Indonesian Physical Review
Volume 7 Issue 1, January 2024
P-ISSN: 2615-1278, E-ISSN: 2614-7904

Synthesis of Nano-Silica from Loa Kulu Rice Husk using the Sol-Gel Method

Dian Mart Shoodiqin[1*], Musyarofah[1], Fadli Robiandi[1], Regita Cahya Chairunnisa[1]
[1] *Physics department, Kalimantan Institute of Technology, Indonesia*

Corresponding Authors E-mail: dianms@lecturer.itk.ac.id

Article Info

Article info:
Received: 04-10-2023
Revised: 18-01-2024
Accepted: 23-01-2024

Keywords:
Debye Scherrer; Crystal; Calcination; Cristobalite; Organic.

How To Cite:
D. M. Shoodiqin, Musyarofah, F. Robiandi, and R. C. Chairunnisa, "Synthesis of Nano-Silica from Loa Kulu Rice Husk using the Sol-Gel Method", Indonesian Physical Review, vol. 7, no. 1, p 125-132, 2024.

DOI:
https://doi.org/10.29303/ipr.v7i1.280.

Abstract

Silica is a material that is widely found in nature and is able to withstand corrosion attacks from corrosive environments. However, this natural material must be extracted to obtain high purity silica. Simple sol-gel method is used to solve the extraction problem (nano-silica with high purity). The natural materials used in this research come from organic materials, namely rice husks from the local area (Loa Kulu area). The main objective of this experiment is studying the effect concentration of HCl for crystalline size. The synthesis of silica was carried out with the preparation of ashes, then mixed with NaOH 7M until a solution of sodium silicate was produced. Silicate sodium solution was pressed with HCl 2M to form a silica gel with pH 7, 5, and 3 then was dried to produce silica powder. Silica powder was then burned at a temperature of 1000°C to produce silica with a crystalline phase. Based on the experiment, silica powder before calcination has amorphous phase and at any pH variation, the crystallite size calculated with the Debye Scherrer approach does not show any change the crystallite size by the variation of the silica gel's pH. In addition, silica powder calcinated at 1000°C has amorphous and cristobalite phases and showed changes in crystal size after calculated with Debye Scherrer's approach.

Introduction

East Kalimantan, as one of the provinces that has rice commodities, can produce 262.43 thousand tons of milled dry grain (GKG) in 2020 [10]. Every ton of rice obtained can contribute 30% of the total weight of the rice harvest [9]. These results have not yet been utilized optimally so further processing needs to be carried out to make it something useful. Several researchers have been interested in developing rice husks as silica-based raw materials such as zeolite, silicon tetrachloride, silica nitride and pure silica [1]. [2] Pramudita et al, successfully conducted research showing that rice husk extract is a good corrosion inhibitor. Nanoscale silica is widely used in industrial fields such as cosmetics, ceramics and paint [3]. Silica can be produced from various methods, one of which is the sol-gel method. The sol-gel method is a chemical reaction process in a solution at low temperatures [4]. The main problem is silica gel's pH might affect the crystallite size and the crystal's structure. To solve the problem, some of

pH variation should be conducted for making sure those effects. The crystallite size of silica which is formed is difficult to be analyzed because the size is small, so the Debye Scherrer's approach should be tried in this research. The research is conducted to study the effect of pH of silica gel in order to create nanoscale of cristobalite structure's silica.

Theory and Calculation

The increasing industrial development every year results in the use of materials also increasing. The material used in industry is metal, but metal is susceptible to corrosion if it is in an unfavorable environment. Corrosion was a decrease in the quality of a metal or material due to physical contact with its environment [11]. There were many ways to prevent corrosion on a material, one of which is coating. This technique was coating process a metal surface with certain materials to inhibit the electrochemical reaction process in the metal [5]. One of the coating methods that could prevent corrosion was organic coating, where the materials used in this method come from organic materials. Several researchers have been interested in developing rice husks as silica-based raw materials such as zeolite, silicon tetrachloride, silica nitride and pure silica.

Silica could be produced from various methods, one of which is the sol-gel method. The Sol-gel method was a chemical reaction process in a solution at low temperatures [4]. There were several factors that can influence silica in the sol-gel method, one of which was pH. Differences in pH in the sol-gel method process could produce nano-silica with different characteristics and silica synthesized with a pH of 7 could be applied as a filler for composite resins [6]. The silica produced in this method generally had an amorphous form and to change its structure to cristobalite it was necessary to calcinate [3].

The silica that has been extracted is then characterized using an X-Ray Diffraction (XRD) test equipment to determine the crystal structure and phases formed from silica powder with CuKα (λ = 1.54060Å). X-Ray Diffraction operating conditions are at 30mA, 40kV and step size 0.0170° in the angle range (2θ) 5-120^0. The data produced in this characterization is the relationship between 2θ and intensity. Qualitative analysis of the X-Ray Diffraction test to determine the FWHM value or peak width. The value of the crystal size can be determined using the Debye Scherrer approach which refers to the peaks of the diffraction pattern and the Debye Scherrer approach is shown in the following equation

$$D = \frac{K\lambda}{\beta \cos \theta}$$

where K = (0.9) is the particle shape factor, λ is X-ray wavelength, βhkl is the half-width of (hkl) reflection, θ = 2θ/2 is Bragg angle corresponding to (hkl) reflection [15] .

Experimental Method

Rice Husk Preparation

The rice husks used come from Loa Kulu Kota Village, East Kalimantan. The rice husks were burned in an open room until become ash, then ground and sifted using a 200mesh sieve. The resulting rice husk ash was heated in a furnace at a temperature of 700°C for 6 hours. Next,

the ash was washed with 2M HCl to remove impurities. The washing results were filtered, and the sediment obtained was rinsed with distilled water until the neutral pH.

Synthesis of Rice Husk Ash

The husk ash from the washing results was mixed with 7M NaOH and heated at 300°C. The resulting mixture was then added with distilled water and filtered to produce sodium silicate solution. The sodium silicate solution obtained was titrated with 2M HCl until pH 7, 5 and 3 were reached. The silica gel was washed with distilled water to remove residual salt from the titration results. After washing, the gel was dried at 100°C until it became powder. The silica powder was then calcined at 1000°C for 1 hour to produce silica in crystalline form.

Characterization

The calcined silica was characterized using X-Ray Diffraction to determine the crystal structure and phases formed from silica powder with CuKα (λ = 1.54060Å). Operating conditions were in the angle range (2θ) 5−120°. The resulting diffraction patterns were analyzed to determine the FWHM value. The crystal size could be determined using the Debye Scherrer approach. Apart from that, characterization was also carried out using X-Ray Fluorescence (XRF) to determine the element content in silica powder.

Result and Discussion

Burning process could reduce the organic compound content in the husk and speed up burning time could produce husk ash with a higher silica content [7]. Rice husk is washed using 2M HCl was tested using XRF and the test results are shown in Table 1 below.

Table 1. XRF test results of rice husk ash burned in an open space and washed with 2M HCl

Element	(wt%)		
	Rice husk ash burned in the open	Rice husk ash heated at 700°C	Rice husk ash washed with 2M HCl
Si	79.54	80.38	9.129
K	9.08	8.80	4.39
Ca	3.76	3.69	1.29
P	3.07	2.94	1.75
Cl	1.53	1.47	-
Mn	0.99	0.96	0.38
Fe	0.95	0.92	0.49
S	0.81	0.57	0.25
Zn	0.09	0.09	-
Ti	0.09	0.08	0.07
Ni	0.04	0.03	0.05
Cu	0.005	0.005	0.002

From the table 1, the heating process of rice husk ash at 700°C for 6 hours remove organic compounds. Apart from that, washing the ash with 2M HCl could reduce the levels of impurities such as K and Fe so that the Si element with high purity is produced by 91.29%. According to research by Putranto et al [12], the addition of strong acid to rice husk ash could release metal oxides such as K_2O and Fe_2O_3.

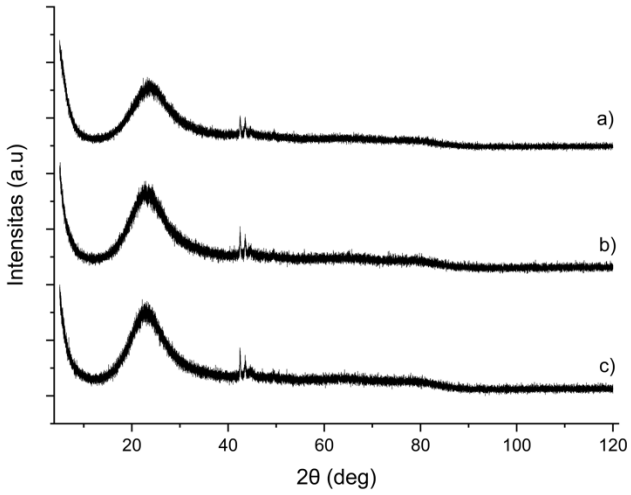

Figure 1. X-ray diffraction patterns (CuKα) of amorphous silica powder after varying the pH of HCl. a) pH 3; b) pH 5; and c) pH 7

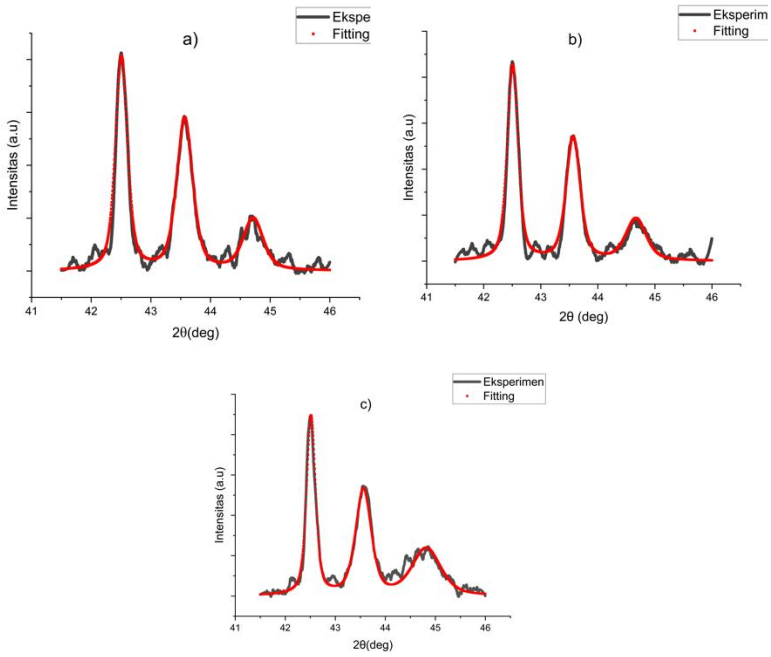

Figure 2. Fitting of X-ray diffraction patterns (CuKα) on silica powder before calcination a). pH 3; b). pH 5; and c). pH 7 with Fityk software.

The XRD diffraction patterns in Figure 1 show that the curve has bumps which are characteristic of amorphous silica and the results show the presence of a quartz phase at angles 2θ = 42.5° and 44°. The formation of mounds from the results of sol-gel synthesis is in accordance with research conducted by Musyarofah et al [8] namely that there are humps from the qualitative XRD results on silica powder. The results of the XRD analysis showing the peak of the quartz phase were then

processed as shown in Figure 2. To determine the FWHM (Full Width Half Maximum) value and the crystal size was calculated using the Debye Scherrer approach. The values from the crystal size calculation results are shown in Table 2 below.

Table 2. Results of calculating the size of silica crystals for variations in pH 3, 5 and 7 using the Debye Scherrer approach

pH	2θ(°)	K (rad.Å^{-2})	λ(nm)	*FWHM* (β) (°)	*FWHM* (β) (rad)	Crystalite Size (nm)
3	42,507 ± 0.001	0.9	0.15406	0.240 ± 0.003	$0.4x10^{-2}\pm 0.6x10^{-4}$	35.5 ± 0.5
5	42,508 ± 0.001	0.9	0.15406	0.234 ± 0.003	$0.4x10^{-2}\pm 0.6x10^{-4}$	36.4 ± 0.5
7	42,508 ± 0.001	0.9	0.15406	0.232 ± 0.003	$0.4x10^{-2}\pm 0.6x10^{-6}$	36.7 ± 0.6

These calculations show that the crystal size does not change with increasing pH. These results are not in line with research conducted by previous researchers, according to research by Indrasti et al [6] who synthesized nano-silica in the pH range 7-10 showing an increase in crystal size with each increase in pH and this explains that as the pH increases, the crystal size increases. The crystal size that does not increase is probably caused by using room temperature during the titration so that the energy required for crystal growth is not sufficient. According to Elma [4], the crystal size at pH < 7 can be ignored because it shows changes that are not significant, so to increase the crystal size at low pH it is necessary to use other supports such as temperature and pressure to achieve high solubility. At pH > 7 the crystal size increases due to low solubility.

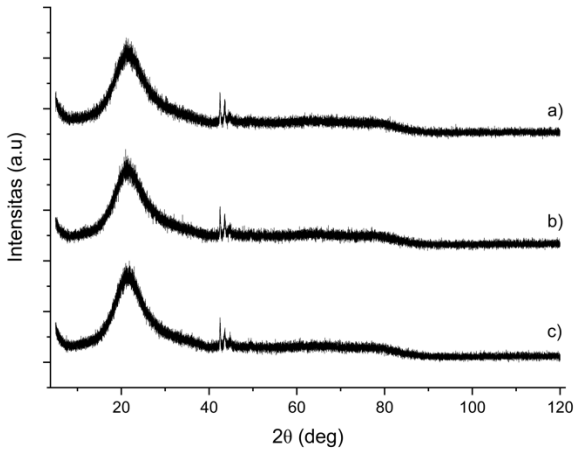

Figure 3. XRD (CuKα) diffraction patterns of silica powder after calcination at 1000°C. a) pH 3; b) pH 5; and c) pH 7.

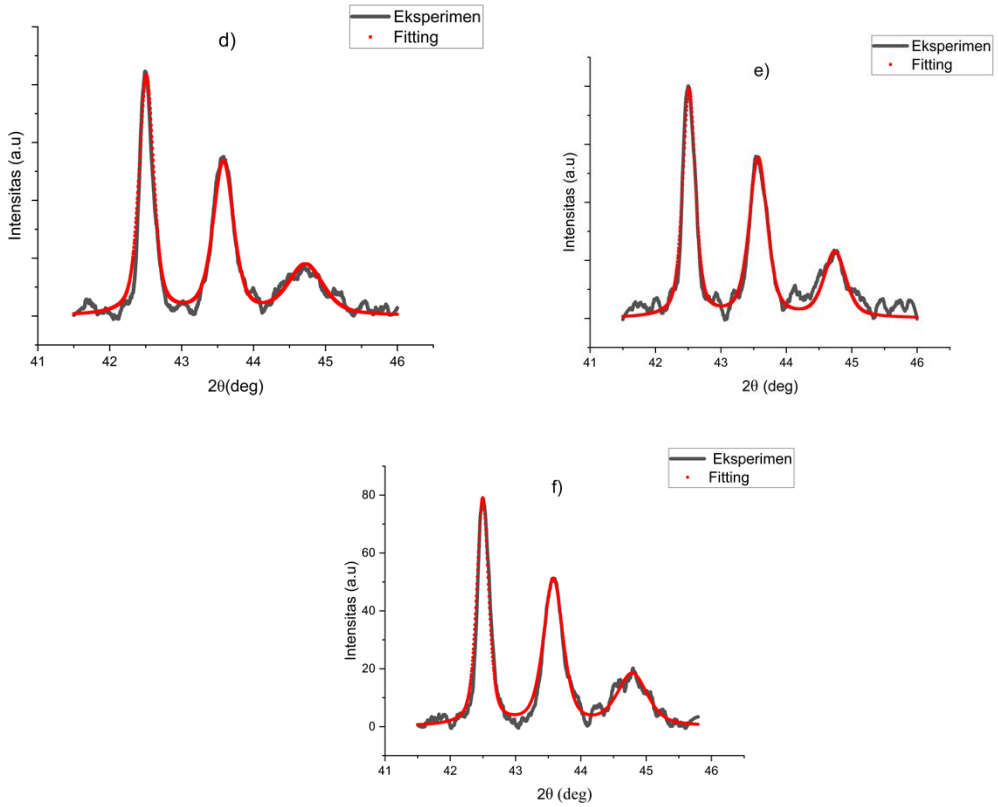

Figure 4. Fitting of X-ray diffraction patterns (CuKα) on silica powder after calcination at 1000°C a). pH 3; b). pH 5; and c). pH 7.

Silica powder is calcined at a temperature of 1000°C with a holding time of 1 hour to change the amorphous phase structure to crystalline. Figure 4 shows the XRD diffraction patterns of calcined silica powder which produces amorphous and crystalline silica powder in the form of cristobalite. Based on qualitative analysis, the cristobalite phase is formed at the peak of 2θ = 22.01°; 42.5°; and 44°. This is in accordance with research conducted by Johan et al [13], namely that silica calcined at a temperature of 1000°C is still in the form of amorphous silica with the presence of a cristobalite phase. The presence of an amorphous phase at a temperature of 1000°C because it requires a longer holding time during calcination.

Table 3. Calculation results of silica crystal sizes varying from pH 3, 5 and 7 calcined at 1000°C using the Debye Scherrer approach

pH	2θ(°)	K (rad.Å^{-2})	λ(nm)	*FWHM* (β) (°)	*FWHM* (β) (rad)	Crystallite size (nm)
3	42,507 ± 0.001	0.9	0.15406	0.230 ± 0.002	$0.4\ x\ 10^{-2} \pm 0.4\ x\ 10^{-4}$	37.1 ± 0.4
5	42,508 ± 0.001	0.9	0.15406	0.228 ± 0.004	$0.4\ x\ 10^{-2} \pm 0.7\ x\ 10^{-4}$	37.4 ± 0.6
7	42,508 ± 0.002	0.9	0.15406	0.222 ± 0.002	$0.4\ x\ 10^{-2} \pm 0.5\ x\ 10^{-4}$	38.4 ± 0.5

The crystal sizes obtained from Debye Scherrer calculations are shown in Table 3. These values show that silica powder with a pH of 3, 5 and 7 experiences an increase in crystal size after being calcined at a temperature of 1000°C. Calcination temperature affects silica crystals, that is, the higher the calcination temperature used, the larger the size of the silica crystals. A high increase in temperature can cause the intensity of the silica peak to increase, so that the FWHM value decreases. According to Lisdawati [14], the increase in crystal size is caused by the faster movement of atoms so that crystal growth is also faster.

Conclusion

Based on the extraction of silica from rice husk ash using the sol-gel method, the pH of HCl has no effect on crystal size. In addition, it was found that silica powder pH 3, 5 and 7 experienced an increase in crystal size after calcination at a temperature of 1000°C and the value of the crystal size was determined using the Debye Scherrer equation.

Acknowledgment

The authors wish to thank farmer in Loa Kulu Village for the rice husk used in this investigation

References

[1] L. Sun and K. Gong, 'Silicon-Based Materials from Rice Husks and Their Applications', *Ind. Eng. Chem. Res.*, vol. 40, no. 25, pp. 5861–5877, Dec. 2001, doi: 10.1021/ie010284b.

[2] M. Pramudita, S. Sukirno, and M. Nasikin, 'Rice Husk Extracts Ability to Reduce the Corrosion Rate of Mild Steel', *Int. J. Chem. Eng. Appl.*, vol. 9, no. 4, pp. 143–146, 2018, doi: 10.18178/ijcea.2018.9.4.715.

[3] F. Rahayu, M. Zainuri, and J. A. R. Hakim, 'Pengaruh Jenis Fasa SiO2 (Amorphous, Quartz, Cristobalite) Terhadap Sifat Hydrophobic pada Media Kaca'.

[4] M. Elma, *PROSES SOL GEL: ANALISIS, FUNDAMENTAL DAN APLIKASI*. Lambung Mangkurat University Press, 2018.

[5] A. Rochmat, M. Pramudita, F. Fathiayasa, and A. Buchari, 'Karakteristik SiO2 - Getah Flamboyan (Delonix regia) sebagai Material Coating Pencegah Korosi', *Tek. J. Sains Dan Teknol.*, vol. 12, no. 1, p. 83, Jun. 2016, doi: 10.36055/tjst.v12i1.6618.

[6] N. S. Indrasti, A. Ismayana, A. Maddu, and S. S. Utomo, 'Synthesis of Nano-silica from Boiler Ash in the Sugar Cane Industry using the Precipitation Method', *Int. J. Technol.*, vol. 11, no. 2, p. 422, Apr. 2020, doi: 10.14716/ijtech.v11i2.1741.

[7] N. Nuryono, N. Narsito, and E. Astuti, 'ENCAPSULATION OF HORSERADISH PEROXIDASE-GLUCOSE OXIDASE (HRP-GOx) IN SILICA AQUAGEL SYNTHESIZED FROM RICE HULL ASH FOR ENZYMATIC REACTION OF GLUCOSE', *Indones. J. Chem.*, vol. 8, no. 2, pp. 169–176, Jun. 2010, doi: 10.22146/ijc.21619.

[8] Musyarofah, N. D. Lestari, R. Nurlaila, N. F. Muwwaqor, Triwikantoro, and S. Pratapa, 'Synthesis of high-purity zircon, zirconia, and silica nanopowders from local zircon sand', *Ceram. Int.*, vol. 45, no. 6, pp. 6639–6647, 2018, doi: 10.1016/j.ceramint.2018.12.152.

[9] M. V. Hermawan, "Pengaruh Variasi Ukuran Partikel Sekam Padi pada Komposit Semen-Sekam Terhadap Kekuatan Tekan dan Serapan Air," S.T. Thesis, Dept. Machine. Eng., Muhammadiyah Surakarta University., Central Java., 2017

[10] kaltim.bps.go.id, 'Luas Panen Padi di Provinsi Kalimantan Timur', 2020. [Online] Available: https://kaltim.bps.go.id/indicator/53/318/1/luas-panen-padi-menurut-kabupaten-kota.html. [Accessed: 7-April-2022]

[11] F. Gapsari, "Pengantar Korosi," UB Press, Malang, 2017.
[12] V. H. Putranto, E. Kusumastuti, Jumaeri, "Pemanfaatan Zeolit dari Abu Sekam Padi dengan Aktivasi Asam untuk Penurunan Kesedahan Air," *MIPA. J,* vol. 38. no. 2, pp. 150-159, 2015.
[13] E. Johan, K. Ogami, N. Itagaki, Y. Aono, "Fabrication Of High Purity Silica From Rice Husk And Its Conversion Into Zsm-5," ARPN, Eng. And App. Sci. J, vol. 11, no. 6, pp. 4006-4010, 2016.
[14] A. N. Lisdawati, "Pengaruh Variasi Suhu dan Waktu Kalsinasi pada Pembentukan Fasa ZrO2," M.Sc. Dissertation, Dept. Physics, Sepuluh Nopember Surabaya Institute of Technology, Surabaya, 2017.
[15] A. O. Bokuniaeva and A. S. Vorokh, "Estimation of particle size using the Debye equation and the Scherrer formula for polyphasic TiO2 powder," *J. Phys. Conf. Ser.*, vol. 1410, no. 1, 2019, doi: 10.1088/1742-6596/1410/1/012057.