International Journal of Ecology and Environmental Sciences
www.ecologyjournal.in
Online ISSN: 2664-7133; Print ISSN: 2664-7125; Impact Factor: RJIF 5.28
Received: 11-12-2020; Accepted: 26-12-2020; Published: 11-01-2021
Volume 3; Issue 1; 2021; Page No. 81-86

Synthesis and characterization of mesoporous silica from sugarcane bagasse industrial fly ash

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Abstract
Sugarcane bagasse is a well-known agricultural residue produced in high quantities around the world and Sugarcane Bagasse Ash (SCBA) is one another waste generated in tonnes as a result of consumption process which is mostly dumped as landfills. These wastes generated out of Sugarcane industry are enriched with silica content and are ecologically safe and biocompatible. The present study was focused on extracting silica from sugarcane bagasse and to synthesize mesoporous silica using sol-technique. The synthesis of mesoporous silica nanoparticles from sugarcane bagasse fly ash involved liquid crystal templating mechanism. Initially, the Sugarcane Bagasse Fly ash extract and HCl concentrate was taken in the ratio of 1:10, to which 1:6 ratio of Sodium hydroxide was added to obtain base solution of sodium silicate wherein H_2SO_4 concentrate solution was put in along with a non-ionic surfactant, polyethylene glycol (PEG) to obtain a white colour precipitate followed by the process of gel formation. The PEG used as surfactant template was then removed through heat treatment using muffle furnace. The resultant mesoporous silica biomaterial synthesized from sugarcane bagasse ash, was characterized with very high surface area that could relatively encapsulate number of bioactive molecules of interest involving eco-friendly techniques.

Keywords: sugarcane bagasse charcoal, sodium silicate, encapsulate, mesoporous silica, solgel

Introduction

Agriculture is a major occupation and is one of the primary sources of livelihood for about 58% of India's population (Indian Agriculture and Allied Industries Industry Report). Though agriculture contributes crucially to Indian economy the processing of wastes generated out of agriculture and allied industries requires limelight. For instance, straw, corn cob and bagasse are the waste produced from rice, maize and sugarcane respectively are rich in silica [1]. The demand for Silica is on high rice in agriculture as it can potentially boost the plant growth, yield and quality of the end produce. Additionally, they play an important role against environmental stress and crop care. India is the leading producer of Sugarcane *(Saccharam officinarum)* with production capacity of 167 million tonnes annually (Annual Report Sugarcane -2012-2013). Around 40 million metric tonnes (MMT) of sugarcane bagasse are generated as waste from sugarcane industry with an average 44,220 tonnes/day. Sugarcane bagasse is rich in silica with a percent content of 53.10. The advantage of using sugarcane bagasse as a source material includes, cost-effectiveness, chemical stability, versatility, biocompatibility and eco-friendly (slowing *et al., 2008)* [2]. The two major fields of silica application are the paper industry (sugarcane fly ash) and agriculture (loading capacity of mesoporous silica). Nano-porous materials are those with a small organic or inorganic framework that facilitates loading of active compounds [10, 18]. The IUPAC classifies porous materials into microporous, mesoporous and Nano porous *(*McCusker *et al., 2001)* [3]. The mesoporous silica is exclusively targeted in agricultural applications as they can be easily functionalized with number of molecules for targeted delivery, their stability which is due to Si-O bond and the tuneable nature of pores is an added strength, (kwon *et al., 2013)* [4].

Functionalization of Mesoporous silica nanoparticles, its high surface area, chemical stability, large pore size, pore volume and its rapid internalisation in plant cell without causing any cytotoxic effects promotes it as a good carrier of any compound of interest for stimuli-based delivery [15]. Apart from being a good carrier, mesoporous silica nanoparticles itself acts as a functional molecule that favours seed germination, root growth, seedling vigour and nutrient availability [17]. Mesoporous silica nanoparticles can be synthesised through various approaches such as sol gel method, micro emulsion and stabber method [13, 14]. But these methods have disadvantages like phase change, difficulty in controlling the particle size, high degree of crystallinity, high cost etc., Thus, green synthesis utilizing agricultural wastes like sugarcane bagasse is considered to be a best alternative method [16]. The low consumption of toxic chemicals, use of waste as raw material etc makes it a better choice [7, 8]. Mesoporous silica nanoparticles provide a non-invasive and biocompatible delivery platform for a broad range of applications in therapeutics, pharmaceuticals and diagnosis [11]. The creation of smart, stimuli-responsive systems that respond to subtle changes in the local cellular environment are likely to provide long term solutions to many of the current drug/gene/DNA/RNA delivery problems. (*Popat et al, 2011*) [9]. The present study aims to synthesize mesoporous silica from sugarcane bagasse ash and to further functionalize it to utilize as a carrier of targeted biomolecule [12].

Materials and methods

Sugarcane bagasse charcoal, the source material for synthesis of mesoporous silica was obtained from local sugarcane industry, Perambalur. Hydrochloric acid (HCl), Sulphuric acid (H2SO4)

and Sodium hydroxide (NaOH) was purchased from Sigma Aldrich of analytical grade and the Poly ethylene glycol (Molecular weight 6000) used as substrate was also obtained from Sigma Aldrich.

The technique followed to synthesize mesoporous silica was the modified protocol reported by Rahman *et al.*, 2015 [16]. The charcoal of sugarcane bagasse obtained was converted into ash by the process of calcination at 600ºC for 6hrs using muffle furnace. The process was repeated twice to obtain ash at desired purity that appears white. The ash acquired from this process after calcination, was taken for alkali treatment, in which the ash was dissolved in 1M HCL and stirred at 400 rpm for 2.30 hours. The solution was then filtered using at room temperature. The filtered ash was further dried at 60ºC for 3 hours. The dried ash was dissolved in 2N NaOH and again stirred for 3 hours at 600 rpm. The dried ash dissolved in sodium hydroxide was filtered using Whatman filter paper no.42 at RT to obtain the resultant sodium silicate solution.

To further synthesize mesoporous silica, sodium silicate was used as a precursor. The non-ionic surfactant (PEG) at 2% concentration was used as a substrate, and added drop wise to 10 ml of sodium silicate under stirring at room temperature, in order to form a precipitate white pigment. It was then left undisturbed until a gel network was formed. The produced gel was then centrifuged for 10 minutes at 6000rpm and then thoroughly washed using distilled water. The resultant milky white pellet obtained was dried in vacuum cum oven drier at 600ºC for 5hours. Finally, to obtain mesoporous silica free from the substrate used (PEG), calcination process was carried out 400ºC for 4 hours. The mesoporous silica was subjected to various characterization including Scanning electron microscopy (SEM), Transmission electron microscopy (TEM) and BET surface area.

Characterization

Transmission electron microscope (TEM)

The morphology and size of silica nanoparticles is assessed from images obtained from the transmission electron microscope, TEM (FEI Technai spirit) has an operating capacity of 120 kV. The nano bio silica samples were dispersed in distilled water and sonicated for 30 minutes. One microlitre of well dispersed sample was placed on carbon coated copper grid. The copper grid was placed undisturbed for complete evaporation of water. The dried copper grid containing nano bio silica was visualised using TEM.

Brunaure- Emmet-Teller (BET)

It is an instrument used to determine surface area, pore size and pore volume. It measures the same by adsorption of nitrogen gas with 16.2Å cross sectional area on the free surfaces of nano bio silica. A desired amount of dry nano bio silica was degassed at a temperature of 300 °C for 180 minutes with a ramp of 20°C/minute**.** The degassed sample was weighed and transferred to liquid nitrogen present in isotherm analysis chamber for nitrogen adsorption and desorption. Based on the amount of nitrogen adsorbed and desorbed surface area, pore size and pore volume were ascertained.

X-ray diffraction (X-RD)

X- ray diffracto meter is used for the determination of crystalline and amorphous nature of sample. An automated X- ray diffraction analysis (XRD) instrument carrying multiplex diffracto meter with Cu anode using k radiation over the range (2Ɵ) at 40 kV and 20ma with a scan time of 0.5x/min of 50-80 º.

Results and Discussion

The Silica nanoparticles were synthesised from sugarcane bagasse fly ash using solgel technique. The charcoal obtained was converted to ash through calcination (600° C) process. To completely remove the carbon content the aforementioned step was repeated twice. The second diluted hydrochloric acid wash of ash was done to remove the other major minerals of bagasse ash such as Aluminium as aluminium chloride, Manganese as Manganese chloride, Copper as copper chloride, Potassium as potassium chloride, Sodium as sodium chloride, calcium as calcium chloride and iron as ferric chloride. A comparative table on the difference in level of contaminants (elements other than silica and oxygen) in ash and silica nanoparticles was represented. (Table.1). The weight percentage of nitrogen, magnesium, aluminium, phosphorous, sulphur, chlorine, potassium and calcium in charcoal and nano bio silica were 25.22, 02.01, 02.37, 01.07, 01.31, 00.95, 00.92, 01.12 and 04.24, 00.10, 0.00, 0.00, 0.00, 00.16, 00.17, 00.17 respectively. This shows the complete reduction other elements due to acid wash. Thus, acid removes the contaminant elements and provides purified form of ash for better preparation of silica nanoparticles. The similar trend of reduction in contaminants were also observed by flak *et al.*, 2019 [5]. The sharp increase in sodium content of nano bio-silica (02.77) was due to alkylation step in the preparation of mesoporous silica nanoparticles. The sugarcane bagasse charcoal and nano bio silica were shown in the figure. The purified ash was used to synthesise sodium silicate solution through alkylation step. Sodium silicate solution was converted to silica gel by reducing the pH of the solution to neutral or nearly acidic. The pH reduction was carried out using PEG ylated sulphuric acid. The PEG in sulphuric acid act as a template such that silicic acid forms intermolecular weak hydrogen bonding with the hydroxyl group of poly ethylene glycol. The synthesised gel was dehydrated to remove moisture and calcinated to remove poly ethylene glycol to form mesoporous silica nanoparticles. The nanoparticles were characterised using TEM, BET and X-RD to analyse the Physico-Chemical nature of the sample. The X-RD spectrum of nano bio silica shows a characteristic amorphous peak of silica at two theta value of 22.75°. However, there was another sharp peak at 31.67° whose crystalline d spacing was calculated using Bragg's law $n\lambda = 2d\sin\Theta$. The calculated d-spacing was 6.46nm. The X- RD spectrum of mesoporous silica nanoparticles was represented in Figure. The bio silica synthesised through alkylation and acidic preparation shows a typical amorphous peak at 22Å (Alves *et al*, 2017) [6]. Similarly, the nano bio silica prepared using cetyl trimethyl ammonium bromide ionic surfactant as a template molecule also characteristic amorphous peak at 22 Å (Rida *et al*, 2014) [19].

The size and morphology of synthesised mesoporous silica nanoparticles was characterised using Transmission electron microscope. The TEM micrograph of mesoporous silica nanoparticles were shown in the figure. The sphere-shaped nanoparticle was observed with size range of 15- 50 nm. Whereas Particle size analyser exhibit a size range of 200 – 400nm with a poly dispersity index of 0.652. The size distribution graph was represented in the figure. Dynamic light scattering analysis of

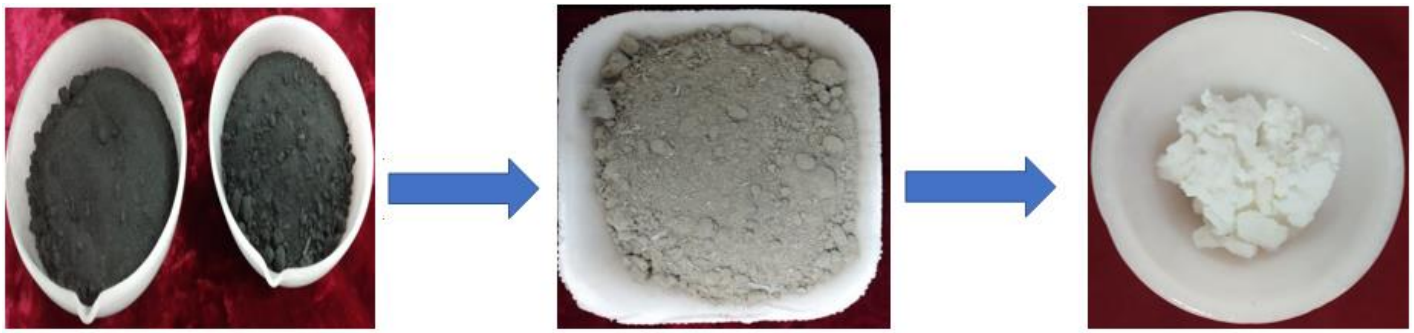
nano bio silica prepared through template assisted method have a particle size of 100–350 nm (Rida *et al*, 2014) [19]. The TEM characterisation of nano bio silica obtained from sugarcane bagasse ash had a size of less than 20 nm (Rovani *et al*, 2018) [7]. The PEG in the nano bio silica was removed through calcination. The pores formed were characterised using surface area analyser. The typical type IV isotherm was obtained. The Surface area, pore volume and pore size of the synthesised nano bio silica were 718.63m^2/g, 7.69 cc/g for 75.11 nm sized particles and 21.4 nm respectively.

Alves *et al*, 2017 [6] reported that the green synthesised bio-silica have a surface area, total pore volume and pore size of about 265 m^2/g, 0.425 cc/g and 6.25 nm respectively. Similarly, the nano-bio silica prepared from sugarcane bagasse ash through solgel technique have a surface area and pore radius of 124, 89 m2/g and 17 nm respectively (flak *et al*, 2019) [5].

They are in similar pattern with the present observed results, but the optimum concentration of PEG and slow addition of PEGylated sulphuric acid results in higher surface area and increased pore radius.

Table 1: Elemental concentration of sugarcane bagasse charcoal and nano bio silica

0	Element	Weight Percent in charcoal (wt %)	Weight percent in Nano bio silica (wt %)
1	Nitrogen	25.22	04.24
2	Oxygen	50.58	40.30
3	Sodium	00.55	02.77
4	Magnesium	02.01	00.10
5	Aluminium	02.37	-
6	Silica	07.60	21.67
7	Phosphorous	01.07	-
8	Sulfur	01.31	-
9	Chlorine	00.95	00.16
10	Potassim	00.92	00.17
11	Calcium	01.12	00.17



Sugarcane Bagasse Industry Charcoal Sugarcane Bagasse Fly Ash Measoporous Bio Silica

Fig 1: Conversion of Sugarcane baggase charcoal to mesoporous bio silica

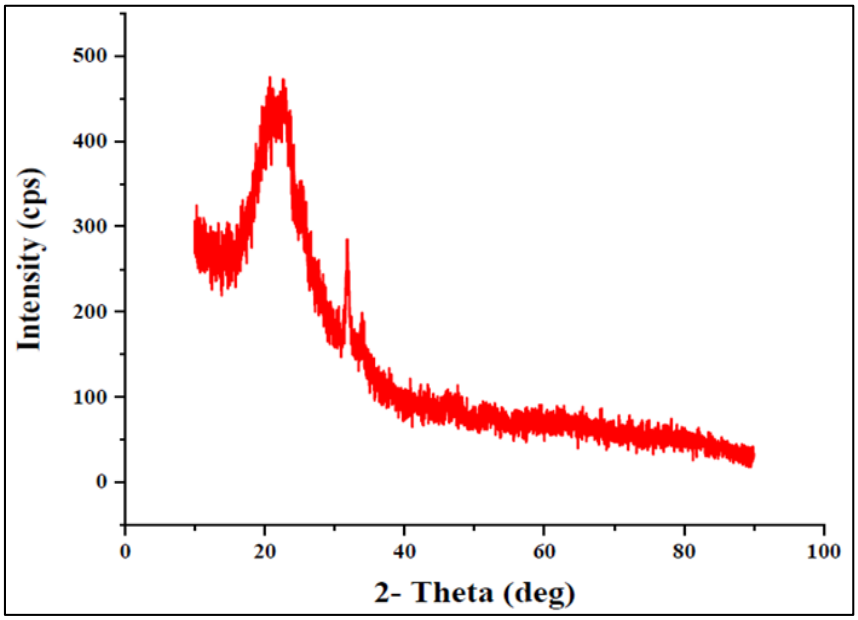


Fig 2: X- RD of mesoporous bio silica

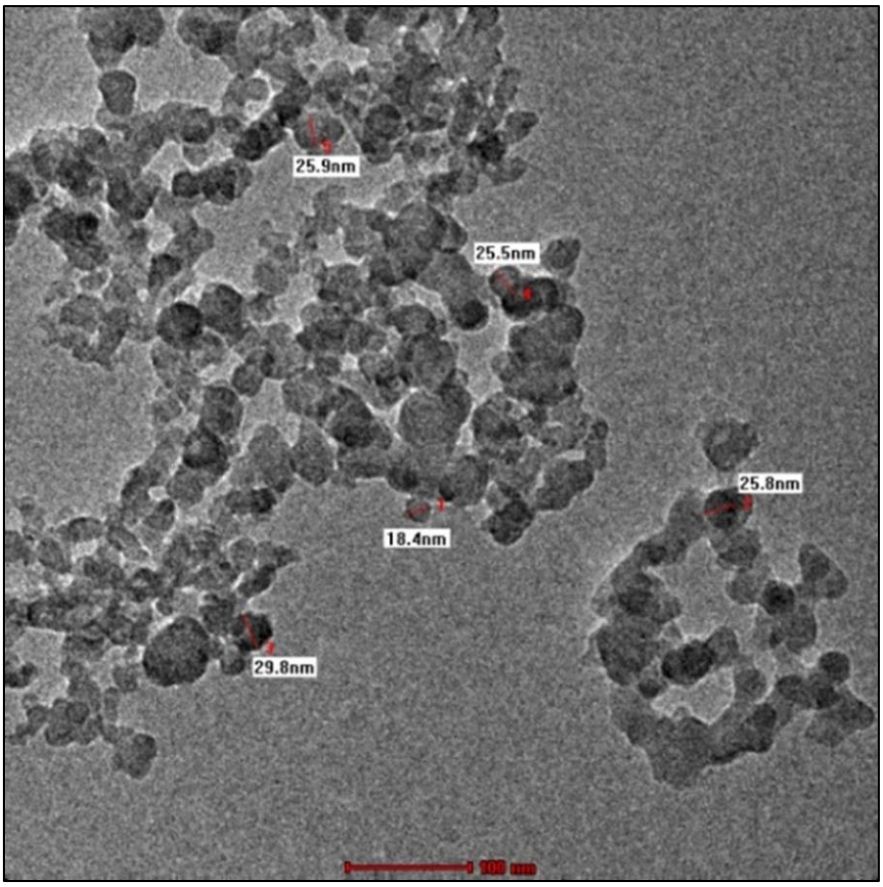


Fig 3A: TEM micrograph of nanobiosilica at 100 nm scale bar

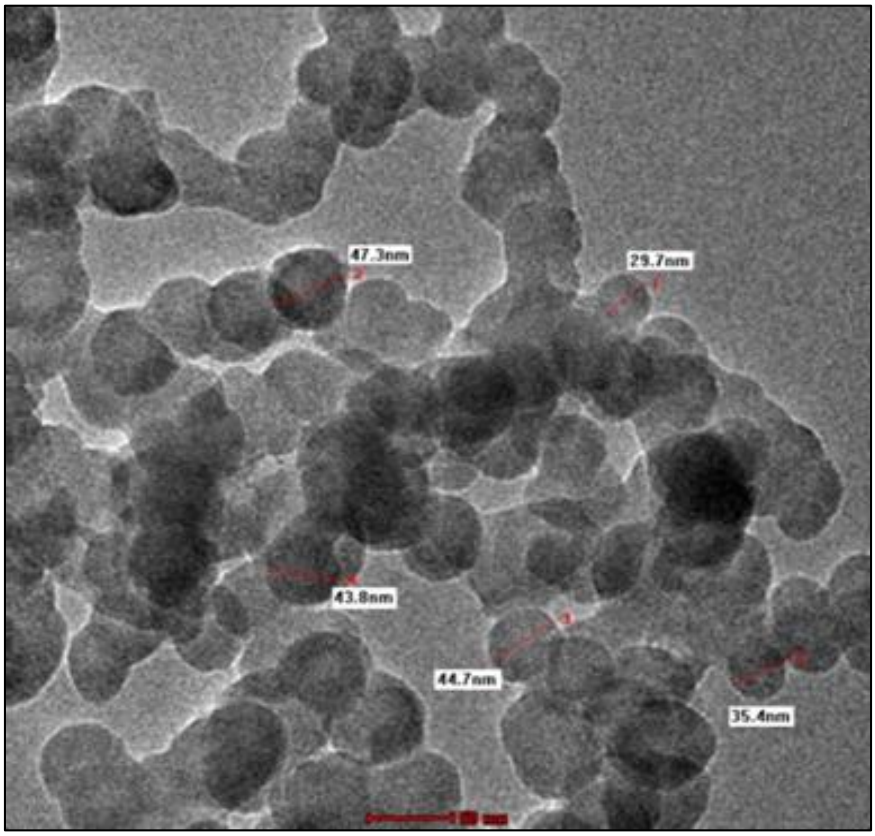


Fig 3B: TEM micrograph of nanobiosilica at 50 nm scale bar

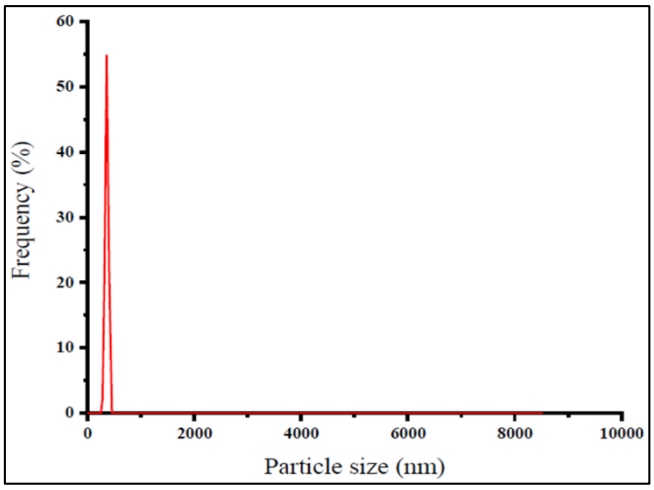


Fig 4: Dynamic light scattering analysis of nano bio silica

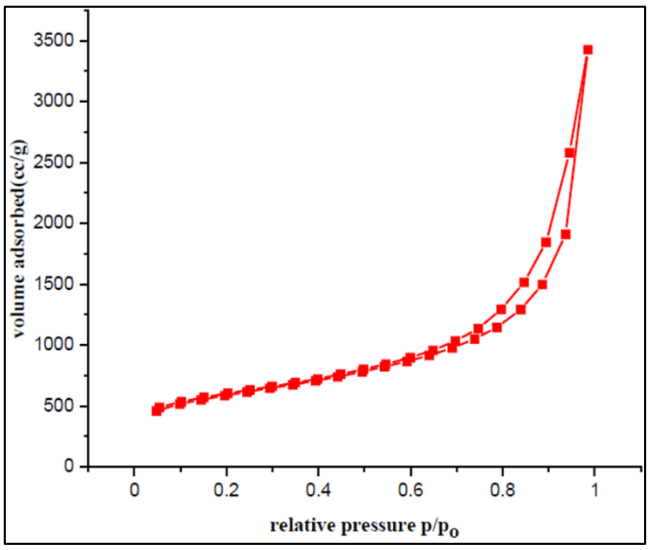


Fig 5: Multi point isotherm of nano bio silica

Conclusion

The results obtained in this study show that the protocols established a sugarcane bagasse fly ash can be purified for the effective alternative approach to obtaining SiO2, either as a commercial silica or stable gel as a powder of nanostructure. The X-RD, TEM, BET, SEM data provide convincing evidence of the high amorphous purity of extracted silica from sugarcane bagasse fly ash. The high silica content of the silica compound can be used for the environmental effect of preparation can be reduced and bagasse ash disposal concerns.

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