

Synthesis of Mesoporous Silica From Beach Sand Using Variation of *Cetyl Trimethyl Ammonium Bromide* (CTAB)

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ABSTRACT

The potential for sand in Indonesia is very abundant because Indonesia has a long coastline than other countries. This research was conducted to explore the potential of beach sand as an alternative raw material to replace commercial silica. To obtain the natural silica, the beach sand was prepared and extracted into mesoporous silica. The reflux method was chosen to extract silica using NaOH solution, HCl solution, and CTAB surfactant. The mesoporous structure was potentially affected by CTAB and SiO₂ ratio, and therefore, this research was focused more on the effect of CTAB weight variation (3; 4,5 and 6 g). Several instruments were used to analyze the characteristics of silica, such as Surface Area Analyzer (SAA), Scanning Electron Microscopy (SEM), and Fourier Transform Infrared Spectroscopy (FTIR). The mesoporous silica has siloxane (Si-O-Si) and silanol (Si-OH) functional group and showed a coral reef-like structure. The porosity properties of these materials ranging from 300-385 m²/g for the specific surface area, 5-8.8 nanometer for pore diameter, and 0.4-0.8 cm³/g for pore volume. Optimal CTAB weight found to be at 6 g, which produces the mesoporous silica with a surface area of 385.928 m²/g, an average pore diameter of 6.015 nanometers, and pore volume of 0.579 cm³/g.

Keywords: beach sand, CTAB, mesoporous, silica

1. INTRODUCTION

Minerals that have developed, such as zeolite, generally have small pores so that the particles cannot run optimally, especially for particle sizes of more than 1.2nm. Porosity plays an important role in various reactions so that the concept of meso-size pore develops and becomes the center of attention today because it can be used for 2-50nm particles. Meso-sized porosity can be formed from silica or

natural minerals and widely used for various purposes [1]. Meso-size pore material can be formed from mineral resources in nature because of its abundance so that it has the potential to become the raw material. One that developed is silica, it applied in various industries, especially in nanometer size with better quality.

Previous research has revealed that mesopore silica can function as a catalyst [2], drug delivery [3,4], and adsorbent [5]. This is because mesoporous silica has a large specific surface area with regular pores. So far, to obtain mesoporous silica, synthetic raw material sources such as tetraethyl orthosilicate (TEOS) are used [6]. However, some of the disadvantages of this raw material are that it is quite expensive and dangerous because it is flammable [7, 8]. Therefore we need an alternative raw material for silica that is non-toxic and safer for the environment, such as sourced from beach sand.

Beach sand contains quartz, therefore it is possible to be a source of silica because quartz is a crystalline form of silica [9]. Apart from quartz, beach sand contains other minerals such as Fe_2O_3 , K_2O , Al_2O_3 , CaO , P_2O_5 , TiO_2 , and so on with different amounts of content including quartz (silica) [10]. Indonesia is a country with the second-longest coastline in the world, owning more than 81.290 km, of coastline [11] and granting Indonesia an abundance amount of sand. The Losari beach sand was known for having a high content of silica, which is 63.76% [12]. Some of the other beach sand research mentioned in previous research [12,13,14].

In general, to obtain silica from sand, we use the acid-leaching process on sand with HCl, the alkaline extraction method (NaOH) to bind SiO_2 , and precipitation process carried out with acid. This acid-base route has been successful in producing amorphous mesoporous structures [15]. In mesoporous materials forming, surfactant micelles are used as a template. The resulting pore properties can be obtained from changes in micelle structure and morphology, for example by variations in the type of surfactant, molecular structure, concentration, and addition [16]. The surfactant commonly used in forming mesoporous is cetyltrimethylammonium-Bromide (CTAB), a cationic surfactant.

2. MATERIALS AND METHODS

2.1. Materials

The materials that were used are Parangtritis Beach Sand, CTAB (Himedia), HCl (Merck), aquades, and NaOH (Merck). The tools that were used in this research are digital scales (OHAUS), chemical glassware, a pH indicator (Merck), a centrifuge, stirrer, furnace, spatula, thermometer, oven (Mettler). The instruments for characterization are a Surface Area Analyzer N_2 (JWGB-Meso 112) FTIR (Thermo Scientific).

2.2 Methods

2.2.1. Silica Extraction from Beach Sand

The sand was collected from Parangtritis Beach. The sand sample was washed and dried overnight at a temperature of 100°C . Afterward, the cleaned sand sieved into 100 mesh in size and weighted 100 g to be refluxed and stirred with 500 mL of HCl solution at a temperature of 80°C for 3 hours. The sample was centrifuged and the solid residue was collected. The residue washed until its freed from HCl then dried overnight at temperature of 100°C . The dried sample was then refluxed and stirred NaOH solution (500 mL) for 2 hours. The solid residue and filtrate were separated using a centrifuge, the filtrate was then collected for further steps.

2.2.2. The Silica synthesis

The CTAB solutions made into three variations by dissolving 3, 4.5, and 6 g of CTAB with 50 mL distilled water. Each of the CTAB solutions added into 100 mL filtrate from previous steps, and then this mixture was added with 3M HCL solution until the pH value reach 7 [17]. The solution was heated at a temperature of 60°C for 4 hours, aged for 66 h to add condensation time, then filtered, washed, and dried at a temperature of 100°C for 2 hours. The cleaned silica was calcined at 550°C for six hours to obtain mesoporous silica.

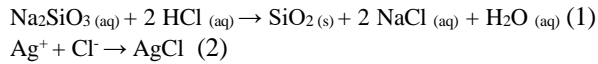
2.2.3. Characterization of Mesoporous Silica

The functional group that presents in mesoporous silica was analyzed using FTIR. The pore characteristics, such as the specific surface area, pore volume and pore diameter, were analyzed and calculated using the Gas Adsorption Analyzer. For morphological characteristics, it is obtained from SEM analysis

3. RESULTS AND DISCUSSION

The synthesis process of mesoporous silica from beach sand was done using surfactant variation. The surfactant used in this research was CTAB, a cationic quaternary surfactant with a long alkane chain that can produce a large pore diameter. In meso-size pore formation, the CTAB has an advantage in a shorter time of synthesis, compared to non-ionic surfactant [18]. The synthesis of mesopore silica was started by mixing CTAB and sodium silicate and then added with dropwise of 1M HCl. The HCl was the chosen acid because of the easiness of removing its side

product, NaCl, which is soluble and easily removed from the system (eq.1). To ensure that NaCl was completely removed, the filtrate was added with the AgNO₃ solution to form white AgCl precipitate if there is any chlorine in the filtrate (eq. 2).



When the synthesis process is carried out, stirring will facilitate the hydrolysis process and the sodium silicate will be condensed in a more stable meso-structure and a high degree of order. Then, continued aging for 24 hours to increase the condensation time to prevent shrinkage of the meso-structure during the calcination stage [19]. Calcination is performed to remove CTAB to form mesoporous silica. From this process, we can obtain the yield of mesoporous silica (table 1).

Table 1. The yield of mesoporous silica with CTAB variation

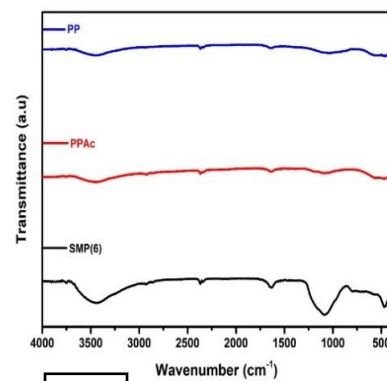
No	Sample	Yield of silica with template before calcination (%)	Yield of mesoporous silica with template after calcination (%)
1.	SMP (3)	2.521	1.67
2.	SMP (4.5)	2.405	1.546
3.	SMP (6)	2.345	1.478

From the table 1, it can be seen that the yield of mesoporous silica from sand is small but bigger than Meyori's (2018) research [12], which obtained a maximum yield of xerogel silica of 0.8%. The sand components are probably one of the factors affected the low yield. There are many other minerals besides silica which have a high composition, such as Fe₂O₃. Then, the acid leaching preparation process is also allegedly affecting the yield, because if the acid leaching does not work perfectly, other minerals will not separate and interfere with the synthesis of mesoporous silica. In the washing process after acid leaching, and after giving NaOH, it will reduce the weight of silica, as well as in the calcination process, and it is also necessary to pay attention to the concentration and time of silica deposition after HCl drops.

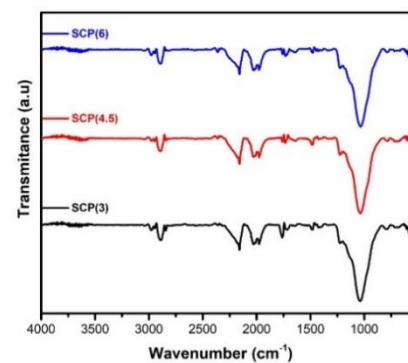
3.1 Functional Group Analysis Using FTIR

Determination of the functional group in the material (beach sand as a raw material (PP), beach sand after acid leaching (PPAc), CTAB, silica with template but without calcination (SCP), and mesoporous silica after calcination (SMP)) was done

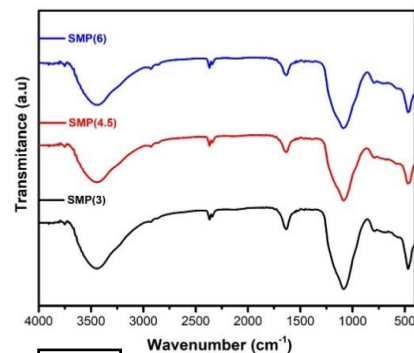
using FTIR, as shown in Figure 1. There is a significant difference in spectral patterns between raw material, SCP and SMP. The spectral patterns of the beach sand before and after the acid leach is not significantly different, so the possibility of the process did not affect the initial structure of the sand much. The CTAB showed to have CH₃, methylene CH₂, C-H in alkyl chain, and C-N group at 2923 cm⁻¹, 2850 cm⁻¹, 1477 cm⁻¹ and 964 cm⁻¹ [20,21], respectively. Those functional groups were matched with the CTAB structure in Figure 1.



1.a



1.b



1.c

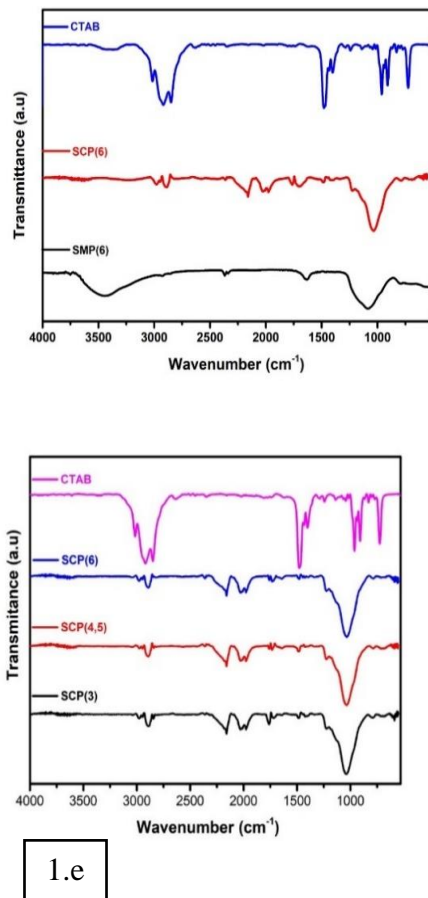
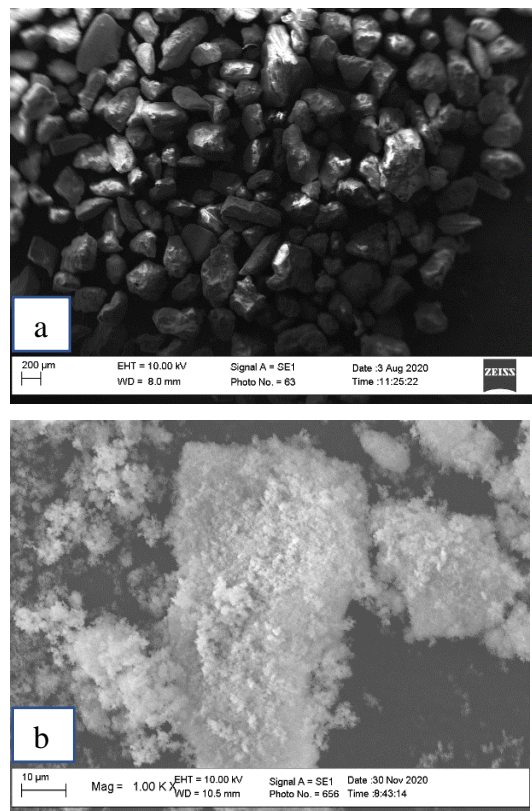


Figure 1. FTIR spectra of PP, PPAc, and SMP 6 (1.a); SCP 3 g of CTAB, SCP 4.5 g of CTAB, SCP 6 g of CTAB (1b), SMP3, SMP4.5, SMP6 (1.c); CTAB, SCP6, SMP6 (1.d), and CTAB, SCP3, SCP 4,5, SCP6 (1.e)

The set of SCP (SCP3, SCP4.5, and SCP6) showed few CTAB distinctive features, 2882 cm^{-1} and 2883 cm^{-1} , which indicates that some of the CTAB still attached on the materials. The CTAB absorption bands disappear in SMP, indicates that the calcination process successfully remove the CTAB(22). The SMP set showed new absorption bands, i.e., hydroxyl (O-H), siloxane (Si-O-Si) symmetric and asymmetric, silanol (Si-OH), Si-O bending, and Si-OH at 3448 cm^{-1} , 1087 cm^{-1} , 470 cm^{-1} , and 794 cm^{-1} , respectively [23,24,25,26]. The silica functional groups that present in SMP indicates that the majority of the silica structure remain intact [22].

3.2 Morphology Characterization Using SEM

Identification of the SMP morphology obtained from SEM analysis and references, shown in Figure 2. In general, the silica morphology has coral reef-like structures, with heterogeneous size due to impurities in sample size [7,27]. The calculation of particle size was difficult due to the aggregation on each sample, but qualitatively, the particle size usually was inversely proportional to the weight of the CTAB used. The formation of the micelle and the enhancement of the bond between CTAB and silica probably cause the phenomenon. The silica surface tends to be heterogeneous, where the particles are hardly seen and appeared to be agglomerated grain [13], with the size under 100 nanometer [28].



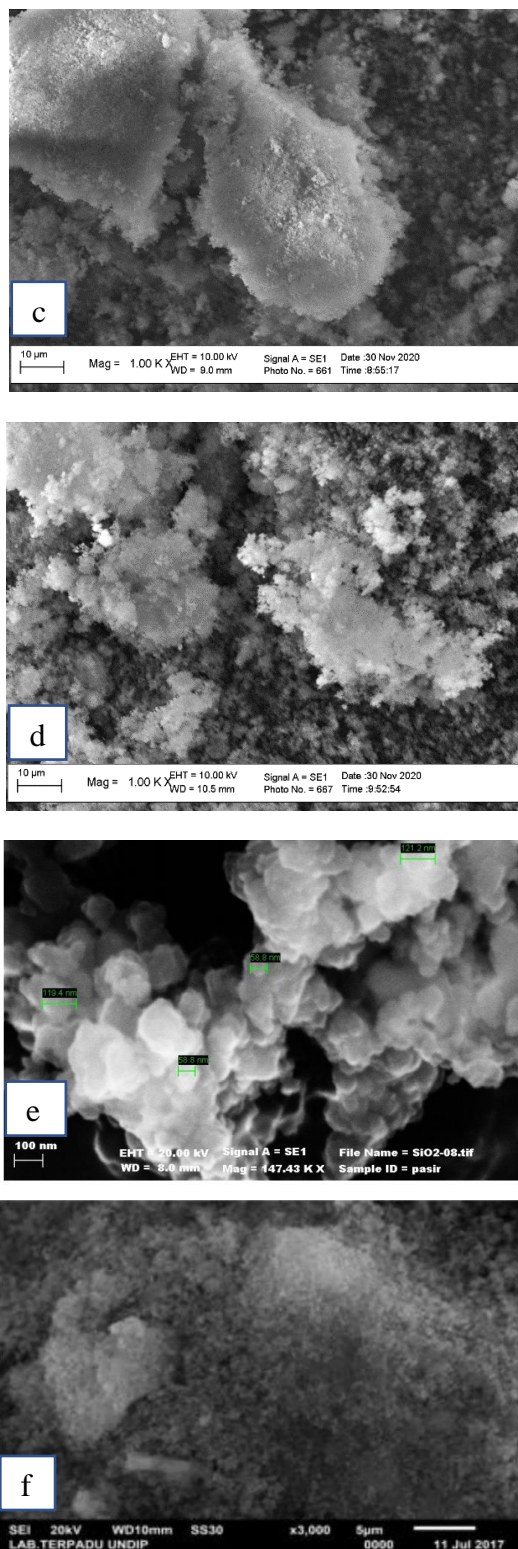


Figure 2. SEM images of the Parangtritis beach sand as a raw material (a), mesoporous silica with 3 g of CTAB (b), 4.5 g of CTAB (c), 6 g of CTAB (d), silica of the Bancar sand beach (e)[29] and silica xerogel from the Panjang-Bengkulu sand beach (f)[12]

3.3 Adsorption-Desorption Analysis of Sample

The nitrogen adsorption-desorption method was done to analyze the sample pore characteristics. Figure 3 shows an adsorption-desorption pattern of all SMP catalysts have a similar trend, both from the sharpness of the curve in the relative pressure area of 0.2-0.4 and the curve pattern formed during the adsorption and desorption processes. The curve sharpness indicates mesoporous uniformity, where a sharper curve gives a more uniform pore size [18].

The porosity properties of the SMP could be seen in Table 1. All the SMP synthesized from beach sand under the variation of the weight of the CTAB template could be classified as mesoporous materials. The surface area of the SMP was an increase as the effect of a higher dose of CTAB. This phenomenon could occur because of

CTAB's role in the system, directing the mesoporous formation so the agglomeration process less possible to take place.

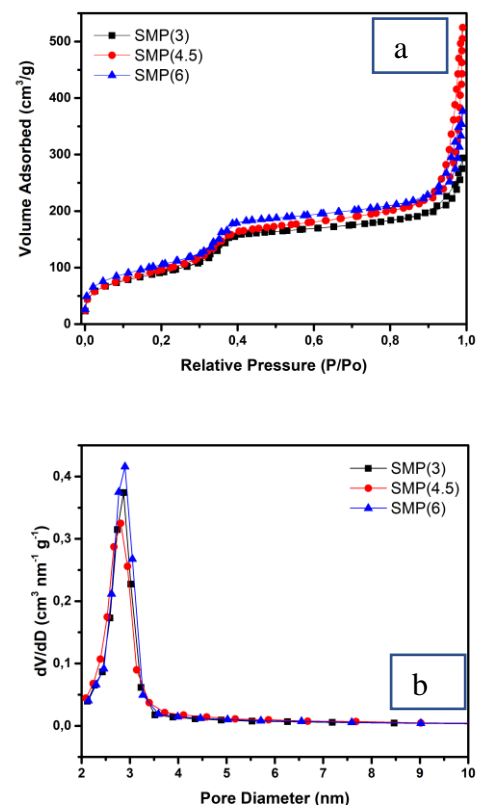


Figure 3. The adsorption-desorption of N₂ isotherm curve (a) and pore size distribution of SMP (b)

Table 2. The properties of mesoporous silica

Sample	Surface Area (m ² /gram)	Average Pore Diameter (nanometer)	Total Pore Volume (cm ³ /gram)
Mesoporous silica from Parangtritis beach sand			
SMP (3)	338.209	5.243	0.443
SMP (4.5)	362.928	8.881	0.806
SMP (6)	385.928	6.015	0.579

The highest surface area and an average pore diameter are 385.928 m²/g and 6.015 nm for mesoporous silica with 6gr CTAB template. These results indicate that mesoporous character from beach sand was higher than Lapindo mud (the surface area of 75.105 m²/g; a pore volume of 0.1974 cm³/g and an average pore diameter of 105.14 A) [30] also silica from natural diatomite (the surface area of 38-250 m²/g; pore volume of 0.071-0.364 cm³/g and average pore diameter of 5-8 nanometer) [31].

4. CONCLUSION

Mesoporous Silica from beach sand can be synthesized with CTAB template. The mesoporous silica has a surface area specific (300-385 m²/g); an average pore diameter ranging from 5-8.8 nm; and a pore volume ranging from 0.4-0.8 cm³/g. The functional groups of silica were Si-OH and Si-O-Si. The CTAB optimum weight based on the highest surface area in this research was found to be at 6 g.

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