

## Synthesis and Characterisation of Nano-silica Based on Pumice Using NaOH

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**ABSTRACT:** *Nano-silica was synthesised from pumice by extraction method using sodium hydroxide (NaOH), sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) and hydrochloric acid (HCl). The raw material of pumice was collected from local area, Tanggamus-Lampung Indonesia. After grinding, the pumice powder was activated at 450°C for 2 h before mixing with NaOH for extraction. After extraction, the powder was heated at 800°C for 4 h, to maintain the silica is in amorphous phase. Physical characteristics were analysed using transmission electron microscopy (TEM) for measuring particle size, Brunauer-Emmett-Teller (BET) technique for surface area measurement, x-ray diffraction (XRD) for structure and x-ray fluorescence (XRF) for determination of oxides. XRD analysis proved that besides amorphous nano-silica, there are peaks of sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) as representation of crystalline structure. The maximum silicon dioxide (SiO<sub>2</sub>) content was found on 3.0 molar (M) NaOH. The highest surface area of 165 m<sup>2</sup>/g was obtained in sample of 3.5 M NaOH. The truly amorphous nano-silica content was found in NaOH of 3.0 M. The formation temperature may occur between 1100°C–1200°C. The particle size is in the range of 9 nm–17 nm.*

**Keywords:** pumice, extraction, amorphous, particle size, formation temperature

### 1. INTRODUCTION

Pumice is a volcanic igneous glassy rock that is hollow and has large pores and low density, also has a white, creamy or grey colour.<sup>1</sup> The light nature of this material is due to rapid cooling of the melting volcanic mass.<sup>2</sup> According to Muralitharan and Ramasamy, pumice has a chemical content of silica (68.56%), alumina

(21.93%), loss on ignition (LOI) (4.40%) magnesium oxide (2.31%), sodium (1.01%), potassium (0.83%), iron (0.96%) and several others in trace amounts.<sup>3</sup> The high level of silica makes this material abrasive and the alumina content responsible for heat resistant of this material. However, the exact chemical composition of pumice is varied between the samples, depends on the location of the deposit. The pumice investigated in this study was found to have the silica content of 78%.

In nature, silica is available abundantly in many minerals and plants. Besides pumice, several important sources of silica are sodium silicate solution, clay, rice husk, rice husk ash, *equisetum arvenses* and olive stones.<sup>4-9</sup> In this research, one of the mineral ingredients chosen is pumice. Since amorphous silica is preferred in some respects to crystalline, attempts have been made to synthesise or to obtain amorphous silica from various sources. While plant-based silica tends to be amorphous the opposite is true for mineral based silica.<sup>6,8</sup>

Silica nanoparticles have found applications in many fields such as catalysis, aggregate in concrete, insecticide industry, and as adsorption materials in recyclable ceramic membrane.<sup>10-13</sup> In recognition of the important roles of nano-silica in different fields, in this research, extraction of nano-silica from pumice was attempted using sodium hydroxide (NaOH) as a solvent. Extraction was conducted under heating to optimise the dissolution of the silica. The mixture was filtered, and the filtrate was then titrated with sulphuric acid ( $H_2SO_4$ ) to convert the dissolved silica into solid. The solid silica was further purified with hydrochloric acid (HCl). The use of NaOH in this study is also based on the reports by several researchers who have conducted studies on the use of NaOH in extracting silica from pumice and other plant materials.<sup>10,14</sup>

In this investigation, extraction of silica from pumice was carried out using NaOH solution of different concentrations, with the main purpose to study the effect of the NaOH concentrations on the amount and some physical characteristics of the silica obtained.

## 2. EXPERIMENTAL PROCEDURES

### 2.1 Materials

The samples of pumice shown in Figure 1 were obtained from Tanggamus Bandar Lampung, Indonesia with latitude and longitude are 5°18' S and 104°33' E.



Figure 1: Local pumice from Tanggamus.

The sizes of pumice are not exactly the same, but the textures are the same. Based on vertical and horizontal diameters, the average diameter of pumice used in this research is 2 cm. The NaOH pellet (99% purity), concentrated  $\text{H}_2\text{SO}_4$  (97%), and concentrated HCl (38%) were purchased from Merck.

## 2.2 Methods

### Preparation of nano-silica

In this study, the procedure for preparation of nano-silica involves several steps. First, pumice was washed using aqua bidest and then dried at  $100^\circ\text{C}$  for overnight. The dried pumice was grinded followed by sieving with size of  $150\ \mu\text{m}$ , and the pumice powder was washed again with aqua bidest and dried  $100^\circ\text{C}$  for overnight and  $450^\circ\text{C}$  for 2 h.

A mass of 2.5 g of the powder was refluxed in 150 ml of NaOH with concentrations of 2.0, 2.5, 3.0, 3.5, and 4.0 molar (M), respectively. The formed sodium silicate was filtered, and the filtrate was collected. The filtrate was titrated with 150 ml of 5 M  $\text{H}_2\text{SO}_4$ , to neutralise the filtrate and produce white silica gel. The gel was aged for 24 h, followed by washing with hot aqua bidest, and finally was heated at  $100^\circ\text{C}$  for 24 h. After grinding, the powder was purified by adding 150 ml of 1 M HCl for 4 h followed by heating at  $100^\circ\text{C}$ . The procedure was completed by calcination of the powder at  $800^\circ\text{C}$  for 4 h.

### 2.3 Instrumentation

The chemical components of the samples were analysed by X-ray fluorescence (XRF) spectrometer (PANalytical Epsilon 3, Netherlands). The Brunauer-Emmett-Telle (BET) surface area was measured by  $N_2$  adsorption-desorption using Quantachrome TouchWin v1.2 (USA). Powder x-ray diffraction (XRD) patterns were obtained by XPERT PRO PANalytical (Netherlands) using  $CuK\alpha$  radiation. The patterns were collected over a range  $10^\circ$ – $100^\circ$  with step size of  $0.026^\circ$ . Transmission electron microscopy (TEM) with SAED of JEOL JEM-1400 (Japan) was used to find microstructure and measure the particle size. Differential thermal analysis (DTA) data was collected with Hitachi model Estar SII 7300 (Japan) with standard of platinum.

## 3. RESULTS AND DISCUSSION

The quantity of silica obtained from pumice using NaOH with different concentrations is shown in Table 1. The experiments were carried out using 2.5 g pumice, followed by calcination of the silica at  $800^\circ C$ .

Table 1: The mass of silica obtained using NaOH with different concentrations.

No	Name of sample	NaOH concentration (M)	Mass of silica (g)
1	NaOH2.0 M	2.0	1.147
2	NaOH2.5 M	2.5	1.316
3	NaOH3.0 M	3.0	1.450
4	NaOH3.5 M	3.5	1.605
5	NaOH4.0 M	4.0	2.124

Table 1 shows that the amount of silica increases with increased concentration of NaOH solution used. The results presented in Table 1 also confirm the existence of amorphous silica in pumice investigated, since it has been acknowledged that amorphous silica is soluble in alkaline solution. The results of this study are in agreement with the earlier observation of Srivastava et al., who stated that the concentration of NaOH solution influences the decomposition of silica in pumice.<sup>15</sup>

### 3.1 Characterisation by XRD

Figure 2 shows the XRD pattern of pumice powder after the sample was subjected to heating at 450°C for 2 h and the silica samples produced from extraction process and heated at 800°C. Phase identification was conducted using Joint Committee on Powder Diffraction Standards (JCPDS) files number 41–1486 for anorthite with formula  $\text{CaAlSiO}_8$ , 19-1184 for albite with formula  $\text{NaAlSi}_3\text{O}_8$ , and 37-1465 for  $\text{Na}_2\text{SO}_4$ .<sup>16–18</sup>

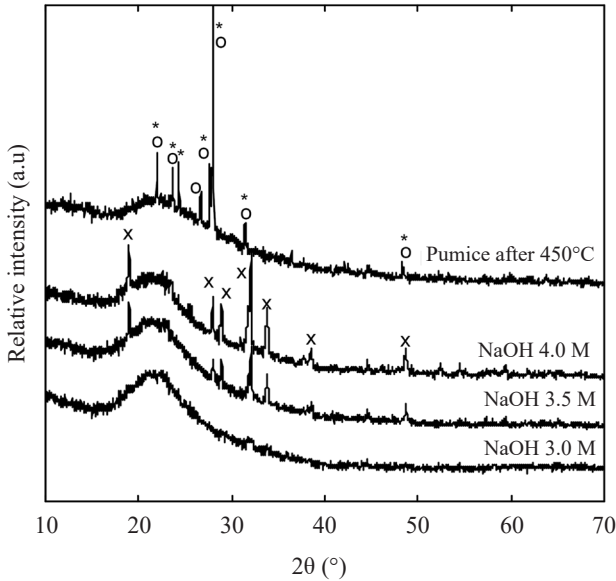


Figure 2: Diffractogram of pumice powder after 450°C and after a series processing at different NaOH concentrations. Legend: o = anorthite, \* = albite and x =  $\text{Na}_2\text{SO}_4$ . The wavelength of x-ray used = 1.54056 Å.

The composition of pumice powder after heating at 450°C for 2 h consisted of two phases i.e., anorthite and albite. The hump of diffractogram around 20°–23° is associated with the presence of amorphous silica. As can be seen in Figure 2, the diffractogram of the silica obtained using NaOH 3.0 M is marked by a broad peak at around 21.5°, which is a characteristic feature of amorphous silica suggests that the sample is practically amorphous. This result is in good agreement with earlier observation of Tuan et al., for silica obtained from rice husk. Carneiro et al., also reported that the main broad peak of nano-silica from *equisetum arvense* was found at around 22°. <sup>8,19</sup> Amorphous nano-silica characteristic is confirmed by the hump around 2θ of 17°–27°. <sup>20</sup>

However, Liou and Wu have observed the peak at  $2\theta = 22.5^\circ$  for nano-silica obtained from acid washed rice husk.<sup>21</sup> Slightly different results reported by workers suggest that silica structure is affected by raw material, water washing and calcination treatments. Ullah et al., reported diffuse peak occurred at about  $20^\circ$  and Naddaf et al., found between  $16^\circ$ – $38^\circ$  centred at  $2\theta$  of  $21.7^\circ$ .<sup>9,22</sup>

In the diffractograms of the sample obtained using NaOH 3.5 M and increased in sample NaOH 4.0 M, it can be seen that besides amorphous silica, weak peak associated with sodium sulphide was detected, with higher intensity in the sample obtained using NaOH 4.0 M. The crystalline part in the two samples is matched with  $\text{Na}_2\text{SO}_4$ , most likely originated from NaOH and  $\text{H}_2\text{SO}_4$  used during extraction process.

### 3.2 XRF Analysis

Chemical composition of different samples investigated, in the form of oxides, was analysed using XRF technique, producing the results as presented in Table 2.

Table 2: Chemical composition of pumice and silica extracted using NaOH solution with different concentrations.

Compound	Pumice	NaOH 2.0 M	NaOH 2.5 M	NaOH 3.0 M	NaOH 3.5 M	NaOH 4.0 M
$\text{SiO}_2$	77.799	92.017	93.716	96.264	91.422	86.764
$\text{Al}_2\text{O}_3$	12.724	0.750	1.058	1.146	1.010	1.206
$\text{SO}_3$	–	5.265	4.771	2.191	6.544	10.531
$\text{K}_2\text{O}$	3.701	0.158	0.037	0.023	0.034	0.089
$\text{CaO}$	1.677	0.168	0.049	0.047	0.115	0.131
$\text{MgO}$	1.518	0.502	0.007	0.000	0.000	0.728
$\text{P}_2\text{O}_5$	0.367	1.031	0.301	0.272	0.784	0.367
$\text{Fe}_2\text{O}_3$	1.422	0.009	0.009	0.007	0.020	0.017
$\text{TiO}_2$	0.281	0.013	0.011	0.010	0.009	0.025
$\text{Ag}_2\text{O}$	0.210	0.069	0.036	0.030	0.057	0.086

Note:  $\text{SiO}_2$  (silicon dioxide),  $\text{Al}_2\text{O}_3$  (aluminum oxide),  $\text{SO}_3$  (sulfur trioxide),  $\text{K}_2\text{O}$  (potassium oxide),  $\text{CaO}$  (Calcium oxide),  $\text{MgO}$  (magnesium oxide),  $\text{P}_2\text{O}_5$  (phosphorus pentoxide),  $\text{Fe}_2\text{O}_3$  (ferric oxide),  $\text{TiO}_2$  (titanium dioxide),  $\text{Ag}_2\text{O}$  (silver oxide)

Data in Table 2 clearly indicate the existence of silica as prime component of the samples. Compared to the pumice sample, it can be seen that the contents of silica in the samples produced from extraction are significantly higher, with the trend as presented in Figure 3.

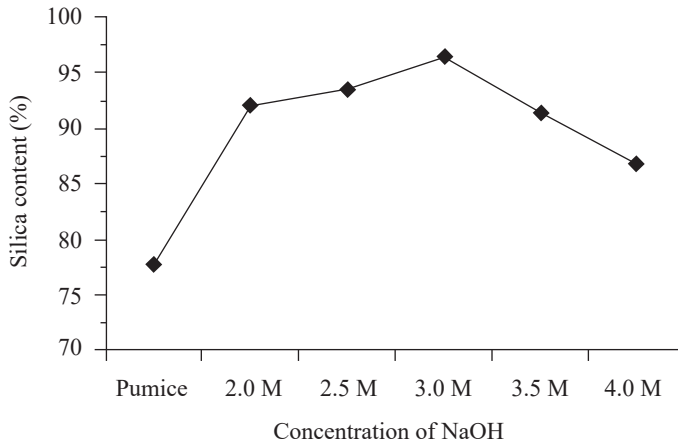


Figure 3: Purity of silica as a function of NaOH concentrations.

As can be seen in Figure 3, the silica with the highest purity (96.264%) was obtained with the use of 3.0 M NaOH solution, while the use of less and more concentrated solution was found to lead to decrease purity of the silica produced. In this respect, it is concluded that 3.0 M is the optimum concentration of NaOH for extraction of amorphous silica from pumice. The presence of  $\text{SO}_3$  in extracted samples is due to the usage of  $\text{H}_2\text{SO}_4$  during titration process, since this oxide was not found in the pumice sample. The nature of solid  $\text{SO}_3$  is complex because of the structural changes caused by traces of water.<sup>23</sup>

### 3.3 BET Analysis

The surface of the samples according to BET analysis is shown in Figure 4, displaying quite significant effect of NaOH concentrations used.

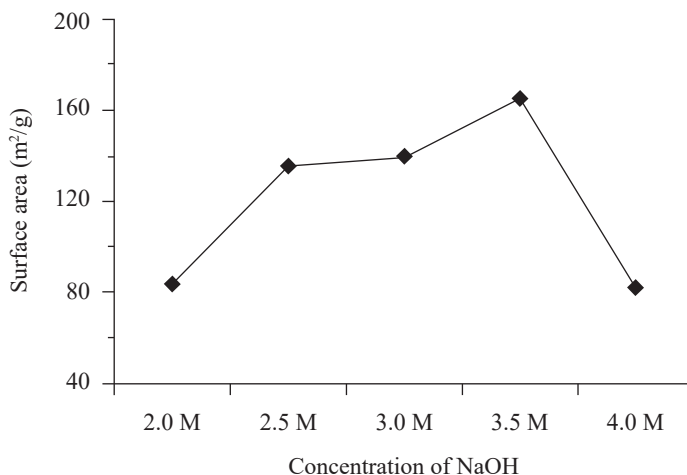


Figure 4: Surface area of amorphous silica obtained using NaOH at different concentrations.

As can be seen in Figure 4, the surface area of the sample increases with the increased concentration of NaOH until 3.5 M, reaching the largest value of 165 m<sup>2</sup>/g, and then decreases to 82 m<sup>2</sup>/g with the use of NaOH 4.0 M. Generally, the surface area of the commercial micro silica and fume is on the range of 15 m<sup>2</sup>/g–28 m<sup>2</sup>/g.<sup>21</sup> Other researches using 0.7 wt% NaOH to extract silica reported the surface area of 60.3 m<sup>2</sup>/g and 169.7 m<sup>2</sup>/g that is relatively the same with the result of this study.<sup>24</sup> In another study, silica nanoparticles from rice husk was reported to have surface area in the range of 81 m<sup>2</sup>/g–120 m<sup>2</sup>/g.<sup>25</sup>

### 3.4 DTA Analysis

To investigate thermal characteristic, the silica obtained using NaOH 3.0 M was analysed using DTA. This particular sample was selected based on its existence as the highest purity silica produced. Measurement was made from room temperature to 1200°C on the basis that the formation temperature of SiO<sub>2</sub> ( $\alpha$ -tridymite form) occurred at elevated temperatures of > 870°C and it converts to  $\beta$ -cristobalite at 1470°C.<sup>26,27</sup> In this research, heating rate of 3°/min was applied, and the DTA curve produced is presented in Figure 5.



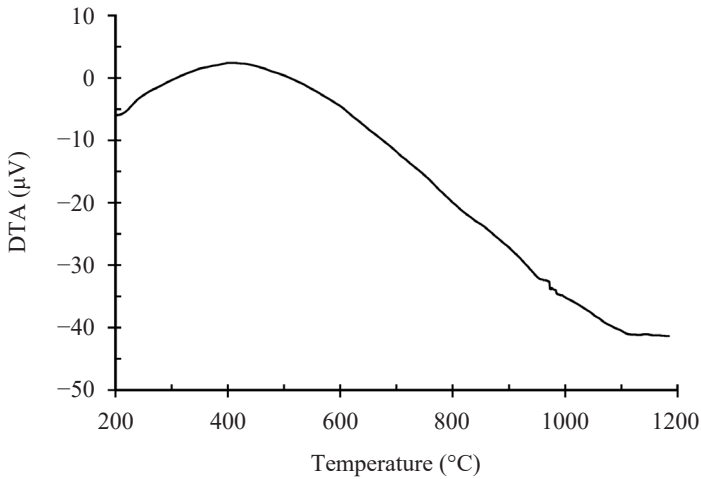


Figure 5: DTA curve of silica sample extracted using 3.0 M NaOH.

As can be seen Figure 5, the formation temperature lies between 1100°C–1200°C. This result is consistent with the formation temperature of silica, which is in the range of 870°C–1470°C as previously mentioned. This result of current study is consistent the finding by others using DTA technique, who reported that formation temperature for silica occurred above 1000°C.<sup>14</sup> There is no endothermic peak detected from 400°C–1100°C, indicating there is no other significant phase formed in that temperature range.

### 3.5 TEM of Nano-silica

In this investigation, the samples prepared using NaOH of 3.0 M and 3.5 M were characterised with TEM to justify the production of nano-silica as expected. TEM images for both samples are depicted in Figure 6.

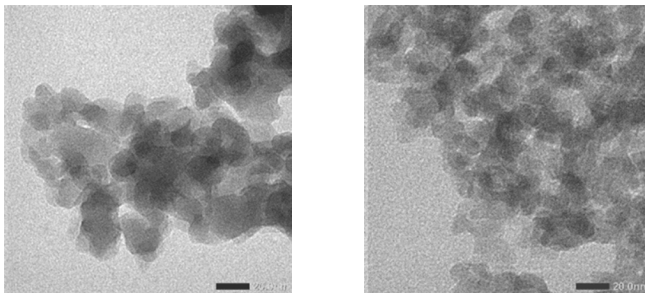


Figure 6: TEM image of nano-silica using NaOH of 3.0 M and 3.5 M. Bar scale — = 20 nm.

The particles of 3.5 M sample look sticks to each other attributing to the particles that experience adhesion.<sup>28</sup> This mechanism can be contributed by its surface area as depicted in Figure 4 which its BET is 165 m<sup>2</sup>/g. Sample 3.0 M (pure amorphous phase) indicates no stick among the particles, which means no cohesive behaviour. By using ImageJ software, the average particle size of selected samples (3.0 M and 3.5 M) is (14.8 ± 3.1) nm with narrow range. The sample morphology is not really spherical may be due to shape factor that make the difference between the spherical nanoparticles and non-spherical nanoparticles.<sup>29</sup> Our results are comparable to finding of in the range of 15 nm.<sup>14</sup> The size of nano-silica obtained in this work was almost the same with that of nano-silica synthesised by other authors, and smaller than nano-silica powder from rice husk.<sup>19,30</sup>

#### 4. CONCLUSIONS

Extraction of high purity nano-silica was successfully achieved in this study using NaOH solution as a solvent, with the highest purity was obtained using 3.0 M NaOH. The existence of nano-silica as amorphous material was confirmed using XRD technique, with the sample produced using 3.0 M NaOH is practically pure amorphous. BET results indicate that the sample obtained using 3.5 M NaOH has the largest surface area (165 m<sup>2</sup>/g), and according to TEM analysis the average particle size of the nano-silica produced is 15 nm with a narrow range of 9 nm–17 nm. Based on DTA data, the temperature of the nano-silica formation has started at temperature of 1100°C.

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