Vol. 14 Special Issue (2023) 33-40

Jurnal Riset
Teknologi Pencegahan Pencemaran Industri

Journal homepage : https://www.jrtppi.id

Kementerian Perindustrian
REPUBLIK INDONESIA

Synthesis of Silica Nanoparticle Made from Lampung Pumice Modified with Sonication Parameters for Size and Purity

Siti Rahmadiarti[1], Yusup Hendrosursito*[2,3]

[1] Department of Physics, FMIPA, Universitas Negeri Lampung.

[2] Mining Technology Research Center - National Innovation Research Agency.

[3] Department of Physics, FMIPA, Universitas Gadjah Mada.

ARTICLE INFO

Article history:
Received April 27, 2023
Received in revised form September 11, 2023
Accepted November 23, 2023
Available online December 22, 2023

Keywords :
ANOVA
Pumice
Silica
Sol Gel
Sonication
Synthesis
Taguchi

ABSTRACT

Silica nanoparticles are widely utilized nanomaterials in various industries due to their unique characteristics. Homogeneous nanoscale size is preferred to obtain superior properties. This research was conducted to determine the sonication parameters of pumice rock synthesis on silica size and purity formation. Silica synthesis was carried out until a white gel formed, followed by sonication at temperatures of 30°C, 60°C, and 80°C for 1, 2, and 3 hours. The purity of silica was analyzed through X-ray fluorescence results, X-ray diffraction, and SEM imaging for morphology analysis. The synthesis results followed by the sonication process had the highest SiO_2 concentration of 98.97%. The sonication temperature had a significant effect and contributed 67.25%, higher than the sonication time of 22.4%. The highest SiO_2 concentration of >98% was achieved at 40°C for 1.5 hrs. Meanwhile, for particle size, both parameters have a significant effect with an error value of α: 3.14%. Particle size <6 nm was obtained with a sonication temperature of 50°C for 2 hours. The sonication process can increase the concentration and reduce the size of the synthesized silica particles by selecting appropriate independent variables.

1. INTRODUCTION

Indonesia possesses a wealth of both metallic and non-metallic mineral resources. Among the non-metallic resources is pumice, a light-colored stone type originating from volcanic eruptions forming distinctive zone atop silicate lava (Kumalawati and Mastaram, 2013). Indonesia ranks among the countries with the most active volcano in the world, with around 129, and comprising about 30% of the world's active volcano (Pratomo, 2006).

Among these active volcano is Mount Krakatau, located in Lampung Province, which erupted in 1883. This eruption has endowed Lampung Province with numerous reserves of pumice originating from volcanic sediment. most of which are SiO_2 (77.79%) and Al_2O_3 (12.72%). These eruption materials were spread to several areas in Lampung Province, one of which can be found around the beach of Gubug Garam, south of Tarahan City, Lampung.

Ersoy et al (2010) reported that pumice contains oxides of SiO_2, Al_2O_3, MgO, Na_2O, CaO, Fe_2O_3, K_2O, and others. The most dominant oxide contained in pumice is SiO_2 of 70.21%. Silica also known as SiO_2 is a mineral composed of two elements: silicon (Si) and oxygen (O_2). Nano silica, on the other hand, is an amorphous material composed of Si-O-Si bond with a silanol group (Si-OH) and is nano-sized.

*Correspondence author.
E-mail : yusuph_ugm07@yahoo.com (Yusup Hendronursito)

doi : https://10.21771/jrtppi.2023.v14.si.p33-40

Accreditation number : (Ristekdikti) 158/E/KPT/2021

The availability of silica is abundant in nature, and so widely used in industrial fields such as raw materials for glass, ceramics, cement, and other industries. Silica can be obtained from quartz sand, granite, and pumice, while plant-derived silica is sourced from bagasse, corn cobs, and rice husks.

Silica dissolves in alkaline conditions and settles in acidic conditions. Therefore, silica extraction from pumice with NaOH was carried out to obtain silica. The highest silica content, 96.3%, was achieved with 3.0M NaOH variation, representing 18.5% increase from the original pumice silica content. Silica settles at pH 7; thus, to achieve this pH condition, the extracted filtrate dripped with H_2SO_4 solution to fasilitate silica settling. Subsequently, the resulting precipitate yields silica gel.

The silica obtained from the extraction still contains impurities such as Fe_2O_3 and Al_2O_3. The Silica purification process is carried out to remove these impurities by washing the silica using an acid solvent (HCl), which is effective in reducing the metal impurity content of 70.22%.

Nanomaterial is a material ranging in size from 1 to 100 nm. Material in nano size has an advantage over the same material in a larger size, nano-sized material has particles with a high interaction surface area. The more particles that interact, the stronger the bond between the particles, so the material is easier to react. One way to make nano-sized material is by sonication.

The sonication method is one method that can be applied to make smaller and homogeneous particle sizes. The key parameter for the utilization of sonication are temperature and time. The sonication method is widely used due to its effectiveness in producing nano-sized samples and separating the agglomeration of particles.

This research aims to determine the effect of variations in temperature and sonication time on pumice-based silica. The research is expected to provide valuable insights into the application of pumice as nano silica, particularly using sonication, in the industrial sector in Indonesia, such as the glass and cement industry, where silica is commonly utilized.

2. METHODS

Pumice stone from Lampung Province was washed with distilled water and dried at 80-110°C for 24 hours. Subsequently, the dried pumice stone was crushed with a mortar and meshed with ASTM: E11 through a 200 mesh sieve to obtain a fine material. It was then washed again using distilled water and calcined at 800°C for 4 hours.

The synthesis of silica begins by mixing 2.5 grams of pumice powder with 150 mL NaOH, followed by refluxing for 24 hours using a magnetic stirrer at 100°C. The extraction result is then filtered, and the filtrate was collected. The filtrate was then dripped with 50 mL H_2SO_4 until pH 7 to get a gel. The gel was dried in an oven for 24 hours at 80-100°C and then crushed to obtain silica powder. Next, the silica was mixed with 150 mL HCl and refluxed for 4 hours at 110°C. The resulting reflux materials were filtered, washed with distilled water and the residue was taken. Finally, the residue was dried for 24 hours at 110°C.

The sonication process started by mixing 100 mL of distilled water and 1 gram of silica powder. The mixture then inserted into the ultrasonic tube for sonication. Variation of temperature and sonication time are determined based on Design of Experiment (DOE) using Minitab 19 software, as shown in Table 1. The silica residue from sonication process was dried for 24 hours at 80°C-110°C and then calcined at 800°C for 4 hours to produce pure white silica. The chemical content of raw materials and results were analyzed using PANalytical's MiniPal 4 energy-dispersive XRF Bench-Top, crystal structure using X-ray diffraction type 3 E'xpert Powder, and morphology using FESEM Thermo Scientific Quattro S.

Table 1. Design of Experiment (DOE) for Sonication Process

No Samples	Temperature (°C)	Time (hrs)
1	80	3
2	80	2
3	60	1
4	30	1
5	80	1
6	60	2
7	30	3
8	30	2
9	60	3

3. RESULT AND DISCUSSION

3.1. X-R Fluorescence Characterization Results of Pumice

The results of the X-RF characterization of pumice are shown in Table 2. This chemical content resulted from the raw material before the synthesis and sonication process.

The results of raw material concentration are in accordance with previous research, indicating that the content of pumice has the most dominant silica compound. This shows that pumice is one of the abundant and easily accessible sources of silica.

The results X-RF characterization of silica after the synthesis are shown in Table 3. After the synthesis of pumice, the silica content reached 98.80 wt%, indicating a 28.99 wt% increase. The pumice synthesis process has reduced the impurities in the formed silica. The highest impurities were P_2O_5 at 0.72% and CaO at 0.37%.

3.2. Analysis of Variance (ANOVA) for Silica (SiO_2) Concentration

The results of the XRF silica test after the sonication process are shown in Table 4. below. The lowest SiO_2 content was formed in the specimen using a temperature of 80°C with a sonication time of 1 hour. Meanwhile, the highest SiO_2 content was obtained at a temperature of 60°C with a sonication time of 2 hours. The ANOVA for SiO_2 concentrations is shown in Table 5.

The highest contribution to the SiO_2 concentration is temperature, accounting for 67.25%. This parameter also has a significant effect, indicated by the P-value <5%, which is 0.018. Therefore, the null hypothesis (Ho) is rejected, concluding that temperature have significant effect on SiO_2 concentration. On the other hand, the time parameter contributes 22.4%, but it does not significantly affect the SiO_2 concentration. An error of 10.36% indicates that other independent variables have an effect.

The prediction of (SiO_2) concentration resulting from the correlation of independent variables shown in Fig. 1.

More than 98% SiO_2 concentration can be obtained by adjusting the temperature and time within the dark green area. Temperatures between 40 and 65 °C and times ranging from 1.5 to 3 hours yield the highest concentration. Notably, at low temperatures, maximum concentrations can also be obtained with a minimum time of 1.5 hrs. This contour plot facilitates the designer's choice of the DoE to produce the maximum SiO_2.

Table 2. X-RF Characterization Results of Pumice

Compound	Concentration (%)
SiO_2	69.81
Al_2O_3	9.24
Fe_2O_3	7.90
CaO	5.05
K_2O	4.96
TiO_2	1.22
P_2O_5	0.93
MnO	0.26
MgO	0.20
ZrO_2	0.10

Table 3. X-RF Characterization of Silica After Synthesis

Compound	Concentration (%)
SiO_2	98.80
Al_2O_3	0.04
CaO	0.37
TiO_2	0.01
P_2O_5	0.72

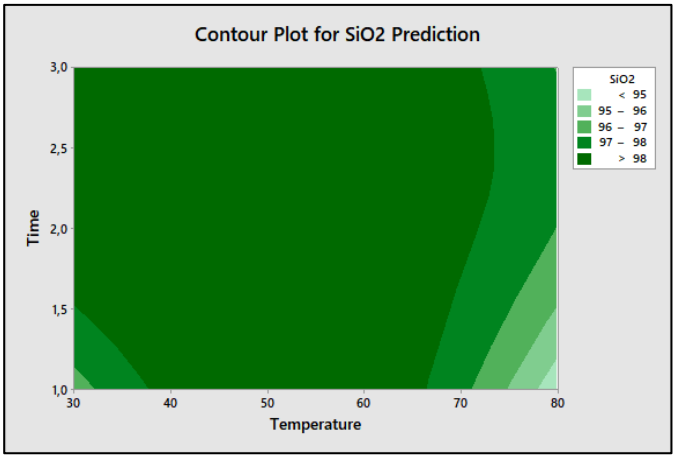


Figure 1. Independent Variables Correlation for SiO_2 Concentration

Table 4. Silica Concentration After Sonication Process

Temperature (°C)	Time (hrs)	SiO_2 (%)
80	3	96.95
80	2	96.99
60	1	98.81
30	1	96.52
80	1	94.24
60	2	98.90
30	3	98.86
30	2	98.82
60	3	98.97

Table 6. Silica Size After Sonication Process

Temperature (°C)	Time (hrs)	SiO_2 Size (nm)
80	3	12.602
80	2	15
60	1	13.536
30	1	16.712
80	1	17.827
60	2	6
30	3	11.383
30	2	14.970
60	3	5.303

Table 5. ANOVA for Transformed Response

Source	DF	Seq SS	Contribution (%)	Adj SS	Adj MS	F-Value	P-Value
Temperature	2	10.594	67.25	10.594	5.2970	12.99	0.018
Time	2	3.529	22.40	3.529	1.7644	4.33	0.100
Error	4	1.631	10.36	1.631	0.4079		
Total	8	15.754	100				

Table 7. ANOVA for Transformed Response

Source	DF	Seq SS	Contribution (%)	Adj SS	Adj MS	F-Value	P-Value
Temperature	2	39975	50.31	39975	19987.4	29.15	0.04
Time	2	36744	46.24	36744	18372.1	26.79	0.05
Error	4	2743	3.45	2743	685.8		
Total	8	79462	100				

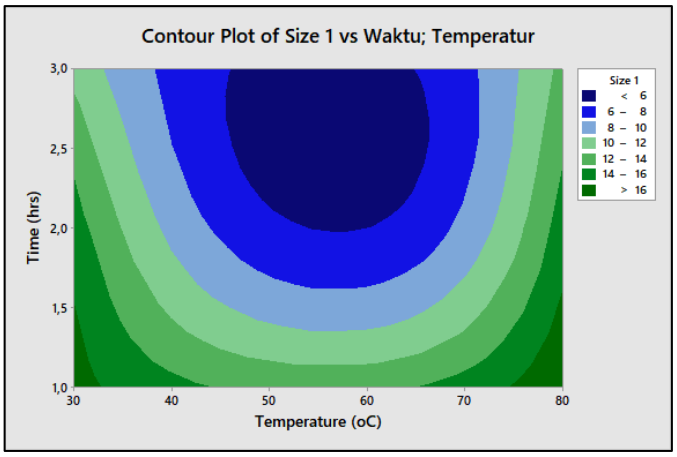


Figure 3. Independent Variables Correlation for SiO_2 Size

3.3. Analysis of Variance for SiO_2 Particle Size

The particle size of the sonicated SiO_2 is shown in Table 6. The smallest size of 5,303 nm, was obtained from the specimen with a temperature of 60°C and a sonication time of 3 hours. The ANOVA for SiO_2 particle size is presented in Table 7.

The independent variables, namely temperature and time, contributed to the particle size of 50.31% and 46.24%, respectively. Both of these variables significantly affect the particle size, as indicated by P-Value <5%, accounting for 0.004 and 0.005, respectively. With a 5% P-value, Ho is rejected and H1 is accepted. Therefore, it can be concluded that the independent variables have a

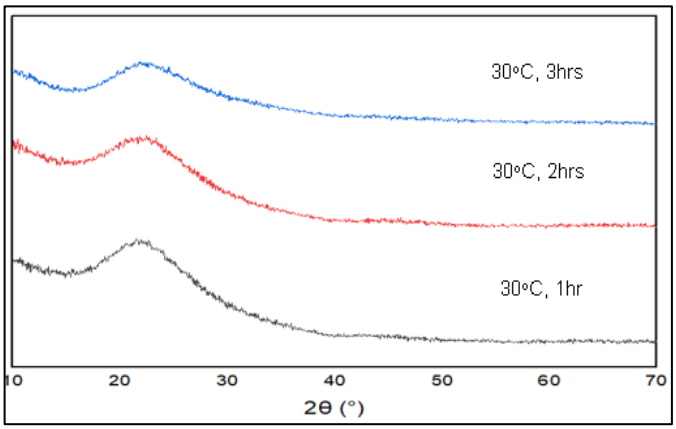
significant effect on particle size. The error, representing variables outside the experimental parameters, is only 3.45%. This value is less than 5%, thus, it can be ignored. This small error value will affect the R-square value of 96.55%. An R-square value close to 1 indicates that the distribution of the data follows a reliable pattern.

The prediction of (SiO_2) size resulting from the correlation of independent variables shown in Fig. 3. It can be observed that the SiO_2 particle size below 6 nm can be obtained by adjusting sonication parameters, particularly with temperature ranging from 50 to 65°C and time between 2 and 3 hours. This contour plot facilitates easier way to choose DoE.

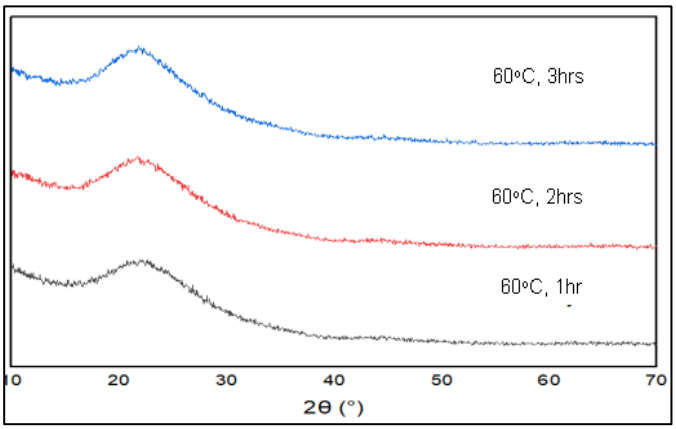
3.4. X-Ray Diffraction

The formed crystalline phase will be determined by the XRD test results. According to earlier investigations (Mourhly et al., 2015), the silica created during the synthesis process was amorphous silica. Fig. 4 presents the XRD results.

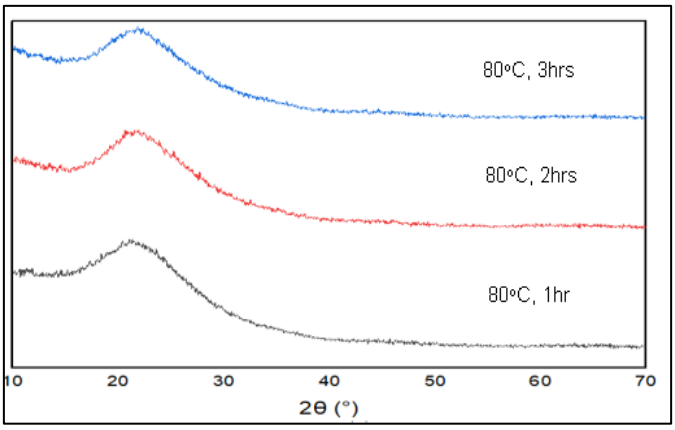
Pumice that has been ultrasonically processed at temperatures of 30, 60, and 80 °C for 1, 2, and 3 hours possesses amorphous silica. The amorphous phase can be identified by the shape of a diffractogram, which exhibits a curved pattern resembling a hill.



a). at 30 °C

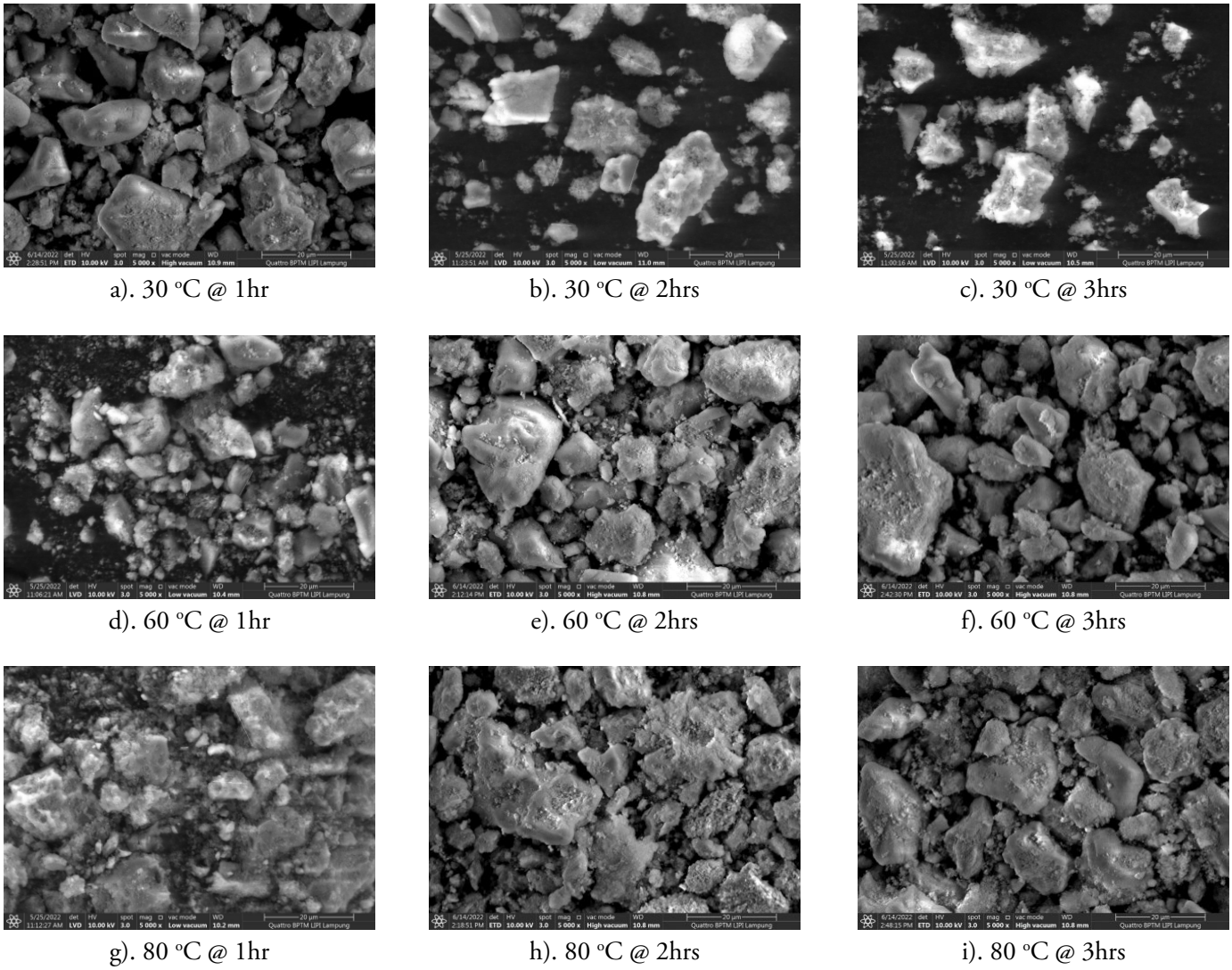


b). at 60 °C



c). at 80 °C

Figure 4. Comparison of Sonicated Silica Diffractogram



a). 30 °C @ 1hr b). 30 °C @ 2hrs c). 30 °C @ 3hrs

d). 60 °C @ 1hr e). 60 °C @ 2hrs f). 60 °C @ 3hrs

g). 80 °C @ 1hr h). 80 °C @ 2hrs i). 80 °C @ 3hrs

Figure 5. Microphotos of Silica After Sonication

3.5. Nanoparticle Morphology Used SEM Image

Fig. 5 depicts the observation of photo micro silica following the sonication procedure. After processing the data from these microphotos, the particle size is determined.

Some of the silica particles have a sub-angular shape, which is characterized by acute angles on certain particles. The particles' surfaces appear rough and amorphous. The sonication process is also successful in producing nano-sized samples and can separate the agglomeration of particles like other research. The silica synthesis treatment using the sol-gel method, followed by the sonication process, did not induce changes in particle shape. It can be seen from the SEM image that the shape of the particles does not change significantly.

An increase in sonication temperature will enhance reaction kinetics in the sol-gel process. This heightened reactivity signifies accelerated hydrolysis and condensation reactions during silica formation. Furthermore, higher temperatures will also reduce the viscosity of the solution. Consequently, the lowered solutions' viscosity, improves the dispersion of silica particles. Therefore, higher temperatures contribute to better mixing and more uniform particle distribution. In this study three temperature variants were applied, ranging from room temperatures of 30°C, 60°C, to 80°C. The SEM image reveals that the

surface structure at a high temperature (80°C) is rougher than at a low temperature. This rough surface indicates increased particle kinetic reactions in response to ultrasonic waves during particle agitation process . The surface conditions align with previous research, which noted that the sonication process at room temperature decreased micro-flotation. However, it's crucial to note that excessively high temperatures can lead to damage or degradation of the particle surface. Hence, selecting an appropriate process temperature is essential. Through Anova, the lowest process temperature can be selected in the predicted range to produce the most optimum size and composition of silica.

Purity, shape, and particle size are critical factors in determining the quality of silica nanoparticles. High purity of SiO_2, typically above 95%, ensures the use nano-silica without impurities from other ingredients. Silica nanoparticles are applicable in various fields, such as a filler or thickening agent in cosmetic products or as a catalyst. Electronic applications demand even higher purity, above 99%, as contaminants can adversely affect the performance of electronic devices. SiO_2 nanoparticle sizes below 10 nm are favorable for catalyst applications, while larger particle sizes around 90 nm, have been utilized as a filler for semiconductor packaging materials. Nanosilica measuring <7 nm was also reported to be successfully grafted with an amino group. The prediction chart from Anova simplifies the selection of parameters that comply particle size requirements.

Silica nanoparticles serve a crucial role in energy storage, acting as templates in making porous carbon for supercapacitor electrodes. Silica nanoparticles function as reinforcement, while increasing the hydrophilic properties of the interface on the surface of carbon pores. Another previous studies also affirmed that adding nano-silica increased the specific surface area of the supercapacitor electrode from 302 to 624 $F.g^{-1}$.

4. CONCLUSION

The pumice synthesis through modified sonication process has succeeded in obtaining amorphous silica particle with sizes ranging from 5,303 to 17,827 nm, achieving silica (SiO_2) purity between 94.24 - 98.97%. The independent variable, temperature, contributed 67.25% and exhibit a significant impact on the SiO_2 concentration. The two sonication variables, namely temperature and time, demonstrating a significant effect on particle size and contributed 50.31% and 46.24%, respectively. Additionally, there are other independent variables accounting for 10.36% that affect the SiO_2 concentration. The sonication process proves to be a reliable method for enhancing the concentration and particle size of the synthesized silica by selecting the appropriate independent variables.

ACKNOWLEDGMENT

The authors would like to express their gratitude to the Research and Development Center for Mining Technology and Non-Metal Laboratory and Chemical Analysis of the National Research and Innovation Agency (BRIN) of South Lampung for providing necessary tools and materials for conducting research and testing. Authors statement: all authors contributed equally to the writing of this paper.

REFERENCE

Anthe S, Pasau G, A. T. Variation of Weak Zone Internal Structure of Mount Loko Based on Seismo-Volcanic Studies. Scientific Journal of Science. 2015;15(1):27–32.

Ersoy B, Sariisik A, Dikmen S, Sariisik G. Characterization of acidic pumice and determination of its electrokinetic properties in water. Powder Technology.2010;197(1–2):129–35. http://dx.doi.org/10.1016/j.powtec.2009.09.005

Firnando HG, Astuti. Effect of Temperature on Sonication Process on Particle Morphology and Nanoparticle Crystallinity. Journal of Physics Unand. 2015;4(1):1–5.

Gungoren C, Ozdemir O, Ozkan SG. Effects of temperature during ultrasonic conditioning in quartz-amine flotation. Physicochemical Problems of Mineral Processing. 2017;53(2):687–98.

Hao X, Wang J, Ding B, Wang Y, Chang Z, Dou H, et al. Bacterial-cellulose-derived interconnected meso-microporous carbon nanofiber networks as binder-free electrodes for high-performance supercapacitors. Journal of Power Sources. 2017;352:34–41. http://dx.doi.org/10.1016/j.jpowsour.2017.03.088

Kim SY, Kim BH. Silica decorated on porous activated carbon nanofiber composites for high-performance supercapacitors. Journal of Power Sources.2016;328:219–27. http://dx.doi.org/10.1016/j.jpowsour.2016.08.011

Kumalawati A, W TM, Mastaram Y. Analisis Pengaruh Penggunaan Abu Batu Apung Sebagai Pengganti Filler Untuk Campuran Aspal. Jurnal Teknik Sipil. 2013;2(2):191–200.

Miloskovska E. Structure-property relationships of rubber / silica nanocomposites via sol-gel reaction (dissertation). Netherlands: Eindhoven University; 2013.

Miskah S. Pemanfaatan Batu Apung (Pumice) sebagai Bahan Pemucat Crude Palm Oil. Jurnal Teknik Kimia. 2010;17(2):2010.

Mourhly A, Khachani M, El Hamidi A, Kacimi M, Halim M, Arsalane S. The synthesis and characterization of low-cost mesoporous silica SiO2 from local pumice rock. Nanomaterial and Nanotechnol. 2015;5(35):1–7.

Pratomo I. Klasifikasi gunung api aktif Indonesia, studi kasus dari beberapa letusan gunung api dalam sejarah. Indonesian Journal on Geoscience. 2006;1(4):209–27.

Putra PS, Yulianto E. Karakteristik Endapan Tsunami Krakatau 1883 Di Daerah Tarahan, Lampung. Riset Geologi dan Pertambangan. 2017;27(1):83.

Sari LV, Manurung P, Yulianti Y. Pengaruh Variasi H2SO4 Pada Pembentukan Nanosilika Berbasis Batu Apung. Jurnal Teori dan Aplikasi Fisika. 2019;7(2):125–32.

Shen Y. Rice husk silica derived nanomaterials for sustainable applications. Renewable and Sustainable Energy Reviews. 2017;80(February):453–66. http://dx.doi.org/10.1016/j.rser.2017.05.115

Singh LP, Agarwal SK, Bhattacharyya SK, Sharma U, Ahalawat S. Preparation of silica nanoparticles and its beneficial role in cementitious materials. Nanomaterial and Nanotechnology. 2011;1(1):44–51.

Srivastava K, Shringi N, Devra V, Rani A. Pure Silica Extraction from Perlite: Its Characterization and Affecting factors. International Journal of Innovative Research Science Engineering and Technology. 2013;2(7):2936–42.

Sun Y, Zhang Z, Wong CP. Study on mono-dispersed nano-size silica by surface modification for underfill applications. Journal of Colloid and Interface Science. 2005;292(2):436–44.

Tiara, Earmpon T. Gambaran Tingkat Pengetahuan Perawat Terhadap Penanggulangan Bencana Di Provinsi Lampung Tahun 2017. Jurnal Ilmiah Kesehatan. 2019;8(2):74–7.

Trabelsi W, Benzina M, Bouaziz S. Physico-chemical characterisation of the Douiret sand (Southern Tunisia): Valorisation for the production of Silica Gel. Physics Procedia. 2009;2(3):1461–7. http://dx.doi.org/10.1016/j.phpro.2009.11.117

Vejayakumaran P, Rahman IA, Sipaut CS, Ismail J, Chee CK. Structural and thermal characterizations of silica nanoparticles grafted with pendant maleimide and epoxide groups. Journal of Colloid and Interface Science. 2008;328(1):81–91. http://dx.doi.org/10.1016/j.jcis.2008.08.054

Wardhani GA paramita kusumah. Silika pada Togkol Jagung yang Dikarakterisasi Menggunakan Spektroskopi Infra Merah dan Difraksi Sinar-X. Jurnal Riset Kimia. 2017;2(1):37.