SYNTHESIS OF PRECIPITATED SILICA FROM CORN COB BY USING ORGANIC ACIDS

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ABSTRACT: *In the present study, precipitated silica was synthesized from the corn cob by using organic acids. Corn cob ash (CCA) was produced by soaking corn cobs in three different organic acids i.e., citric acid, acetic acid, oxalic acid and combined solution of (50 % of each) citric acid and acetic acid. Organic acids were used to adjust the quality of the raw material and helped to dealuminate the corn cob ash before the extraction of precipitated silica. CCA was mixed with alkali solution to produce sodium silicate solution and precipitated silica was produced by the neutralization of sodium silicate solution. Corn cobs soaked in citric acid produced the maximum amount of the sodium silicate solution and precipitated silica i.e., 39.43 % and 35.3 % by weight respectively. Sodium oxide (Na_2O) content and silica (SiO_2) content in the sodium silicate solution were also determined. Extracted precipitated silica particles were characterized by Fourier transform infrared (FTIR), X-Ray diffraction and Optical microscopy techniques.*

Keywords: Corn Cobs, Sodium Silicate, Organic acids, Sodium oxide, Precipitated Silica.

1. INTRODUCTION

Corn is the most abundantly cultivated crop around the globe. According to International Grain Council, 861 million tons of corns were produced in the year 2013 worldwide. Approximately 18 kg of corn cobs are produced from 100 kg of corn grains [1].

Pakistan is an agricultural country. Different kinds of food crops are grown in the country on a large scale. Corn has distinct position among all the food grains grown in Pakistan. After wheat and rice, it attains third highest share in country's grain production [2]. It is cultivated on an estimated area of 0.9 million hectare with the annual grain production of 1.3 million tons, which contributes 6.4 % of overall grain production of the country [3].

Corn cobs, which are the by-product of corn grains are usually thrown out as a waste or burnt as a low grade fuels. This causes a serious problem in storage as well as in disposal. Un- controlled combustion of corn cobs causes an increase in the concentration of CO_2 in the atmosphere. Carbon dioxide is a greenhouse gas, which causes global warming [4].

Silica (SiO_2) has wide range of applications. It is used in adhesives, ceramics, pharmaceutical products, detergents and electronics [5]. Different agricultural materials were used previously for the extraction of silica (SiO_2). Studies have been done by Hai Le et al, 2013; Hariharan and Sivakumar, 2013; Rungrodnimitchai et al, 2009; Affandi et al, 2009 and Worathanakul et al, 2009.

Hai Le et al, 2013 [6] synthesized silica in solid form at nanoscale with the application of heat on vietnamese rice husk by adopting the sol–gel methodology. Rice husk being heated in controlled environment for 4 hrs at 600°C to produce rice husk ash (RHA). This RHA was latter mixed with sodium hydroxide to form sodium silicate solution and followed by precipitation with the addition of HCl at pH = 4 in water/butanol mixture with cationic presence. Scientific analysis which includes X-ray diffraction, scanning electron microscopy and transmission electron microscopy confirmed the extraction of amorphous silica.

Hariharan and Sivakumar, 2013 [7] studied on bagasse consumption in sugar industry as a fuel. They used sol-gel technique with reflux method for the production of pure and nano silica. XRD, FTIR and SEM with EDS used for synthesized nano silica characteristics confirmation.

Rungrodnimitchai et al, 2009 [8] used microwave heating for the separation of silica gel from rice husk ash. Multiple samples of rice husk ash in sodium hydroxide solution having different concentrations were kept in microwave oven for 5-10 minutes. Latter, neutralization process performed to get silica gel from sodium silicate. They concluded that if 2.0 M sodium hydroxide kept at microwave power of 800 W for 10 minutes, the optimum results can be achieved.

Affandi et al, 2009 [9] produced sodium silicate from bagasse ash by dissolving in NaOH solution. Then silica gel was synthesized by neutralization reaction with HCl. Ion exchange treatment and washing with de-mineralized water methods were used to successfully produce highly pure silica xerogels (>99 wt.%).

Worathanakul et al, 2009 [10] investigated heating temperature, time and acid treatment parameters on bagasse ash for silica extraction. X-ray fluorescence, X-ray diffraction, Scanning electron microscopy, and Fourier Transform Infrared Spectroscopy methods were used to characterize the synthesized silica.

The objective of the present work is to synthesize the maximum amount of silica (SiO_2) from corn cob by using three different organic acids. In this way, silica (SiO_2) can be produce at lower cost with reducing disposal as well as pollution challenges. The synthesized sodium silicate and precipitated silica has been analyzed by using chemical titration, FTIR, XRD and Optical microscopy techniques.

2. MATERIALS AND METHODS

Corn cobs were ground upto 20-30 mesh size. After washing and sun-drying, corn cobs were soaked in 25 % of three different organic acids i.e., citric acid, acetic acid, oxalic acid and combined solution of (50 % of each) citric acid and acetic acid for 24 hr. Then combustion of soaked corn cobs were carried out after washing and drying at 550 °C for 2 hr in a furnace.

Silica (SiO_2) was synthesized from corn cob ash by applying the method developed by Okoronkwo et al 2013 [11].

Initially, appropriate amount of pretreated corn cob ash was mixed with 1N NaOH solution and boiled for 1 hr with constant stirring to produce sodium silicate solution. The solution was filtered and the filtrate was then allowed to cool to room temperature. The sodium oxide (Na_2O) content of sodium silicate solution was determined by a chemical titration of a sample with standard hydrochloric acid to pH 4.3 and a suitable indicator such as methyl orange.

$$\% Na_2O = \frac{\text{ml HCl} \times \text{Normality} \times 3.1}{\text{Sample weight}}$$

The silica (SiO_2) content of sodium silicate solution was determined as weighed sample is diluted with deionized water and acidified with dilute hydrochloric acid. After evaporating to dryness on a hot plate, the resultant silica gel is rinsed free of chlorides. The residue is ignited in a muffle furnace in a carefully weighed crucible. After cooling and weighing, the residue is calculated directly as SiO_2.

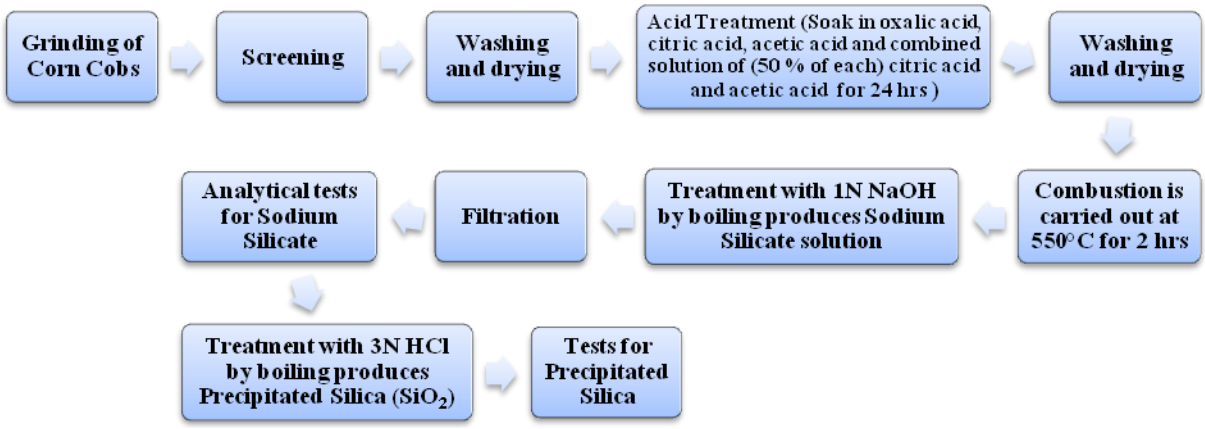
The filtrate was boiled with 3N HCl solution with constant stirring so that the pH of the solution was reduced to 7.0. Precipitated silica was produced after 1 hr boiling of filtrate with 3N HCl solution as shown in the flowchart 1. The same procedure was followed with citric acid, acetic acid and combined solution of (50 % of each) citric acid and acetic acid.

The reaction between NaOH and silica (SiO_2) of corn cob ash can be expressed as follows:

$$2x\ NaOH + y\ SiO_2 \rightarrow x\ Na_2O.y\ SiO_2 + x\ H_2O \quad \text{---- (1)}$$

And precipitated silica (SiO_2) can be produced by neutralization of the obtained sodium silicate solution (x Na_2O.y SiO_2) with HCl reported by Rungrodnimitchai et al, 2009 [12]:

$$x\ Na_2O.y\ SiO_2 + 2x\ HCl \rightarrow y\ SiO_2 + 2x\ NaCl + x\ H_2O \quad \text{--- (2)}$$



Flowchart 1: Steps of experimentation for the synthesis of precipitated silica from corn cob by using organic acids

3. RESULTS AND DISCUSSIONS

Corn cobs contain approximately 39.1 % cellulose, 42.1 % hemicellulose, 9.1 % lignin, 1.7 % protein and 1.2 % ash [13]. Organic acids are used to adjust the quality of the corn cobs before the extraction of precipitated silica. The acid treatment helped to dealuminate the corn cob ash and to remove the iron to the certain extent for adjusting the raw material quality [14]. The used three organic acids were citric acid, acetic acid and oxalic acid. All the used organic acids are weak acids but the citric acid having higher molecular weight is the stronger one from the acetic acid and oxalic acid.

The synthesized sodium silicate from the corn cobs soaked in citric acid, acetic acid, oxalic acid and combined solution of (50 % of each) citric acid and acetic acid were 39.43 %, 34.3 %, 15.8 % and 29.4 % by weight respectively as shown in table 1. The weight percentages of synthesized sodium silicate and precipitated silica from the corn cobs soaked in citric acid were high as compared to the other two acids because citric acid, being stronger one, dealuminated the maximum amount of ash from the corn cobs as shown in the fig 1. While the weight percentages of synthesized sodium silicate and precipitated silica from the corn cobs soaked in oxalic acid were low because crystals were formed when corn cobs soaked in oxalic acid as shown in the fig 1. The crystal formation created hindrance for the removal of ash from the corn cobs.

The sodium oxide (Na_2O) content of the sodium silicate solution which was synthesized from the corn cobs soaked in citric acid, acetic acid, oxalic acid and combined solution of (50 % of each) citric acid and acetic acid were 11.2 %, 8.1 %, 4.3 % and 7.4 % by weight respectively as shown in table 1. The silica (SiO_2) content of the sodium silicate solution which was synthesized from the corn cobs soaked in citric acid, acetic acid, oxalic acid and combined solution of (50 % of each) citric acid and acetic acid were 21 %, 17.6 %, 9.4 % and 16.7 % by weight respectively as shown in table 1. While the extracted precipitated silica from the corn cobs soaked in citric acid, acetic acid, oxalic acid and combined solution of (50 % of each) citric acid and acetic acid were 35.3 %, 31.5 %, 20.4 % and 25.7 % by weight respectively as shown in table 1.

The extracted precipitated silica from the corn cobs soaked in citric acid was identified by FTIR spectrum as shown in figure 2. The band at 791 cm^{-1} to 964 cm^{-1} is due to the Si-O-Si symmetric bond stretching vibration, while the band at 1010 cm^{-1} to 1098 cm^{-1} is due to the Si-O-Si asymmetric bond stretching vibration as observed by Nayak, 2010 [15]. The band at 1635 cm^{-1} to 1645 cm^{-1} is due to the bending vibration of the water molecules,

Table 1: Weight percentages of synthesized sodium silicate, sodium oxide and silica in the sodium silicate, and extracted precipitated silica from the corn cobs soaked in organic acids

Sr. No.	Corn cobs soaked in organic acids	Percentage of synthesized sodium silicate (wt. %)	Percentage of sodium oxide (Na_2O) in the sodium silicate (wt. %)	Percentage of silica (SiO_2) in the sodium silicate (wt. %)	Percentage of extracted precipitated silica (wt. %)
a.	Corn cobs soaked in citric acid	39.43	11.2	21	35.3
b.	Corn cobs soaked in acetic acid	34.3	8.1	17.6	31.5
c.	Corn cobs soaked in oxalic acid	15.8	4.3	9.4	20.4
d.	Corn cobs soaked in combined solution of (50 % of each) citric acid and acetic acid	29.4	7.4	16.7	25.7

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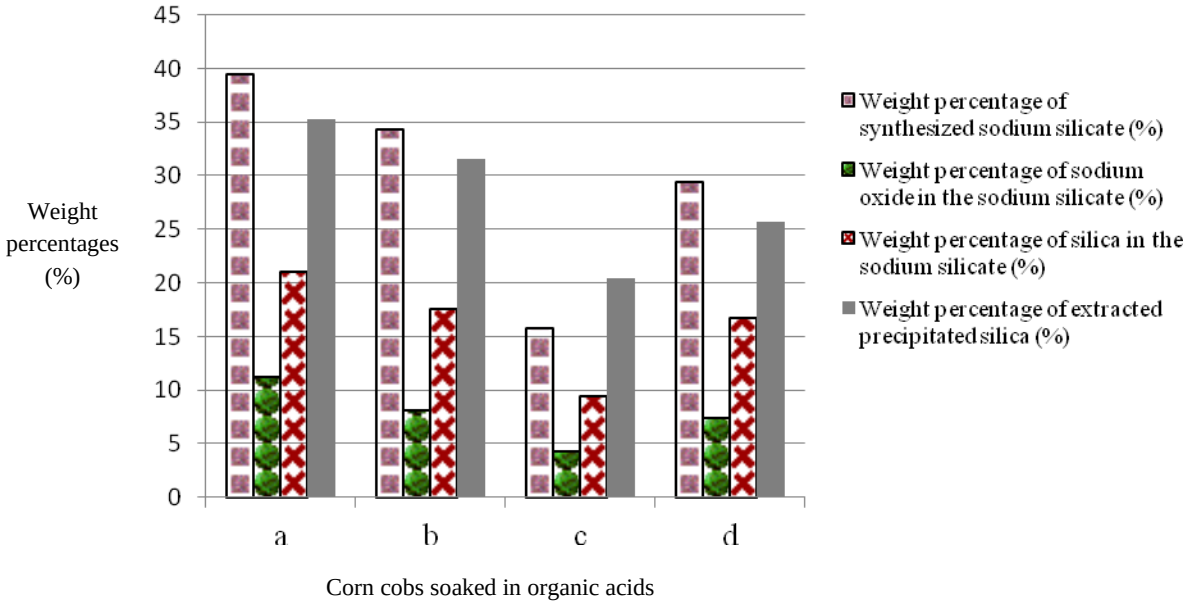

Fig 1: Comparison of weight percentages of synthesized sodium silicate, sodium oxide and silica in the sodium silicate, and extracted precipitated silica from the corn cobs soaked in organic acids

which are trapped in the matrix of the silica. The board band at 3310 cm^{-1} to 3490 cm^{-1} is due to the stretching vibration of the O-H bond from the silanol groups (Si-OH) and is due to the absorbed water molecules on the silica surface as reported by Javed et al, 2011 [16].

Figure 3 shows the optical micrograph of extracted precipitated silica from the corn cobs soaked in citric acid at X 10 magnification. In the optical micrograph, spherical nature particles of extracted precipitated silica are freely disposed on the surface which may be due to synthesized silica has lower hydroxyl number and hence reduced silica-silica agglomeration as observed by Kalapathy et al, 2002 [17]. However, some agglomeration forms are seen. Average size of silica is approximately 100 µm

Figure 4 shows the XRD pattern of extracted precipitated silica from the corn cobs soaked in citric acid. A broad band is detected between 2 θ = 10° and 35° which is confirmed the amorphous nature of silica as reported by Leny Mathew et al, 2010 [18].

4. CONCLUSION

Precipitated silica can be successfully synthesized from the corn cobs by using organic acids. But the highest percentage of sodium silicate i.e., 39.43 wt. % having sodium oxide and silica contents are 11.2 wt. % and 21 wt. % respectively and precipitated silica i.e., 35.3 wt. % can be extracted from those corn cobs which are soaked in 25 % of citric acid. FTIR analysis shows the presence of siloxane and silanol groups in the precipitated silica. XRD pattern confirms the amorphous nature of the silica and optical microscopy shows the spherical nature of silica particles.

5. ACKNOWLEDGEMENT

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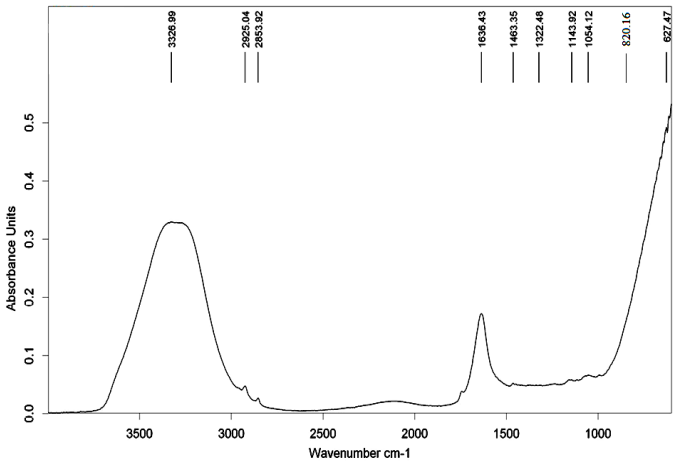

Fig 2: FTIR spectra of extracted precipitated silica from the corn cobs soaked in citric acid

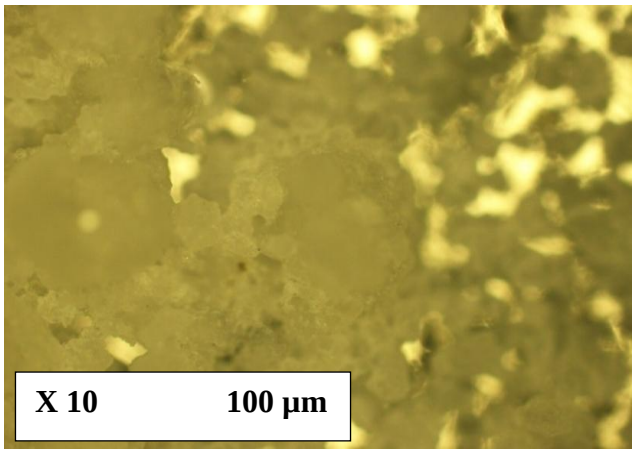

Fig 3: Optical micrograph of extracted precipitated silica from the corn cobs soaked in citric acid

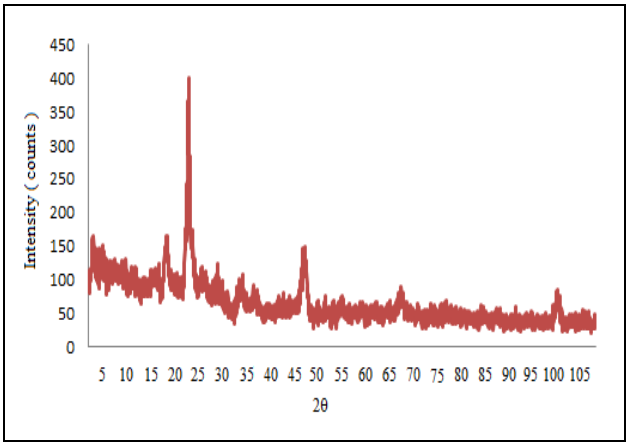

Fig 4: XRD pattern of extracted precipitated silica from the corn cobs soaked in citric acid

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