Extraction High Purity Nanosilica Corn Cob by Modified Precipitation Technique

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Research

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Extraction high purity nanosilica corn cob by modified precipitation technique

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Abstract. Corn cob considers the agricultural waste in Iraq. High purity SiO\textsubscript{2} NPs were extracted from corn cob by enhanced precipitation and developed leaching processes. In this study, pre-treatment with 3N H\textsubscript{2}O\textsubscript{3} has achieved then calcination of the corn cob at 700°C, then follows with the leaching process with (2, 2.5, 3)N NaOH. The characterizations of the prepared SiO\textsubscript{2} NPs were analyzed with atomic force microscopy (AFM), and X-ray fluorescence (XRF). The results were found that the prepared SiO\textsubscript{2} NPs have an amorphous structure with a high purity of 97.13 %. Also, the AFM results indicated that the average diameter of the SiO\textsubscript{2} NPs was 85 nm. It was noted that the leaching processes and pretreatment methods determine the structure, particle size, and quality of the synthesized SiO\textsubscript{2} NPs.

Keywords: Nanosilica (SiO\textsubscript{2} NPs), Corn cob ash (CCA), Precipitation method, Leaching process.

1. Introduction

High purity nanosilica has unique properties that make it widely used in many applications as photovoltaic devices, electronic devices, solar energy conversion, electric devices, high capacity anodes, and biomedical applications [1-3]. Silica exists in the crust of the earth as a crystalline structure or amorphous structure. Corn cob is obtained as a by-product from the process of milling for cobs [3]. In corn cobs, silica considers the main inorganic component [4]. Per year, the corn world harvest is almost 600 million tons. 20% of corn is considered as grains, through the combustion of the cobs, the cobs are converted to ash. Usually, corn cob and the ash of corn cob remained as unutilized industrial waste. Using corn cobs as cheap resource material to obtain significant material like nano-silica produced a big economic benefit because of reducing the cost and utilizing from the wastes. The CCA preparation process was studied with many important investigations [5]. The nature of silica products (crystallinity and microstructure) is highly related to their application because the low reactivity of crystalline silica is limited to its direct applications [6]. Generally, the extracted Silica from CCA has an amorphous structure and also has a high surface area. However, amorphous silica has many chemical applications, such as thermal insulators, catalysts, and absorbents as a result of its proprieties of the high specific surface area [7-9]. Various synthetic methods of extracting nano silica from agriculture waste were used like chemical precipitation, ion exchange, solvent extraction, and electrolysis deposition method. Yafei Shen [10] produced nano silica from RHA by chemical method. they found the preparation conditions, time, temperature of combustion have controlled the nature of the produced nano-silica thus the silica with amorphous structure was obtained at 550–800 °C, and the silica with crystalline structure forms at higher temperatures than this. Nittaya thuadaij et al. [11], using the precipitation method to obtain amorphous silica with a specific surface area reaching 656 m\textsuperscript{2}g\textsuperscript{-1}. Carmona et al. [12], extracted amorphous and white silica with both micro and nanometric particles from rice husk using mild acid solutions. They conducted that the prepared nano-silica was prepared by a precipitation process which was extracted from Iraq.
agriculture sources. Therefore, the main objective of the present investigation is to produce high purity nanosilica from agricultural wastes of corn cob by developed chemical extraction techniques. Many factors are effected on nano-silica purity such as the type of raw material, precipitation temperature, pretreatment steps, and the final purification process. All these parameters determine the quality and quantitative of produced nano-silica.

2. Materials and methods

2.1 Materials

The raw corn cob (CC) was obtained from Iraq. The materials chemicals, such as sodium hydroxide (NaOH, 99.9%) (LOBA chemie), ammonium hydroxide (NH₄OH, 25%) (UK GCC), hydrochloric acid (HCl, 35%), and sulfuric acid (H₂SO₄, 98.079%) (thomas baker), were obtained from Fluka Co.

2.2 Preparation corn cob ash (CCA)

For the preparation of corn cob, the first step includes washing the corn cobs by water (three times) for removing the dust and contaminations soluble after that dried for 24 hours at room temperature. The pretreatment process was carried out by soaking 30 g of the dried CC in one liter of 3N HCl solution at 75 °C for 5 hours. The mixture was then subjected to refluxing in the same acid at room temperature for 12 hours. CC was then washed with deionized water and filtered three times to make it free-acid after that dried inside the oven for temperature reaching for 100 °C at 5 hours. The corn cob (CC) pre-treatment produced was burned inside a muffle furnace for 700°C, at the rate of 10 °C/min for 4 hours. The obtained corn cob ash (CCA) becomes almost white color.

2.3 Preparation of nanosilica from CCA

SiO₂NPs was extracted by treating 20 g of CCA with 150 ml of (2, 2.5, 3) N NaOH. The samples were stirred via magnetic stirrer under heated in a covered beaker of 250 ml at 80 °C for 3 hours, as shown in Fig. 1. The solution of sodium silicate was filtered by the paper of filter (Whatman No. 41 ash less). So an obtained solution is (Na₂SiO₃) as revealed in the below equation.

\[
\text{SiO}_2 + 2\text{NaOH} \rightarrow \text{Na}_2\text{SiO}_3 + \text{H}_2\text{O}
\]  

Fig. 1. Production process of SiO₂NPs.
The residue solution was carefully washed with (100 mL) of boiling water, as shown in Fig. 2. Then sulphuric acid (5N H$_2$SO$_4$) was added to precipitate the silica gel as a white gelatinous solid by a gelation process.

$$\text{Na}_2\text{SiO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{SiO}_2 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$$ (2)

A residue soft gel was aged for 4 hrs, after aging, the slurry was washed and filtration via using the vacuum pump. NH$_4$OH was added to make the pH = 8. Then, it left at room temperature for 4hrs. The product was washed and filtered through whatman (No. 41 ash less) than added 20 ml of warm deionized water many times to become free-alkali and dry at 90 °C for 10 hours in the oven. An produced powder was refluxed with 6N HCl for 4 hours and washed with deionized water, after washing, 2.5N NaOH will added and stirred by magnetic stirrer then heated for 70 °C at 3 hours inside covered beaker with capacity (250 ml ) then 5N H$_2$SO$_4$ was added to obtain white nanoparticles with high purity of (SiO$_2$) after washing and filtering by whatman (No. 41 ash less).

**Fig. 2.** The high purity nanosilica preparation flow chart by precipitation method.
SiO$_2$NPs precipitated was washing with warm deionized water until becomes completely alkali free then filtered through whatman (No. 41 ash less) filter paper and then the produced were collected then dried for 110°C at 12 hours inside an oven. The final product is SiO$_2$NPs by precipitation method, as shown in the following sequence steps Fig. 3.

3. Results and discussion

3.1 XRF analysis

The purity of prepared SiO$_2$NPs from CC was analyzed by (XRF) X-ray fluorescence. The Table 1 shows a chemical analysis for the prepared silica at (2, 2.5, 3)N NaOH.

| Components | Treatment with NaOH |
|------------|---------------------|
|            | 2 N | 2.5 N | 3 N     |
| SiO$_2$    | 96.338 | 96.952 | 97.416 |

The purity of SiO$_2$NPs increases with increasing the concentration of NaOH from 96.338 to 97.416 respectively. This result is an agreement with researches [14-16]. The relationship between the degree of purity for extraction SiO$_2$NPs and NaOH concentration is show in Fig. 4. It indicates that within an increase in NaOH concentration, the purity increases.
Fig. 4. The relationship show effect NaOH concentration on purity nanosilica.

3.2 Morphology of CC silica

Fig. 5 shows the surface morphology of CC-SiO$_2$NPs, which was analyzed using FE-SEM. Accordingly, it has a sphere-like shape with a large agglomeration of particles.

Fig. 5. FE-SEM image of extracted CC-SiO$_2$NPs, at a) 2 NaOH, b) 2.5 NaOH, c) 3 NaOH.
3.3 Atomic force microscopy (AFM) and particle Size of Nanosilica

According to AFM analysis, the diameters of SiO$_2$NPs extracted at 2N NaOH with range of (21–125 nm) and the average diameter of 77.20 nm. The AFM images of SiO$_2$NPs obtained at 2.5N NaOH display keeping the spherical shape of particles with the increase in the size of particles in which the range of particle diameters is 75–100 nm and the average diameter is 79.76 nm as shown in Fig. 6. The 3D surface image of SiO$_2$NPs prepared at 3N NaOH appears the surface of SiO$_2$NPs has the shape of the hills and valleys. Fig. 6c shows the diameters of prepared nano-silica are in the range of 70–165 nm and the average diameter equal to 88.93 nm. In general, all these results reveal that the increasing the concentration of NaOH leads to rise in size of the particles. In the other hand, the shape of particles can be changed from spherical which was obtained at NaOH concentration led from 2 - 2.5 to crystal-like structures at 3N NaOH concentration.
4. Conclusions

An amorphous SiO$_2$NPs was successfully prepared from corn cob by chemically modified precipitation technique. The chemical treatment processes were the main affective parameters for producing high purity nano-silica (97.416%). The current study investigated to find out the best suitable treatment for the extraction of amorphous silica nanoparticles from CC at 3N NaOH solution. The main particle size of the prepared SiO$_2$NPs was 40-89 nm. From an engineering point of view, the modified production method is economic, flexible non-complicated, and produced high-quality amorphous nano-silica. Then, the process could be used for production on an industrial scale.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Availability of data and materials

The datasets supporting the conclusions of this article are included within the article.

Authors’ contributions

The manuscript draft was interpreted and written by Dr. Naser Korde Zedin. Prof. Dr. Sami A. Ajeel and Prof. Dr. Khalid A. Sukkar provided technical support, revised the manuscript, and also supervised the research. All authors read and approved the final manuscript.

References

1. Sami A. Ajeel, Khalid A. Sukkar, Naser K. Zedin, "New magnesio-thermal reduction technique to produce high-purity crystalline nano-silicon via semi-batch reactor", Materials Today: Proceedings 42, 1966–1972, 2021.
2. M. Al Mubarok, L. P. Setiawan, M. Utami, and W. Trisunaryanti, "Study of Acid Leaching in the Preparation of Silicon from Lapindo Mud". International Journal of Academic and Scientific Research, V 2, Issue 4 (2014), PP 31-36.
3. P. P. Nayak, S. Nandi & A. K. Datta, "Comparative assessment of chemical treatments on extraction potential of commercial grade silica from rice husk". Engineering Reports, (2019), PP: 1-13.
4. V.B. Carmona, R.M. Oliveira, W.T.L. Silva, L.H.C. Mattoso, J.M. Marconcini, "Nanosilica from rice husk: Extraction and characterization". (Industrial Crops and Products 43 (2013) 291–296.
5. N. Soltani, A. Bahrami, M.I. Pech-Canul, L.A. González, "Review on the physicochemical treatments of rice husk for production of advanced materials". Chemical Engineering Journal 264 (2015) 899–935.
6. Davide Barana, Anika Salanti, Marco Orlandi, Danish S. Alia, Luca Zoia, "Biorefinery process for the simultaneous recovery of lignin, hemicelluloses, cellulose nanocrystals and silica from rice husk and Arundo donax". Industrial Crops and Products 86 (2016) 31–39.
7. Dae Soo Jung, Myung-Hyun Ryoua, Yong Joo Sung, Seung Bin Park, and Jang Wook Choi, "Recycling rice husks for high-capacity lithium battery anodes". PNAS 2013, vol. 110, no. 30, pp. 12229–12234.
8. Noratiqah Syahirah Mohd Zarib, Shahrul Azam Abdullah, Noorina Hidayu Jamil, "extraction of silica from rice husk via acid leaching treatment". The European Proceedings of Social & Behavioural Sciences EpSBS, 2019, pp.176-183.
9. Usman, b. and Rufai, i.a., "extraction and characterization of solar-grade biosilica from rice husk". Cafei2012, pp.225-231.
10. Yafei Shena., "Rice husk silica derived nanomaterials for sustainable applications". Renewable and Sustainable Energy Reviews 80 (2017) 453–466.
11. Nittaya Thuadaij and Apinon Nuntiya, "Synthesis and Characterization of Nanosilica from Rice Husk Ash Prepared by Precipitation Method". (Special Issue on Nanotechnology, 2008) Vol. 7(1) 59.
12. Văn Hải Lê, Chi Nhan Ha Thúc and Huy Ha Thúc, Mostafa Feyzi and Mahdi Shaterzadeh, "Synthesis of silica nanoparticles from Vietnamese rice husk by sol–gel method". International Nano Letters 2013, 8:58.
13. Linqi Zong, Bin Zhu, Zhenda Lu, Yingling Tan, Yan Jin, Nian Liu, Yue Hua, Shuai Gu, Jia Zhu, and Yi Cui, "Nanopurification of silicon from 84% to 99.999% purity with a simple and scalable process". PNAS, 2015, vol. 112, no. 44, pp. 13473–13477.
14. Sami abualnoun Ajeel, Khalid A. Sukkar and Naser Korde Zedin, "Extraction of high purity amorphous silica from rice husk by chemical process", IOP Conf. Series: Materials Science and Engineering 881 (2020) 012096, doi:10.1088/1757-899X/881/1/012096.
15. Naser Korde Zedin, Sami abualnoun Ajeel, and Khalid A. Sukkar, "Nanosilicon powder Extraction as a sustainable source (From Iraqi Rice husks) by hydrothermal Process", AIP Conf. Proc. 2213, 020155-1–020155-8; https://doi.org/10.1063/5.0000147.
16. R. Yuvakkumar, V. Elango, V. Rajendran & N. Kannan, "High-purity nano silica powder from rice husk using a simple chemical method". Journal of Experimental Nanoscience, 2014, 9:3, 272-281.
17. Sami A. Ajeel a, Khalid A. Sukkar b, Naser K. Zedin, "Chemical Extraction Process for Producing High Purity Nanosilica from Iraqi Rice Husk", Engineering and Technology Journal Vol. 39, Part A (2021), No. 01, Pages 56-63.
18. Sami abualnoun Ajeel, Khalid A. Sukkar and Naser Korde Zedin, "Evaluation of acid leaching process and calcination temperature on the silica extraction efficiency from the sustainable sources", Journal of Physics: Conference Series 1773 (2021) 012014, doi:10.1088/1742-6596/1773/1/012014
