**Extraction and physical characterization of amorphous silica made from corn cob ash
at variable pH conditions via sol gel processing**

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Abstract

Herein, we disclose a novel approach for the synthesis of nano-silica using corn cob ash (CCA). Also, we identify that silica is stable at pH 7 and unstable at pH 10 at the critical salt concentration for monovalent NaOH. A zeta potential study was used to characterize the surface charge of nanoparticles. The silica nanoparticles were characterized by SEM-EDS, XRD, FTIR, TEM and XRD confirmed the crystalline nature and TEM images showed spherical silica nanoparticles. Brunauer–Emmett–Teller, cation exchange capacity, and N₂ analyses showed increased stability at pH 7. The CCA-mediated synthesized particles showed excellent stability at pH 7.

Key words: Corn cob, silica, different pH; characterization

1. Introduction

Corn cobs are a major waste from corn/maize production and contain 30–35% hemicellulose, 40–45% cellulose, and 10–20% lignin [1, 2]. As a low-cost lignocellulosic biomass, corn cobs are a reliable and renewable source for the production of various value-added products such as biofuel enzymes [3], proteins [4], fuels [5], absorbents [6], and cements [7]. With such a huge availability of raw materials, keeping corn cob waste as a resource is likely to become more economical for a greater number of commercial applications. Presently, having no inherent commercial value, corn cobs usually end up being burned in open spaces, creating environmental pollution and disposal problems. Due to the need to conserve energy and resources, efforts have been made to burn the cobs under controlled conditions and to utilize the resultant ash as building, semiconductor, composite, and abrasive materials [8-12]. Due to the high surface area present in ash, it can act as an active catalyst and has the potential to be a good catalytic support material. Corn cob ash (CCA) contains >60% silica by mass with minor amounts of metallic elements [7,13,14] and could be an economically-viable raw material for the production of silicates and silica nanoparticles. The chemical composition of CCA may vary as a factor of their environmental, geographical, and soil conditions where the corn was grown in addition to the methods used during sample preparation [13]. In a variety of fast growing research arenas, nano-silica (nS) occupies a prominent position because of its easy preparation and multi-industrial applications such as its use in catalysis, pigments, pharmaceuticals, electronics, ceramics, polymer material industries, thin film substrates, thermal insulators, and humidity sensors [15]. The size, shape, and distribution of these nanoparticles determine their quality.

In this study, nSs were prepared using sol–gel processing with an agro-industrial residue corn cob [16]. Generally, smelting quartz sand with sodium carbonate at 1300 °C is used to provide the precursor for silica [17]. Commercial silica is manufactured in a process

involving multiple steps that involve high temperatures and pressure. This makes the process less cost effective and not very environmentally-friendly. Conversely, the extractable amorphous silica from CCA is cost effective, providing a low-energy method as an alternative to current high-energy methods. Additionally, natural silica from corn cobs is made up of organic materials and hydrated silicon [15,16]. Earlier nSs have been synthesized using rice husks [17], wheat husks [18,19], *Fusarium oxysporum* [20], and corn cobs [13,14]. The emphasis of this paper is to optimize the conditions for the preparation of highly-purified amorphous nS from CCA at variable pH conditions via sol gel processing. Various characterizations and the stability analysis of these materials are also carried out.

2. Experimental

2.1 Materials

The raw materials (corn cobs), which were obtained from a local agricultural field (Iksan-si, Jeollabuk-do, South Korea) during the process of removing kernels, were washed thoroughly with distilled water to remove adhering dust, soluble particles, and other contaminants. This process also removed heavy impurities such as sand. The material was then dried in an air oven at about 110 °C for 24 h. All of the reagents that were used were of analytical grade, and their solutions were made up twice using reverse osmosis (RO) in nanopure purified water (conductivity = 18 µΩ/m, TOC < 3 ppb, Barnstead, Waltham, MA, USA). H₂SO₄ and NaOH were of laboratory grade from DaeJung Chemicals (Siheung-si, Gyeonggi-do, South Korea).

2.2 Ash preparation

A weighed quantity of corn cobs was subjected to heat treatment in order to obtain the ash. Samples were burned inside of a programmable furnace (Nabertherm controller B 170, Nabertherm GmbH, Lilienthal, Germany) at 700 °C and heated at a rate of 5 °C/min. We designated these as corn cob ash (CCA). The above ash preparation method was followed

according to the optimized method provided by Rafiee et al. [12], which they used for preparation of ash using rice husks.

2.3 Extraction of silica at pHs of 7 and 10

A 10.0 g sample of CCA was stirred in 60 mL of a 1N NaOH solution. The solution was stirred for 3 h with constant heating in a covered beaker and filtered using a Whatman No. 41 ashless filter. The obtained residue was cleaned with 100 mL of nanopure water. Silica was extracted using this residue. The residue was then washed with 100 mL of boiling nanopure water. The obtained solution was allowed to cool down to room temperature and adjusted with different pHs (7 and 10) with 1N H₂SO₄ to form a silica hydrogel. This was followed by several washings of the hydrogel and then separation by 15 min of centrifugation at $1325 \times g$ for 5 min. The supernatant was discarded. This step was repeated several times to effectively remove minerals and impurities from the silica. The obtained gel was transferred to a fresh beaker and dried at 80 °C for 24 h in order to obtain xerogels. Scheme 1 shows the simple procedure and details of the extraction of corn cob silica.

2.4 Characterization of the extracted silica at variable pHs

The Energy-dispersive X-ray spectroscopy (EDX) spectra were recorded by placing the corn cob silica (CCS) on a copper substrate (JEOL JSM 6360). X-ray powder diffraction (XRD) was performed on drop-coated and air-dried samples on a glass substrate to analyze the structure and phase using Cu K_α radiation in the 2θ range from 20° to 90° (Philips PW-3710). Transmission electron microscopy (TEM) micrographs were used to determine the morphology and size of the CCS (Hitachi, H-n650, Japan). Fourier transform infrared spectroscopy (FT-IR) spectra of the CCS were obtained by a Perkin-Elmer FT-IR spectrophotometer (Perkin-Elmer, Norwalk, CT, USA) using the diffuse reflectance mode at a resolution of four particles cm⁻¹ in KBr pellets. The zeta potential was analyzed in order to examine the electrokinetic potential of CCS, and the specific surface areas of the CCS

samples were obtained by Brunauer-Emmett-Teller (BET) using a Micromeritics ASAP 2020 surface area analyzer. The cation exchange capacity was performed to identify the maximum quantity of the total cations present in the CCS. Ion chromatography (IC) was also performed (Spectro Analytical Instruments, Fitchburg, MA, USA).

3. Results and discussion

3.1 EDX spectra

Fig. 1(a) shows the EDS spectrum of the nS obtained at pH 7. A strong intensity of Si and O peaks between 0 and 5 keV, confirming the presence of silica, are predominant in this sample. **Fig. 1(b)** shows the EDS spectrum of the CCS obtained at pH 10; the spectrum clearly shows the impurities that are present in the silica prepared at pH 10. The silica surface consists of two types of functional groups, namely silanol (SiO-H) and siloxane (Si-O-Si), with silanol being more reactive and possessing more adsorptive properties. Because more cations appear on the surface of silica nanoparticles at a higher pH, greater mineral contamination occurs.

3.2 X-ray diffraction and amorphous form analysis

Generally, it is important to evaluate the amorphous form of silica. To evaluate this, we followed an earlier method described in [12, 21]. The ‘silica activity index’ method is used to estimate the degree of the amorphous form of silica by calculating the percentage of silica dissolved in an excess of boiling 4 M KOH after a three minute extraction period [12]. This method was used to investigate the extracted nano-silica; the results showed that the material was 98.5% of the amorphous form. **Fig. 2(a)** shows the XRD patterns of the CCSs at each pH composition. CCS at pH 7 has a typical amorphous shape that shows a broad peak centered $2\theta = 22^\circ$, which is associated with amorphous silica. The lack of sharp peaks indicates the absence of any ordered crystalline structure, confirming the results obtained from the silica activity index and the lack of a crystalline phase. The CCS samples showed the presence of an ordered crystalline structure with no other contaminants. The CCS at pH 10 showed

various sharp crystalline peaks [Fig 2\(b\)](#). The fact that there is no peak around $26^{\circ} 2\theta$ confirms the absence of crystalline quartz or cristobalite and also shows several peaks, proving its low-crystalline nature.

3.3 FT-IR analysis

[Figures 3\(a and b\)](#) show that the FT-IR bands between 490 cm^{-1} and $4,480\text{ cm}^{-1}$ belong to the stretching and bending vibration of Si-O and O-Si-O. The peaks at $1,100$ and 800 cm^{-1} are due to the asymmetric, symmetric, and bending modes of SiO_2 for pH 7 ([Fig. 3\(a\)](#)) and pH 10 ([Fig. 3\(b\)](#)), respectively. The unique peak at 600 cm^{-1} , present at pH 7 but not found at pH 10, might be caused by impurities found in the CCS. The broad band between $3,200\text{ cm}^{-1}$ and $3,800\text{ cm}^{-1}$ is due to the stretching vibration of the O-H bond from the silanol groups (Si-OH) and is caused by the adsorbed water molecules on the silica surface at pH 7 ([Fig. 3\(a\)](#)) and pH 10 ([Fig. 3\(b\)](#)), respectively. The band around $1,600\text{ cm}^{-1}$ is assigned to the bending vibration of water molecules that are bound to the silica matrix at both pHs. No peaks were found between $1,800$ and $3,000\text{ cm}^{-1}$ at either pH. This suggests that there were no original organic compounds in the silica after the controlled combustion and extraction. The intensity of the Si-peak as a function of the concentration of the given nanoparticles varies according to the degree of hydroxylation on the surface of the silica nanoparticles, which is caused by changes in the pH [\[1,13,14,22-24\]](#).

3.4 TEM analysis

[Figure 4](#) depicts the TEM micrographs of the nano-silicas. The shape of the silica grains is spherical with an average particle size of 60 nm for both pHs, which is in agreement with the size estimated using Scherer's formula. [Fig. 4\(a\)](#) shows that the silica grains consist of aggregated spheres at pH 7. [Figs. 4\(b and c\)](#) show the shape at pH 10 and a magnified image of the shape at pH 10, respectively. More aggregation occurs at pH 10 compared to pH 7.

3.5 Zeta potential and ion chromatography (IC) analyses

The surface charge of metal-oxide particles in water vary between a negative charge and a positive charge due to deprotonation caused by increasing the pH. Figure 5 show the CCS zeta potentials between pHs 7 and 10. The zeta potential of CCS at pH 10 has a more negative charge then at pH 7 within the test range. Table 1 show that the minimum absorption of anions on the surface of silica was achieved at pH 7. This may be caused by the static resistance between the silica surface, which has a negative charge, and the anions.

3.6 Estimation of the porosity, pore size, and cation exchange capacity (CEC)

The physical properties of the CCSs synthesized at pHs 7 and 10 are shown in Table 2 and Figs. 6(a, b, and c). The BET surface area and micropore volume were calculated by the absorption in the N₂ isothermal line (Table 2 and Fig. 6(a)). The BET and N₂ absorption isothermal lines for each sample are shown in Fig. 6(b). pH 7 is superior for a higher surface area and larger pore volume, compared to pH 10. It was confirmed that the surface area and diameter of the air gap increased with an increase in pH. It should be noted that the CCS formed at a higher pH (pH 10) showed a greater number of impurities and that the lower pH (pH 7) yielded an increase in the crystallization of silica. The specific surface area also decreased with increasing pH (Table 2). This decrease of S_{BET} can be attributed to the portion of the pores that were destroyed during processing. Amorphous silica of high purity and relatively high surface area was prepared at pH 7. This shows that CCS prepared at pH 7 has greater potential for ion-adsorption on its surface compared to CCS prepared at pH 10. As a result of analyzing the CEC of CCSs synthesized at pHs 7 and pH 10, the CCS prepared at pH 10 showed a CEC (Fig. 6(c)) value that was about twice as high compared with the CES value of CCS prepared at pH 7. Therefore, CCS prepared at pH 7 is better suited as an absorbent for removing heavy metals.

4. Conclusions

In summary, we report a novel biomaterial (CCA) for the synthesis of nS. The synthesis of

nS is eco-friendly, inexpensive, and rapid. At pH 7, nano-sized, highly purified silica (99.5 mass percentages) was produced with a high surface area, high reactivity, and that is 98.5% amorphous. The formed CCS had an average particle size of 60 nm and was crystalline in nature. Due to presence of more acidic sites at pH 7 (as compared to pH 10), CCS prepared at pH 7 yielded a good support material for catalysts. The synthesized CCS, which was mostly aggregated in multiple shapes and elemental compositions, confirmed the presence of nS with other biomolecules attached to it. FT-IR spectrum analysis at 1110 cm⁻¹ (indicative of Si-bond) using FT-IR showed structural changes on the surface of the silica particles as a factor of the pH of the solution. South Korea is both an agro-based country and a producer of silica; on the basis of our work, CCS can be obtained from agricultural waste rather than through synthetic routes.

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Figure legends

Scheme 1. Flow chart showing corn cob nano silica preparation at different pH conditions.

Fig. 1. SEM-EDS spectra of CCS: (a) pH 7 and (b) pH 10.

Fig. 2. XRD patterns of CCS: (a) pH 7 and (b) pH 10.

Fig. 3. FT-IR spectra of CCS at pH 7 and pH 10.

Fig. 4. HR-TEM image of CCS: (a) pH 7, (b) pH 10, and (c) magnified image of pH 10.

Fig. 5. Mean zeta potentials of CCS at different pHs (7 and 10).

Fig. 6. BET plot of CCS at (a) pHs 7 and 10. The N₂ adsorption/desorption isotherms of CCS at pHs 7 and 10 and the CEC of CCS at pHs 7 and 10.

Figure

Scheme 1.

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Table 1

Ion chromatography (IC) analysis for anions.

	F ⁻ (mg/L)	Cl ⁻ (mg/L)	NO ₂ ⁻ (mg/L)	NO ₃ ⁻ (mg/L)	PO ₄ ³⁻ (mg/L)	SO ₄ ²⁻ (mg/L)
pH 7 CCS	0.23 ± 0.04	2.14 ± 0.51	ND	ND	6.26 ± 0.97	0.30 ± 0.04
pH 10 CCS	0.04 ± 0.05	3.51 ± 1.0	0.10 ± 0.02	0.08 ± 0.15	408.51 ± 15.01	0.54 ± 0.38

Table 2

Surface area of CCSs obtained by BET and their textural properties.

	BET (m ² /g)	Approximate values of C	Total pore volume (cm ³ /g)	Mean pore diameter (Å)
pH 7 CCS	39.9	137.12	0.3299	33.08
pH 10 CCS	56.498	93.944	0.6692	47.378