Extraction of Silica from Bengkulu Beach Sand using Alkali Fusion Method

Soraya Nur Ishmah[1], M. Diki Permana[1], M. Lutfi Firdaus[2], Diana Rakhmawaty Eddy[1*]
[1]Department of Chemistry, Faculty of Mathematics and Natural Sciences, Padjadjaran University
[2]Graduate School of Science Education, University of Bengkulu
*Corresponding author: diana.rahmawati@unpad.ac.id

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ABSTRACT

Silica is one of the potential minerals to be developed and applied in various industrial fields. High purity of silica can be obtained by utilizing natural materials such as beach sand. In this research the solid-liquid extraction (leaching) method was used in three main steps. Bengkulu beach sand as precursors reacted with NaOH (alkaline fusion) at 95°C to form Na_2SiO_3, then addition of HCl to form $Si(OH)_4$, and drying the silica gel becomes SiO_2. Based on the initial content analysis in Bengkulu sand contained 69.87% silica and other compounds with a lower percentage. The extracted silica was characterized using XRF and the purity of silica increase to 97.3%. The XRD characterization results showed that the silica formed was in the amorphous phase. Si-O-Si and Si-O bonds which are characteristics of SiO_2 were identified in the FT-IR spectrum with absorption bands of 798.8 cm^{-1} and 475.1 cm^{-1} respectively.

Keywords: silica sand, SiO_2, solid-liquid, alkali fusion.

INTRODUCTION

Silicon dioxide (SiO_2) or known as silica is the example of minerals in natural resource that very potential to be developed. In general silica found in gel, crystalline, and amorphous forms (Todkar *et al*., 2016). Silica can be obtained through synthesis or extraction from natural materials both biological and non-biological. Based on the types of natural resources, silica can be obtained from agricultural waste such as rice husk ash (Bakar *et al*., 2016), coconut pulp (Anuar *et al*., 2018), and bagasse ash (Megawati *et al*., 2018; Norsuraya *et al*., 2016) with the acquisition reaching 99%. While from the non-biological materials silica can be obtained from beach sand (Eddy *et al*., 2015) and coal waste such as flying ash sludge (Cheng *et al*., 2018) with the acquisition of 91.19%. Bengkulu Province is one of the potential regions in Indonesia which has coastal sand with high silica mineral content (55.30-99.87wt%) (Madina *et al*., 2017).

Silica generally used as precursor for various materials such as catalyst, thin layer or coating for electronic and optical materials (Yang *et al*., 2018; Mc Daniel & Kelly 2018). Now the use of silica is also growing in many industrial fields such as glass, mirrors, ceramics, silicon carbide, and sand blasting. Moreover silica is widely used as a supporting material in the cast steel, oil and mining industries, and refractory bricks (Munasir *et al*., 2015). Silica with the addition of calcium now developed into a new nanoparticle composite as a bioactive material for bone tissue replacement (Tavafoghi *et al*., 2018). Silica can also be applied to strengthen composites of a polymer as an anti-corrosion agent (Yeganeh *et al*., 2019). The use of high purity silica in industrial applications is relatively expensive because it requires a high melting point of 1700°C (Omar *et al*., 2016). Thus, the process of extracting silica by utilizing natural materials such as beach sand is one of the ways to reduce costs production.

The existence of silica in nature is mixed with oxides and other minerals so separation is required to obtain pure silica. Various methods for obtaining silica have been developed such as precipitation, electrocoagulation (Zhang *et al*., 2019), emulsions (Gustafsson & Holmberg 2017), Stöber method (Meier *et al*., 2018), sol-gel (Azlina *et al*., 2016), hydrothermal (Munasir *et al*., 2015), and alkaline fusion (Munasir *et al*., 2013). In this research, an alkaline fusion method is used which aims to obtain high purity silica. The principle of this method is to break the chemical bonds in the sand using a alkaline solution such as KOH, NaOH, and Na_2CO_3 followed by the binding of silicon with oxygen to form SiO_2.

METHODS

Leaching method was used in this research in extraction process. The initial content of sand from Bengkulu beach has been analyzed using ICP then mashed using a ring mill afterwards sieved with 325 mesh siever. After that the sand soaked in a 2 M HCl solution for 12 hours. The residue from filtration washed with distilled water until there is no yellowish color, then dried at 110°C until the water content is reduced. Next, reacted the sand with 3 M NaOH solution at 95°C while stirring for 4 hours. The suspension then filtered using Whatmann filter paper No. 42 and rinse with 100 mL of distilled water. Afterwards the filtered filtrate (sodium silicate) stirred and add 6 M HCl solution to form a gel (pH 7). The formed gel stored for 18 hours. After that filtered and rinse silica gel with distilled water. Silica gel then dried at 110°C. The obtained silica powder then characterized using XRF, XRD, and FTIR. This research was conducted in February to March 2019 at Physics and Inorganic Chemistry Laboratory Department of Chemistry, Faculty of Mathematics and Natural Sciences, Padjadjaran University.

RESULT AND DISCUSSION

Silica Extraction

Based on the initial composition test using ICP, it shows that the silica content from Bengkulu beach sand reaches 69.87% which is higher than other regions in Indonesia such as Bali and Lombok (**Table 1**).

Bengkulu beach sand was extracted using the solid-liquid extraction method (leaching) via the alkaline fusion route to obtain SiO_2. Bengkulu beach sand pounded using a ring mill in order to reduce the particle size. The smaller particle size would wider the contact surface area between the sand and the solvent, so there more interactions occur during the sand washing process that can maximize the process of dissolving impurities. Then the sand sifted using a 325 mesh siever.

Table 1. Results of the initial sand content from several regions in Indonesia using ICP.

Origin	Minerals compositions (%)		
	SiO_2	Al_2O_3	Fe_2O_3
Bali	19,54	0,70	1,47
Lombok	21,08	1,28	0,75
Bengkulu	**69,87**	11,99	3,55

After that soaked the sand in 2 M HCl solution for 12 hours. The process of soaking with acid aims to reduce impurities or other compounds besides SiO_2 that contained in sand. HCl was chosen as a solvent because impurities dissolve easily in acidic solvents such as HCl, whereas under normal conditions SiO_2 can only dissolve in very strong acids such as HF. Then the sand is filtered using a Buchner funnel and rinsed with distilled water until there is no yellowish color. Washing sand is then dried at 110 °C for 2 hours to reduce the water content.

Next, sand was immersed in 3 M NaOH solution while stirring and heated at 95°C for 4 hours. Silica compounds dissolve easily in an alkaline solution, and will settle to an acidic solution. Heating will accelerate the rate of reaction and stirring aims to speed up contact between solute and solvent also distribute the temperature, besides that the stirring function is to reduce the occurrence of precipitation. The reactions that occur during the extraction process are as follows:

$$SiO_{2\ (sand\ powder)} + NaOH_{\ (aq)} \rightarrow Na_2SiO_{3\ (aq)} + H_2O_{\ (l)}$$

The mechanism formed during the formation of sodium silicate shown in **Figure 1**. Based on this mechanism it shows that sodium hydroxide will dissociate completely to form sodium ions (Na^+) and hydroxyl ions (OH^-). An OH^- ion which acts as a nucleophile will attack the Si atom in SiO_2 which is electropositive. Then the electronegative O atom will break one double bond and form SiO_2OH^- intermediates. In the next step, the intermediates formed will release H^+ ions. Whereas on the O atom there will be a break of the double bond again and form SiO_3^{2-}. At this stage dehydrogenation will occur, where the second hydroxyl ion (OH^-) will bond with hydrogen ions (H^+) and form a water molecule (H_2O). SiO_3^{2-} molecules that are formed with negatively charged will be balanced by two Na^+ ions that are formed so that sodium silicate (Na_2SiO_3) will be formed.

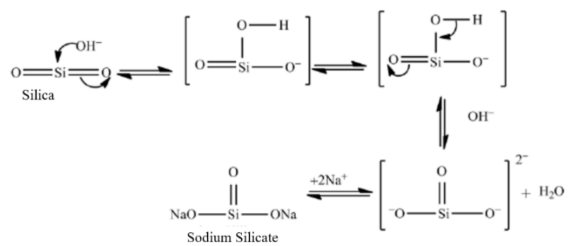

Figure 1. The mechanism of reaction of the formation of sodium silicate (Yusuf *et al*., 2014).

The sodium silicate solution (Na_2SiO_3) formed is then filtered to separate the filtrate from the residue. After that, the filtrate (Na_2SiO_3) obtained was added with 6M HCl while stirring to form a gel then stored for 18 hours. The formation of silica gel is obtained by adding HCl solution to Na_2SiO_3 solution with an initial pH of 11 to reach pH 7 to form tetraortosilicate acid ($Si(OH)_4$) and sodium chloride (NaCl). The reaction is as follows:

$$Na_2SiO_{3(aq)} + H_2O_{(l)} + 2HCl_{(aq)} \rightarrow Si(OH)_{4(aq)} + 2NaCl_{(aq)}$$

HCl solution acts as a precipitation agent, the purpose of adding HCl to Na_2SiO_3 solution is to allow ion exchange between Na^+ with H^+ to produce silicic acid. The addition of HCl solution was stopped at pH 7 because the precipitate obtained at pH less than 7 was less, this happened because under these pH conditions the precipitate that had formed would dissolved again. While the sediment obtained at a pH of more than 7 is also small, this is due to the pH conditions that the HCl solution used to react with sodium chloride is only slightly so that the exchange between Na^+ and H^+ ions that occur is also small. At pH 7, silica does not dissolve so it is expected that under these conditions silica deposition takes place optimally. The addition of HCl solution to the precursors causes the protonation of the siloxy group (Si-O-) to silanol (Si-OH). The addition of acid causes a higher concentration of protons (H^+) in the sodium silicate solution and some siloxy groups (Si−O−) will form a silanol group (Si−OH). The silanol group formed is then attacked further by the siloxy group (O-Si-O-) with the help of an acid catalyst to form a siloxane bond (Si-O-Si). This process occurs quickly and continuously to form an amorphous silica network. The reaction mechanism that occurs in the formation of silica gel from acidifying Na_2SiO_3 solution shown in **Figure 2**.

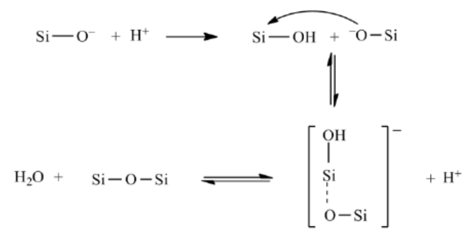

Figure 2. Mechanisms reaction of the formation of siloxane bonds in the process of gel formation (Yusuf *et al*., 2014).

The precipitate was filtered using whatmann filter paper No. 42. This filter paper has a dense pore size so that any deposits that pass through the screening process can be minimized. Next, the precipitate was rinsed with distilled water to remove excess acid and dried in an oven at 110°C for 2 hours. Heating at 110°C results in dehydration of silicic acid to form silica gel ($SiO_2.H_2O$) which is then pounded to obtain SiO_2 powder. The reactions that occur in this process are as follows:

$$Si(OH)_{4\ (aq)} \rightarrow SiO_{2\ (s)} + 2H_2O_{\ (l)}$$

Table 2. Element content in Bengkulu beach sand before and after extraction.

Minerals	Composition (%)	
	Before extraction	After extraction
SiO_2	**69,87**	**97,30**
Al_2O_3	11,99	2,56
Fe_2O_3	3,55	0,14

The SiO_2 then characterized using XRF to determine its composition after extraction process. The results of the analysis silica content shown in **Table 2**.

Based on these data is known that the SiO_2 content of Bengkulu beach sand extraction results was 97.3% where there was an increase about 27.43% from the initial content analysis which 69.87%. This shows that the washing of quartz sand with acids has dissolved other metal oxides (impurities).

XRD Analysis of SiO_2 Extraction Results

The extracted SiO_2 was analyzed using XRD to determine the characteristics of SiO_2 formed. The XRD pattern of SiO_2 are shown in **Figure 3.** It match with ICSD 98-016-2660 where there is a gentle slope at $2\theta = 22.5873^\circ$ which indicates that the SiO_2 formed is an amorphous phase. In addition, the highest absorption absorption typical also appeared at $2\theta = 31.6397^\circ$ which was identified as aluminum dioxide (Al_2O_3) according to ICSD 98-002-8920. This result is also relevant to the results of the XRF analysis which shows that there are still small amounts of Al_2O_3 compounds in the extracted SiO_2.

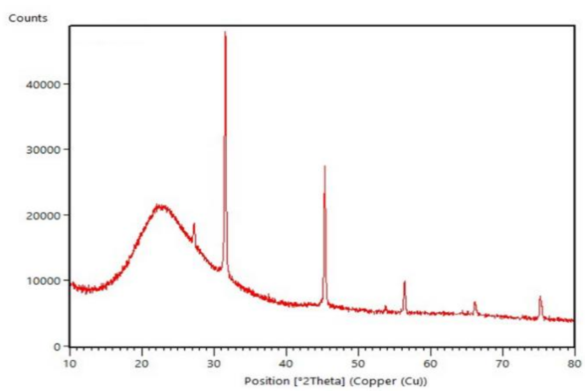

Figure 3. XRD Pattern of SiO_2 extraction results.

FTIR Analysis of SiO_2 Extraction Results

IR analysis was carried out to confirm the results of the XRD analysis. The functional group that contained in the extracted SiO_2 were analyzed using FTIR. The SiO_2 spectrum is shown in **Figure 4.** The characteristics of the IR absorption band at the wave number 3,466 cm^{-1} are stretch-OH vibrations while at 1,638.2 cm^{-1} is a typical absorption for bend-OH vibrations. The strong and dominant absorption peak found in wave number 1099 cm^{-1} is asymmetrical stretching of Si-O-Si (siloxane) bonding. The presence of a peak at wave number 798.8 cm^{-1} indicates the vibrational strain of the Si-OH bond (silanol) in the amorphous SiO_2 structure. The appearance of Si-OH bonds shows that there is still water that binds to silica. Whereas the absorption peak at wave number 475.1 cm^{-1} is caused by O-Si-O bond tension (siloxy).

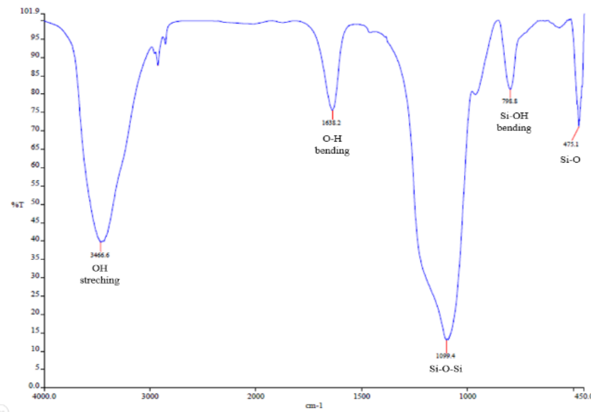

Figure 4. Infrared spectrum of extracted SiO_2.

CONCLUSION

Silica can be extracted using the alkaline fusion method at low temperature conditions. Based on XRF analysis results obtained 97.3% silica purity from Bengkulu sand and XRD characterization results indicate the silica formed is in the amorphous phase. Si-O-Si and Si-O groups which are characteristics of SiO2 were identified in the FTIR spectrum with typical absorption bands of 798.8 cm-1 and 475.1 cm-1, respectively.

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