Synthesis and characterization of mesoporous silica from beach sands as silica source

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Abstract. The amorphous mesoporous silica was successfully synthesized from beach sand sources. Dodecyl amine, DDA, was used as a mesoporous template under a sol-gel reaction. The synthesized mesoporous silica has a high specific surface area 766.40 m²/g, pore volume 0.51 cc/g, average pore diameter in mesoporous range 3.04 nm, and relatively high acidity value 0.88 mmol/g. It was found that rotation speed during the addition of DDA affects greatly the porosity formation, with higher rotation speed favors porosity formation.

Keywords: Characterization; dodecyl amine; mesoporous silica; beach sand;

1. Introduction
Beach sand contains various important components such as silica. Every beach sand has its silica composition depending on their geographical location. Beach sand is an example of carbonate sand and has a silicon dioxide content of 72-84% [1]. High silica content could increase the economic value of respective beach sand if converted into a more valuable product. Silica and silicon dioxide could be used for any kind of purpose, i.e. adsorbent, desiccant, filter media, and catalyst component. Silica-based material shows great promises in the adsorbent and catalyst industry if treated or converted into mesoporous material [2].

Mesoporous materials are defined as material that has a pore size in the range of 2-50 nm. Mesopore structure could resolve and avoid diffusion limitation of bulky molecules during the catalytic process, hence, expected to have better catalytic activity [3]. There are many synthesis routes to achieve mesoporous silica material, i.e. hydrothermal, sol-gel, and the latest sonochemistry.
Previous literature stated that alkaline medium could affect the control of mesopore size distribution using sol-gel methods, hence, making it easier to control the material porosity [4].

Well-known ordered mesoporous silica, i.e. MCM-41, SBA-15, etc., are known for their ordered porosity and excellent performance in various applications. These materials are usually synthesized either from tetraethyl orthosilicate (TEOS) or sodium silicate solution [5]. Their great performance was demonstrated in catalytic dehydrogenation of propane (MCM-41) [6], transesterification of used cooking oil (MCM-41) [7], hydrocracking of α-cellulose (SBA-15) [8], etc. These examples showed the great versatility of silica as a catalyst and its potential to be used for many other purposes.

The use of beach sand to synthesize mesoporous silica has not yet been studied. In this study, the silica content in beach sand was extracted from three beach sand: Sepanjang, Parangtritis, and Glagah Beach. The extracted silica is then being used to synthesize silica and mesoporous silica. In mesoporous silica synthesis, dodecyl amine (DDA) was used as a template to create mesoporous using the sol-gel method. The effect of rotation stirring speed was studied by analyzing the properties of the materials.

2. Materials and methods

2.1. Materials

Sand beach was collected from three beaches: Sepanjang, Glagah, and Parangtritis. Distilled water, hydrochloric acid (HCl 37%, Mallinckrodt), sodium hydroxide (NaOH, PA VWR Chemicals), silver nitrate (AgNO3), pyridine (Sigma Aldrich), dodecyl amine (C12H27N), and Fisher Scientific.

2.2. Sample preparation

2.2.1. Silica Synthesis. Silica was synthesized from beach sand that contains SiO2 [9]. The synthesis steps consisted of washing the sand to remove excess Cl and impurities. The washed sands then sieved with 100 mesh, refluxed with 6M HCl at the temperature of 90 °C for 4 h, filtered, and washed with distilled water until the pH is 7. The neutralized sand then dried at 120 °C for 2 h. Silica extracted from the sand sample by refluxing each sample with 6M NaOH at a constant temperature of 80 °C for 4 h, then filtered and washed. Concentrated HCl then added dropwise into the filtrate, until the pH reaches the value of 12 and the solution turned white. The solution was then stored for 24 h until the gel was formed. Afterward, the gel separated and washed until the filtrate has no Cl. The synthesized silica dried in an oven at 120 °C for 4 h.

2.2.2. Mesoporous Silica Synthesis. Mesoporous silica was prepared from previously synthesized silica using n-dodecyl amine (DDA) surfactant as a template [10]. Powder SiO2 was dissolved in a solution of 1.5 M NaOH and stirred at temperature 40 °C for 30 minutes to obtain soluble sodium silicate. As much as 1 g DDA was dissolved in 25 mL solvent mixture, distilled water, and ethanol (1:1), at temperature 40 °C for 30 minutes. Sodium silicate was added dropwise to DDA solution under rotation speed of 60 rpm (MSA) and 120 rpm (MSB) at room temperature. The mixture was left for 1 h before it was added with 6M H2SO4 to get pH value to 5. The reaction mixture was under the static condition at room temperature for 18 h. The product was then filtered and washed with distilled water until filtrate reaches the pH value of 6 and dried at 50 °C for 4 h. Dried products were then calcined at 600 °C for 5 h with a heating rate of 5 °C/min to remove the surfactant template.

2.3. Characterization

The chemical composition of silica and mesoporous silica was analyzed using X-ray Fluorometer (XRF). The functional group in silica, as well as the presence and disappearance of the DDA template from silica, was observed and analyzed using Fourier-Transform Infra Red Spectrometer (FTIR) using the KBr disc technique. Pore size and volume were analyzed using N2 gas sorption analysis which was carried out using Quantachrome NOVA touch. Adsorption and desorption isotherms were measured.
by the multipoint method. The total surface areas were calculated by the BET method. BJH desorption model was used to provide pore size distribution. The mesoporous silica crystallinity was analyzed using X-ray diffraction (XRD) analysis and was performed using Rigaku Miniflex 600 with Cu Kα monochromatized radiation source (λ = 1.54 Å), operated at 30 kV, 10 mA, scan speed 10°/min, and scan range 2-80°. Morphology of mesoporous silica was characterized using scanning electron microscope (SEM) and transmission electron microscope (TEM) to analyze its pores structure [11]. The acidity of sand, silica, and mesoporous silica were analyzed using gravimetric base adsorption. In this research, pyridine was used as base probe molecules. The acidity was calculated with the following formula, where WC₅H₅N is the weight of adsorbed pyridine vapor (g), W_Y is the weight of mesopore silica and MC₅H₅N is the molecular weight of pyridine (79.01 g/mol).

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\text{Acidity} = \frac{W_{C_5H_5N}}{W_Y} \times \frac{M_{C_5H_5N} \times 1000}{g} \text{ mmol} \]

### 3. Result and discussion

#### 3.1. Silica

Beach sand samples that were used in this research were taken from Sepanjang Gunung Kidul, Parangtritis Bantul, and Glagah Beach Kulon Progo Yogyakarta Indonesia. The elemental composition of each sample was shown in Table 1.

| Elements | Sepanjang Beach | Mass Percentage (wt.%) | Parangtritis Beach | Glagah Beach |
|----------|----------------|------------------------|--------------------|--------------|
| Al       | 5.54           | 16.15                  | 3.70               |
| Si       | 39.17          | 46.12                  | 9.14               |
| P        | 0.21           | -                      | 0.25               |
| K        | 0.45           | 0.84                   |                    |
| Ca       | 53.6           | 15.47                  | 2.70               |
| Fe       | 0.94           | 19.37                  | 75.91              |
| Zn       | 0.08           | 0.02                   | 0.10               |
| Ag       | -              | 0.05                   | -                  |
| Cd       | -              | 0.07                   |                    |
| Ti       | -              | 1.41                   | 6.94               |
| V        | -              | -                      | 0.52               |
| Mn       | -              | -                      | 0.74               |
| Al₂O₃    | 6.15           | 16.78                  | 4.90               |
| SiO₂     | 49.19          | 54.24                  | 13.00              |
| PO₄      | 0.38           | -                      | -                  |
| K₂O      | 0.32           | 0.55                   | 2.00               |
| CaO      | 43.90          | 11.90                  | 2.00               |
| TiO₂     | -              | 1.30                   | 8.24               |
| Fe₂O₃    | -              | 15.22                  | 70.46              |

Based on data shown in Table 1, each beach sand sample had its unique characteristics. Sepanjang Beach sand contained a relatively high amount of calcium Ca, 43 wt.% and a fair amount of silica SiO₂, 49.19 wt.%. The high calcium content could affect silica preparation steps, especially in reflux with 6M HCl, where the exothermic reaction of CO₂ formation would take place. Glagah Beach sand contained the lowest amount of silica (SiO₂), 13.0 wt.% and was dominated with iron (Fe, 75.91 wt.%). This could bring up an additional issue in which the high density of iron makes the stirring process with magnetic stirrer heavier and difficult just to get a little amount of silica. Parangtritis
Beach sand was composed of a high amount of silica (SiO$_2$), 54.24 wt.%, with relatively minimal amount of Ca 15.47 wt.% and Fe 19.37 wt.%. Therefore, Parangtritis Beach sand was chosen to be extracted.

The silica was extracted from the beach sample after treated with 6M NaOH and was selectively precipitated by adding 6M HCl until a pH value of 12. Silica precipitation started at a pH of 12 and reached its optimum at a pH of 8. H$_2$SiO$_3$ precipitate was then separated by the filtration method. The precipitate was dried to release its water content, forming SiO$_2$, as shown in these reactions below.

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\begin{align*}
\text{SiO}_2 (s) + 2 \text{NaOH (aq)} & \rightarrow \text{NaSiO}_3 (aq) + \text{H}_2\text{O (l)} \\
\text{NaSiO}_3 (aq) + \text{HCl (l)} & \rightarrow \text{H}_2\text{SO}_3 (s) + \text{NaCl} \\
\text{H}_2\text{SO}_3 (s) & \rightarrow \text{SiO}_2 (s) + \text{H}_2\text{O}
\end{align*}
\]

The SiO$_2$ obtained from the previous steps visually resembled the commercial SiO$_2$. Generally, SiO$_2$ is a white brittle powder, which makes it easier to grind. The composition of SiO$_2$ powder then analyzed using XRF, shown in Table 2. The high content of silica showed its potential as a silica source [12].

| Mineral | Unit   |
|---------|--------|
| Si      | 58.67% |
| Cl      | 40.52% |
| Ti      | 0.29%  |
| Fe      | 0.39%  |
| Ni      | 543 mg/kg |
| Br      | 86.8 mg/kg |

The presence of silica was also confirmed by FTIR data, shown in Figure 1. The broadband at 3448 cm$^{-1}$ appeared from the stretching vibration of -OH from adsorbed water, H-OH. The adsorbed water was also confirmed with the appearance of a peak at 1635 cm$^{-1}$, which was assigned to be water that binds to Si-OH. There was a strong intensity band at 1095 (asymmetric vibration) and 470 cm$^{-1}$ (bending vibration), indicating the presence of Si-O-Si. It was generally known that the 450 – 1300 cm$^{-1}$ range was the silica unique band. Alongside the XRF data, this spectrum data confirmed the presence of silica in the sand sample, which could be used as a silica source for mesopore silica synthesis with dodecyl amine as a template.

![Figure 1. FTIR spectra of extracted silica (S)](image)
The expressed in the region of the wave number 450-1300 cm\(^{-1}\) identified as the typical absorption of silica [13].

3.2. Mesoporous Silica
The synthesized mesoporous silica produced was characterized using FTIR before and after calcination at 600 °C to remove its template, as shown in Figure 2. The mesoporous silica before calcination as MSB* and after calcination as MSB. The broadband at a wavenumber of 1566 cm\(^{-1}\) showed the presence of primer amine, N-H bending vibration. The stretching vibration of N-H appears at 2924 and 3332.9 cm\(^{-1}\). These bands indicating that the DDA template was still a presence in the MSB*. Besides that, there are also wave numbers indicate the presence of silica. This shows that the silica surface has coated the dodecyl amine. According to [14] the wave number at 1000-1200 cm\(^{-1}\) shows Si-OH and Si-O-Si stretching. After the calcination process, the DDA template was expected to be removed. The DDA removal from MSB* was proofed by the disappearance of 1566 and 2924 cm\(^{-1}\) peaks. Calcination also makes the silica MSB more freely to adsorb water, compared to when there was a template in the MSB*, as there were new bands at 1635 cm\(^{-1}\) and strong band at 3448.7 cm\(^{-1}\) after the calcination, which represented water O-H bending and O-H stretching, respectively.

![Figure 2. FTIR spectra of MSB* (a) and MSB (b)](image)

3.3. Gas Sorption Analysis
The synthesized silica and mesoporous silica were analyzed using Gas Sorption Analyzer (GSA) to determine their porosity character. The isotherm graph and specific surface area were determined using the BET equation. Pore volume, average pore diameter, and pore size distribution were determined using BJH. The character of mesopororous silica (MS) was shown in Table 3.

| Samples     | Specific Surface Area (m²/g) | Total pore volume (cc/g) | Average Pore Diameter (nm) |
|-------------|------------------------------|--------------------------|----------------------------|
| Silica (S)  | 54.43                        | 0.006                    | 3.13                       |
| MSA         | 65.03                        | 0.16                     | 13.94                      |
| MSB         | 766.40                       | 0.59                     | 2.29                       |

Mesoporous Silica A(MSA), was the mesoporous silica synthesized with the rotation speed of 60 rpm, while MSB was at 120 rpm. It was shown in Table 3, that all the samples were in the mesoporous range, 2-50 nm [15]. [16] synthesized hexagonal mesoporous silica with a pore diameter of 2.1 nm. Although silica without template was in the mesoporous material range, its pore volume was very low, compared to SMA and SMB, indicating that low porosity formation occurred in that material. It was seen that stirring rotation speed affects the porosity formation in MS synthesis, higher rotation speed
gave significantly while higher porosity properties, i.e. specific surface area, pore volume. This phenomenon was as reported by the previous research [10].

Isotherm graph on both MSA and MSB was shown in Figure 3. Both MSA and MSB were confirmed to have a mesoporous structure, based on the presence of their hysteresis loop. These isotherm patterns resembled the IUPAC type IV isotherm model, with the hysteresis loop resembled type H4. The hysteresis loop of type H4 was well known for materials that have narrow slit-like pores, particles with internal voids of irregular shape, and broad size distribution [17,18]. The irregular internal voids were later confirmed in Figure 8.

![Figure 3. Nitrogen sorption isotherm of MSA (black) and MSB (red)](image)

The pore size distribution of MSA was relatively more homogenous compared to MSB, despite having low porosity. On the other hand, MSB has higher porosity, but its pore diameter is dominated by several sizes (6 peaks in 1, 2, 3, 4, 5, and 6 nm). Both MSA and MSB have the potential to be used in a further application, i.e. catalytic reaction, due to the presence of mesopore in the materials, but MSB was more superior than MSA, therefore further characterization will be focused more on MSB.

![Figure 4. The pore size distribution of MSA (square symbol) and MSB (triangle symbol)](image)

3.4. Mesoporous Silica Crystallinity
MSB crystallinity was examined using XRD, Figure 5. It was found that MSB has an amorphous silica phase, where it was inagreement with previous studies [5,16,19].
3.5. Mesoporous Silica B (MSB) Characterization with SEM and TEM

Characterization of MSB with SEM-EDX and TEM was done to reveal the morphology of synthesized mesoporous silica structure. SEM imaging was necessary to characterize the 3D surface morphology of mesoporous silica. It was seen from Figure 6. that extracted silica has a large irregular chunk of silica. On the other hand, MSB has many spherical silicas that seem connected by intercrystalline joints.

| Element Number | Element Symbol | Element Name | Atomic Conc. | Weight Conc. |
|----------------|----------------|--------------|--------------|--------------|
| 14             | Si             | Silicon      | 21.19        | 34.00        |
| 8              | O              | Oxygen       | 34.22        | 31.27        |
| 6              | C              | Carbon       | 43.17        | 29.62        |
| 35             | Br             | Bromine      | 1.00         | 4.57         |
| 11             | Na             | Sodium       | 0.42         | 0.55         |

Figure 6. SEM imaging (left) and EDX analysis (right) of Silica (S)

| Element Number | Element Symbol | Element Name | Atomic Conc. | Weight Conc. |
|----------------|----------------|--------------|--------------|--------------|
| 8              | O              | Oxygen       | 64.21        | 57.80        |
| 14             | Si             | Silicon      | 11.96        | 18.90        |
| 6              | C              | Carbon       | 16.41        | 11.09        |
| 11             | Na             | Sodium       | 5.41         | 7.00         |
| 35             | Br             | Bromine      | 1.51         | 3.02         |

Figure 7. SEM imaging (left) and EDX analysis (right) of MSB

TEM images of MSB were shown in Figure 8. The white dots on the TEM images represent the porosity that presents in the MSB. The pore distribution data, Figure 4, could help to confirm that the white dot at the MSB was a small mesopore that was detected by GSA. From SEM and TEM imaging,
it could be concluded that dodecyl amine could function as a template, forming small particles that later could form a bigger aggregate through intercrystalline joint, which has a small mesopore. This phenomenon was in agreement with previous study[16].

![Figure 8. TEM imaging of MSB [18]](image)

3.6. Acidity Test

The MS surface acidity was determined using a gravimetric acidity test with pyridine as a base probe molecule. The results are 0.2 mmol/g for sand, 0.85 mmol/g for silica, and 0.88 mmol/g for MS. The higher acidity of MS showed its potential to be used as a catalyst that requires acid sites, such as hydrocracking.

4. Conclusion

Parangtritis Beach Sand was successfully used as a silica source for mesoporous silica synthesis with high porosity properties. MSB has a specific surface area of 766.40 m$^2$/g, a total pore volume of 0.51 cc/g, and an average pore diameter at 3.04 nm. The presence of mesopore silica formation was supported by SEM and TEM imaging and had a relatively high acidity of 0.88 mmol/g. This study also found that rotation speed at the templating step was very influential as the porosity properties of MSA and MSB differ significantly.

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