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Synthesis and Characterization of Silica from Ragi Husk Ash (Finger Millet) by a Sol-gel Method

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Abstract
Silica aerogel, a mesoporous material, was prepared from ragi husk ash by sol–gel method and dried under atmospheric pressure. In this method, ragi husk ash, which is rich in silica, was extracted with sodium hydroxide solution to produce a sodium silicate solution. This solution was neutralized with acid to form a silica aerogel. The aged gel was washed carefully by de ionized water and ethanol and finally dried under atmospheric air. A temperature of 700^0C was found to be optimum ashing temperature with maximum amorphous silica content. From a morphological analysis obtained by SEM and diffraction patterns (XRD), a longitudinal fibrous and amorphous structure was observed for Ragi Husk. FTIR characterization indicated the presence of silanol and siloxane groups. Thermo gravimetric was used to characterize burning behaviour and also to determine the activation energies. This economic technology, as applied to waste material, also provides many benefits to the local agro-industry.
Keywords: Ragi husk Ash, Sol- gel method, Amorphous silica, Aerogel

1. Introduction

Silica has been widely used in pharmaceutical products, chromatograph column packing, detergents, adhesives, electronics, dental material, and ceramics. Silica has also been used as a major precursor for a variety of inorganic and organometallic materials which have applications in synthetic chemistry as catalysts, and in thin films or coatings for electronic and optical materials. A low energy method to produce pure silica from rice husk ash with 91% extraction yield, has been developed, acid leaching and gasification methods have also been investigated for recovering silica from ragi hull. Bio mass is an important renewable energy resource and accounts for 15% of the total global energy supply. Finger millet is an annual, tufted grass and varies in height from as little as 25 cm up to more than 120 cm. It tillers at a population of less than 10 plants per square meter (1). It accounts for 8% of the area and 11% of production of all millets in the world (2). It is grown in over 25 countries in Africa (East and South) and Asia (Middle East and Far East), mainly for grain (International Centre for Agricultural Research in the Semi Arid Tropics [ICRISAT], 1997). For several years, this species was considered one of the most important crops grown in the oasis of Gabes. It had prominently occupied an important place in the oasis. The finger millet remains largely unknown and unstudied in oasis conditions and it is threatened by extinction, despite it's important role in these ecosystems. Finger millet (*Eleusine coracana*) can add substantial value to the diet in terms of protein and carbohydrates which is comparable to other cereals. In addition it contributes vitamins, minerals and fibre as it is consumed whole, in comparison to ragi which is usually consumed after milling and polishing (3). This ragi husk ash (RHA) can be an economically viable raw material for the production of silicates and silica. Sodium silicate can be produced very cheaply from the RHA by simply boiling it with refluxed sodium hydroxide solution for 1 hour whereas this sodium silicate, the precursor for silica production, is currently manufactured by melting quartz sand with sodium carbonate at 1300°C (4). Silica gel has been used as a desiccant for many years to protect sensitive materials from damage due to excess humidity. As the gel is normally white or colourless, and shows no obvious change in colour during use, it is difficult to tell when it has become saturated with moisture and needs to be regenerated by heating, or replaced. There is therefore a need for a visible indication when the gel is saturated (5).

Subsequently various procedures have been developed to convert RHA to silica: fluidized bed (6), chemical pre and post treatment using acid and base solution (7), pressurized hot water treatment processes (8), carbonization and combustion (9), non isothermal decomposition in oxidizing atmosphere (10). Thus any process to produce this silica has the benefit of not only getting valuable material but also reducing disposal and pollution problems of the husk.

This paper reports to a prepare nano silica from ragi husk ash without adding chemicals and any extra surfactants by using sol -gel technique. This technique has benefits reduces as a disposal pollution challenges and also environmental impacts.

2. Materials and methods

Among chemicals used in this study include HNO_3 and NaOH. All chemicals were used as received without any purification. Initially, locally collected Ragi 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 ºC and 700 ºC

for 5 hrs.

2.1. Sample preparation

Washing and pretreatment of RH was carried out according to the procedure reported by Adam *et al.,* [10]. Washed and dried RH (30.0 g) was stirred in 500 mL of 1 M HNO_3 overnight, to enable the removal of metals from the RH (11). This acid treated RH was washed thoroughly with copious amount of distilled water to ensure the absence of NO_3 - and subsequently dried in an oven at 110°C for 24 h. The sodium silicate solution was kept in a covered container to be used as the source of silica but the pH was maintained at 3. RH-Silica was synthesized by titrating the sodium silicate with 3.0 M HNO_3 until it reached pH 3. A yellowish- brown suspension was observed during the titration. The observed suspension was aged for 2 days in a covered container. The gel was filtered, washed with copious amount of distilled water and oven dried at 110°C. The resultant product is RH - Silica.

3. Result and discussion

3.1. XRD Analysis:

According to diffraction theory, the intensity of peak depends on the amount of ordered semi crystalline structures on the differences in electron density between amorphous and crystalline. Fig(1) shows the sharp peaks can be directly correlated to crystalline region and the diffused peaks to amorphous region of the samples. The lower peak intensities indicate the presence of lower degree of crystallinity. In the diffractogram, a broad halo is observed at 2θ= 15˚ to 40˚ which is due to disorder structure of Si-O band. It implies that silica particle in the ash undergoes structural transformation under increased calcination temperature which is supported to the comments suggested by P.K.Jal et al (12). According to their report, naturally occurring silica is crystalline whereas synthetically obtained silica is amorphous in nature. It implies that, further increase the temperature, the ash again turned from amorphous to crystalline. From the XRD analysis amorphous SiO_2 is determined at 700 °C which is a suitable condition prepare the nano SiO_2 from the pre treated ash SEM analysis of ash at 700 °C.

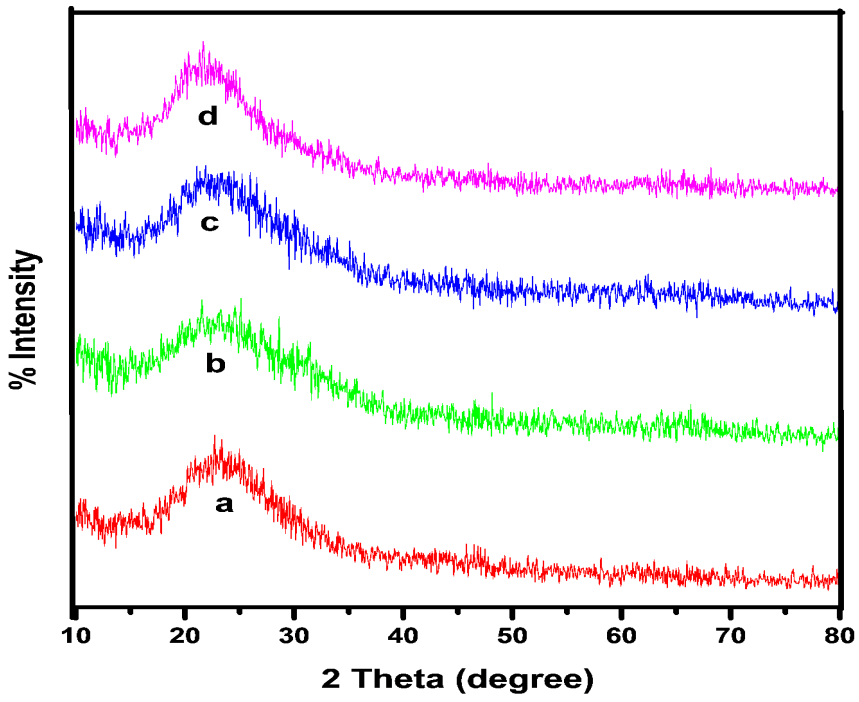

Fig 1. XRD pattern Ragi Husk Ash a) 400^0C b) 500^0C c) 600^0C d) 700^0C e) silica gel

Crystallization had taken place due to the high temperature employed during calcinations . The XRD results indicated that the temperature affected the crystallization of the RHA samples.

3.2. FTIR Analysis:

Fig (2) shows that the broad band in the range at 3490 cm-1 is due to the stretching vibration of O-H band. This band is due to the silanol OH groups (Si-OH) and the adsorbed water bound to the silica surface The vibration of oxygen atom joined with the adjacent silicon atom in the asymmetric stretching of Si-O-Si band appeared at

1098 cm-1, while a symmetric stretching vibration of Si-OH band appeared at 964 cm-1 (13). The peaks between 1055 and 711 cm^{-1} indicates the vibration modes of Si – O – Si network.

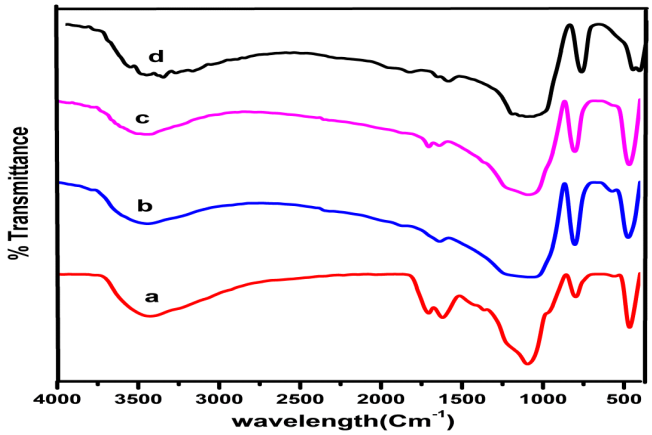

Fig 2. FTIR pattern Ragi Husk Ash a) 400^{0}C b) 500^{0}C c) 600^{0}C d) 700^{0}C e) silica gel

3.3. TG- DTA Analysis:

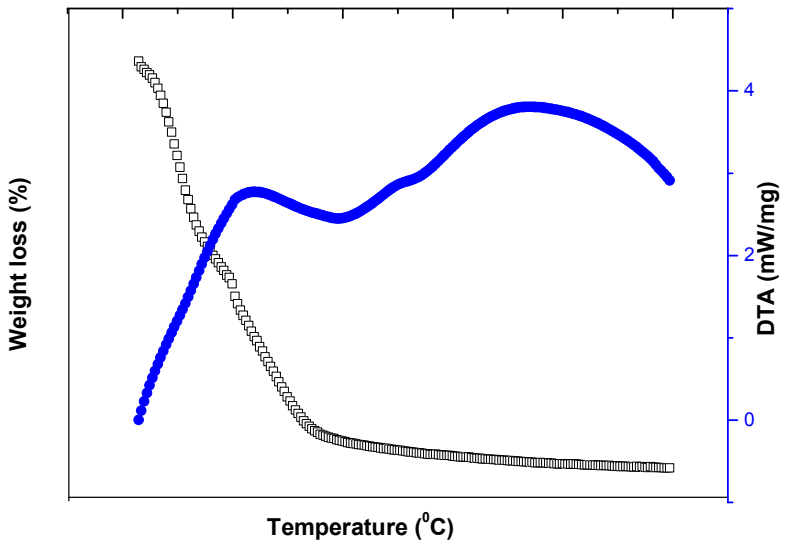

Fig 3. Tg- DTA spectrum for raw ragi husk ash

The burning of organic material (hemicelluloses and most of the stratch) begins at approximately 180 °C and extends up to 200 ºC. Between 300 and 600 ºC the decomposition of lignin occurs. From the moment that the percentage of mass reaches the second level, all of the organic part of the bark has been burned, leaving mainly inorganic compounds, e.g., silicon oxide, which is more stable at high temperatures (14). In DTA curves of Fig. 3 there are two exothermic peaks at 370 and 680^{0}C, which are correlated with removal of organic groups by oxidation and rapid decomposition of the sample, respectively

3.4. SEM/EDX analysis:

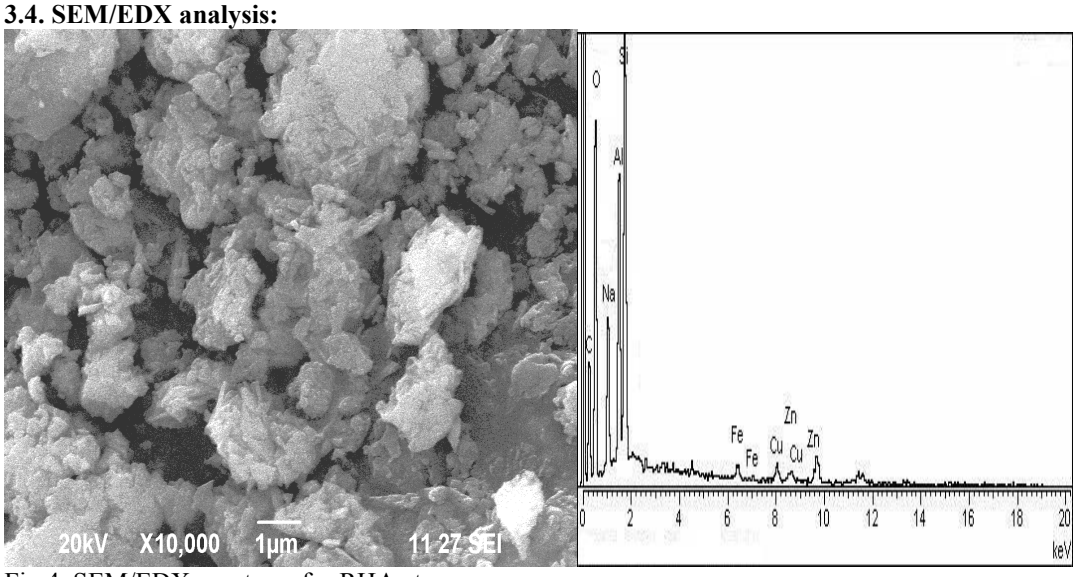

Fig 4. SEM/EDX spectrum for RHA at

The observations of X-ray diffraction were confirmed by the scanning electron microscopic studies. The microstructure of the native as well as the processed Ragi Husk Ash products are illustrated in Figure 4.In the SEM image, Fibrous nature of particles are freely disposed on the surface which may be due to synthesized silica has lower hydroxyl number and hence reduced silica-silica agglomeration (15). In EDS Spectrum A strong intensity of Si is alone in the spectrum which is confirmed predominant of silica in the sample and some traces due to impurities.

4. CONCLUSION:

It is concluded from the study, Ragi Husk ash is a suitable source for silica preparation and expensive for preparation cost is to be less with equivalent properties to commercial silica and that silica xerogels with 52.32% silica content and minimal mineral contaminants can be produced from RHA using the sol gel method. XRD analysis reveals the amorphous nature of the silica; Fourier transform infrared (FTIR) data indicated the presence of siloxane and silanol groups. SEM/EDX was confirmed that the highest percentage of the silica matrix.

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