5-7). The calcinations temperature and time are two important deputies to define whether the silica in the rice husk ash amorphous is become crystalline. Some studies have been performed the amorphous silica from rice husk, found that the temperature 400- 700^0C is the appropriate by reviewing literatures (8). The rice husk ash(RHA) make may certain several metallic impurities like Fe, Mn, Na, Ca, K......... etc., can decrease its surface area and purity. If these elements can be made good use to residue problems would be cleared, and at the same time great profits could be gained.

In most applications, rice husk ash is more favourable compared to rice husk. The silica in the ash undergoes structural transformation depending on the conditions (time, temperature, chemical composition, minerals content) of combustion. At 400-1200^0C amorphous ash is formed and at temperature greater than the crystalline ash is formed (9).

In the present study to extract active amorphous silica obtained from rice husk either via complete composition or by solvent extraction. It may be concluded that amorphous silica of rice husk ash can be used for different novel applications. This amorphous silica has a promising future as a biomaterial because it originates from biomass (10). Silica based materials are frequently used for different bio applications due to their good bioactivity and biodegradability characteristics.

2. EXPERIMENTAL DETAIL

2.1. *Materials*

Among chemicals used in this study include HCl, NaOH and H_2SO_4. All chemicals were used as received without any purification. Initially, locally collected rice husk waste was cleaned by distilled water to remove the dirt and then dried at 24 hr. An appropriate amount of cleaned sample was calcined at 400 °C, 500 °C, 600 °C and 700 ºC for 5 hr.

Table -1

Properties of rice husk

Proximate analysis wt% (as received)	
Moisture	2.4
Ash	20.3
Volatile	75.8
Main constituent's wt% (on air – dry basis)	
Hemi cellulose	20.2
Cellulose	38.6
Lignin	19.8
Silica (pure)	18.7
Metallic oxides	0.39 (Mgo, Al_2O_3, Cao, K_2o, Nao)

2.2. *Instrumentation*

2.2.1. *XRD studies*

X- ray diffraction experiments of rice husk ash were performed with a Rigaku miniflex diffractometer for 2Θ values from 10^0 to 90^0 using Cukα target at wavelength of $\lambda = 1.5406A^0$

2.2.2. *Infrared spectroscopy (FT- IR)*

The obtained materials from the burnt rice husk were characterized in a Perkin Elmer Spectrum 1000 spectrometer. In the wave number range from 4000 – 400 Cm^{-1} at a resolution $4Cm^{-1}$ using 64 scans using KBR powder as reference. Typically, samples between 10 – 40 mg used.

2.2.3. *Morphology Studies (SEM)*

Our samples were characterized by scanning electron microscopy (SEM) (Jeol – JSM – 6360LV) at a voltage 20kV and previously coated with gold under vacuum by sputtering using a BAL – TEC'S apparatus. Secondary electron images were obtained.

2.2.4. *Thermal analysis*

Treated rice husk ash TGA and DTA analysis were performed in thermo gravimetric equipment (Pyris7, Perkin – Elmer) to verify the mass loss behaviour of rice husk and the effect of the chemical treatments, as well as their activation energies from the application of the Ozawa method.

TGA were carried out with 10 – 60 mg rice husk samples in platinum pan in air atmosphere under $10 – 20^0C$ min- 1 heat rate providing the percentage composition of volatiles, organic compounds and the residue created by the rice husk burning.

3. PROCEDURES

The proposed method consists of the following stages.

3.1.1. *Acid pre treatment of material*

Rice husk (RH) and dilute HNO_3 were mingled into a 500ml two necked flask. The suspension was boiled for 5h under reflux condenser, and vigorous stirring was applied during the whole reaction processes. Finally, the suspension was filtered, and solid residue was washed throughouly with deionised water to ensure the absence of NO_3^- and subsequently dried in an oven at 155^0C for 48h.

3.1.2. *Preparation of rice husk ash*

The dried rice husk then was taken in crucible and placed it in electrical furnace for 5h at 400^0C to get a black ash. The ash then was ground into powder and later heated again at 600^0C 5h complete combustion. Pure amorphous white silica was obtained by burning this rice husk at 800^0C in a muffle furnace for 5h. Finally produce the rice husk silica (RHS).

3.1.3. *Preparation of silica gel particles*

A schematic flow chart for preparation of silica gel particles from rice husk ash is proposed as shown in fig. 5g rice husk ash was mixed with 250mL of 1N sodium hydroxide aqueous solution. The mixture was refluxed for 3h at 110^0C. The solution was filtered and stored in a refrigerator for further usage.

A 5ml sample of sodium silicate solution was taken from the stock solution and poured into 15ml distilled water at a time and stirred for a specific time. The pH of the solution was adjusted to 10-12 by drop wise addition of hydrochloric acid under stirring speed to form silica gel. The time want for gelation is approximately within five minutes after sol solution was neutralized. Agitation was continued for another one hour to obtain wet gel

nano particles. The prepared gel was aged at 800^0C for 3h under finalized condition. Distilled water, NaCl and other impurities were separated from the gel by solvent exchange with dilute and pure methanol in 4-5 times. The dilute methanol (75%) was used to avoid any structural shrinkage during the solvent exchange. Completely, methanol exchange was done six times and aged at 800^0C. The total time of aging was 52 h. The wet gels were then dried.
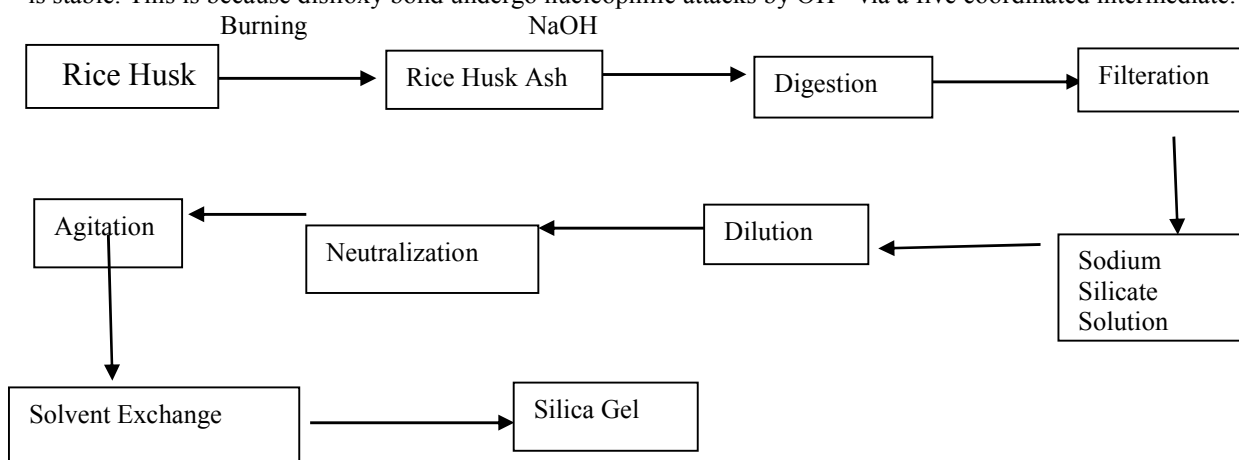
Nano silica was obtained from sodium silicate solution using a sol -gel technique. The reaction is as follows:

$$SiO_2 (Ash) + 2NaOH \longrightarrow Na_2SiO_3 + H_2O$$

The silica particles were generated from the solution by adding nitric acid as catalyst. The acidic condition of pH 5 indicates approximately the complete precipitation of silica from sodium silicate by the following reaction:

$$Na_2SiO_3 + H_2SO_4 \longrightarrow SiO_2 + Na_2SO_4 + H_2O$$
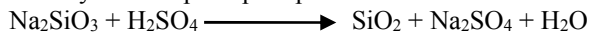
At a lower silicate concentration and with the pH less than 8, Si $(OH)_4$ is the dominant species in its aqueous solution. At higher concentrations, the silanols, the Si (OH) groups, spontaneously polymerize to yield higher oligomers linked by a disiloxy bond. Such a reaction is most favourable when one of the silanols is deprotonated to a Si- O- group (11). These oligomers grow into colloid - sized silica particles in which larger particles grow at the expense of smaller ones. At higher pH (greater than 8), however, the much more concentrated silicate solution is stable. This is because disiloxy bond undergo nucleophilic attacks by OH - via a five coordinated intermediate.

Burning   NaOH

Rice Husk → Rice Husk Ash → Digestion → Filteration

Agitation ← Neutralization ← Dilution ← Sodium Silicate Solution

Solvent Exchange → Silica Gel

Scheme1. Schematic diagram of preparation of rice husk ash to silica gel

3.2. *Visual Inspection of RHA after combustion:*

The RH powder was combusted under different conditions, including varying amounts of the husk powder combustion temperature and soaking times (12). Different colour changes were observed and the results are shown in table 2.

Table.2. Combustion temperature and soaking duration for dry rice husk powder

Component	Combustion temperature (^0C)	Soaking duration (h)	Observation
Dry RH powder	400^0C	5	Coarse powder, Incomplete combustion, Fully black
Dry RH powder	500^0C	5	Fine, Pinkish white
Dry RH powder	600^0C	5	Fine, white
Dry RH powder	700^0C	5	Fine, Pure White

4. RESULT AND DISCUSSION

The physical appearance of untreated rice husk was seen to be brownish before pre treatment. After pre-treatment, it was seen to be light yellowish colour due to the concentration of acid added to the husk. The light yellowish colour indicates that the pre - treatment of the rice husk has increased the surface area of the rice husk after treatment. Burning out temperature and time are the two important factors to define whether silica remains amorphous, as in RHA, or become crystalline.

It has been found that reheating the ash to remove carbon residues takes a relatively long period of time and temperatures, with the consequent effect that silica is converted into crystalline forms (13). This behaviour was not evidenced along the burning cycles here applied.

4.1. *Experimental work & results*

The experimental work has different parameters that affect quantity and quality of silica produced. The quality of silica produced mainly depends mainly on the precipitation conditions (14).

4.2. *Digestion*

Studies were carried out by the varying process parameters such as temperature, concentrated HNO_3 solution used for the digestion.

a) Quality of silica extracted from ash increase with temperature

b) Silica yield increased marginally with increase in concentration caustic (at same caustic to ash ratio). It was observed that as the caustic to ash ratio increases the yield increases up to a ratio of 1:3 after which the yield decreases (15).

4.3. *Structural and phase changes Investigation*
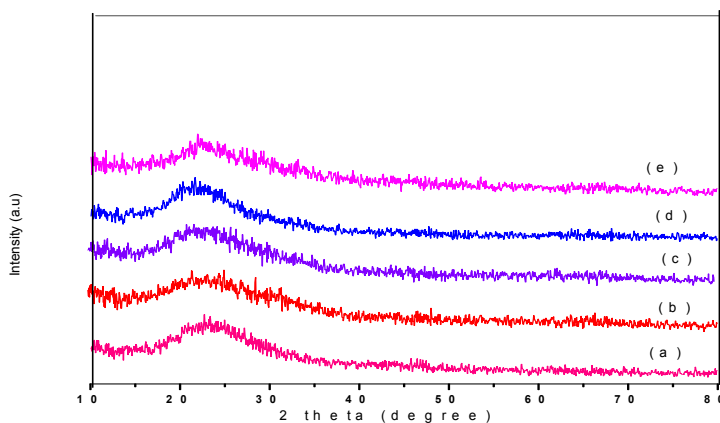
Fig 1. XRD Spectrum RHA a) 400^0C b) 500^0C c) 600^0C d) 700^0C

The X- ray spectroscopy of the rice husk ash is shown in figure (1). It is important to prepare high purity SiO_2 ashes with amorphous structures from rice husk, because IARC (International Agency for Research on Cancer) one part of WHO (World Health Organisation), strongly points that the crystal SiO_2 have carcinogenic risk to humans (16). The structure of RHA strongly depends on the burning temperature and time. There are no sharp peaks. A strong peak is observed at about 23^0 2theta angle. This generally indicates that the solid is either not crystalline (or) it consists of micro crystalline structures. No peak at region of around 23^0 confirms absence of crystalline quartz or crystoballite. The other X-rays diffract grams showed semi crystalline and crystalline phase of silica for combustion at varying temperatures are 400^0C, 500^0C, 600^0C and 700^0C shows that amorphous substances display an atomic arrangement that is either random (or) has a very short range in order (17). The existence of several sharp peaks indicates the presence of crystalline phase in the matrix. Crystallization had taken place due to the high temperature employed during calcination.

4.4. *Structural characterization of silica gel nano particles:*
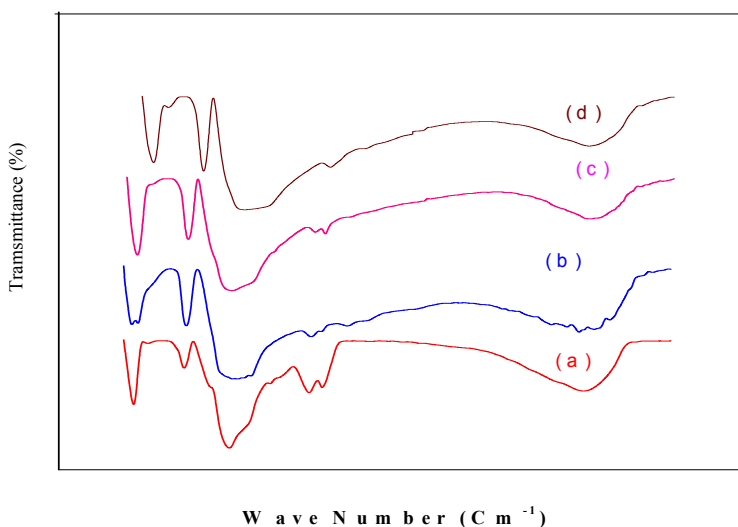
Fig 2. FTIR Spectrum for RHA a) 400^0C b) 500^0C c) 600^0C d) 700^0C

FTIR spectroscopic tool is used to identify the key functional groups indicating structural changes in the samples (Figure 2). A broad band in the range of 3670-3000 cm^{-1} responsible for the isolated and surface -OH

groups of -Si-OH whereas the band at 1630 cm^{-1} assigned to the bending mode (HOH) of coordinated water (18). The results indicates that the intensity of these peaks is decreased after calcination whereas is increased after silica extraction. The predominant absorbance peak between 1200 and 1050 cm^{-1} is associated with the Si-O-Si asymmetric band stretching vibration and the corresponding symmetric stretch at ~802 cm^{-1} (19). The intense peak in the range of 470-450 cm^{-1} is attributed to the Si-O asymmetric bending vibration of Si-O-Si bond. After thermal activation and silica extraction, the intensity of all these peaks is shifted towards higher wave number (20) AS is exhibited a relatively strong peak at about 817 cm^{-1} and it can be distinguished from the band of crystalline silicate (21). The presence of more pronounced Si-O-Si bending vibrations at 473 cm^{-1} confirms the highly condensed silica network in Amorphous Silica spectra. No peak was found between 2800 and 3000 Cm^{-1}. It means that there were no original organic compounds in the silica after controlled combustion and extraction
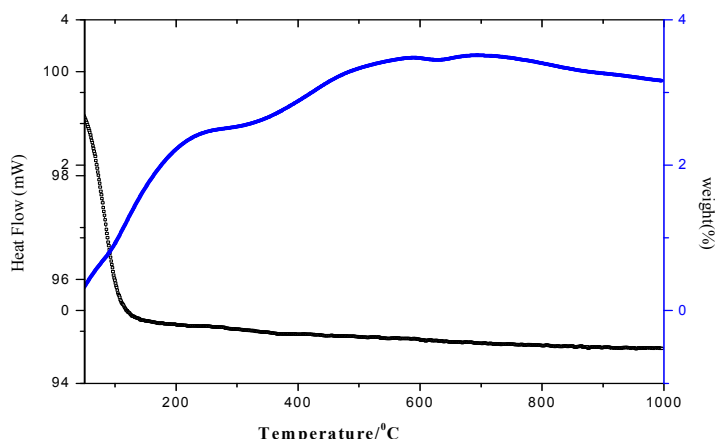
4.5. *Thermal analysis:*

Fig 3. *TG-DTA curve for Raw Rice husk ash*

The organic compounds content was in the range of 75- 84 % (depending on the rice husk variety and chemical treatment), which is constituent with the literature. This phenomenon can be explained on the basis of the thermal decomposition behaviour of its major organics constituents (Fig. 3) In TG curves the weight loss observed up to 100^{0}C is attributed to evaporation of physically absorbed water and perhaps the remaining ethanol. The next weight loss occured at 102 to 600^{0}C which was related to evaporation of water formed from poly condensation reactions and removal of organic groups by oxidation reaction. The first stage of thermal decomposition is the loss of volatile compounds followed by the decomposition of the cellulose and lignin to the intermediate, which may be an organic material of smaller molecular weight. In the second stage, there is no peak was observed. Hemicelluloses decomposes between 200^{0}C to 260^{0}C, while the cellulose between 250^{0}C to 360^{0}C, and lignin from 280^{0}C to 360^{0}C (26), it was not possible to separate the degradation process of rice husk components due to the complexity reaction and the superposition of the degradation peaks.

4.6. *Morphology analysis of silica gel nano particles*

Fig. 4(a & b) shows the SEM and EDS analysis of corn cob ash at 700 °C. In the SEM image, corn cob ash particles are polygonal shape and the strong intensity of Si in the EDS spectrum is confirmed the silica at higher weight percentage and also due to some trace of other impurities.
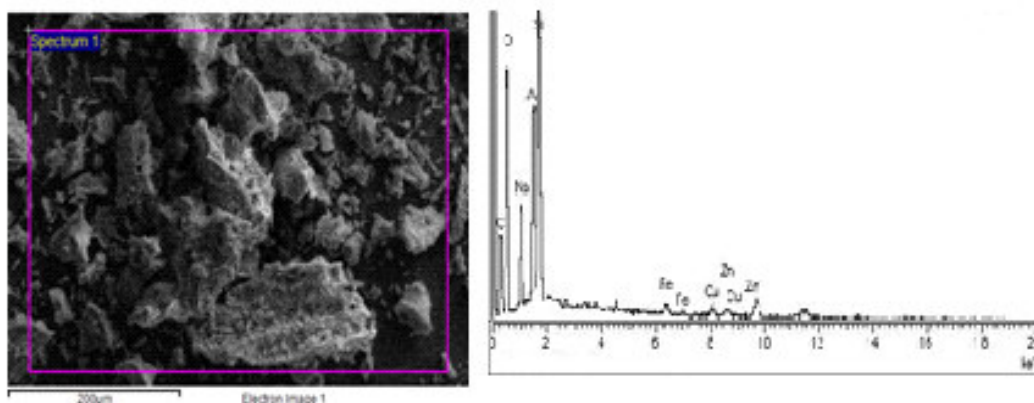

Fig 4. (a) SEM image of RHA and **(b)** EDS spectrum of RHA at 700 ˚C for 5hr

5. CONCLUSION

This study revealed the process for extraction of silica from Rice husk and also transition metal doped rice husk silica nano particles was synthesized via sol – gel method under mild conditions. Effect of two main parameters (heating temperature and heating hours) on the formation of black and white particles in rice husk silica ash was also studied. All existing techniques for obtaining silica are primarily operated at temperatures of around 1000^0C while this process used in this work has been made possible in the temperature varying from 400 to 700^0C. However, at low temperature (400^0C) the oxidation of carbon in the acid treated rice husk is slugggish. Rice husk is a potential green resource. This proves to highly energy effective and also a useful technique for waster disposal and utilization.

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