



## Efficient Pretreatment and Microwave Assisted Leaching of Silica from Biomass and Their Optimization

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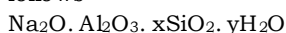
### Abstract:

In recent study optimization and leaching of silica from biomass i.e. rice husk. Rice husk (RH) is converted into rice husk ash (RHA) by heating at 400-500°C in furnace and obtained ash was calcined at 1000°C to remove carbon contained and other several volatile materials present in the RHA formed Calcined rice husk ash (CRHA). Efficient pretreatment by mineral acid to activate CRHA and remove metallic gangue. The CRHA further treated with alkali solution followed by microwave irradiation gives silica liquor. The obtained silica liquor is neutralized by mineral acid and optimizes specific pH, time and concentration. The synthesized silica gel is characterized by Spectrophotometer, Fourier transfer infra red (FTIR), Scanning electron microscopy (SEM), X-ray diffractometer (XRD).

**Keywords:** Pretreatment, Biomass, CRHA, optimization and leaching of silica, Silica liquor and gel,

### 1. Introduction:

Zeolite is crystalline, porous aluminosilicate with completely cross-linked open framework structures made up of corner-sharing SiO<sub>4</sub> and AlO<sub>4</sub> tetrahedra. A general empirical formula is as follows



Where Na is exchangeable cation which may balance the negative charge created by the presence of Al in the structure. The framework may contain cages and channels of discrete size, which are ordinarily occupied by water. The main constituents of zeolite are soda, silica and alumina. There is lots of byproduct available to extract silica such as fly ash, rice husk, Pedy husk, corn cobe husk etc. In recent study we are using rice husk as silica source to synthesis zeolite. Rice husk is the major byproduct of rice processing industries. Rice husk is agriculture wastage of rice mill and it is easily found in India. In current strategy rice husk use as silica source, they contain 60-90% SiO<sub>2</sub>. Around world India is a second largest production of rice it is accounted for that around 0.27 tons of rice husks (rice frame) are shaped from each ton of rice produced. World rice production is approximately 480.13 million tons. Asian farmers produce rice about 90% of total production of 106,500,000 tons or more, with two countries, China and India, growing more than half of the total crop. In recent investigation, calcined rice husk ash (CRHA) has been used as a source of silica. Rice husk easily converted into rice husk ash at 700°C heating by muffle furnace. Initially, RHA is completely burned to produce carbon-free white ash and followed by calcinations of siliceous material of the husk ash into calcined

rice husk ash (CRHA). In past days conventional method use to synthesis of zeolite which is tedious and time taking process. In this synthesis of zeolite-RH, approach to use green techniques such as microwave irradiation and ultrasonic waves. Leaching of silica by microwave irradiation to optimization of specific concentration and their pH to convert into silicate gel.

### 2. Experimental:

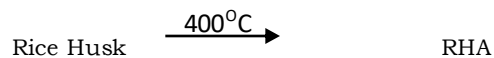
#### 2.1 Materials and methods:

The crude rice husk is collected from vidharbha area, Maharashtra, India, (EMPLURA), Sodium hydroxide pellets (LOBA Chemie), Muffle furnace (Bio-Technics, India), Green method i.e. Microwave irradiation (MW-IFB 20PMIS), Magnetic stirrer (Bio-Technics, India), Spectrophotometer (UV201, thermofisher), Flame photometer (Systronic), XRD, XRF, SEM.

#### 2.2 Synthesis of Silica gel by biomass:

##### 2.2.1 Conversion of Rice husk (RH) to Rice husk ash (RHA):

Initially refined rice husk material stored in well equipped muffle furnace at 400°C for 2 hours in mediatory intermixing is converted to rich husk ash for removing some organic impurity.



##### 2.2.2 Conversion of RHA to CRHA:

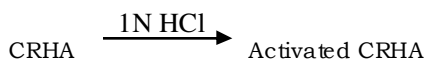
1000°C

Rice husk ash (RHA) is calcined (in absence of oxygen or limited supply of oxygen) at 1000°C for 1 hour to form calcined rice husk ash (CRHA) to remove carbon contained and other several volatile materials present in the RHA.



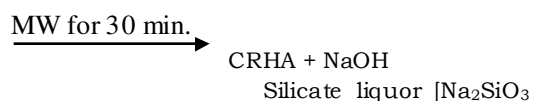
**2.2.3 Activation of CRHA by mineral acid:**

Efficient pretreatment with 1N hydrochloric acid (HCl) to activate CRHA by removing other impurities and metallic gangue to increase efficiency of CHRA in production of silica.



**2.2.4. Leaching of silica liquor by microwave irradiation:**

The activated CRHA is mixed with calculated amount of sodium hydroxide solution. To extract silica by microwave irradiation for 30 minutes, the obtained slurry filter to remove residual part and the filtrate having silica in the form of sodium silicate about 60 % this is characterized by spectrophotometer.

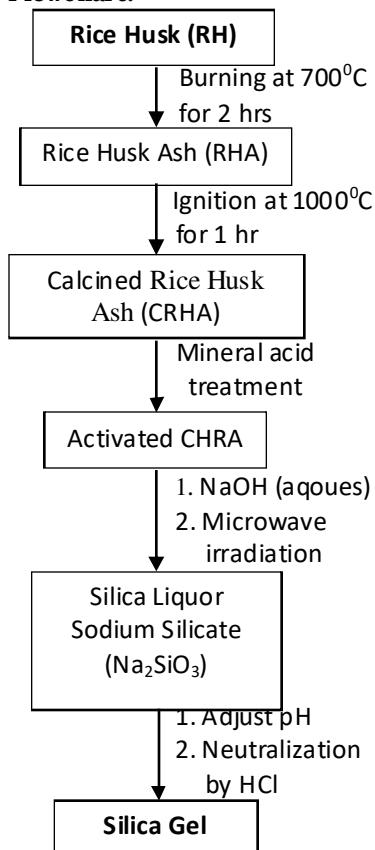


(Sodium silicate)]

**2.2.5 Synthesis of silica gel:**

The obtaining silicate liquor on adjusting their pH and neutralize by hydrochloric acid to form silica gel. To optimize specific concentration of acid and exact pH of liquor.

**Flowchart:**



**Figure.1** Flowchart of synthesis of silica gel from rice husk (RH).

**3. Result and discussions:**

**3.1 Physicochemical characteriza**  $\xrightarrow{1000^{\circ}C}$

**3.1.1 Sample Preparation:**

Take 0.25 gm of sample in a platinum crucible including 3 gm of Sodium carbonate and 1 gm Boric acid mix well and fuse in muffle furnace (Bio-Technics, India), the temperature expanding step by step to the full temperature of the furnace. Keep in the molten condition for 15-20 minutes. Expel the crucible from the furnace and allow to cool. Dissolve the melt in 100 ml water in borosil beaker, add HCl (1:1) and boil for 15 minutes. Filter the solution through whatman No. 40 filter paper in 250 ml volumetry flask. Wash the filter paper several times with hot water, allow to cool the solution then make up to mark with water and mix thoroughly. Reserve the filtrate for analysis.

**3.1.1a Spectrophotometry analysis of SiO<sub>2</sub>:**

Silicic acid react with a solution of molybdate in the acidic medium to give an intense yellow coloration due to the formation of complex silicomolybdic acid H<sub>4</sub>(SiMo<sub>12</sub>O<sub>40</sub>) which can be measured at 400 nm wavelength. It is better to reduce the complex acid to molybdenum blue. A solution of Ascorbic acid is generally used after reduction, the absorbance can be measured at 810 nm wavelength. Compute the percentage of SiO<sub>2</sub> from the standard graph.

**3.1.1b Spectrophotometry analysis of TiO<sub>2</sub>:**

Take an aliquot equivalent to 0.1 gm, include 5 ml phosphoric acid and 5 ml 1:1 sulphuric acid (final acidity may vary from 105 to 3.5 N), add 5 ml dilute hydrogen peroxide. A yellow color will develop. Make up the volume to 100 ml in a volumetric flask and measure the absorbance in a spectrophotometer (SHIMADZU, Japan) at 410 nm. Compute the percentage of SiO<sub>2</sub> from the standard graph.

**3.1.2: Titrimetric analysis**

**3.1.2a Determination of Al<sub>2</sub>O<sub>3</sub> (EDTA Complexometry):**

The pH of the principle aliquot is acclimated to a suitable range (5.5). An excess of EDTA solution added and boiled to form a stable complex. After cooling, the excess of EDTA is determined by titrating with a solution of zinc acetate and the percentage of Al<sub>2</sub>O<sub>3</sub> is calculated from the amount of actual EDTA used up.

**3.1.2b Determination of Fe<sub>2</sub>O<sub>3</sub> (Volumetry):**

The main aliquot is disintegrated with concentrated hydrochloric acid, and iron is reduced to its divalent state with stannous chloride. The excess of reductant is removed by oxidation with mercuric chloride. Ferrous iron is determined by sulphuric-phosphoric acid

medium, employing diphenylamine barium sulphate as indicator.

**3.1.3: Determination of Na<sub>2</sub>O, MgO and CaO:**

Take 0.1 gm of sample in a platinum crucible and add 3 gm of Boric acid mix well and fuse in muffle furnace, the temperature increasing gradually to the full temperature of the furnace. Keep in the molten condition for 15-20 minutes. Remove the crucible from the furnace and allow to cool. Dissolve the melt in 100 ml water in borosil beaker, add HCl (1:1) and boil for 15 minutes. Allow to cool at room temperature and make up in 250 ml volumetric flask. Mix thoroughly and allow to settle for about 2 hours. Decant the supernatant liquid through a dry funnel in a dry beaker and determine the Na<sub>2</sub>O by flame photometry (flame photometer 128, Systronic). MgO and CaO is determine by Inductively Coupled Plasma Atomic Emission Spectrometer (ICP Thermo elemental, USA).

**3.1.4 Determination of loss on ignition (Gravimetry):** Weigh accurately one gram of sample into a weighed platinum crucible. Heat gently first and then at a gradually increasing temperature. Finally, ignite at 1000°C for 30 minutes, cool in a desiccators and weigh.

$$L.O.I = \frac{[(A-B) \times 100]}{C}$$

Where

A = initial weight in gm of the crucible with the sample.

B = final weight in gm of the crucible with the residue after ignition.

and C = weight in gm of the sample taken.

**3.2 X-ray diffraction patterns (XRD)** were recorded utilizing the X-ray diffraction (XRD) spectra of synthetic zeolites were obtained using

**Bruker AXS D8 advance analysis from 180° C to 430°C measuring circle diameter 435, 500 and 600mm pre define angle range 360° max. usable angular range 3° to 135° x-ray source Cu, wavelength 1.5406 Å detector Si(Li) PSD.**

The samples were scanned from 10–50° (2θ, where θ is the angle of diffraction). Various crystalline phases exists in the samples were identified with the help of JCPDS (Joint Committee on Powder Diffraction Standards) files for Inorganic compounds. Quantitative measure of the crystallinity of the synthesized zeolite was made by using the summed heights of major peaks in the X-ray diffract were ascertained.

**3.3 Scanning electron microscopy (SEM):**

Scanning electron microscope was performed on ZEISS. SEM experiments were directed to explore of the morphology of coal fly ash and zeolite structure Fig. 2a and 2b shows SEM micrographs of the coal fly ash at 6.32KX and Zeolite at 3.12 KX

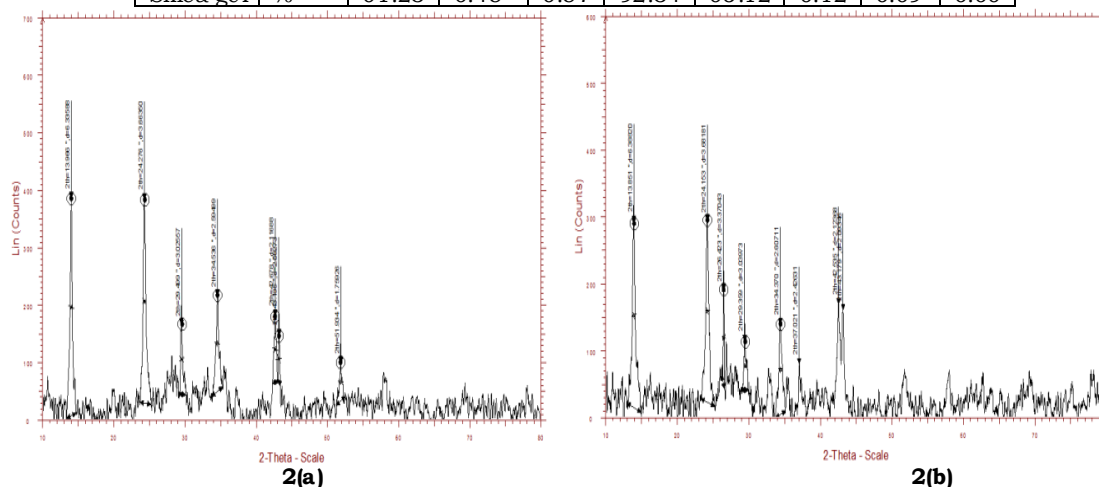
**3.4 Fourier transform infrared spectroscopy (FTIR):**

The main IR bands [1] were as follows: internal tetrahedra 1250 - 920 cm<sup>-1</sup>, asymmetrical stretch (n<sub>asym</sub>); 720 - 650 cm<sup>-1</sup>, symmetrical stretch (n<sub>sym</sub>); 500 - 420 cm<sup>-1</sup>, T-O bend; external linkages: 650 - 500 cm<sup>-1</sup>, double ring vibrations; 420 - 300 cm<sup>-1</sup>, pore opening vibrations; 1150 - 1050 cm<sup>-1</sup>, asymmetrical stretch; 820 - 750 cm<sup>-1</sup>, symmetrical stretch.

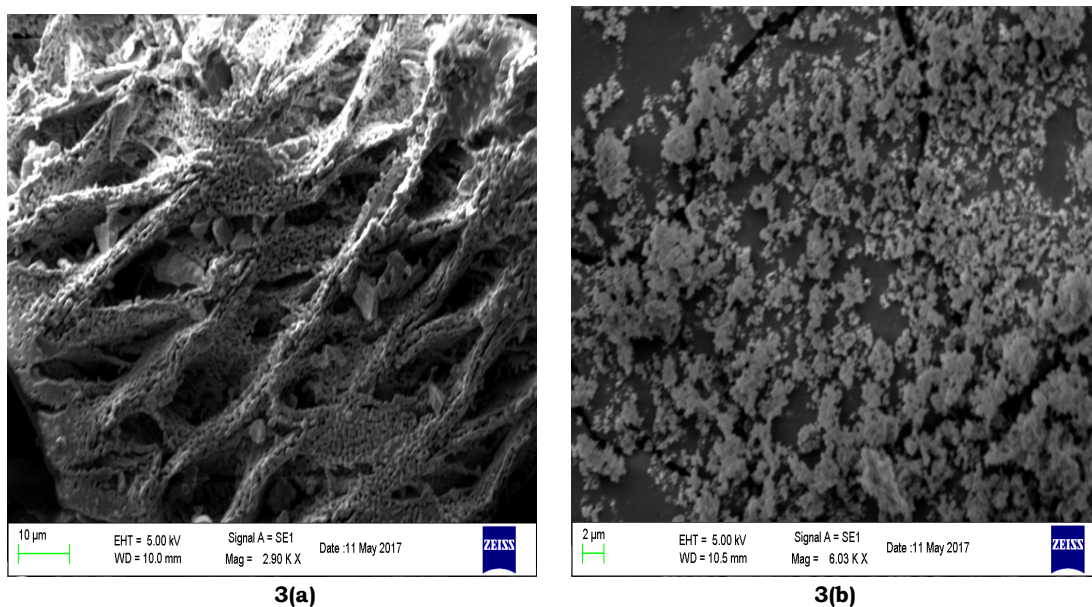
3396.23 symmetrical stretch for hydrated group presence The positions of bands due to vibrations of external linkages are often very sensitive to structure.

**Table No. 1: Physicochemical characterization of CHRA and zeolite.**

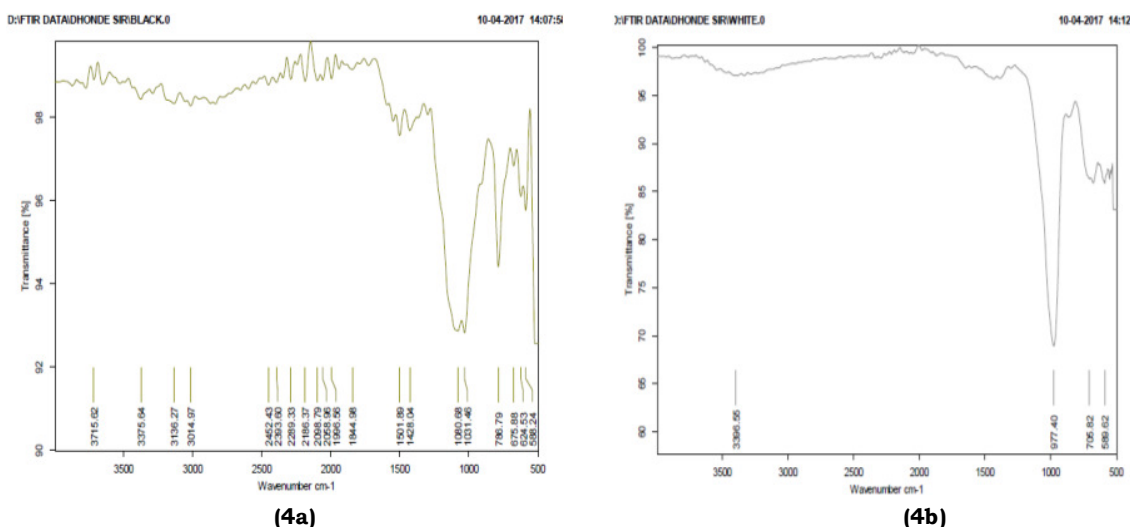
Samples	Conc.	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	SiO <sub>2</sub>	Na <sub>2</sub> O	CaO	MgO	LOI
CHRA	%	20.31	7.67	1.12	63.39	0.08	1.01	0.35	0.20
Silica gel	%	01.23	0.45	0.57	92.34	06.12	0.12	0.09	0.00



**Figure 2:** XRD patterns of rice husk and silicate gel.



**Figure 3:** Morphological study by SEM a) rice husk and silicate gel



**Figure 4:** Fourier transform infrared spectroscopy (FTIR) peak of a) CRHA and b) Silicate Gel

**4. Conclusion:**

RH to CRHA via RHA in mediatory mixing to reduce time and efficient pretreatment by hydrochloric acid to activate CRHA gives better result for silica leaching. In conventional synthesis leaching of silica from digestion of CRHA with aqueous Sodium hydroxide for 4 hours with continuous intermixing and heating is replaced by microwave irradiation i.e green technology for 30 minutes.

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**5. References:**

1. Supitcha Rungrodnimitchai, Wachira Phokhanusai And Natthapong Sungkhaho, "Preparation Of Silica Gel From Rice Husk Ash Using Microwave Heating", Journal Of Metals, Materials And Minerals, Vol.19 No.2 Pp.45-50, 2009.
2. Ragini Patil ,Rajendra Dongreand Jyotsna Meshram, "Preparation Of Silica Powder From Rice Husk" , IOSR Journal Of Applied Chemistry (IOSR-JAC), PP26-29 , 2014
3. Ram Prasad, Monika Pandey, "Rice Husk Ash as A Renewable Source for the Production of

Value Added Silica Gel and Its Application: An Overview”, Bulletin Of Chemical Reaction Engineering & Catalysis, Vol. 7 (1), PP 1 -25, 2012.

4. M. M. Rahman, N. Hasnida, W. B. Wan Nik, “Preparation of Zeolite Y Using Local Raw Material Rice Husk As A Silica Source” J. Sci. Res.1(2), 285-291 (2009)

5. E. A. Okoronkwo, P. E. Imoisili, S.O.O. Olusunle, “Extraction And Characterization Of Amorphous Silica From Corn Cob Ash By Sol-Gel Method”, Chemistry And Materials Research Vol.3 No.4, PP 68-72, 2013

6. Abhishek Mehta, Dr. R. P Ugwekar , “Extraction of Silica and other related products from Rice Husk”, Int. Journal of Engineering Research and Applications , Vol. 5, Issue 8, (Part-4) August 2015, pp.43-48.

7. K.V. Selvakumar, A. Umesh, P. Ezhilkumar, S.Gayatri, P. Vinith, V. Vignesh, “Extraction of Silica from Burnt Paddy Husk”, International Journal of ChemTech Research CODEN (USA): IJCRGG Vol.6, No.9, pp 4455-4459, 2014.

8. HadiNur, “Direct synthesis of NaAzeolite from rice husk and carbonaceous rice husk ash”, Indonesian Journal of Agricultural Sciences, Vol. 1, PP40-45, 2001.