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Original Paper

Review: Synthesis of Nanosilica Materials from Various Sources Using Various Methods

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Abstract

Synthesis of nanosilica materials today has become a considerable concern because of its higher-level of physicochemical properties and potential applications in various fields. The aim of this paper is to conduct a literature review on the synthesis method of SiO_2 nanoparticles based on 53 papers from 2002 to 2020. This paper will present a study of several methods and materials that can be used for synthesis of SiO_2 nanoparticles, including: sol-gel method, coprecipitation, spray flame pyrolysis, ultrasonication, alkali-fusion, autoclave, wet chemical, hydrolysis, and condensation reactions. The results showed that synthesized materials have a high level of purity so that it can be used as an alternative source of silica in several technological fields, such as optics, electronics and biomedicine where the particle size, crystal structure, purity, and morphology are depend on the synthesis method used.

1. Introduction

Silica is a compound obtained from polymerization of silicic acid which is composed of tetrahedral SiO_4 unit chains with general formula SiO_2. Silica compounds are found in several natural materials, such as: sand, quartz, glass, etc. Natural silica has a crystalline structure, while synthetic silica has an amorphous structure. Synthetically, silica compounds can be prepared from silicate solutions or from cross-reagents. Silica gel is an example of synthetic silica compounds that have an amorphous structure (Sulastri & Kristianingrum, 2010). Silica

(SiO_2) naturally occurs in three main phases and five minor phases, they are quartz, tridymite, and cristobalite; keatite, coesite, melanophlogite, fibrous, and faujasite. (Hong et al., 2009).

Silica can be synthesized from various natural sources, including Lapindo mud (Herdianto & Zahwanul, 2012), rice husk ash (Andreas et al., 2016; Meliyana et al., 2019), kettle ash of sugar industry (Ismayana et al., 2017), bagasse ash (Falk et al., 2019; Nazriati et al., 2010), and natural silica sand (Munasir et al., 2013, 2014, 2015; Silvia & Zainuri, 2020).

Various methods are used to synthesize SiO_2 nanoparticles, including: Spray Flame Pyrolysis Method for Lapindo Mud (Herdianto & Zahwanul, 2012), Sol-gel method for Rice Husk Ash (Meliyana et al., 2019), Sol-gel with Ethanol solvent method for Rice Husk (Andreas et al., 2016), Ultrasonication with the addition of surfactants for Kettle Ash of Sugar Industry (Ismayana et al., 2017), Sol-gel and calcination, then Nano-Si is made by Magnesiothermic reactions from Bagasse Ash (Abu Bagasse) (Falk et al., 2019), Sol-Gel with the addition of TMCS for Bagasse Ash (Nazriati et al., 2010), Dry Method / dry method and Hydrothermal Method for materials Natural silica sand (Munasir et al., 2015), hydrothermal and coprecipitation for natural silica sand (Munasir et al., 2014), coprecipitation using NaOH for natural silica sand (Silvia & Zainuri, 2020), and Alkali Fusion using Silica Sand material (Munasir et al., 2013).

In this paper, several methods of synthesizing silica nanoparticles with various natural materials will be discussed and hope it can provide information to readers about natural materials that are generally considered hazardous or non-reusable which actually can be used as a source for manufacture of SiO_2 nanoparticles in various sectors. **Table 1** provides a summary of some of the methods discussed in this paper.

Table 1. The advantages and disadvantages of method used

Bahan	**Grup Penelitian**	**Method**	**Hasil**
Lapindo Mud	(Herdianto, Hengky dan Mochamad Alfi Z. F., 2012)	*Spray Flame Pyrolysis*	Diameter ranges of nanosilica particles are from 10.00-45.00 nm depending on the pressure of spraying and the concentration of silica acid solution. The strength development of ML silica concrete is better than flow concrete. DSA Value; MOR; MOE; and IB that was achieved were 16.25%; 67.42 kg/cm^2; 56.28 kg/cm^2; and 63.56 kg/cm^2.
Rice Husk	(Andreas et al., 2016)	Sol-gel with ethanol solvent	Obtained silica has a purity of 93.08% and has an amorphous structure. In variation of aging time, nano cups have an amorphous structure, non-uniform size and low purity around 20.00-30.00%. The best variation of solvent ratio is 1:16 with the highest silica purity, namely 56.85%.
	(Meliyana et al., 2019)	Sol-gel with rice husk ash washing using	Cleaning and washing rice husk ash with 1 N HCl effectively removes organic substances and other elements to form Silica Rich WRHA with the largest contained silica of

Ash		HCl 1 N	93.27%. However, in the nano silica synthesis process, the silica content decreased to 89.17% for silica obtained from treated WRHA and 82.18% for silica obtained from untreated WRHA. The silica peaks are seen in waves of 1068.56 cm^{-1} and 1121.11 cm^{-1}. Size of formed silica particles was not much different with and without treatment ranging from 92 ± 25 to 98 ± 25 nm.
Kettle Ash Of Sugar Industry	(Ismayana et al., 2017)	Ultrasonication with surfactant addition	The degree of obtained crystallinity was 76.96% without addition of surfactants and 84.04% with addition of 10.00% CMC surfactant. Crystal size becomes smaller with the addition of 10.00% CMC, which is 37.69 nm from the 41.40 nm crystal size without surfactant addition.
Bagasse Ash	(Falk et al., 2019)	Sol-gel and calcination, Nano-Si made by Magnesiothermic reaction	Uniformity of SiO_2 nanoparticles with method 1 (sol-gel) is ~ 10.00 nm with a high purity level of ~ 97.00% and most of them are amorphous, while silica nanoparticles obtained by method 2 (direct calcination and deep leaching HCl) shows the characteristic biogenic structure of bagasse. Specific surface area values obtained by the BET method were 124.89 $m^2g - 1$ for silica prepared by method 1 (sol-gel) and 8.28 m2g − 1 for silica prepared by method 2. In addition, nano-Si was successfully synthesized by a magnesiothermic reaction carried out at 800°C for 5 hours.
	(Rovani et al., 2018)	Wet chemical method: Hydrolysis and Condensation reaction	Obtained SiO_2 nanoparticles have a purity of >99.00%. Then, the results of SiO_2 nanoparticle characterization with TEM showed a nanoparticle size of <20.00 nm and characterization using the BET method shows a specific surface area of 131.00 m^2g^{-1}, about 23 times higher than the initial material of bagasse ash.
	(Nazriati et al., 2014)	Sol-gel with TMCS addition	Characteristics of silica aerogel with variations in the composition of SA: TMCS: HMDS have a surface area between 50.00 to 468.00 m^2/g, a pore volume of 0.20-0.90 m^3/g, and a contact angle of 48-119°.
	(Munasir et	Dry Method and	Obtained SiO_2 nanoparticles by hydrothermal method have a purity of 98.90%, consisting of

	al., 2015)	Hydrothermal Method	spherical particles with size about 30.00 nm, containing quartz and cristobalite phases.
	(Munasir et al., 2014)	Hydrothermal and Coprecipitation	Synthesis and characterization of SiO_2 powder have been successfully carried out using hydrothermal and coprecipitation methods. Nano Silica powder formed at pH 2.00; 7 M is amorphous SiO_2.
Natural Silica Sand	(Silvia, L., & Zainuri, M., 2020)	Coprecipitation using NaOH	Synthesis of natural sand-based quartz (SiO_2) with the coprecipitation method using NaOH produces a single phase in the form of quartz (SiO_2) with an amorphous background and the estimation results of calculating quartz crystal size.
	(Izzati & Munasir, 2013)	Alkali Fusion Route	Synthesis of silica (SiO_2) from natural sand by alkali fusion method using NaOH produces silica (SiO_2) with amorphous morphology and has a crystal shape, namely oval and circle with a size of ~ 60.00 nm, and the purity of silica obtained is 98.90%.
Olivine minerals	(Stopic et, al., 2019)	Mineral Carbonation Using High Pressure in Autoclave	Obtained nanosilica has a spherical amorphous shape with diameter of 400-500 nm. The pressure used is 121.60 to 159.70 bar.

2. Silica Nanoparticles Synthesis

There have been many studies reporting the synthesis of silica nanoparticles using various methods, such as chemical processing which includes the use of organic and inorganic materials and thermal processing. The use of these methods has advantages and disadvantages that are adjusted to physicochemical properties of the material to be synthesized.

2.1. Sol-Gel Method

Synthesis method that is commonly used nowadays is the sol-gel method. According to (Muslim, Safpriseini, & Aini, 2017), sol-gel method is a provide alternative for synthesis of silica nanoparticles because it is able to adjust the geometric structure and particle size through chemical reactions at a certain temperature. Where in the process, there is a phase change from colloid suspension (sol) to form a continuous liquid phase (gel). In addition, sol-gel process has been widely proven to be a highly flexible chemical synthesis method for the manufacture of a wide variety of photonic materials in a variety of configurations, such as: monoliths, coatings, fibers, and films for optical device applications. (Rovani et al., 2019)

In study by (Silvia & Zainuri, 2020), extraction stage was carried out using a leaching process by two variations of solvents, namely immersion in 2 M HCl solution

for 12 hours and immersion in NaOH solution. Same process was done by (Meliyana et al., 2019) with addition of acetic acid p.a and washing rice husk ash using 1 N HCl solution to analyze the purity effect of synthesized silica. In contrast to (Andreas et al., 2016), isolation of silica from rice with a leaching process was carried out using ethanol solvent. Variation in solvents affects the particle size, however does not affect the purity of silica in product obtained. Other than that, the addition of a silylating agent solution like TMCS as reported by (Nizar et al., 2016) has better nanoparticle size results.

The fundamental differences between each synthesis path and sol-gel method lies in solvent used and addition of reaction process. Sol-gel method research by (Falk et al., 2019) produced xerogel silica with 96.80% by weight of SiO_2 purity because synthesized material was reduced magnesiothermally, therefore the material could maintain morphological similarity to silica precursors, show high crystallinity, small size, and give it superior performance over traditional materials. Synthesis of nanoparticles using the sol-gel method gave better results in terms of specific surface area, porosity, pore volume, and average pore diameter. (Falk et al., 2019)

Sol-gel method research by (Meliyana et al., 2019) produced SEM testing that showed white rice husk ash (WRHA) was treated with the addition of 1 N HCl (WRHA 1), and looked more alike than without treatment (WRHA 0). Whereas, cleaning and washing rice husk ash with 1 N HCl produced a synthetic product with a nano silica content of 89.17% and an untreated synthesis product with a nano silica content of 82.18%. The size of the silica particles between without and with a treatment were not that much different, ranging from 92 ± 25 nm to 98 ± 25 nm.

2.1.1. Bagasse Ash

Among the various natural resources that are available, sugarcane is a potential source of material for silica extraction and transformation of nanostructured silicon. Bagasse ash shows a high enough silica content therefore it has potential to be a source of silica extraction. (Nazriati et al., 2014)

Silica nanoparticles, obtained from bagasse ash using sol-gel method, produce silica particles with a similar average size of ~10.00 nm with a purity content of up to ~97.00%. The silica particles obtained are mostly amorphous. Meanwhile, the silica nanoparticles obtained by method 2 (direct calcination and leaching in HCl) showed characteristic biogenic structures typical of bagasse. Silica that is synthesized in method 1 (sol-gel) has a surface area value of 124.89 and silica prepared by method 2 has a surface area value of 8.28 m^2g^{-1}. It is unique that nano silica prepared by sol-gel method gave better results in specific surface area, porosity, pore volume, and average pore diameter compared to nano silica obtained by direct calcination. As a result, the nanosilica obtained by method 1 (sol-gel) showed a greater potential for use as an adsorbent material. **Figures 1 (a, b)** show SEM images of materials obtained by different preparation methods. The silica synthesized by sol-gel method **(Figure 1 (a))** shows agglomerates of irregular size, characterized by transformation of gel into xerogels, and particles of size on the nanometric scale (confirmed in TEM analysis). The sample obtained by method 2 **(Figure 1 (b))** makes it possible to observe the structure of biogenic silica formed by the presence of agglomerates with irregular shapes, characterized by raw

material processing, and presence of several spherical particles distributed in a porous structure. The EDX analysis is additionally shown in **Figure 1 (c).** Whereas, the mapping of main chemical elements found in silica nanoparticles prepared by method 1 (sol-gel) can be observed. (Falk et al., 2019)

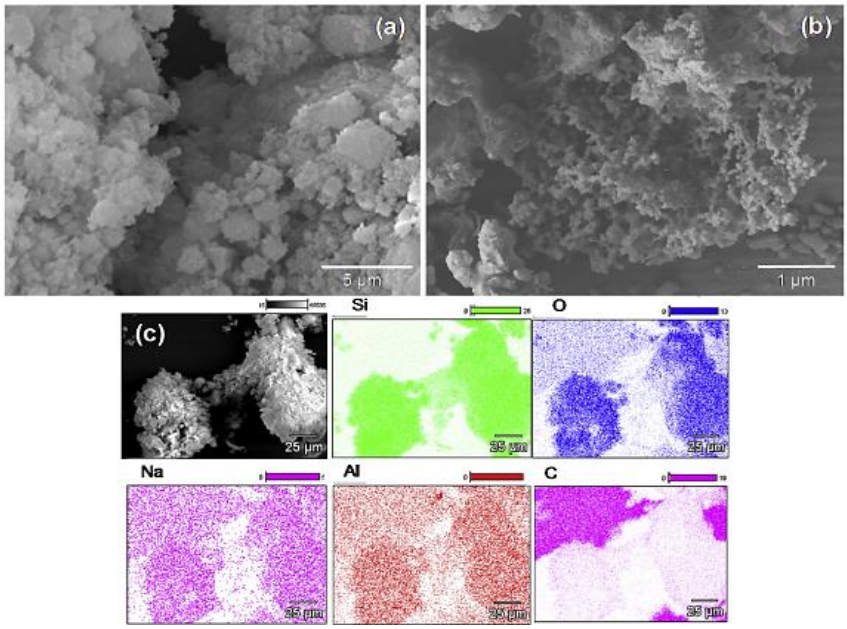

Figure 1. SEM analysis results of powders prepared by different methods and mapping images of EDX elements from silica prepared with sol-gel method. (a) and (c): sol-gel method and (b) acid washing method. Adopted from reference (Falk et al., 2019)

Powder morphology after magnesiothermic reduction was evaluated by scanning electron microscopy (SEM) as shown in **Figure 2 (a, b).** Whereas, the selective removal of synthetic residues using acidic solutions results in the formation of silicones with a morphology similar to xerogel silica (characteristics of materials on a nanometric scale). The efficiency of reaction and leaching process was evaluated by energy dispersive X-ray spectroscopy (EDX) as shown in **Figure 2 (c, d).** The magnesiothermic reduction process may support the formation of 2MgO (s) + Si (s) **(Figure 2 (a))**. After going through the leaching process **(Figure 2 (b))**, the EDX spectrum proves that the product is rich in silicon plus a percentage of residual oxygen, this is likely due to the highly active silicon surface during exposure to aqueous solutions of HCl, and possibly relate to the small presence of silica that didn't react.

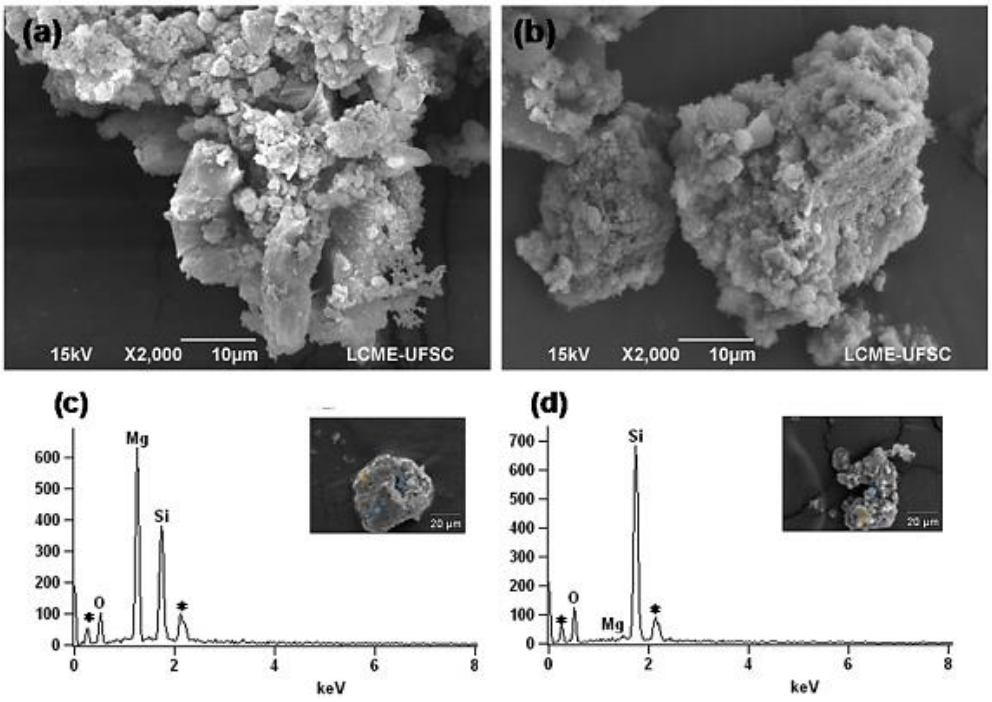

Figure 2. SEM micrographs of Si were obtained by magnesiothermic reactions (a, b) and EDX spectrum from nano-Si before (c) and after the leaching process (d). Adopted from reference (Rovani et al., 2018)
(*) Au coating sample for analysis.

The silica aerogel obtained has a lump, coarse powder, and fine powder shaped morphology. The greater the HMDS content added, the more likely silica aerogel tends to be in powder form. FTIR analysis produces the spectrum shown in **Figure 3.**

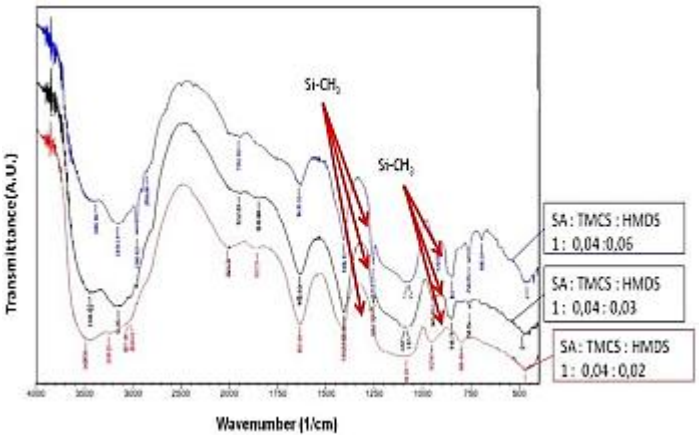

Figure 3. FTIR analysis of the synthesis results. Adopted from reference (Falk et al., 2019)

Figure 3 shows the peaks that appear at wave numbers 850 and 1260 cm^{-1} indicating the presence of Si–CH_3 groups. This proves that the surface modification has occurred in which the silanol groups are replaced by alkyl groups.

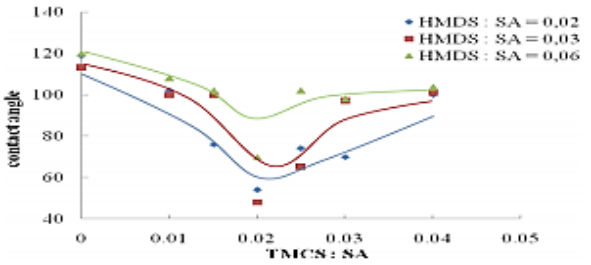

Figure 4. Hydrophobicity of silica aerogel at various contents of HDMS and TMCS. Adopted from reference (Falk et al., 2019)

Figure 4 shows that the greater HMDS content, the greater resulting contact angle, which means that more hydrophobic silica aerogel is obtained. The increase in HMDS contents causes more silanol groups to be replaced by alkyl groups, therefore hydrophobicity increases. The contact angle of the synthesized silica aerogel ranged from 48-119.

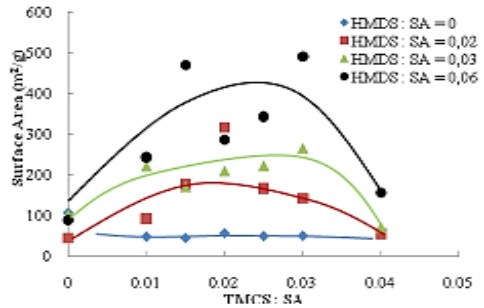

Figure 5. Surface of silica aerogel at various contents of HDMS and TMCS. Adopted from reference (Falk et al., 2019)

Figure 5 shows that there is an increase in surface area with an increase in HMDS contents, and there is a difference in surface area between the synthesis of silica aerogel particles with and without the addition of HMDS. The addition of surface modification will stop the condensation process further so that the particles obtained are not too large and particle surface area becomes large along with the increase in HMDS contents. The surface area of synthesized silica aerogel was between 50.00-468.00 m^2/g.

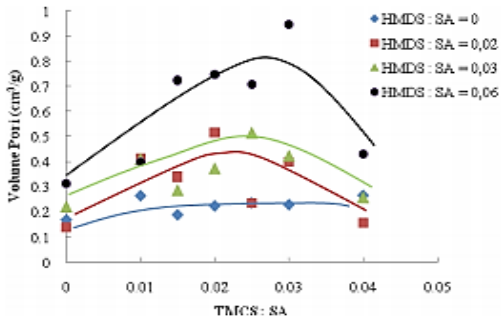

Figure 6. Silica Aerogel Pore Volume at various contents of HDMS and TMCS. Adopted from reference (Falk et al., 2019)

Figure 6 shows that the more HMDS is added to salicylic acid, then the pore volume of silica airgel produced increases. Increasing contents of HMDS to SA from 0 to 0.06 will increase pore volume up to 78.15%. In the process of surface modification mechanism, the higher HMDS content against SA, the more H from (OH) group in silica pore that is modified into O-Si-$(CH_3)_3$ groups, therefore springback effect that occurs is greater and prevents enlargement of shrinkage excess. In other words, the higher content of HMDS, the less the increase in shrinkage pore volume between 5.70-22.56 nm. Based on the pore types defined by IUPAC, it can be concluded that silica aerogel particles are mesoporous. (Falk et al., 2019)

Researchers (Rovani et al., 2018) reported that the production of SiO_2 nanoparticles (SiO_2NPs) has been successfully synthesized. This process produces nanoparticles with high purity (>99.00% of SiO_2). In its manufacture, cetyltrimethylammonium bromide is used as a stabilizer and size regulator. SiO_2NPs characterization carried out by the TEM method showed the presence of small nanoparticles (<20.00 nm) and the BET method showed a specific surface area of 131 m^2g^{-1}, about 23 times higher than the bagasse ash of the starting material. The kinetic and isothermic results, apart from the thermogravimetric analysis, show that AO8 is adsorbed onto SiO_2NPs and forms multiple layers. The results show that it is possible to obtain environmentally friendly adsorbents from renewable sources at low cost. Apart from its application as an adsorbent, the highly pure SiO_2NP has the potential to be applied in catalysts, biopolymers, paints, and others.

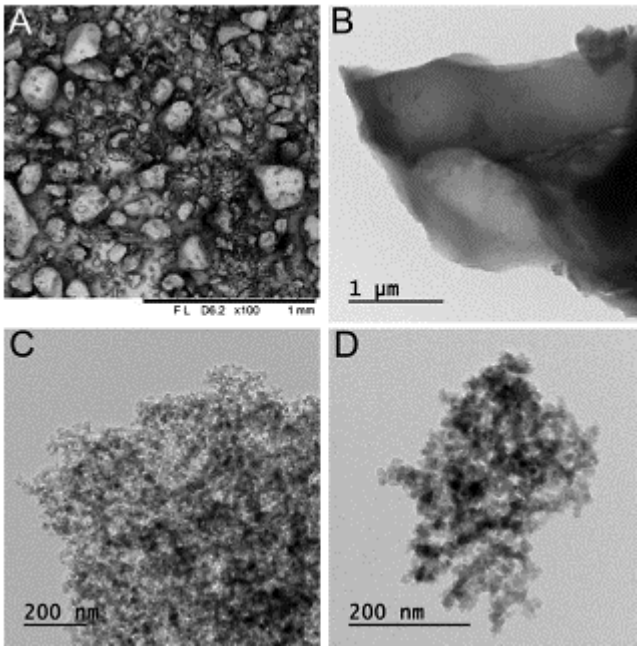

Figure 7. SWA image : (A) SEM and (B) TEM. TEM silica nanoparticles with two different magnifications at (C, D). Adopted from reference (Rovani et al., 2018)

The SEM analysis results of Sugarcane Waste Ash (SWA) in **Figure 7 (A)** show heterogeneous material with irregular shapes. Where, the sizes are in the range of 5 and 500 µm. The high level of roughness is related to the release of

organic matter during the burning process of bagasse to produce energy in the sugar alcohol industry. The morphology obtained from the SWA sample was similar to that observed (Batra et al., 2008) and (Faria et al., 2012).

Figure 7 (B) shows the results of TEM analysis of single ash which has a relatively large size, making it difficult to analyze single ash using this method. In contrast, **Figure 7 (C, D)** shows a TEM image of SiO_2NP that shows a drastic change in material size and morphological shape when compared to real ash. The size ranges from a few micrometers for ash reduced to 20 nm. The observed synthesized nanoparticles did not have a defined shape, however the nanoparticles not larger than 50 nm were definitely similar to the SiO_2NP size reported by (Rafiee et al., 2012); (Hassan et al., 2014); (Le et al., 2017); (Bahrami et al., 2017) and (To et al., 2017).

2.1.2. Rice Husk Ash

Rice husk ash is one of the highest or highest silica-producing natural materials. Rice husk contains 87-97% silica so it is suitable to be used as a silica-producing material (Agung, Hanafie, & Mardina, 2013; Handayani, Nurjanah, & Rengga, 2014). In addition, according to (Chandrasekar et al., 2006) in his research suggested that the silica characteristics of rice husks, such as amorphous; ultra fine size; and highly reactive, can produce better quality silica based products. Complete burning of rice husk produces rice husk ash which is rich in silica, which is more than 60%. (Kalapathy et al., 2000)

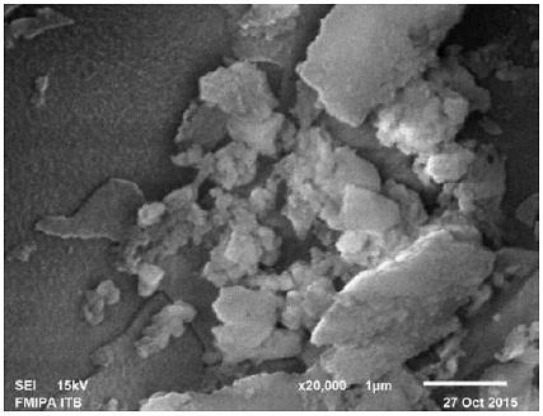

Figure 8. SEM test with a 20,000 magnification for rice husk ash. Adopted from reference (Andreas et al., 2016)

The morphology of rice husk ash shown in **Figure 8** shows that rice husk ash particles have a smooth surface, no visible protrusions and fine hairs. Where, research (Chandra, 2012) reports that fine hair shows the presence of impurities. In addition, it can be seen that in the research conducted (Andreas et al., 2016), rice husk ash was obtained without other impurities besides silica. Based on the results of the analysis of the composition of rice husk ash by (Andreas et al., 2016), there are two compounds, namely carbon by 6.92% and silica (SiO_2) of 93.08%.

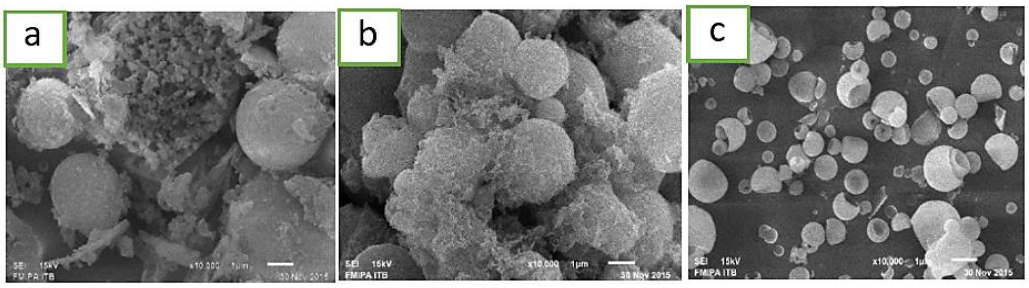

Figure 9. SEM test magnification of 10,000 times for nanosilica: a) 1: 9 variation of solvent, b) 1:16 variation of solvent, c) 1:23 variation of solvent. Adopted from reference (Andreas et al., 2016)

The SEM test of nanosilica research results (Andreas et al., 2016) in **Figure 9** shows the smallest nano silica particle size obtained from the variation of the 1:23 solvent ratio (the highest amount of solvent). According to (Andreas et al., 2016) this happens because of the polymerization and syneresis processes at the aging stage. Increasing the amount of ethanol solvent causes condensation to continue during the aging time. The more the amount of ethanol solvent used, the polymerization process and the syneresis process will occur more frequently so that the particles shrink. Changes in the characteristics and integrity of silica can additionally occur with changes in temperature. Temperature control needs to be done on the silica that has been synthesized to eliminate the presence of impurities and increase the purity of the silica obtained. (Mahmud et al., 2016).

Composition analysis using EDX from the three solvent variations in the study (Andreas et al, 2016) used the highest composition, namely the 1 : 16 solvent variation, namely 56.85%.

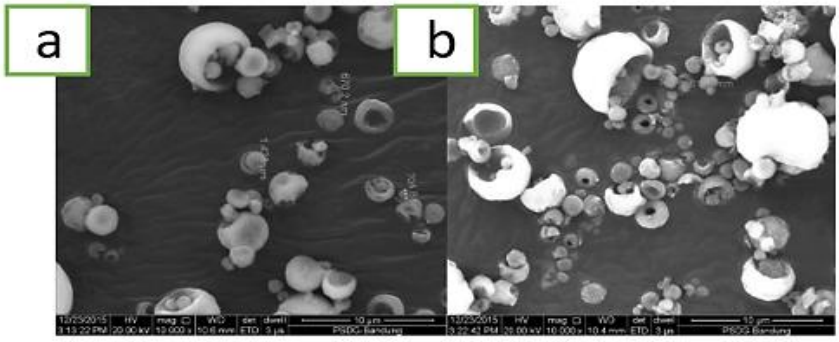

Figure 10. SEM test for nanosilica a) 3 days aging time, b) 7 days aging time. Adopted from reference (Andreas et al., 2016)

The results of the morphological analysis in **Figure 10** show that from the two variations carried out, the shape of the particles obtained were round but crushed and not intact, the particles had non-uniform sizes and closely resembled the shape of silica nano cups. Particles with a 3 day aging time had a particle diameter ranging from 670.2 nm - 1.428 μm. Particles with an aging time of 7 days had a particle diameter ranging from 582.8 - 993.4 nm. This shows that the particle diameter with an aging time of 7 days has a smaller size than the particles with an aging time of 3 days.

Analysis of the composition by EDX in an experiment with an aging time of 3 days, the obtained information on the silicon composition is 11.07%. While

the experiment with 7 days aging time, the obtained silicone composition was 17.86%. So it can be concluded that the silicon composition is greater at the longest aging time, which is 7 days. (Andreas et al., 2016). The results of the research conducted (Meliyana et al., 2019), WRHA was tested using XRF first to determine its chemical composition and the results obtained were the percentage of SiO_2 of 93.27%. The percentage of silica obtained is quite high and is almost the same as the research (Nittaya & Apinon, 2008). WRHA morphology was observed by SEM. Observations focused on the microstructure in the form of material homogeneity and morphology, all of which were related to the effect of adding 1 N HCl (Meliyana et al., 2019)

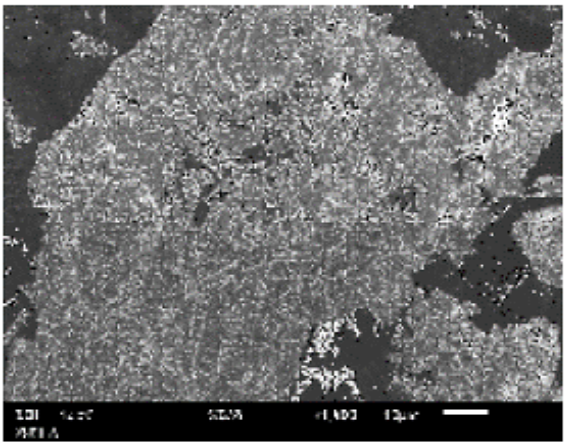

Figure 11. SEM WRHA with 1N HCl Addition Treatment. Adopted from reference (Meliyana et al., 2019)

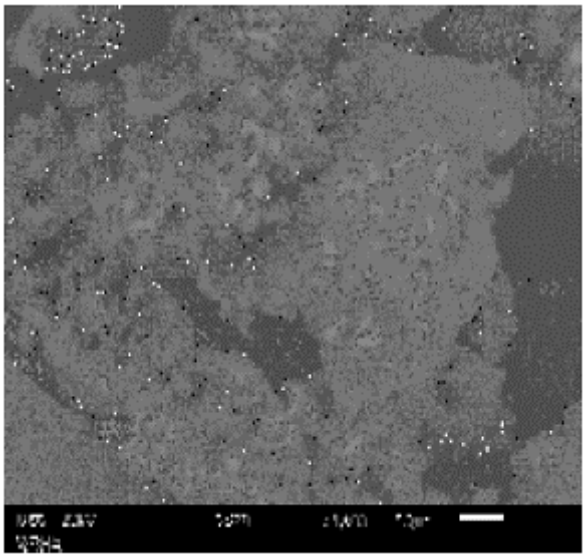

Figure 12. SEM WRHA without additional 1 N HCl treatment. Adopted from reference (Meliyana et al., 2019)

Cleaning and washing WRHA with 1 N HCl is more effective than WRHA without treatment. This is because HCl is able to dissolve organic substances and other elements in WRHA. This is consistent with the XRF test results for silica

content in WRHA with a treatment that has a much higher percentage of SiO_2. (Meliyana et al., 2019)

In the synthesis process of WRHA into silica nanoparticles by mixing 2.5 N NaOH and forming silica gel with 1 N HCl and drying process, the composition and content of silica in WRHA 0 (without treatment) and WRHA 1 (with treatment) were 82.18 and 89.17%, respectively. In the nano silica synthesis process with treatment, the silica content decreased from 93.27% to 89.17%. This is because in the synthesis process there is a reduction in silica due to unstable temperature, manual filtering, and the acid cleaning process when the phase changes from sol to less clean gel. (Meliyana et al., 2019)

Based on FTIR analysis, the silica peaks were seen at the wave numbers 1068.56 and 1121.11 cm^{-1}. This did not differ greatly between treated, untreated and commercial silica WRHAs. Based on the results of the Particle Size Analyzer (PSA) test, the size of the silica particles formed was not much different with and without treatment ranging from 92 ± 25 nm to 98 ± 25 nm. (Meliyana et al., 2019)

2.2. Flame Spray Pyrolysis Method

The flame spray pyrolysis method is reported (Herdianto, Hengky and Mochamad Alfi Z. F., 2012) to produce silica particle diameter of about 10-45 nm relative to the spraying pressure and concentration of silica acid solution. The silica nanoparticles that have been synthesized through this method can be used as an aggregate mixture to make and produce high-performance concrete by testing physical and mechanical properties.

2.2.1. Lapindo Mud

Lapindo mud contains minerals and chemicals that are provided for the manufacture of cementitious materials with high silica content. Apart from that, the results of preliminary inspection of hot mud from Lapindo Sidoarjo for ceramic products were additionally carried out by Dr. Ir. Aristanto from the Bandung Center for Ceramics, Ministry of Industry. The SiO_2 content in the Lapindo mud based on TPSA-BPPT was 54.92%, while based on the Ministry of Industry was 53.08%.

Based on research (Herdianto, Hengky and Mochamad Alfi Z. F., 2012), the sodium silicate solution obtained has an average diameter of 9 μm with a yield of more than 80% using sodium hydroxide (15%) in the washing method of pre-combination ML particles. The washing method of pre-combined ML particles has a silica percentage of about 92.5%. Hydrogen ion exchange resins are used to remove Na^+ ions in sodium silicate solution and produce a silica acid solution with a Na^+ ion concentration of less than 95 ppm.

The amorphous silica nanoparticles produced using silica acid solution by the flame spray pyrolysis method have a particle diameter of about 10 - 45 nm, relative to the spraying pressure and the concentration of the silica acid solution. Silica acid solution for the synthesis of silica nanoparticles using a speed of 3.00 cm/s. Ethanol was added to the silica acid solution in order to obtain a concentration of 0.30 mol/L to adjust the precursor concentration and flame temperature. The air pressure in the two-fluid nozzle varies, ranging from 0.50-3.00 kgf/cm^2 with variations in the discharge. **Figure 13** shows the results of SEM analysis of nanoparticles made at (a) 1.50 and (b) 3.00 kgf/cm^2. The morphology of

the nanoparticles obtained is homogeneous and almost spherical. (Herdianto, Hengky and Mochamad Alfi Z. F., 2012)

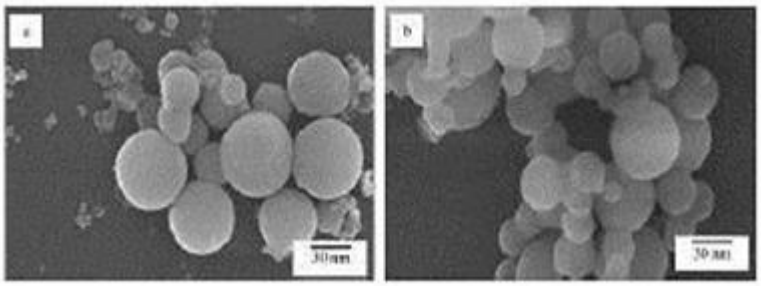

Figure 13. SEM images of Silica Nanoparticles (a) 1.50 and (b) 3.00 kgf / cm2. Adopted from reference (Herdianto, Hengky and Mochamad Alfi Z. F., 2012)

The specific surface area and mean particle diameter were 52, 182, and 297 m^2/g; 60, 17, and 11 nm when the pressures are 1.2, 1.6, and 2.2 kgf/cm^2. **Figure 14** shows a graph of the specific surface area and mean particle diameter in relation to the concentration of silica acid in solution at a pressure of 2.5 kgf/cm^2. When there was an increase in concentration from 0.28 to 0.55 mol/L, the mean particle diameter increased from 10.00 to 45.00 nm and the specific surface area decreased from 298.00 to 62.00 m^2/g. This occurs due to the growth of the nucleus produced by condensing and sintering particles at high temperatures. (Herdianto, Hengky and Mochamad Alfi Z. F., 2012)

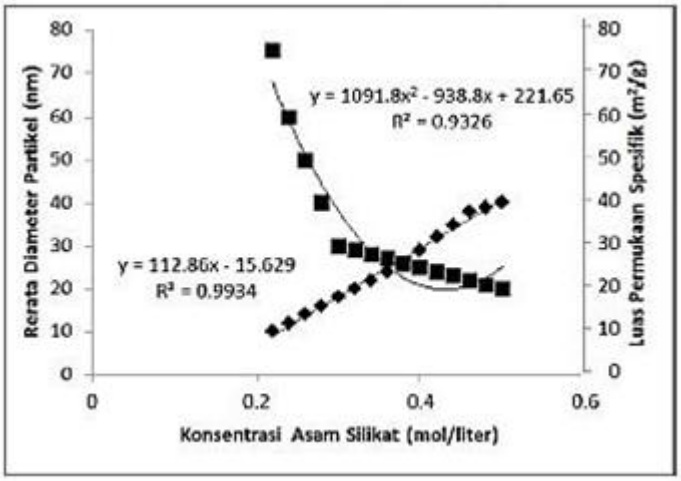

Figure 14. Effect of Silica Acid Concentration on Particle Size and Specific Surface Area of Silica Particles. Adopted from reference (Herdianto, Hengky and Mochamad Alfi Z. F., 2012)

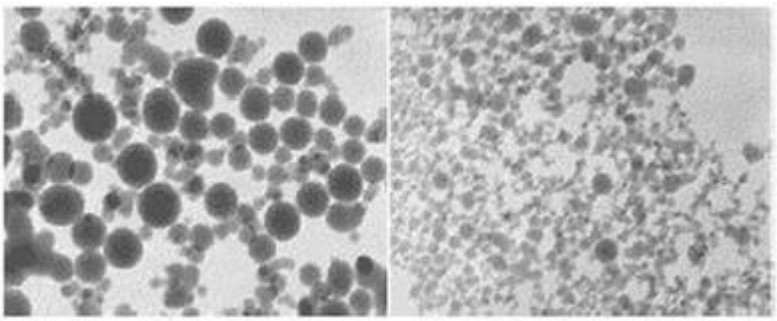

Figure 15. Two Fluid Nozzles at Fixed Process Conditions ((a) 1.50 and (b) 3.00 kgf / cm TEM Silica Nanoparticles Produced in Different Pressure Input Air at 2). Adopted from reference (Herdianto, Hengky and Mochamad Alfi Z. F., 2012)

The strength development of ML silica concrete is better than flow concrete. Score DSA, MOR, MOE, and IB achieved 16.25%, 67.42, 56.28 and 63.56 kg / cm2, respectively. (Herdianto, Hengky and Mochamad Alfi Z. F., 2012)

2.3. Coprecipitation Method

Research on the synthesis of silica nanoparticles using the coprecipitation method has been reported (Munasir Nanda Iriawan, 2014). The advantages of this method when compared to other conventional methods, namely: it has a high level of purity, the deposition process is definitely simple so that it is easy to separate at low temperatures, the time required is relatively fast, the equipment used is simple, and requires relatively low cost so that it is possible to obtain a powder with a certain crystal size. The same result reported by (Silvia & Zainuri, 2020) regarding the synthesis and characterization of SiO_2 powder using hydrothermal and coprecipitation methods. Where, the purity of the SiO_2 sample increases after experiencing coprecipitation.

2.3.1. Silica Sand

Silica sand is a mineral that is abundant in nature and can be used in various applications. Where, silica material derived from nature has been successfully purified in several previous studies. (Silvia & Zainuri, 2020)

The results of the diffraction pattern after the sample went through the leaching process showed a reduction in the number of crystalline peaks. In the initial state, the diffraction patterns were found as many as 18 crystalline peaks with three phases. After the leaching process, the number of crystalline peaks is reduced to 15 and is single-phase. Then, when the coprecipitation stage is complete, the silica product obtained from the synthesis process has an amorphous form and increases in purity. (Munasir et al., 2014)

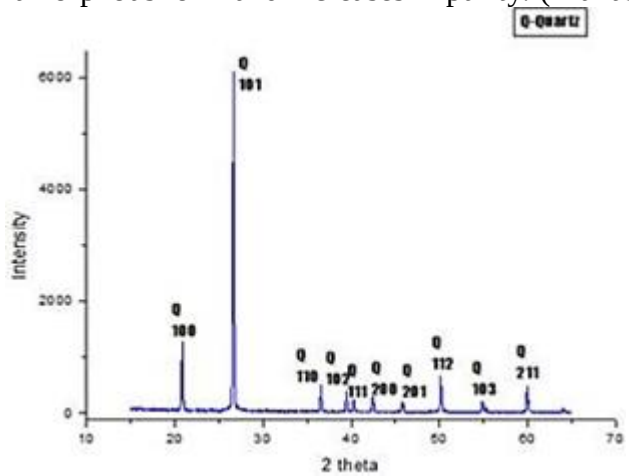

Figure 16. Results of diffraction pattern after powder leaching. Adopted from reference (Munasir et al., 2014)

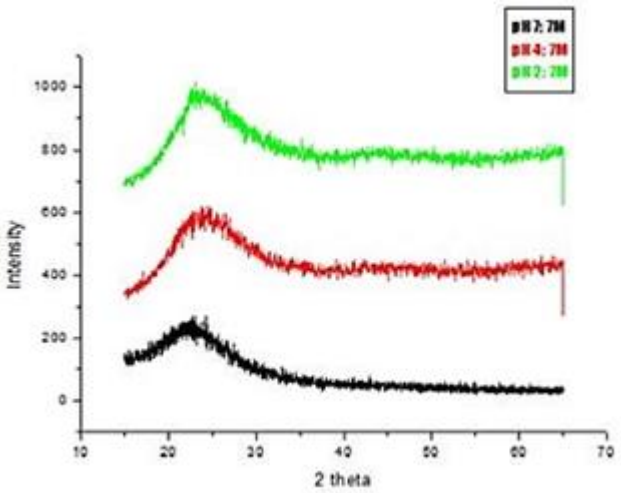

Figure 17. Synthesis results with variation pH of coprecipitation at 7 M NaOH. Adopted from references (Munasir et al., 2014)

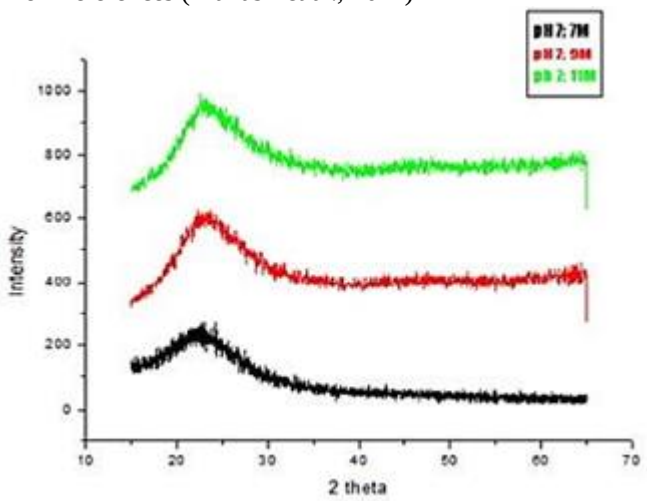

Figure 18. Comparison of the diffraction pattern of silica with molarity variations of NaOH at pH 7. Adopted from references (Munasir et al., 2014)

Synthesis and characterization of SiO_2 powder were successfully carried out by hydrothermal and coprecipitation methods (Yan et al., 2017). Result of silica powder formed at pH 2; 7 M is the amorphous form of SiO_2. The purity of the SiO_2 sample increases after experiencing coprecipitation (Yan et al., 2016). This indicates that impurities other than SiO_2 have dissolved into the HCl solution. Particle size reduction was performed using wet milling at a speed of 150 rpm for 10 hours. This reduction in particle size causes the particles to become smaller and more easily dissolved in the NaOH solution to become a sodium silicate solution (Hadi et al., 2011).

The synthesis of quartz (SiO_2) based on natural sand from Bancar beach with the coprecipitation method using NaOH was successfully carried out and produced a single phase in the form of quartz (SiO_2) with an amorphous background and the results of estimating size calculations obtained the form of quartz crystals (Munasir, Triwikantoro, Moch. Zainuri, 2013). Treatment changes in the sequence of HCl and distilled water at the initial stage before synthesis did not have a significant effect on the resulting X-ray diffraction pattern. Based on the analysis of the X-ray diffraction pattern after the coprecipitation process using Match 2 software, the dominant single-phase form of quartz (SiO_2) with an

amorphous background was obtained from the synthesis results. The purity of the natural sand samples at Bancar beach has increased after the coprecipitation process is carried out (Izzati & Munasir, 2013).

SiO_2 nanoparticles obtained from hydrothermal methods have high purity (more than 98.00%) and consist of spherical particles with a size of about 30.00 nm and containing quartz and cristobalite phases. This was confirmed by the presence of silanol (Si-O), siloxane (Si-O-Si), and hydroxyl groups on the surface of the sample. Meanwhile, the SiO_2 nanoparticles obtained from the dry method only had a purity of 72.90%. In addition, the formation of quartz and cristobalite phases in all SiO_2 nanoparticles that have been synthesized is an interesting discovery obtained in this study (Susilo et al., 2016).

Synthesis of nanosilica from silica sand using the alkaline fusion method produces silica nanoparticles that are not much different from the previous method (Nisa & Munasir, 2015). Nanosilica obtained was 98.90%, proven by XRD results and DTA / TG results data.

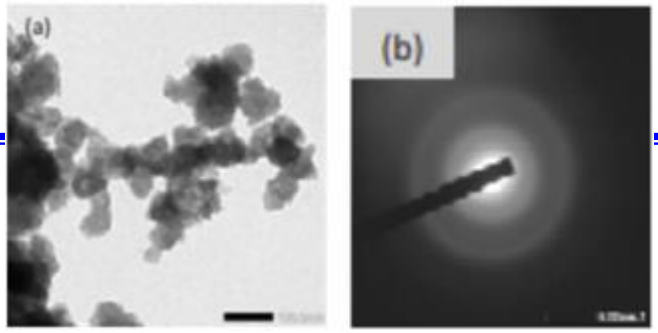

Figure 19. TEM image of the resulting silica (extraction with 87.50% NaOH), (a) agglomerated granules with a particle size <100.00 nm and (b) a ring pattern indicating the presence of an amorphous phase. Adopted from references (Munatsir, 2013)

Figure 19 (a) shows the morphology of a sample of silica powder with an agglomerated oval grain and a circular shape having a nanometer particle size (<200.00 nm). Further analysis using a ring pattern (**Fig. 19 (b)**) shows that the amorphous phase predominates over the crystal phase.

The synthesis was initiated by immersing the sample in 2 M HCl for 10 hours to dissolve materials other than SiO_2 because HCl has the ability to dissolve several compounds so that Na can optimally bind SiO_2 to form sodium silicate (Na_2SiO_3) during the alkaline fusion process which is marked by a decrease impurities in the sample, namely the change in mass of sand from 7 g to 6.20 g. HCl titration is carried out in low pH conditions (pH 1-2) so that Na, Al, Ca, and Cu can dissolve in the solution and reduce unwanted elements. The purity of SiO_2 obtained is definitely high, namely 98.90% (Alfaiz & Hutahaean, 2015).

2.4. Ultrasonication Method with Addition of Surfactants

The synthesis of nanosilica from kettle ash by the ultrasonication method with the addition of surfactants was reported (Ismayana et al., 2017) in several stages, namely preparation of boiler ash, extraction of silica from furnace ash, and synthesis of nanosilica. Where, the results of research (Ismayana et al., 2017) show that the nano silica synthesis process using the ultrasonication method produces particles with an orderly crystal arrangement. This happens because the ultrasonication method generates heat which can encourage the formation of nanosilica crystals to become more regular. In

addition, the synthesis of nanosilica by the ultrasonic method can be produced with a high degree of crystallinity.

The use of the ultrasonication method is reported (Safitri, 2012; Kurniawan, 2013) has advantages over commonly used methods, such as one of which is the relatively faster precipitation or synthesis time and the ability to manipulate the characteristics of nanosilica into crystals.

In research by (Ismayana et al., 2017), ultrasonication methods were improved with the addition of surfactants. This is in line with research (Fahyuan et al., 2013) which stated that the addition of surfactants can provide a higher pressure effect to compress crystals and cause the distance between fields to be closer so that the crystal size becomes smaller. Besides the decrease in crystal size, the addition of surfactants in research by (Ismayana et al., 2017) can increase crystallinity levels and minimize the agglomeration process so that particle uniformity can occur.

2.4.1. Kettle Ash

In kettle ash, which is produced from the burning of sugar cane in the sugar industry, it contains the dominant silica mineral. Thus according to (Ismayana et al., 2017), this kettle ash becomes one of the potential sources of silica minerals. Which is, the improvement of silica characteristics by synthesizing in nano size can expand the utilization of silica, especially silica in kettle ash.

Based on the characterization of kettle ash by (Ismayana et al., 2017), it is known that SiO_2 content reaches 49.69%. After the burning of kettle ash into furnace ash, silica levels in the furnace ash increased to 78.75%. The size of nanosilica in the results of the study by (Ismayana et al., 2017) is shown in **Table 2**. The particle size shows the average particle size in a sample without a template. The minimum nanosilica size is obtained with a size of 203.94 nm with pdi 0.638. This value of the Particle Dispersion Index (PDI) is relatively greater. This indicates that the uniformity of particle size is small. Unlike samples that used surfactants, the PDI value obtained was relatively smaller. This indicates the uniformity of particle size is large. (Ismayana et al., 2017) explained that the addition of surfactants minimizes the agglomeration process. Based on the results of the study (Ismayana et al., 2017) with the addition of surfactants, the most uniform size distribution is a sample that uses 2.50% CMC surfactant with a size of 408.76 nm and (PDI) 0.047. Nanosilica produced with the addition of CMC 10% indicates a small size uniformity with PDI 0.496. (Ismayana et al., 2017)

Table 2. The size of silica nanoparticles. Adopted from reference (Ismayana et al., 2017)

Sample	Range (nm)	Average (nm)	PDI
No Template	22.39 - 3716.34	203.94	0.638
PEG 6000	44.68 - 1698.69	259.99	0.244
CMC 10%	35.39 - 3891.48	294.73	0.496

CMC 5%	213.85 - 1023.56	462.89	0.045
CMC 2.5%	186.26 - 933.50	408.76	0.047
Tween 80 3%	48.79 - 2239.31	300.02	0.320

The degree of crystallinity of the resulting nanosilica particles **Table 3** indicates that nanosilica synthesized using surfactants have a higher degree of crystallinity than nanosilica without surfactants

Table 3. Degree of nanosilica crystallinity. Adopted from reference (Ismayana et al., 2017)

Sample	**Degree of Crystallinity (%)**	**Crystal Size Flattening (nm)**
No Template	76.96	41.40
PEG 6000	78.58	38.84
CMC 10%	84.04	37.69
CMC 5%	82.07	39.29
CMC 2.5%	78.45	39.53
Tween 80 3%	79.59	41.48

In nanosilica synthesized using CMC, the large concentration of CMC provides a difference in the degree of nano silica crystallinity. In the study (Ismayana et al., 2017) explained that the more surfactants are added, then the degree of crystallinity of the nanosilica crystals obtained will increase. The addition of higher surfactants leads to the growth of more guarded crystals so that the degree of crystallinity of the obtained crystals becomes higher.

Reported by (Ismayana et al., 2017), the addition of surfactants can lower the average size of nanosilica crystals. This is explained by (Fahyuan et al., 2013) that the addition of surfactants gives a higher pressure effect to compress crystals so that the distance between fields becomes closer and the size of the crystal becomes smaller.

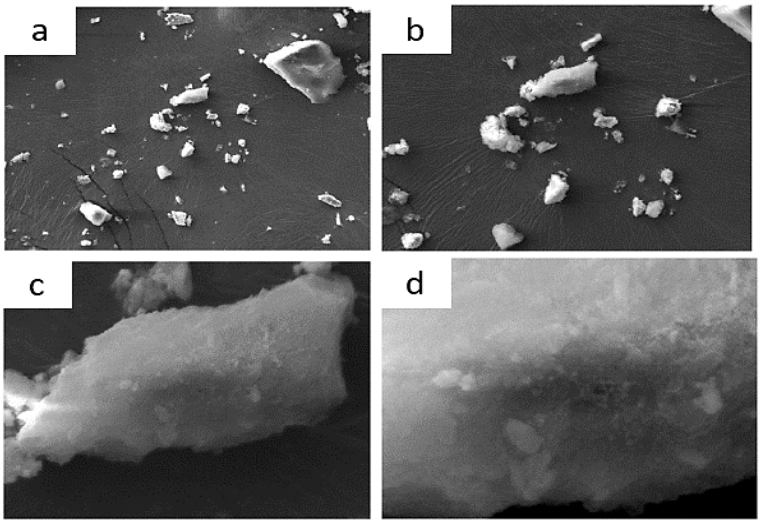

Figure 20. Morphology of nanosilica with CMC surfactants uses SEM magnification (a) 500x, (b) 1000x, (c) 5000x, and (d) 10,000x. Adopted from reference (Ismayana et al., 2017)

The nanosilica morphology results in **Figure 20** show irregular shapes and some particles are larger in size than others. According to (Ismayana et al., 2017), these large particles are particles composed of small particles that have the agglomeration process.

2.5. High Pressure Autoclave Metabundanhod

Silica nanoparticles synthesized by high-pressure autoclave method use Amorphous Calcium Carbonate (ACC) compounds, which are premade by carbonation method. ACC is created using the ACC dissolving procedure on methanol solvents to form a $Ca(OCH_3)_2$ layer on ACC particles. (Nakashima et al., 2018)

CO_2 separation uses olivin as the raw material and this separation is carried out in autoclaves at 175°C and 100 bar in a water solution and gas phase that is rich in CO_2 for 0.50 to 12 hours. (Turri et al., 2017) shows that the fraction that separated from silica can be maintained in carbonate and olivin inert states.

The characterization of retained solids indicates that carbonate dominates with particle sizes ranging below 40.00 μm. The silica of synthesis result obtained is in the form of smooth ball particles. The addition of 0.64 M of hydrogen carbonate sodium, oxalic acid 0.50 M and ascorbic acid 0.01 M was successfully applied to obtain maximum carbonation and lead to complete silica formation. Optimal reaction conditions are reported to be in the temperature range of 15–185°C and in the pressure range of 135.00–150.00 bar. (Rahmani et al., 2014)

2.5.1. Olivin Rocks

Saprolite is the layer after Limonit, which is distinguished from its richness of magnesium silicate content. Laterite ore generally has low Ni levels (1.00-3.00%), Co (max. 0.10%), Fe (20.00-30.00%) and high SiO_2 levels (over 50.00%). The treatment of silicate ores with different acids and under atmospheric pressure leads to the formation of silica gels and melting processes. Silica gels obtained are amorphous and porous silicon dioxide that consist of irregular three-dimensional skeletons of silicon atoms and oxygen alternates with nanometer-scale pores. (Moskalyk et al., 2002).

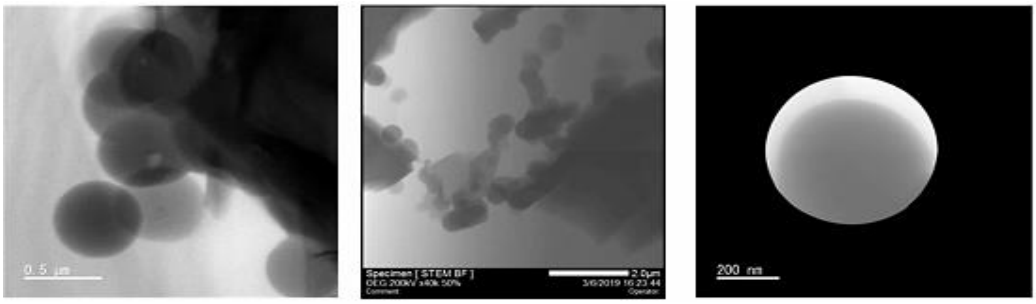

Figure 21. TEM and SEM analysis for nanosilica of the products used

Figure 21 shows the results of TEM analysis of silicon oxide. The data obtained from **Figure 21** is the shape of silica particles produced in the shape of a ball with a diameter of about 400.00-500.00 nm and has amorphous particle morphology. Based on these results, it is possible that the high stirring speed and high pressure in the autoclave are decisive in the ideal formation of silica particles, along with the formation of a larger fraction of magnesium carbonate. (Srecko et al., 2019)

Research by (Wang et al., 2019) reports that in the kinetics and carbonation mechanisms of olivine minerals there is an increase in ion strength that helps the process of dissolving Si into H_4SiO_4 aqueous with the addition of sodium bicarbonate. The process is temporarily continued with the decomposition of the sample into amorphous silica resulting in the removal of the layer that is rich in Si. Silicon aqueous is unstable and can be decomposed into amorphous silica that can be observed extensively in aqueous solutions after carbonation and settles for more than a month at room temperature.

2.6. Fusion Alkaline Methods

Synthesis using the fusion alkaline method consists of several stages, i.e : using HCl to separate desired compound from the impurity compound, purification using NaOH alkali above 80.00% at a temperature of 500-200°C for 2 hours, the addition of HCl until the pH reaches 1-2 for 10 hours, and finally the process of removal of NaCl using aquades as much as 1-10 times.

Generally, fusion alkaline methods are used to extract silica from inorganic materials such as sand and glass waste. Alkali in this method serves as an activating agent of SiO_2 so that it is easily dissolved and easily separated from other compounds in the sample. The alkaline fusion method is easy to do because the synthesis material used is easy to obtain and the energy requirements needed for synthesis are quite low, at a temperature of about 500°C compared to the method of using Na_2CO_3 as an alkaline compound that requires higher energy, at a temperature of 1400-1500°C. (Wahyuni, T., 2016)

2.7. Wet Chemical Method: hydrolysis and condensation reactions

Wet chemical methods include direct hydrolysis reactions performed in the steam phase in the absence of fire. In the study (Chen et al, 2014), $SiCl_4$ vapor was hydrolyzed

using water vapor at 150°C as a first step for the formation of oxychloride particles. Then, the sample was converted into silica particles through further hydrolysis at a temperature of 1000°C to produce silica particles in the size range of 250.00-300.00 nm. The advantages of this method include synthesizing silica nanoparticles with cheap initial materials (silicon tetrachloride and water), environmentally friendly and simple processes, lower energy consumption, and large-scale production capabilities. In the experiment section, the preparation of the silica nanoparticle vapor phase hydrolysis system was synthesized by a vapor phase hydrolysis system consisting of three parts: the feed system, the core reaction system, and the product collection system. (Yan et al, 2013).

In research by (Park & Park, 2008), the synthesis of nanosilica using wet chemical methods was carried out through 2 stages of hydrolysis. In the first stage, $SiCl_4$ vapor partially hydrolyzed with water vapor at 150°C forms an intermediate oxychloride, represented by $SiO_xCl_y(OH)_z$. In the second stage, the intermediate substance is fully hydrolyzed into silica at higher temperatures. The reactor used in the first stage is a batch type reactor to allow uniform particle growth. While in the second stage of the reactor used in the form of tubes for ease of operation. Compared to the Stober method, the advantage of this method is that the dried silica obtained has a quality comparable to dry silica from the direct production, without any filtration, washing, drying, and calcination. This advantage will give many effects in ceramic and composite applications that require dry silica as a starting material.

3. Conclusion

Synthesis methods include methods with chemical processing, both organic and inorganic initial materials and thermal processing processes, from various methods that exist, have their own advantages and disadvantages that can be selected and used based on the characteristics of materials that are used as other alternative sources of silica. The results showed that there are many materials that are successfully synthesized with high purity levels as well as various physicochemical characteristics so that it can be utilized as an alternative source of nanosilica manufacture as well as the use of such materials in several fields according to the characteristics and properties of the resulting materials, both in the field of technology, such as optics and electronics, and biomedical.

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