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Maize Husk Ash as a Renewable Source for the Production of Value Added Silica Gel and Its Application

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Abstract
Nowadays, silica gels have developed a lot of interest due to their extraordinary properties and their existing and potential applications in science and technology. Silica gel has a lot of applications such as a desiccant, as a preservation tool to control humidity, as an adsorbent, as a catalyst and as a catalyst support. Silica gel is a rigid three-dimensional network of colloidal silica, and is classified as: aquagel, xerogel and aero-gel. Extraction of amorphous silica from Maize Husk Ash (MHA) was carried out in this study. Silica xerogel was produced by dissolving MHA with alkali solution to form sodium silicate solution and lowering the pH to7 by adding hydrochloric acid to form silica aquagel followed by drying to form silica xerogel. The silica xerogel was characterized using SEM, XRD and FTIR techniques. Silica and mineral contents of MHA and xerogel were determined by EDS, X-ray diffraction patterns revealed amorphous nature of extracted silica. Fourier transform infrared (FTIR) data indicates the presence of siloxane and silanol groups. Silica yield from MHA was 56.32% while moisture content was 2.89% and also the SEM presented appropriated morphological characteristics of the best silica. MHA proved to be a potential low cost raw material for the production of silica gel.
Keywords: Maize husk ash, amorphous silica, xerogel, surface properties
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1. INTRODUCTION

Amorphous Silica has been extracted from different agricultural biomass like rice husk, sugar cane Bagasse, coffee husk, and wheat husk and corn cob. Silica has been widely used in different fields such as pharmaceutical products, chromatograph column packing, detergents, adhesives, electronics, dental material, and ceramics (1). Silica as a major precursor for a variety of inorganic and organic metallic materials which have applications in synthetic chemistry as catalysts, and in thin films or coatings for electronic and optical materials (2).

Maize is one of the most widely plant food crop in the world. For every 100 Kg Maize grain 18 Kg of corn cob is approximately produced. According to International Grain Council, 824 million tonnes of maize were produced worldwide in the year 2011. India is the seventh largest producer, and the maize cobs are either thrown out as waste or burnt an application with low added value, causing environmental impacts (3). In India, about 28% of maize is produced for food purpose, about 11% as livestock feed, 48% as poultry feed, 12% in wet milling industry and 1% as seed (4). Aerogels are a diverse class of porous, solid materials composed of a network of interconnected mono structures that exhibit porosity up to 95-99%, high surface area and low density. These unique properties of aerogels attracted many researchers to explore them as drug delivery vehicles (5). Most commonly used raw materials for preparation of silica aerogels are tetra ethylorthosilicate (TEOS), tetramethylorthosilicate (TMOS) and sodium silicate solution. Synthesis of nano SiO_2 is currently of great interest because it is a basic raw material that is widely used in electronics and polymer material industries (7). Recently, Mohanraj *et al*. (2012) prepared and characterized nano SiO_2 from corn cob ash by precipitation method. Using the sol-gel technique has a benefit of producing valuable silica particles at lower cost. The objective of this present work is to extract silica from corn cob by sol-gel method and nanostructured the extracted silica without template material. The ash extracted silica was characterized using X-ray diffraction *(*XRD), Fourier transform infrared spectroscopy (FTIR) and Scanning Electron Microscopy/Energy Dispersive X-ray spectroscopy (SEM/EDX) and thermo gravimetric analysis (TG/DTA).

2. Materials and methods

All the chemicals used in this study include HCl, NaOH and H_2SO_4. All chemicals were used as received stage. First, locally collected maize husk ash was cleaned by distilled water to remove the dirt and then dried at 24 hrs. An appropriate amount of cleaned sample was calcined at 400 °C, 500 °C, and 600^{0}C, 700 ºC for 5 hrs.

2.1 Characterization

Powder X-ray diffraction pattern was obtained from a Rigaku miniflex diffract meter for 2ɵ values from 10^0 to 90^0 using Cukα target at wavelength of λ = 1.5406A^0. The FTIR analysis was carried out in a Perkin Elmer Spectrum 1000 using the KBr pellet method. The UV-Vis spectra were recorded with a Hitachi, UV3501 spectrometer. Scanning electron microscopy (SEM), (JEOl – JSM – 6360LV) was used to record the

morphology of the prepared materials and the elemental analysis was carried out by energy dispersive analysis (EDX) and Treated rice husk ash TGA and DTA analysis were performed in thermo gravimetric equipment (Pyris7, Perkin – Elmer).

3. Experimental Procedures

3.1. Preparation of Maize Husk Ash

Preparation of Maize husk ash is done by cleaned and washed with distilled water. The cleaned 100 gm maize husk was shocked in 500 ml of 3M HNO_3 and the mixture was stirred for 3 hours at 80^0C temperature. After the reflux, the solids are washed with de ionized water until neutral (acid free) and dried at a temperature of 120^0C overnight. Maize husk that have been dried and then calcined at temperature of 700^0C for 5 hours.

3.2. Preparation of silica gel nano particles

5g maize husk ash was added 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 [8]. 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 half an hour to obtain wet gel nano particles. The prepared gel was aged at 700^0C 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 700^0C. The total time of aging was 52 h. The wet gels were then dried [9]. The final product labelled at RH-Silca.

$$SiO_2\ (Ash) + 2NaOH \longrightarrow Na_2SiO_3 + H_2O \quad \text{---------- (1)}$$

$$Na_2SiO_3 + H_2SO_4 \longrightarrow SiO_2 + Na_2SO_4 + H_2O \quad \text{---------- (2)}$$

During the addition of sulphuric acid, Si-OH formed and condensed to form siloxane bond as shown below

$$Si - OH + HO - Si \longrightarrow Si - O - Si + H_2O \quad \text{---------- (3)}$$

4. Results and Discussions

4.1. XRD Analysis:

The X-ray analysis of bio silica extracted from corn cob ash is shown in Figure 1. The broad X-ray diffraction pattern shows that the bio silica is predominantly amorphous. Diffraction peak at $2\theta = 22^0$ confirms the formation of amorphous silica.

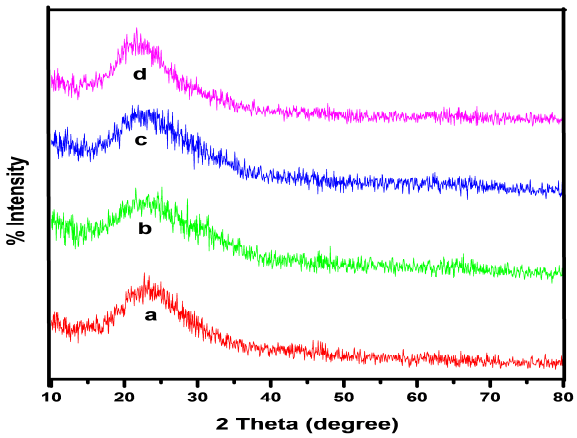

Fig1.XRD spectrum for MHA a) 400^0C b) 500^0C c) 600^0C d) 700^0C

In general, it has been reported that diffraction broad peak at $2\theta = 22^0$ degree indicates amorphous silica along with some of the other impurities peaks are presented. In the diffractogram, a broad hump is observed at $2\theta = 22^\circ$ to 28° which is due to disorder structure of Si-O band.

4.2. FTIR Analysis:

The major chemical groups present in the sample were determinded by FTIR spectral as shown in figure 2.

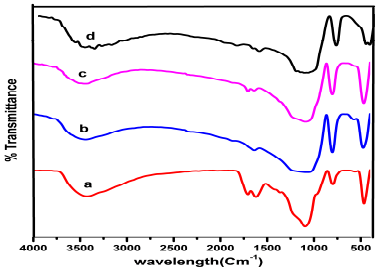

Fig.2.FTIR spectrum of MHA a) 400^{0}C b) 500^{0}C c) 600^{0}C d)700^{0}C

Fig 2(a - d) shows an FTIR spectrum at RHS. A broad band in the range of 3362 cm^{-1} is due to the stretching vibration of the O – H band. This band is due to silanol groups (Si – OH) and the adsorbed water bound to the surface. The weak band 1642 cm^{-1} is assigned to H – O – H bending vibrations mode where also represented due to the adsorption of water in air when FTIR samples disk were prepared in an atmospheric pressure. Also, there is a tiny dip in the spectra at 2354 cm^{-1} due to the presence of atmospheric CO_2. These peaks are trapped in the matrix of silica surface. The predominant peak at 1383 cm^{-1} is due to silaxone bonds (Si – O – Si). The adsorption bands between 474 and 993 cm^{-1} are because of silica structures and other peaks observed in the range of 1247 and 2764 cm^{-1} are because of impurities such as carbonate and sodium groups. The peaks between 1055 and 711 cm^{-1} indicates the vibration modes of Si – O – Si network. A most intense band at 1110 cm^{-1} and a peak 765 cm^{-1} are due to asymmetric and symmetric stretching mode at Si – O – Si. The bending vibration of Si – O is shown by strong band at 475 cm^{-1}. The vibration of oxygen atoms joined with the adjacent atoms in the asymmetric stretching vibrations of Si – OH bond appeared at 1150 cm^{-1} [10].

4.3. SEM/EDS analysis:

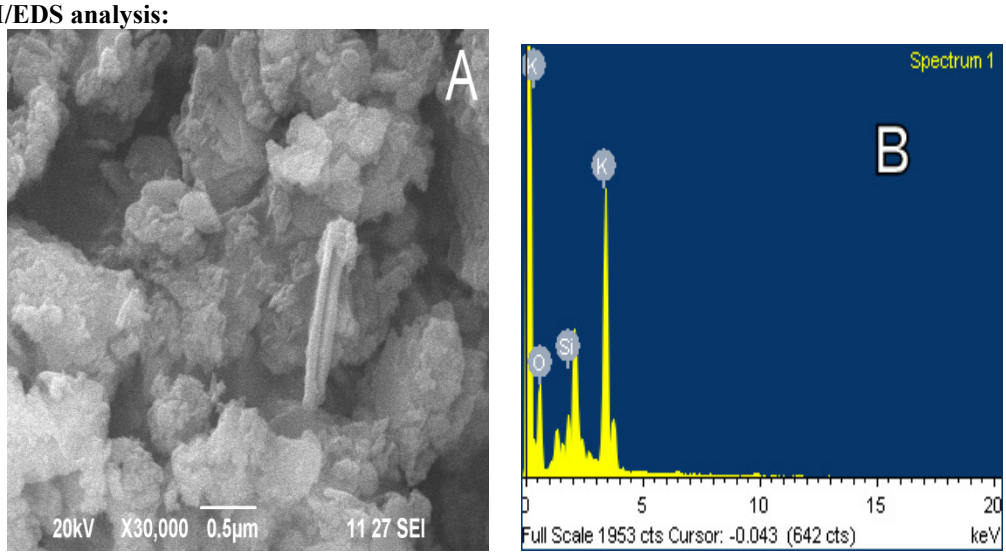

Fig.3. (a) SEM image of MHA and (b) EDS spectrum of MHA at 700 ˚C for 5hr.

Fig. 3(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 with different sizes. The major intensity of Si in the EDS spectrum is confirmed the silica at maximum weight percentage and also due to some trace of other impurities.

4.4. TG/DTA analysis:

The results of TG/DTA analysis conceded for an estimate of the temperature range that corresponds to important chemical and structural transitions of the obtained system. The TG analysis revealed three distinct stages of mass loss namely, removal of moisture content, release of volatile matter and burning of combustion material. In fig (4), the overall decomposition behaviour of MHA was attributed to decomposition of hemicelluloses, cellulose and lignin. Previous reports claim that contributors to the evolution of the volatile matter.

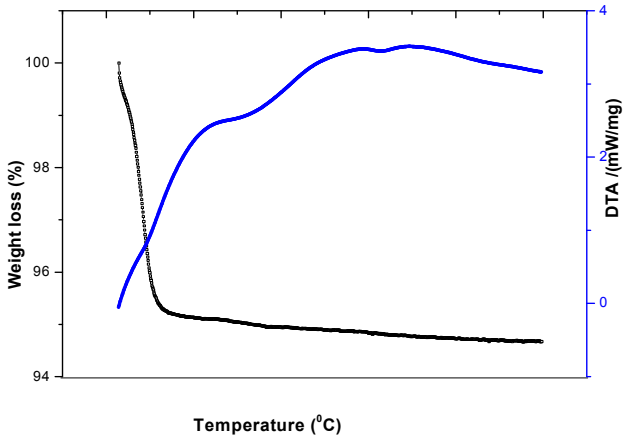

Fig 4. TG-DTA curve for MHS

In the study on the thermal degradation, it can be reduced from these removals that decomposition of hemicelluloses starts first followed by cellulose and finalizes with decomposition of lignin. The gaseous volatiles were released from organic and inorganic material during thermal degradation. In this figure, it was noted that there was a decrease in the temperature of the sample around 200^0C. The weight of the sample remains almost constant for certain duration of time with decreasing temperature and after certain duration there is again increase in the temperature. This typical behaviour of rice husk ash sample of very fine size must be connected with some structural changes, since whenever there are any structural changes associated with sample, a certain amount of energy has been adsorbed and there is an endothermic reaction. The weight trace suddenly acquired along the abscissa and then continued its forward movement as usual. The TGA were mainly exhibits the initial weight around 100^0C which is due to loss of water content of the sample. The decrease in weight over a temperature range of 150^0C can be attributed to the thermal combustion of organic groups present in the ash and rapid decomposition of the sample.

Maize Husk ⟶ Intermediate + Volatiles ---------- (4)

In DTA curve, there are two exothermic peaks at 250^0C and 450^0C which are correlated to the removal of organic groups by oxidation and rapid decomposition of the sample respectively [11]. In Fig (4) TG – DTA for RHS/TiO_2, curve of the mass loss occurring in the range from 180^0C to 310^0C may be attributed to the decomposition of organic and inorganic materials. This occurred due to the removal of impurities with less thermal stability. The increase in temperature to about 400^0C resulted in the weight loss depending of Rice husk variety and chemical treatment due to the loss of water present in the sample and external water bounded by surface tension.

5. CONCLUSION

It is concluded from the study, Maize Husk ash is a suitable source for silica preparation and expensive for preparation cost is to be less with equivalent properties with 52.32% silica content and minimal mineral contaminants can be produced from MHA using the sol gel method. XRD analysis MHA are the amorphous nature of the silica; Fourier transform infrared (FTIR) data indicated the presence of siloxane and silanol groups.

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