Preparation and characterization of nano SiO_2 from corn cob ash by precipitation method

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In this paper, nano silica was prepared from corn cob ash by precipitation method. Initially, received corn cob ash was calcined at 550 °C, 650 °C, and 750 °C for 2 hr to remove the volatiles in the sample and determine the amorphous structure of SiO_2. Next, the thermally treated corn cob ash was mixed with various concentration of NaOH to extract pure SiO_2. 1% of polyvinyl alcohol (PVA) also used as the dispersing agent. Finally, nano silica was synthesized from pure silica by precipitation method. The prepared nano silica particles were characterized by XRD, FTIR and SEM with EDS techniques. From the XRD analysis, amorphous characteristic nano silica is observed a broad hump at 2θ=15˚ to 40˚ and average size is found to be 34 nm for normally prepared and 22 nm for 1% PVA addition. It reveals that PVA has reduced the size of the particles. Infrared spectral data confirmed the presence of hydrogen bonded silonal group and siloxane group. SEM images reveal the spherical nature of SiO_2 particles and average size of the particles is found to be 25 nm in 1% PVA. A strong signal in the EDS spectrum is confirmed the SiO_2.

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1. Introduction

Corn is one of the most widely plant food crop in the world. For every 100 Kg corn grain 18 Kg of corn cob is approximately produced. According to International Grain Council, 824 million tones of corn were produced worldwide in the year 2011. India is the seventh largest producer, and the corn cobs are either thrown out as waste or burnt an application with low added value, causing environmental impacts [1]. In India, about 28% of corn is produced for food purpose, about 11% as livestock feed, 48% as poultry feed, 12% in wet milling industry(for example starch & oil production) and 1% as seed [2]. Usually these are discarded as waste or as low grade fuels. This possesses a serious problem not only in storage but also for disposal, for example the combustion of corn cob is contributing to an increase in the concentration of CO_2 in the atmosphere. It is one of the green house gases and can result in global climate change. It contains a high amount of SiO_2 (>60%) which is being occupied by useful land or treated as waste [3]. Due to the high pozzolanic activity, this corn cob silica finds applications in high strength concrete and it is used in polymers to enhance the mechanical and thermal properties of the materials.

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. Recently many authors have been synthesized nano SiO_2 from agro waste materials.

Suh Cem Pang et al., [4] have been prepared nano structured ceramics and nano composites from cellulosic waste materials and TEOS (Tetraethylorthosilicate) in ethanol medium in the presence of ammonium hydroxide. D.A.Adensanya et al., and A.A. Raheem et al., [5-7] were studied the influence of corn cob ash in blended cement concrete and the study found that corn cob ash is a suitable pozzolanic material for cement replacement. Qing Cao et al., [8] have investigated the pyroelectric behavior of the corn cob ash. Samit Kumar et al., [9] have prepared nano particles form corn cob ash by chemical treatment method. F.Yu et al., [10] have studied the characteristics of corn cob ash by microwave Pyrolysis. To the present knowledge of the authors, there is no report on preparation of nano silica from corn cob ash by precipitation method.

Hence, objective of the work is to prepare nano silica particles from corn cob ash by precipitation method. This method is a combined benefit, not only producing valuable silica particles at lower cost but also of reducing disposal as well as pollution problems. The prepared nano silica particles have been characterized by using XRD, SEM with EDS, and FTIR techniques.

2. Materials and methods

Among chemicals used in this study include HCl, NaOH, H_2SO_4 and polyvinyl alcohol (PVA). All chemicals were used as received without any purification. Initially, locally collected corn cob 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 550 °C, 650 °C, and 750 ºC for 2 hr.

Synthesis of silica

The method suggested by Nithaya Thudaij and Apinon Nunthiya [11] is adapted to synthesis nano silica from calcined corn cob ash. Initially, appropriate amount of pretreated corn cob ash was mixed with 2N, 2.5N, and 3N NaOH solution, boiled at 70 °C for 4 hr with constant stirring, collected sodium silicate precipitation. The precipitation was filtered to obtained impure silica particles. Next, the impure silica particles was extracted by using H_2SO_4 solution under constant stirring at 70 °C for 2 hr, washed and dried at 100 °C for 20 hr to get pure silica particles. Finally, the pure silica particles were mixed with HCl solution, refluxing at 70 °C for 6 hr, collected the precipitation, cleaned and dried at 100 °C for 35 hr. The same procedure was followed in 1% PVA addition.

3. Results and discussion

Thermally treated corn cob ash, synthesized nano silica were subjected to XRD, FTIR and SEM with EDS techniques. The XRD patterns of the samples were recorded by PANalytical X-PERT PRO diffractometer, FTIR spectra were recorded in the range 4000-400 cm^{-1} by using Perkin Elmer FTIR Spectrometer (Model RX1). SEM images were recorded by using JEOL SEM (Model, JSM-5610 LV) with an accelerating voltage of 20 kV, at high vacuum (HV) mode and Secondary Electron Image (SEI).

The mixture of NaOH solution has strongly influences on the dissolution of silica in the pretreated corn cob ash is reported in Table 1.

Table 1. Effect of NaOH concentration with yield of pure silica percentage.

Concentration of NaOH (N)	Yield of pure Silica (%)
2.0	50
2.5	60
3.0	88

Fig. 1 (a-c) shows the X-ray diffraction patterns of calcined corn cob ash at 550 °C, 650 °C, and 750 °C for 2 hr. In Fig. 1(a) a strong peak is noticed at $2\theta = 28.4^{\circ}$ due to the quartz (JCPDS No: 79-1915). A medium intensity peaks at 32.2° and 66.4° are corresponds to tridymite (JCPDS No: 86-0681, 89-3141) and 73.7° by crystobalite (JCPDS No: 89-3434) and peak at 40.5° due to α-SiO_2 (JCPDS No: 81-0068).

Fig. 1(b) shows the XRD pattern of calcined corn cob ash at 650 °C for 2 hr. The diffraction pattern shows that the ash is predominantly amorphous. In the diffractogram, a broad hump is observed at $2\theta = 15^{\circ}$ 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. However, there are two sharp peaks are corresponds to quartz and crystoballite. At 750 °C, the XRD pattern shows that the ash is crystalline phases as it similar as that of 550 °C. 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 650 °C which is a suitable condition prepare the nano SiO_2 from the pretreated ash SEM analysis of ash at 650 °C.

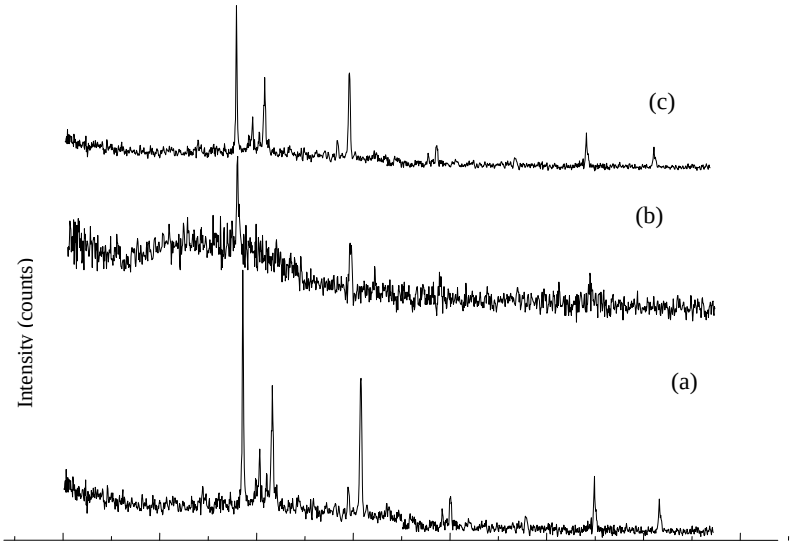

Fig. 1. XRD patterns of calcined corn cob ash at (a) 550 °C ,(b) 650 °C, and (c) 750 °C for 2 hr.

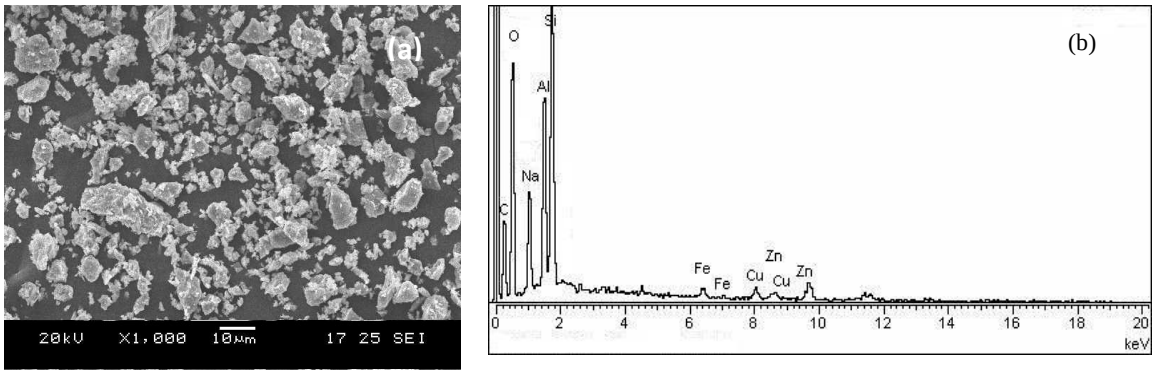

Fig. 2. (a) SEM image and (b) EDS spectrum of calcined corn cob ash at 650 ˚C for 2hr.

Fig. 2(a&b) shows the SEM and EDS analysis of corn cob ash at 650 °C. In the SEM image, corn cob ash particles are polygonal shape with different sizes. Average size of the particles is ≈10-30 µm. A strong intensity of Si in the EDS spectrum is confirmed the silica at higher weight percentage. Fig. 3(a) shows the XRD pattern of nano silica, a broad band is detected between 2θ = 10˚ and 35˚ which is confirmed the amorphous nature of silica [13]. The particle size of the silica was determined from the X-ray diffraction data using Debye Sherrer's formula,

$$D = 0.94\lambda / \beta \cos\theta$$

Where, D is the particle size , λ is the wavelength of the incident X-ray beam, β is the full width at half maximum of the X-ray diffraction peaks and θ is Bragg angle of X-ray diffraction peak. The average particle size of the prepared silica is found to be 34 nm.

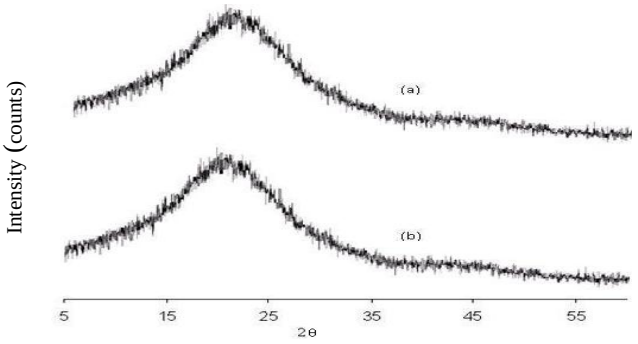

Fig. 3. XRD patterns of nano silica: (a) without PVA, and (b) 1% PVA treated nano silica.

The XRD pattern (Fig. 3b) of nano silica prepared with 1% PVA is almost similar fashion as that of nano silica prepared without PVA. From the pattern average particle size is found to be 22 nm. It implies that PVA influences on reduces the size of the particle. It is supported to the results reported by Leny Mathew et al [14]. Fig. 4(a) shows the SEM micrograph of nano silica at X1000 magnification. In the SEM image, spherical nature particles are freely disposed on the surface which may be due to synthesized silica has lower hydroxyl number and hence reduced silica-silica agglomeration. Average size of silica is approximately 30-50 nm. However, some agglomeration forms are seen. Fig. 4(b) shows the EDS spectrum of nano silica. 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.

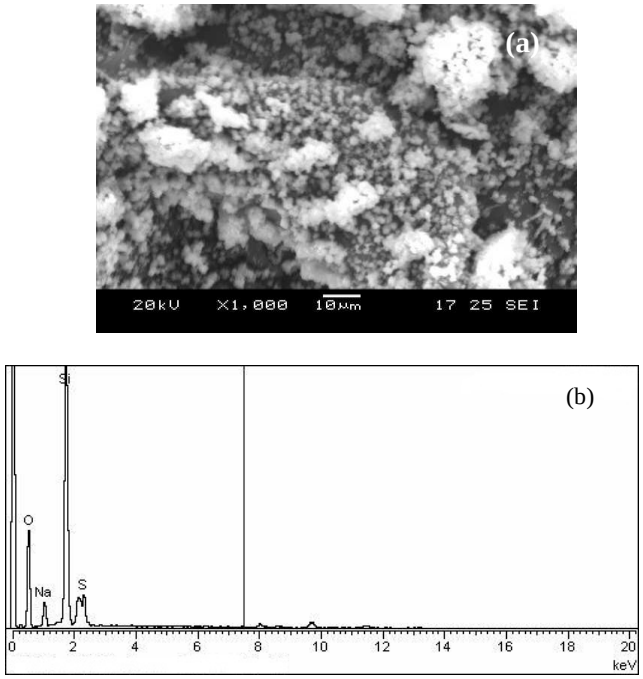

Fig. 4.(a) SEM and (b) EDS results of nano silica.

Fig. 5(a&b) shows the FTIR spectrum of nano silica without and with 1%PVA respectively. Both spectrums are almost similar result. The broad band in the range at 3440-3490 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 band at

1647 cm^{-1} is due to the bending vibration of the water molecules, which are trapped in the matrix of the silica. 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}.

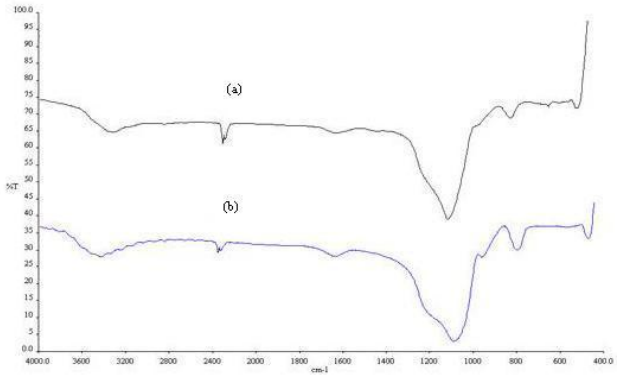

Fig. 5. FTIR spectra of nano silica (a) without PVA and (b) with 1% PVA.

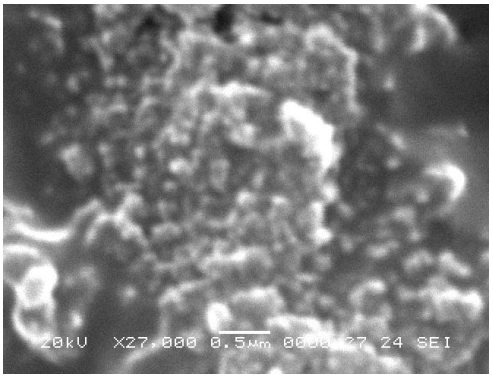

Fig. 6. SEM image of nano silica prepared with 1% PVA.

In the SEM image (Fig. 6), spherical silica particles are freely dispersed on the surface and average size of the particle is about 25 nm which is nearly supported with the XRD result. This micrograph shows that the prepared silica has lower particle size than without PVA addition. It implies that PVA has strongly influence on reduces the size of the particle.

4. Conclusion

Nano silica can be successfully prepared from corn cob ash by precipitation method under controlled condition. 88% of pure silica was extracted in the 3.0N NaOH solution mixture. From the results, the nano silica is predominantly amorphous nature and average particle size is found to be 34 nm for without PVA and 22 nm for 1% PVA. It suggests that the 1% PVA has reduced the size of the particles. It is concluded from the study, corn cob ash is a suitable source for silica preparation and expensive for preparation cost is to be less with equivalent properties to commercial silica.

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