ADSORPTION ISOTHERM OF MESOPORE-FREE SUBMICRON SILICA PARTICLES FROM RICE HUSK

RISTI RAGADHITA[1], ASEP BAYU DANI NANDIYANTO[1,*],
WILLY CAHYA NUGRAHA[2], AHMAD MUDZAKIR[1]

[1]Departemen Kimia, Universitas Pendidikan Indonesia,
Jl. Dr. Setiabudi 229, Bandung 40154, Indonesia
[2]Research Center for Clean Technology, Lembaga Ilmu Pengetahuan Indonesia
Jl. Cisitu Sangkuriang, Bandung 40135, Indonesia
*Corresponding Author: nandiyanto@upi.edu

Abstract

The purpose of this study was to evaluate adsorption isotherm of mesopore-free submicron silica particles. In this study, mesopore-free submicron silica particles were prepared from acid-base extraction of rice husk ash under a surfactant-free condition. The adsorption isotherm analysis was done in the borosilicate batch reactor system under constant pH condition as well as room temperature and pressure. Then, the results were compared to the Langmuir and the Freundlich models. As a model of adsorbate, curcumin was used. To support the adsorption analysis, several characterizations were conducted, including electron microscope, x-ray diffraction, and Fourier transform infrared. The experimental results showed that the present mesopore-free submicron silica particles were effectively adsorbing curcumin molecules. The adsorption isotherm test showed that the equilibrium adsorption data of the present silica particles were fit to the Freundlich isotherm model, confirming the adsorption occurs on heterogeneous surfaces with multilayer adsorption. This informs molecule-molecule interaction on the adsorption layers. Low adsorption rate is found, which is due to the existence of mesopore-free structure on the silica adsorbent. This study gives information for the importance of a critical variable influencing the adsorption capacity.

Keywords: Adsorption properties, Education, Isotherm Langmuir, Rice husk, Silica.

1. Introduction

Silica is one of the most abundant materials. This material has superior and unique characteristics due to its ability to have porous structures, making it applicable for super low density, high surface area, low thermal conductivity, and low dielectric constant [1-4]. Silica is also applied in various fields. In daily life, silica is found in cosmetics, toothpaste, and detergents. In industry, silica has been used as raw materials and fillers for electronics, cements, and rubber. Silica is also used as adsorbents and catalysts [5, 6].

To fabricate silica, many reports have suggested the use of several methods, such as sol-gel, precipitation process, vapor phase reaction, and hydrothermal method. The reports were also completed the information of various feasible raw materials for producing silica [5, 7-10]. Although the reports showed the successful preparation of silica with possible applications, they did not focus on the analysis of the adsorption process. In fact, analysis of adsorption process is important for understanding the beauty of silica for further applications, such as adsorbents, catalysts, lens, etc.

Here, the present study was to evaluate adsorption isotherm of mesopore-free submicron silica particles. Mesopore-free silica particles were used to understand the realistic conditions during the adsorption process in the material. In short, the existence of mesoporous structure allows the additional factors in the analysis of adsorption process.

To produce mesopore-free submicron silica particles, we used an acid-base extraction process under surfactant-free condition. Surfactant-free reaction is important to be utilized in this study for preventing the formation of porous structures in the particle. As a raw material, we used rice husk ash. Rice husk was used due to its largely available in South East Asia. Thus, the information regarding the possible creation of silica from this raw material will also give ideas for solving rice husk waste problems [11, 12], while rice husk is potentially used due to its high silica content (reaching 20%) [13]. Further, due to its abundant condition, this raw material is also one of the alternative low-cost silica raw materials [14]. As a model of dye, we used curcumin. Curcumin was used due to its molecule size (reaching about 1.4 nm). This size range is fit for describing other types of dyes and molecules.

2. Materials and Method

Mesopore-free silica particles were prepared using the following raw chemicals: rice husk (purchased from Jaya Makmur Farm Shop, Bandung, Indonesia), sodium hydroxide (NaOH; Bratachem, Indonesia), and phosphoric acid (H_3PO_4, Bratachem, Indonesia). The mesopore-free silica particles were prepared by extracting rice husk ash (Fig. 1). In short, in the experimental procedure, rice husk was washed, soaked in water for 15 minutes, dried in the oven for 4 hours at 200°C, and grinded using a saw-milling process. Detailed information for the saw-milling process is reported in our previous studies [15]. Then, the dried rice husk was put in the electrical furnace for 2 hours at 600°C to obtain rice husk ash. The rice husk ash was then washed in water using a centrifugation (3 times; 11,000 rpm for 5 minutes). The washed rice husk was then put into NaOH solution (with concentration of 0.07 M) and heated for 2 hours at 70°C.

To get silica extract (as silicic acid ($Si(OH)_4$ solution) and separate carbon residue from the rice husk ash, the mixed solution was centrifuged at 11,000 rpm

for 5 minutes. Then, silica extract was dropped wise by phosphoric acid until the pH reaches 10 and a white precipitate is formed. Finally, to produce silica particles, the white precipitate was settled, centrifuged (11000 rpm for 5 minutes), washed by methanol, and dried in an oven at 50°C.

To analyze the adsorption properties of the prepared silica, curcumin was used as a model. Curcumin was selected because of its ideal size for a model of organic molecule (less than 1.4 nm) [16]. The curcumin was produced using the same manner with our previous studies [17, 18]. In general, the adsorption test was done by adding silica particles into 200 mL of curcumin solution (varied from 24 to 100 ppm) in the constant pH and room temperature and pressure. The mixed solution was mixed in a 400-mL capacity of borosilicate batch glass reactor having dimension of 10 and 8 cm for height and diameter, respectively. The adsorption test was done by stirring the mixed solution at 600 rpm and taking aliquot sample at a specific time. The aliquot solution was then put into a centrifugation (11,000 rpm; 5 minutes). The filtrate was then analyzed using Visible Spectroscopy (Model 7205; JENWAY; Cole-Parmer; US; analyzed at maximum wavelength at a maximum wavelength in the range of between 280 and 600 nm).

To get information about the isotherm adsorption model, we selected the Langmuir and Freundlich isotherm models as a comparison. These models were the most commonly studied models for evaluating adsorption phenomena [19]. The Langmuir isotherm model assumes that monolayer adsorption occurs on the surface of the adsorbent [20], whereas the Freundlich isotherm model assumes multilayer adsorption [19]. Both equations were used the concentration of the adsorbate in equilibrium conditions (Ce; in mg/L) and the amount of adsorbed substance per gram of adsorbent (Qe; in mg/g). The Langmuir equation is shown in Eq. (1) [19]:

$$\frac{1}{Q_e} = \frac{1}{K_L Q_{max}} \frac{1}{C_e} + \frac{1}{Q_{max}} \tag{1}$$

where K_L is the Langmuir adsorption constant and $Qmax$ is the monolayer adsorbent capacity (mg/g).

Freundlich adsorption model is stated in Eq. (2) [19]:

$$\log Q_e = \log k_f + \frac{1}{n} \log C_e \tag{2}$$

where k_f and n are the Freundlich constants and the nonlinear degree, respectively.

In short, the adsorption data was compared to these models (by fitting curves and equations). Efficiency adsorption was measured using the following calculation in Eq. (3):

$$\%E = \left(\frac{C_o - C_e}{C_o} \right) \times 100\% \tag{3}$$

where C_o is the initial concentration of adsorbate (mg/L), C_e is the equilibrium concentration (mg/L), and E is efficiency adsorption (%).

To support the analysis, several characterizations were used: Fourier Transform Infrared (FTIR-4600, Jasco Corp., Japan), Energy Dispersive Spectroscopy (EDS-7000/8000; Shimadzu Scientific Instruments Inc., Japan), Scanning Electron

Microscopy (JSM-6360LA; JEOL Ltd., Japan), and X-Ray Diffraction (XRD; PANalytical X'Pert PRO; Philips Corp., The Netherland).
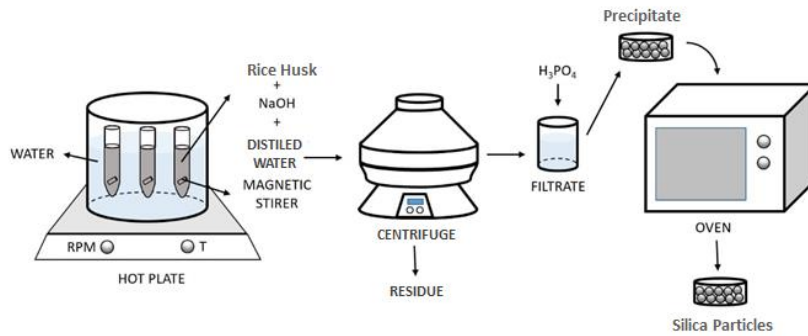

Fig. 1. Schematic process of the extraction silica from rice husk.

3. Results and Discussion

3.1. Physicochemical Properties of the Prepared Silica Particles

Figure 2 shows the SEM analysis images of rice husk before and after the silica preparation process. Figure 2(a) confirms that the initial rice husk after the saw-milling process has sizes of about 500 nm (Fig. 5(a)). After adding the silica preparation process, the particles were spherical and had sizes in the range of between 50 and 200 nm. Some aggregations were found. Since the process was done without additional surfactant, the prepared particles were mesopore-free structure.
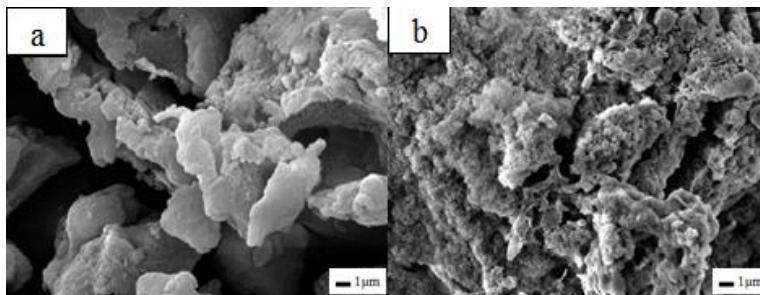

**Fig. 2. (a) SEM analysis of milled rice husk, and
(b) Prepared mesopore-free submicron silica particles.**

Figure 3 shows the FTIR analysis of the prepared silica particles. Several peaks were detected in the FTIR spectrum. However, some peaks were in the fingerprint area, making us difficult to identify them. The presence of absorption between wavelengths of 450 and 1300 cm^{-1} shows typical absorption of silica [21]. The absorption occurs at wavelengths of 488.20; 862.75; and 1057 cm^{-1}, in which these three sequential sequences of peaks are siloxane (Si-O-Si), Si-OH bond, and Si-O bond, respectively. The absorption peaks at wavelengths of 3455 and 1633 cm^{-1} show the presence of water molecules trapped in the sample [21, 22]. The peak in the area of 980 cm^{-1} is related to Si-O stretching vibration of non-bridging oxygen atoms. The absorption bands in the 647 and 554-599 cm^{-1}, respectively, show the stretching vibration of the siloxane group and Si-O-Si bending vibrations [23, 24].

The absence of absorption bands at wavelengths of 2800 and 3000 cm^{-1} indicates the absence of organic compounds from silica after the extraction process [25, 26].
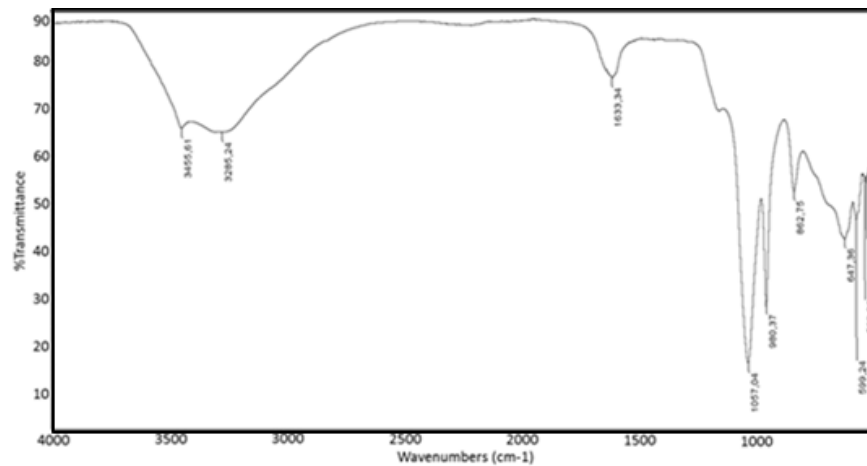

Fig. 3. The FTIR analysis of mesopore-free submicron silica particles.

The results of EDS analysis (as shown in Fig. 4) confirm the atomic content of oxygen (O) and silicon (Si), in which these atoms are the most elements in the material (with concentration of 47.20 and 25.66% respectively). But, based on the results of EDS, there are other elements contained in silica such as elements of sodium (Na), phosphor (P), and potassium (K). Na has a fairly large content of around 8.20%. This is because of the use of NaOH during the silica extraction process. However, this amount can be neglected since this element is typically easily diluted in water. Thus, it will not disturb the adsorption analysis.
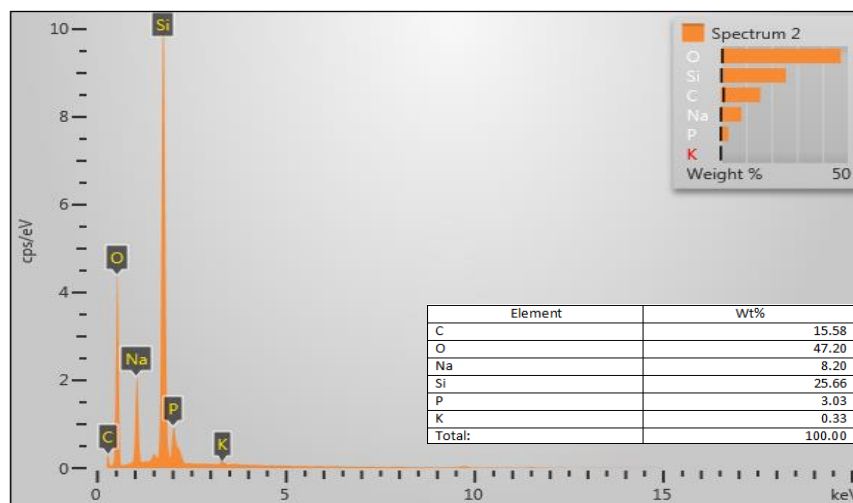

Element	Wt%
C	15.58
O	47.20
Na	8.20
Si	25.66
P	3.03
K	0.33
Total:	100.00

Fig. 4. The EDS analysis of mesopore-free submicron silica particles.

Figure 5 shows the XRD analysis of the prepared silica. The results of the XRD analysis showed the presence of sharp peaks at 22°, confirming the presence of

amorphous silica [19]. In addition, some peaks were obtained. However, these peaks are relating to the cristobalite phase in silica, especially it can be found for the sharp peaks at between 0 and 40°.
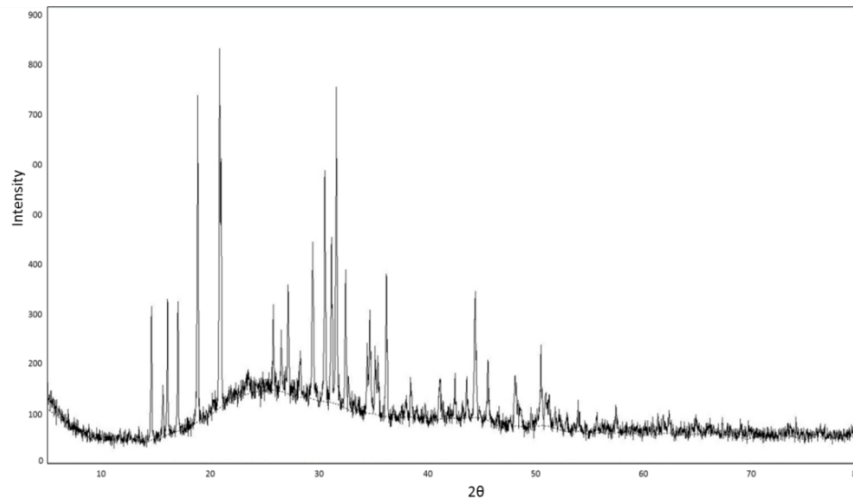

Fig. 5. The XRD result of mesopore-free submicron silica particles.

3.2. Adsorption Properties of Silica

Figure 6 is the effect of adsorbent amount on the adsorption efficiency of silica. This analysis is important for understanding the optimum condition for mass of adsorbent. The experiment was done in the 200 mL of curcumin solution (20 ppm) under various loadings of silica (i.e. 0.10; 0.25; and 0.50 g). In this study, the amount of adsorbents with less than 0.10 g was not carried out because of its difficulties in analysis. The results showed that the silica adsorption efficiency decreased with increasing the mass of the adsorbent. This is because excessive dosages of the adsorbents make them agglomeration. As a consequence, the adsorption sites on the surface of the adsorbents should be less [27]. Based on the analysis, the optimum mass of silica for the adsorption process was 0.10 g. This optimal mass is then used for further investigation of silica adsorption properties.
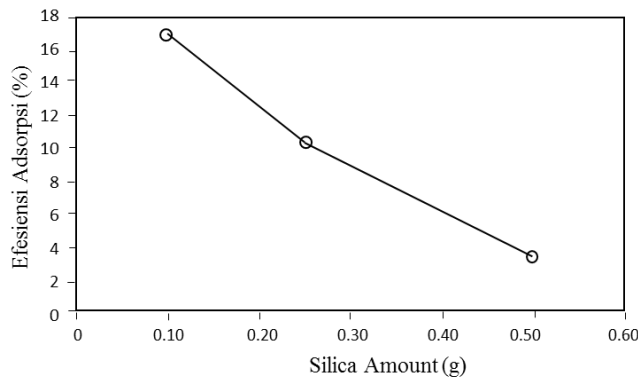

Fig. 6. Effect of adsorbent amount on adsorption properties of mesopore-free submicron silica particles.

Figure 7 shows the effect of adsorption time on the adsorption efficiency. To confirm the analysis, the adsorption time was tested at 10, 30, 50, 70, 90, and 110 minutes. In this study, the mass of adsorbent and concentration of curcumin were fixed at 0.10 g and 50 ppm, respectively. This figure confirms that the longer the contact time of the adsorbent with the adsorbate (turmeric solution), the more effective the adsorbent adsorbs curcumin molecules. In short, the rate for the adsorption can reach 8 ppm in 70 minutes. If the adsorption time is longer than 70 minutes, no more amount can be adsorbed (compared to the concentration at 70 minutes). This informs the saturation of the adsorption site on the adsorbent's surface. Adsorbent surfaces are not able to do more adsorption process. Thus, we can conclude that the optimum adsorption time is 70 minutes.
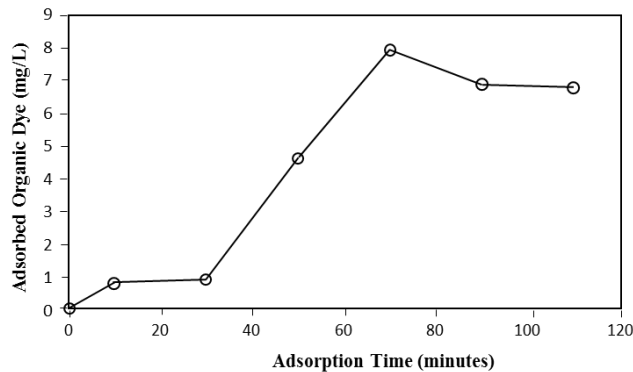

Fig. 7. Effect of adsorption time on adsorption efficiency of mesopore-free submicron silica particles.

Figure 8 shows the effect of initial concentration of curcumin on the adsorption properties of silica. In this test, we varied the initial concentration of curcumin under constant adsorbent dosage of 0.10 g. The adsorption process was done for 70 minutes based on the analysis in Fig. 7. Parabolic curve was obtained and the maximum curve was detected when using concentration of curcumin of 78 ppm. If the initial concentration of curcumin solution exceeds the maximum concentration, the efficiency of its adsorption is no change. The adsorption site on the adsorbent surface reaches saturation condition. Thus, the adsorbent can no longer absorb optimally.
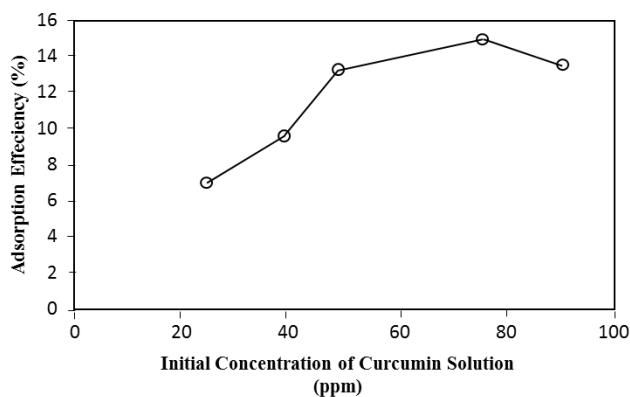

Fig. 8. Effect of initial concentration of curcumin on adsorption efficiency.

Based on the above analysis, experimental data for determining the adsorption of curcumin with silica adsorbent was done by fitting data on the Langmuir and Freundlich isotherm adsorption models. Experiments were carried out under optimum condition based on Figs. 6, 7, and 8.

Figure 9 is the fitting analysis results of the initial concentration of adsorbate C_e and the amount of adsorbed substance per gram of adsorbent Q_e. The fitting of the Langmuir and Freundlich adsorption isotherm models is presented in Figs. 9 (a) and (b).

The experimental results showed that the Freundlich isotherm adsorption model has the regression value approaching 1 ($R^2 = 0.9626$) with the Freundlich parameter obtained in this work is $k_f = 11.978$ and $n = 1.817$. In the Freundlich parameter, this analysis shows that if $n = 1$, adsorption is linear. Meanwhile, if $n < 1$, the adsorption follows a chemical process. If $n > 1$, the adsorption follows a physical process [19]. From the Freundlich parameter results in this study, $n > 1$ was obtained. The adsorption is a type of adsorption followed a physical process. Physical adsorption characteristics are molecules bound to the adsorbents through van der walls bonds, forming a multilayer adsorption, and the adsorption process is not specific at the adsorption site. Langmuir adsorption model has $R^2 = 0.9505$ with the Langmuir parameter obtained in this work is $Q_{max} = 82.64$ mg/g and $K_L = 1$ L/mg. In addition, the main ideas for the obtainment of heterogeneous type adsorption of curcumin on the silica are possibly because the silica forms microporous. Microporous itself is formed due to the existence of folds between Si-O-Si.
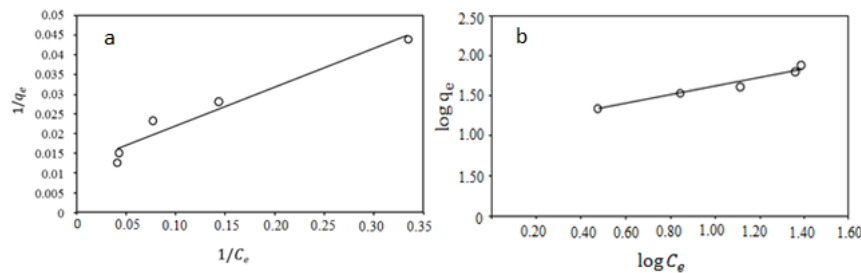

Fig. 9. (a) Model isotherm Langmuir and (b) Model isotherm Freundlich.

In this study, the adsorption rate of the present silica was not very significant. There are several reasons. The first reason is because the adsorbent has relatively large sizes. The sizes varied from nanometer to submicron scale. The second reason is due to the existence of aggregation. The third reason is because of the mesopore-free structure in the adsorbent. These reasons lead to the obtainment of less surface area.

4. Conclusions

The present study analyzes the adsorption isotherm of mesopore-free submicron silica particles. To support the analysis we varied initial amount of silica, adsorption time and initial concentration of curcumin solution. The experimental results showed that the present mesopore-free submicron silica particles were effectively adsorbing curcumin molecules, in which the equilibrium adsorption data is fit to the Freundlich isotherm model. This result confirms the adsorption occurs on heterogeneous surfaces with multilayer adsorption. In general, there are molecule-

molecule interaction happens on the adsorption layers. Low adsorption rate is found, which is due to the existence of mesopore-free structure on the silica adsorbent. This study gives information for the importance of a critical variable influencing the adsorption capacity.

Acknowledgments

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