FACILE EXTRACTION AND CHARACTERIZATION OF SILICA NANOPARTICLES FROM CORN STALK BY SOL-GE L HYDROTHERMAL METHODS

Patrick Ehi Imoisili 1* and Tien-Chien Jen 1*

1University of Johannesburg, Auckland Park, Johannesburg, South Africa
*Corresponding author: tjen@uj.ac.za, patrickehis2002@yahoo.com

Abstract
Lightweight aggregates, drug delivery and energy storage are some of the numerous applications of silica nanoparticles. Amorphous silica was extracted from corn stalk using the sol-gel hydrothermal method and nanostructured using Hexadecyl trimethyly ammonium bromide (CTAB) as template. The crystallographic structures of synthesized silica nanoparticles was characterized using X-Ray Diffraction (XRD). Functional groups was determined using fourier transform infrared (FT-IR) techniques, specific surface area was determine using the Brunauer Emmett Teller (BET) method. The presence of SiO2 was confirmed by Energy dispersive X-ray (EDX), surface morphology and particle size was examine using scanning electron microscope (SEM) and transition electron microscope (TEM). This study provide a silica nanoparticles sourced from agricultural biomass for cutting-edge applications including drug delivery.

Keywords; Corn stalk, hydrothermal, nanoparticles, silica, sol-gel

1. Introduction
Silica (SiO2) gel, are a strong three-fold addition of colloidal silica. Amorphous silica gels are known as aqua gel, xerogel and aerogel depending on the process of synthesis [1]. Silica has been successfully derived from variations in agricultural bio-resources, such as palm kennel shell ash, sugar cane, rice husk, corn cob, bagasse and wheat and rice husk [1-11]. Several procedures for silica extraction from biomass including; sol–gel, hydrothermal, gasification, precipitation and acid leaching methods have also been reported [12].

The increasing awareness in the production of silica (SiO2) nanoparticles is as a results of the widespread utilization as a simple raw compound in the production of various advanced materials classes for advanced technological applications [2-6]. Methods developed for silica nanoparticles production includes, templating, chemical vapour condensation, reverse micro emulsion (RME), sol–gel and precipitation technique [13-15].

The Sol-gel hydrothermal processes combines two process that are used for the manufacture of silica, ceramic and glass due to its capacity to produce solid, durable materials in trifling circumstances [1-9]. This study developed amorphous silica nanoparticles from corn stalk (CS) using the sol–gel hydrothermal extraction process, using CTAB as template. Extracted silica was characterized using XRD, FTIR, EDX, SEM, TEM and BET surface Area

2. Materials and methods
Corn stalk (CS), was collected after the harvest season in south-south Nigeria, and burnt in open air and the ashes further combusted in a muffle furnace at 750 °C, for 2 hrs at a heating speed of 20 °C/min. The sol-gel hydrothermal method was used in the silica extraction were 25 g of CS was dissolved with 2 N NaOH and heated with constant stirring for 2 hrs. The solution was filtered using an ashless filter paper. The filtrate pH was adjusted to 7.5-8.5 and
placed in an oven at 50 °C for 24 h for formation of gel. The gel was dissolve with 100 ml deionized water and centrifuge and the supernatant was dispose of and the filtrate dried in an oven at 70 °C for 12 h to obtain silica zero gel. The extracted silica was nanostructure by adding 0.50 g of CTAB to 50 ml deionized water and stirred with a magnetic stirrer for 10 minutes to produce a clear homogeneous solution. 0.50 g of NH₄OH was applied with constant stirring for 10 mins, during which 2.5 g of silica was gradually added and permitted to mature under stirring at room temperature for 48 hrs. The samples were calcine in a muffle furnace at 600 °C to obtain CS-Nano silica. The Sample was characterize using XRD, FTIR, BET, EDX, SEM and TEM.

3. Results and discussions

Fig. 1, displays the XRD spectral for CS-ash and extracted CS-Nano silica. Results sequence for the CS-ash indicates the presence of quartz at theta = 21.54, 22.6, 41.35, 46.78 and 54.65° (SiO₂PDF Card # 331161) and Calcite at = 21.5, 43.65, 46.56 and 56.21° theta (CaCO₃PDF Card # 050586). XRD collection of isolated CS-Nano silica particles at theta = 23.25, is the characteristic of amorphous solid, supports the development of amorphous silica; related findings have been obtained by other researchers [1-3, 16-18]

FTIR spectral has established the primary chemical compound that occurs in Nano-structured CS-silica as shown in Fig. 2. Band 465 cm⁻¹– 478 cm⁻¹ is linked to the network of O Si O, whilst the band 789 cm⁻¹ – 809 cm⁻¹ was assigned to the symmetrical stretching vibration network of Si-O-Si [1]. Band, 1068 cm⁻¹ – 1092 cm⁻¹ is attributable to Si-O-Si abnormal broadening and bandwidth at 1631 cm⁻¹ – 1648 cm⁻¹ and 3335 cm⁻¹ to 3470 cm⁻¹ is owed to O-H bonding vibration from silanol Si-OH groups and is attributed to H₂O molecules adsorbed on the silica sheet [2-8].
Nano-structured silica extracted from CS-silica has been successful; however, from Fig. 3 and 4, SEM and TEM spectral, silica-silica agglomerations have been observed. Maximum particles sizes varies from 54-98 nm. High Si and O amplitude as seen in the EDX spectrum Fig. 4, reveals that the primary element in the sample is silica (SiO$_2$). It contains about 98.59 per cent of the overall output. This are residual impurity commonly found in the extraction process.
The surface area (SBET) of the prepared CS-Nano silica developed was assessed at 750 °C for 2 hrs after calcination. The surface region of CS-Nano silica was estimated to be 422 m²g⁻¹. This particular surface area is comparable to 438 m²g⁻¹ observed for PKSA silica [1] and greater than the values stated for RHA extracted silica nanoparticles [21].

4. Conclusion
Silica nanoparticles have been removed from corn stalk (CS) using a sol-gel hydrothermal method. The findings indicate that amorphous silica nanoparticles with a 58.75 percent yield of silica with marginal mineral pollutants can be generated from CS-ash. The XRD research confirmed the occurrence of SiO₂ in CS-ash and the existence of amorphous silica. The notable chemical groups occurring in CS-silica were identified by the FTIR results. The FTIR investigation indicates the presence of classes of silanol and siloxane. Silica-silica agglomeration in different sizes (54-98 nm) and shapes was detected from the SEM and TEM analyses. The silica existence in the samples was recognized by the EDX analysis. This research offers silica nanoparticles from biomass for advanced substance applications, including drug delivery.

Acknowledgement
Authors would like to appreciate funding support from URC of University of Johannesburg, and Prof T. C. Jen would also like to appreciate funding support from NRF of South Africa.

Reference
1. Patrick E. Imoisili, Kingsley O. Ukoba, Tien-Chien Jen. (2020). Green technology extraction and characterisation of silica nanoparticles from palm kernel shell ash via sol–gel. J Mater Res Technol. 9(10), 307-313. https://doi.org/10.1016/j.jmrt.2019.10.059
2. Patrick E. Imoisili, Kingsley O. Ukoba, Tien-Chien Jen. (2019). Synthesis and characterization of amorphous mesoporuous silica from palm kernel shell ash, Bol. Soc. Esp. Cerám. Vidr. https://doi.org/10.1016/j.bsecv.2019.09.006
3. Channoy, C., Maneewan, S., Punlek, C., Chirarattananon, S., (2018). Preparation and characterization of silica gel from bagasse ash, Adv. Mater. Res. 1145 44–48. https://doi.org/10.4028/www.scientific.net/amr.1145.44
4. Rovani, S., Santos, J.J., Corio P., Fungaro D.A, (2018). Highly pure silicananoparticles with high adsorption capacity obtained from sugarcane waste ash, ACS Omega 3 (3) 2618–2627. https://doi.org/10.1021/acsomega.8b00092
5. Sapawe N., Osman N.S., Zakaria M.Z., Fikry S. A. S. S. M, Aris M. A. M, (2018). Synthesis of green silica from agricultural waste bysol–gel method, Mater. Today: Proc. 5 (10) 21861–21866. https://doi.org/10.1016/j.matpr.2018.07.043
6. Costa J.A.S., Paranhos C.M., (2018). Systematic evaluation of amorphous silica production from rice husk ashes, J. Clean. Prod. 192 688–697.  https://doi.org/10.1016/j.jclepro.2018.05.028
7. Okoronkwo E.A., Imoisili P.E., Olusunle S.O.O., (2013). Extraction and characterization of amorphous silica from corn cob ash by sol–gel method, Chem. Mater. Res. 3 68–72
8. Elvis A. Okoronkwo, Patrick Ehi Imoisili, Smart A. Olubayode, Samuel O. O. Olusunle, (2016). Development of silica nanoparticle from Corn Cob Ash, Adv. Nanopart. 5 135–139. https://doi.org/10.4236/anp.2016.52015
9. Samsudin Affandi, Heru Setyawan, Sugeng Winardi, Agus Purwanto, Ratna Balgis (2009). A facile method for production of high-purity silica xerogels from bagasse ash, Adv. Powder Technol. 20 (5) (2009) 468–472. https://doi.org/10.1016/j.apt.2009.03.008
10. . Terzioğlu, S. Yücel, C., Kus, , Review on a novel bio-silica source for production of advanced silica-based materials: wheat husk, Asia-Pacific J. Chem. Eng. (2018) 2262. https://doi.org/10.1002/apj.2262
11. Marag R.K., Giri P.A., (2018). Experimental investigation of temperature and reaction time for preparation of silica from wheat husk, Int. J. Eng. Technol. Sci. Res. 60–65.
12. Kaliannan, D., Palaninaicker, S., Palanivel, V., Mahadeo, M. A., Ravindra, B. N., & Jae-Jin, S. (2018). A novel approach to preparation of nano-adsorbent from agricultural wastes (Saccharum officinarum leaves) and its environmental application. Environmental Science and Pollution Research, 26(6), 5305–5314. https://doi.org/10.1007/s11356-018-3734-z
13. Bagwe RP, Hilliard LR, Tan W. (2006). Surface modification of silica nanoparticles to reduce aggregation and nonspecific binding. Langmuir. 22(9):4357–62. https://doi.org/10.1021/la052797j
14. Liu, S., & Han, M.-Y. (2009). Silica-Coated Metal Nanoparticles. Chemistry - An Asian Journal, 5(1):36. https://doi.org/10.1002/asia.200900228
15. Jal PK, Sudarshan M, Saha A, Sabita P, Mishra BK. (2004). Synthesis and characterization of nano-silica prepared by precipitation method. Colloidal Surf. 240:173–178. https://doi.org/10.1016/j.colsurfa.2004.03.021

16. Chandrasekhar S., Satyanarayana K. G, Pramada PN, Raghavan P, Gupta TN. Review processing, properties and applications of reactive silica from rice husk—an overview. J. Mater Sci 2003;38(15):3159–3168. https://doi.org/10.1002/chin.200406243

17. Athinarayanan J, Periasamy V. S., Alhazmi M., Alatiah K. A., Alshatwi A.A. (2015). Synthesis of biogenic silica nanoparticles from rice husks for biomedical applications. Ceram Int. 41(1):275–281. https://doi.org/10.1016/j.ceramint.2014.08.069

18. Yan Liu, Yupeng Guo, Yanchao Zhu, Dongmin An, Wei Gao, Zhuo Wang, Yuejia Ma, Zichen Wang. (2011). A sustainable route for the preparation of activated carbon and silica from rice husk ash. Journal of Hazardous Materials 186 (2-3), 1314–1319. https://doi.org/10.1016/j.jhazmat.2010.12.007

19. Costa J. A. S., Paranhos C. M. (2018). Systematic evaluation of amorphous silica production from rice husk ashes. J Clean Prod. 192, 688–697. https://doi.org/10.1016/j.jclepro.2018.05.028

20. Hongxi Zhang, Xu Zhao, Xuefeng Ding, Hong Lei, Xue Chen, Dongmin An, Yunling Li, Zichen Wang (2010). Preparation and characterization of nano-structured silica from rice husk. Bioresource Technol 101, 1263–1267. https://doi.org/10.1016/j.biortech.2009.09.045

21. Zhang, Hongxi, Xu Zhao, Xuefeng Ding, Hong Lei, Xue Chen, Dongmin An, Yunling Li, and Zichen Wang. (2010). A study on the consecutive preparation of d-xylose and pure superfine silica from rice husk. Bioresource technology 101(4), 1263-1267. https://doi.org/10.1016/j.biortech.2009.09.045