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SYNTHESIS AND CHARACTERISTIC OF NANO SILICA FROM GEOTHERMAL SLUDGE: EFFECT OF SURFACTANT

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Abstract

In the synthesis of nanoparticles, the phenomenon of agglomeration is an undesirable condition because the particles formed can be larger. The use of surfactants can prevent the occurrence of this phenomenon. In this study, the use of surfactants was studied in the synthesis of nano silica from geothermal sludge. The method applied in the synthesis of nano silica is the sol-gel method. A 1 M NaOH (sodium hydroxide) solution was used to prepare of the precursor solution, while the SiO_2 gel formation was carried out at a pH of 5 using a 1.5 M HCl (hydrochloric acid) solution. The surfactants used were ABS (alkyl benzene sulfonate), CTAB (cetyltrimethylammonium bromide), SDS (sodium dodecyl sulfate), and PVP (polyvinylpyrrolidone). The surfactant added to the precursor solution was at the CMC (critical micelle concentration), where the CMC value for each surfactant was 0.15; 0.05; 0.50; and 1.00 wt% for ABS, CTAB, SDS, and PVP, respectively. As a comparison, nano silica synthesis was also carried out without adding of surfactants. The experimental results showed that the synthesis of nano silica without surfactant produced a product with a purity of 98.03%. Based on PSA (particle size analyzer) testing, the average particle size was 4.82 μm. Although the purity was already high, the resulting product experiences agglomeration and surfactants were needed to minimize the occurrence of agglomeration in the product. The surfactant that gives the best product quality is PVP, whose average particle size is 66% smaller than the product without surfactant. However, the effect produced with PVP has a low purity, which is 56.67%. This condition occurs because NaCl was trapped in the surfactant template. The presence of this surfactant template causes the washing process more difficult because the templates become an obstacle for water to diffuse into the particles and dissolve the impurities.

Keywords: *Agglomeration, nano silica, geothermal sludge, surfactant*

1. INTRODUCTION

In general, nanoparticles can be defined as particles having sizes in nanometers or more precisely, in the range of 1 and 100 nm [1]-[2]. By having a smaller size, nanoparticles have different characteristics from their bulk particles in several properties, such as the properties of physical (especially particle surface area), chemical, magnetic, electrical, and optical [3]-[6]. One of the nanoparticles that has excellent potential to be utilized is silica-based nanoparticles or usually referred to as nano silica. Nano silica has a large surface area, high stability, good heat and electrical resistance, and is inert [7]. Those properties are the reasons why nano silica is widely applied in various sectors. Utilization of nano silica as the main and/or supporting material is carried out for applications in the sectors of adsorption, catalysts, drug delivery systems, insulators, sensors, polymers, paints, and energy [8]-[12].

Based on several previous studies, the synthesis of nano silica has been widely studied using raw materials or precursor solutions, such

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as TEOS (tetraethyl orthosilicate), rice husks, and silica sand [13]-[15]. Raw materials that can be employed to synthesize nano silica must contain high silica. In addition to the three materials previously mentioned and studied, there is another raw material that has excellent potential to be employed as a source of silica, namely geothermal sludge.

Geothermal sludge is solid waste generated from geothermal power plants. The amount of geothermal sludge produced from one power plant can reach hundreds of thousands of tons per month and this value is classified as very abundant for a waste [16]. If this waste is left alone, it will cause environmental problems. Based on its characteristics, this geothermal sludge contains several mineral elements or compounds that can be utilized. The most prominent mineral in geothermal sludge is silicon dioxide (SiO_2) compounds in amorphous form. The SiO_2 content in this sludge can reach 98% [17]-[19]. These data indicate that this geothermal sludge has enormous potential to be used as raw material for nano silica synthesis. On the other hand, studies on the utilization of this waste as raw material for nano silica have not been studied much and deserve further study because there is still unknown information.

In the synthesis of nano silica, the most widely used method is the sol-gel method. The sol-gel method involves the polymerization of inorganic compounds through chemical reactions in a precursor solution to form oxide compounds. The formation of these oxide compounds includes the stages of hydrolysis (formation of the sol phase-colloid) and changes in shape from the sol phase to the gel phase through the gelation stage [20]-[22]. This method has several advantages, such as producing homogeneous and high purity products, cheap, simple, and easy to operate [22]-[23]. However, the biggest challenge of synthesizing nano silica using the sol-gel method is agglomeration between particles during the gelation stage.

Agglomeration is a phenomenon in which two or more particles bind to each other for an extended period [24]. This phenomenon will cause the particles formed to be larger or the worst conditions; the resulting product is not nanometer in size. Efforts to prevent this phenomenon can be done by adding surfactants to the solution [25]-[28]. Singh, et. al., [29] have conducted studies regarding the use of several surfactants, such as CTAB (cetyltrimethyl-ammonium bromide), TTAB (tetradecyltrimethyl-ammonium bromide), and DTAB (dodecytrimethyl-ammonium bromide), in the synthesis of nano silica. The results of their research proved that the use of CTAB surfactant was able to reduce the nano silica particle size by almost 70%. In addition, another study conducted by Rakhmasari, et. al., [30] also proved that the use of ABS (alkyl benzene sulfonate) surfactant with a certain concentration can reduce the nano silica particle size by about 30% for the treatment without sonication and 47% for the treatment with sonication.

The focus of this work emphasizes the use of surfactants in the nano silica synthesis using geothermal sludge as raw material. It needs to be studied more deeply because there is no detailed and specific information regarding surfactants in the nano silica synthesis from geothermal sludge, especially the effect of the type of surfactant used. This work will study the use of various types of surfactants (cation and anion surfactants). Different types of surfactants will affect the characteristics of the nano silica formed, including particle size and morphology [29], [31]. Therefore, it will also be seen how the characteristics of the formed product where the use of surfactants with the right concentration is expected to give better characteristics to the nano silica product.

2. MATERIALS AND METHODS

2.1 Materials

For this work, geothermal sludge was the main raw material in the synthesis of nano silica. The sludge was derived from PLTP Geo Dipa Dieng, Indonesia. The sludge contained several mineral compounds and the composition of the sludge is shown in Table 1.

Table 1. The composition of geothermal sludge

Element	Composition (wt.%)
SiO_2	96.79
K_2O	0.91
P_2O_5	0.89
Fe_2O_3	0.89
CaO	0.40
Others	0.12

Other main materials employed for this synthesis of nano silica were NaOH (sodium hydroxide) and HCl (hydrochloric acid). In addition, the surfactant types varied for this work were ABS (alkyl benzene sulfonate), CTAB (cetyltrimethyl-ammonium bromide), SDS (sodium dodecyl sulfate), and PVP (polyvinylpyrrolidone). Demineralized water was applied as a solvent for all materials.

2.1 Procedures

In general, this research procedure can be illustrated a workflow as shown in Figure 1. Geothermal sludge was ground with a mortar and pestle to a size of particle less than 74 microns. Then, 20 grams of geothermal sludge were mixed with 800 ml of 1 M NaOH solution. The mixture was stirred using a magnetic stirrer and a hot plate at 90 ^{o}C for 60 minutes isothermally. After the reaction occurred, the mixture was filtered under vacuum conditions to obtain a supernatant containing Na_2SiO_3 (sodium silicate). This supernatant will act as a precursor solution for nano silica synthesis.

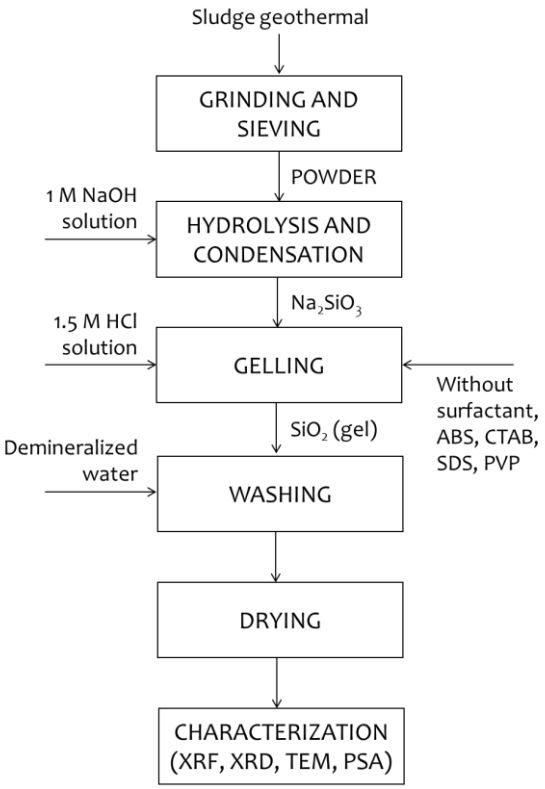


Figure 1. The procedure of this research

A total of 400 mL of the precursor solution was taken and added with surfactant. There were four types of surfactants studied, namely ABS (alkyl benzene sulfonate), CTAB (cetyltrimethyl-ammonium bromide), SDS (sodium dodecyl sulfate), and PVP (polyvinylpyrrolidone). The addition of surfactant was carried out at the CMC (critical micelle concentration). CMC was obtained first by testing the turbidity and surface tension of the precursor solution mixture with surfactants. In this experiment, the surfactant concentration was varied in a particular range according to the character of surfactant. The variation of surfactant concentration is presented in Table 2.

A turbidity meter was used to measure the turbidity level in a mixture of precursor solutions and surfactants. Meanwhile, the Du-Nouy tensiometer was used to measure the surface tension of the mixture. The CMC value was confirmed by making a graph between the surfactant concentration and the values of both physical parameters. Then, the graph was evaluated and compared with the graph of CMC determination, as depicted in Fig. 2.

Table 2. The range of surfactant concentration in the confirmation of CMC

Surfactant	Surfactant (wt.%)
ABS	0 – 2.0
CTAB	0 – 0.5
SDS	0 – 10.0
PVP	0 – 20.0

The precursor solution, added with surfactant in CMC, was stirred with a magnetic stirrer for 60 minutes. The 1.5 M HCl solution was then dripped while stirring until the pH of the solution reached 5 and a SiO_2 solid (gel) was formed. The solution was left for 18 hours so that the aging stage could occur. After the aging stage was complete, the separation process between the solid and liquid was carried out in a vacuum condition.

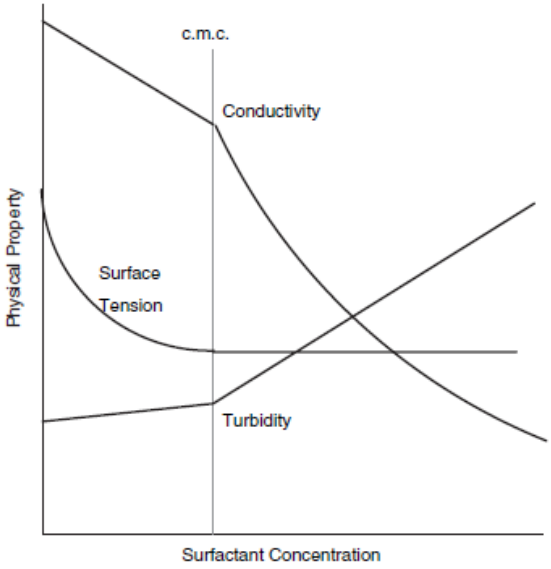


Figure 2. Comparison chart for confirmation of CMC value [32]

The solid formed was washed using 250 mL of demineralized water. The washing process was carried out with a stirring process for 10 minutes in four stages. It carried out in four stages aims to ensure the SiO_2 product has a high purity where the salt impurities (NaCl) dissolve in water. The solid was then dried using a microwave at 700 watts of power for 30 minutes. The final step is that the solids formed are characterized. The characterizations carried out were testing the

product composition using XRF (x-ray fluorescence), the mineral phase of the product using XRD (x-ray diffraction), particle size distribution using PSA (particle size analyzer), and product morphology using a TEM (transmission electron microscope). As a comparison, this study also synthesized nano silica without surfactants. The synthesis steps are the same as previously described.

3. RESULT AND DISCUSSION

3.1 Characterization of Nano silica without Surfactant

Before studying further the effect of surfactants in the synthesis of nano silica from geothermal sludge, the synthesis of nano silica without surfactants needs to be observed first so that it is obtained sharper observations regarding the effect of these parameters. This section shows how the results of nano silica synthesis without the addition of surfactants. The first result observed is the purity of the resulting nano silica product. The results of the analysis can be observed in Table 3.

Table 3. The composition of nano silica without surfactant

Compound	Composition (wt.%)
SiO_2	98.03
P_2O_5	0.97
Fe_2O_3	0.57
CaO	0.31
Others	0.12

Based on the analysis results in Table 3, the purity of the resulting nano silica has increased from the initial raw material. It can be seen that there is an increase of 1.24%, where the product purity is 98.03%. When compared with several other studies [33]-[34], the purity of the product obtained in this study is relatively high.

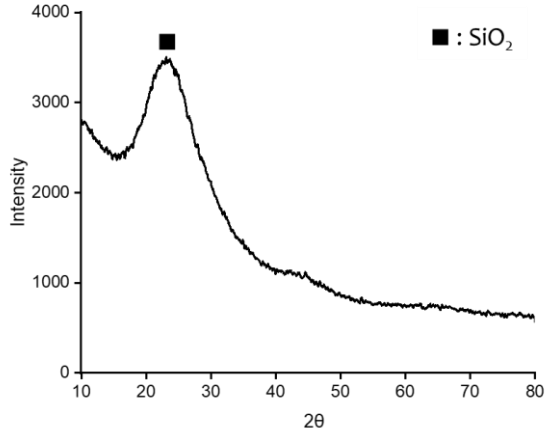
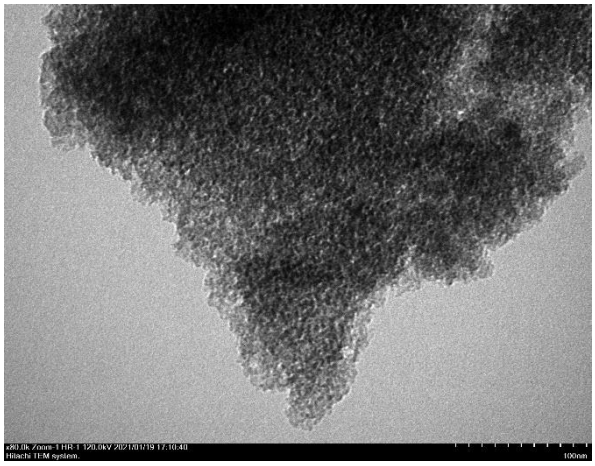
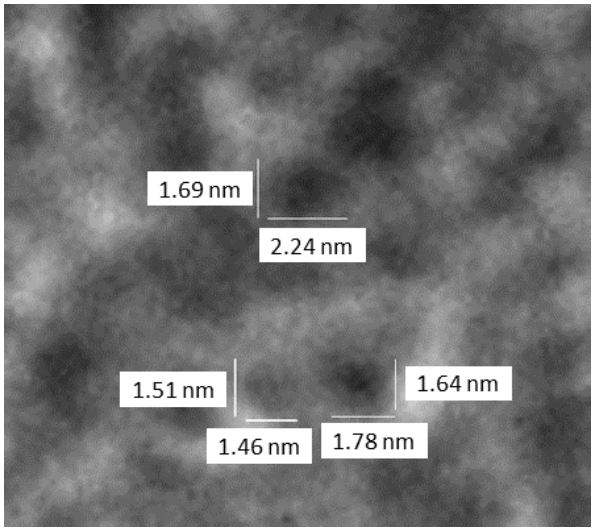


Figure 3. XRD analysis of nano silica products formed without surfactants

To strengthen the results of XRF (x-ray fluorescence) analysis, the mineral phase of the formed nano silica was also analyzed using XRD (x-ray diffraction). The results of the analysis are presented in Fig. 3. Based on Fig. 3, it can be observed that the nano silica product has a peak of about 23.5^o where this peak appears in the range of 16.3-33.8^o. Based on the range of peaks presented in Fig. 3, it also prove that the product formed is an amorphous compound.



(a)



(b)

Figure 4. (a) TEM analysis and (b) size measurement using ImageJ software of nano silica products formed without surfactants

Morphologically, the resulting product was also characterized using TEM (transmission electron microscope) and the characterization results are presented in Fig. 4. Figure 4 indicates that the shape of the resulting nano silica is spherical. Meanwhile, the resulting silica product has a size in nanometers or, more precisely, in the range of 1.46-2.24 nm (see Fig. 4(b)). However, Fig. 4(a) proves that even though the product size is in nanometer units, the nano silica product experiences an enormous agglomeration

phenomenon. In the synthesis of nanoparticles through the sol-gel method, the phenomenon of agglomeration is a common thing to occur. Therefore, this study will be continued to study the use of surfactants as an effort to prevent the agglomeration phenomenon.

3.2 Confirmation of CMC (Critical Micelle Concentration) for Nano silica Synthesis from Sludge Geothermal

In the synthesis of nanoparticles using surfactants, the confirmation of the CMC (critical micelle concentration) is a crucial step. This step has a significant role in forming particles with the size of the nanometer scale because it reduces the possibility of agglomeration. In this study of nano silica synthesis from geothermal sludge, the CMC was confirmed by observing two parameters, namely the surface tension and turbidity in the mixture solution between precursor solution and surfactant. The experimental results for confirming the CMC can be seen in Fig. 5. The graph depicted in Fig. 5 was then compared with Fig. 2 so that CMC could be confirmed. The CMC results of comparing both figures are presented in Table 4.

The synthesis of nano silica without surfactants will make the silica product easier to agglomerate as illustrated in Figure 6a. When the system is in the CMC, the surfactants will aggregate to form micelles. The formation of micelles occurs because the positive groups of surfactants will be adsorbed on the negatively charged nano silica surface to envelop and surround the Na_2SiO_3 solution. It causes SiO_2 (nano silica) formation (gelling stage) to occur in the template or micelles. Under this condition, the possibility of nano silica to agglomerate is low (see Figure 6c).

However, at surfactant concentrations below the CMC, the amount of surfactant present in the solution is not sufficient to protect the entire surface of the surfactant and form micelles. As a result, the formed nano silica still undergoes an agglomeration process between particles (see Fig. 6(b)).

Table 4. The CMC value in the synthesis of nano silica from geothermal sludge

Surfactant	Surfactant Concentration (wt%)
ABS	0.15
CTAB	0.05
SDS	0.50
PVP	1.00

Meanwhile, if the system is above the CMC, the surfactant will form a double layer in which the surfactant previously adsorbed on the silica surface will bind to other surfactants (see Fig. 6(d)).

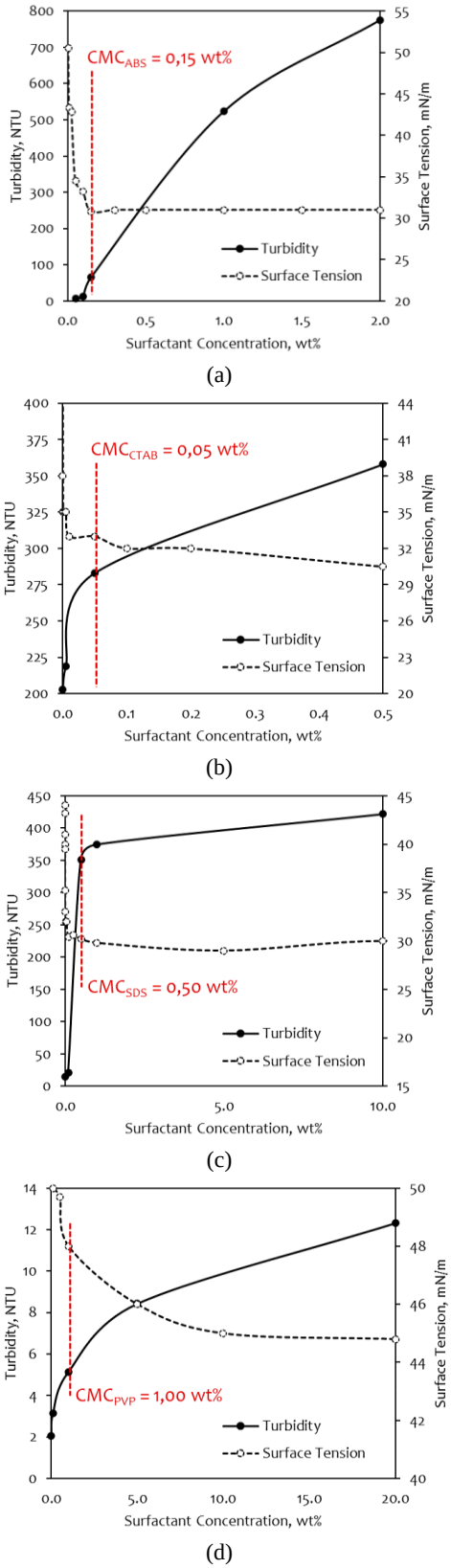


Figure 5. The value of turbidity and surface tension in the solution using surfactant (a) ABS, (b) CTAB, (c) SDS, and (d) PVP

It is due to the excessive amount of surfactant in the solution, which can cause the attractive

force (van der Waals force) between the surfactant and the nano silica surface to be weak so that the surfactant will be released from the nano silica so that the nano silica becomes unprotected and easily agglomerates [35].

Therefore, the surfactant concentration in CMC is the most optimal concentration to protect the nano silica particles from clumping or agglomeration.

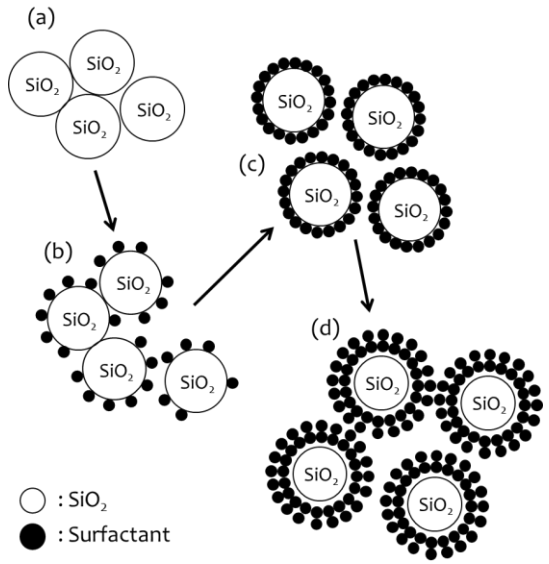


Figure 6. The illustration of the role of surfactants in the synthesis of nano silica (SiO_2)

3.3. Characterization Nano silica with the Addition of Surfactants

This section discusses the effect of using surfactants on the formed nano silica products. The first thing to be discussed is the composition of the nano silica product. The characterization results are presented in Fig. 7. The figure shows a significant decrease in SiO_2 levels in the products synthesized using surfactants. The purity of nano silica with surfactants ranged from 56.77-80.21 wt.%. This reduction in product purity occurs because there is Cl (chloride) based impurities detected in the product. Based on the characterization results, the composition of the Cl impurities ranged from 17.85 to 41.33 wt.%.

The nano silica product with this surfactant was further characterized, especially the compounds contained in this nano silica product. In particular, the determination of the mineral phase is aimed at identifying the impurity compounds in the product. The results of the characterization of this compound are presented in Fig. 8. In general, the formed nano silica products are still dominated by SiO_2 compounds in amorphous form. However, when observed in more detail in Figs. 8(b) to 8€, there are new peaks identified as NaCl (sodium chloride) crystals. It further confirms the test of the composition of the nano silica product in which there is a large amount of chloride-based impurities.

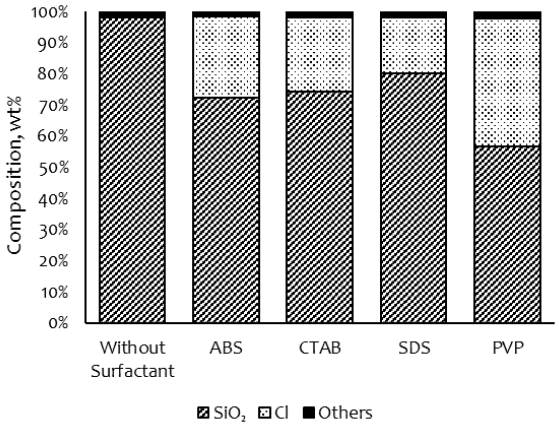


Figure 7. The composition of nano silica formed without and with surfactant

The formation of this NaCl salt is possible during the nano silica synthesis process using the sol-gel method.

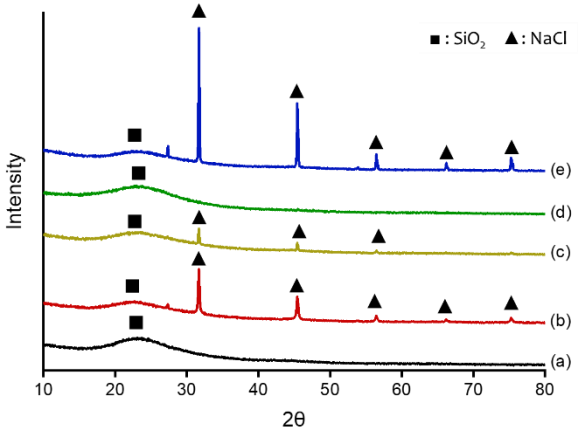


Figure 8. XRD results of nano silica formed (a) without surfactant, with surfactant (b) ABS, (c) CTAB, (d) SDS, and (e) PVP

It can be seen from the following mechanism and chemical reaction equation [22], [36]-[38].

Hydrolysis (basic catalyst)

$OH^- + \equiv Si–OR \rightarrow \equiv Si–OH + OR^-$ (1)

$OR^- + H_2O \rightarrow ROH + OH^-$ (2)

Condensation

$\equiv Si–OH + OH^- \leftrightarrow \equiv Si–O^- + H_2O$ (3)

$\equiv Si–OH + \equiv Si–O–R \rightarrow \equiv Si–O–Si\equiv + ROH$ (4)

$\equiv Si–OH + \equiv Si–O–H \rightarrow \equiv Si–O–Si\equiv + H_2O$ (5)

Gelling

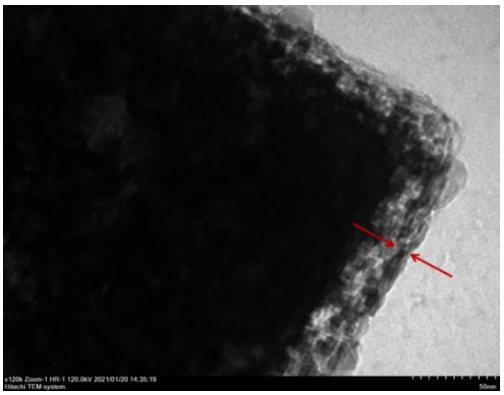
$Na_2SiO_3 + HX \rightarrow SiO_2 + NaX + H_2O$ (6)

Overall reaction (for this study):

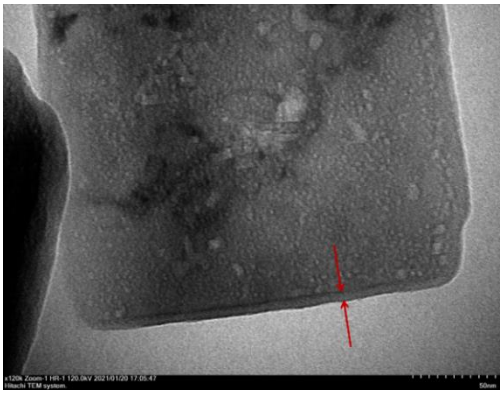
$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$ (7)

$Na_2SiO_3 + HCl \rightarrow SiO_2 + NaCl + H_2O$ (8)

In nano silica synthesis, surfactants will form micelles (or can be considered as templates) where the SiO_2 gel (solid) formation process occurs in the template. Therefore, based on equation (2), the formed NaCl is trapped in the template and a saturated condition, NaCl will crystallize into salt and be bound in nano silica products.



(a)



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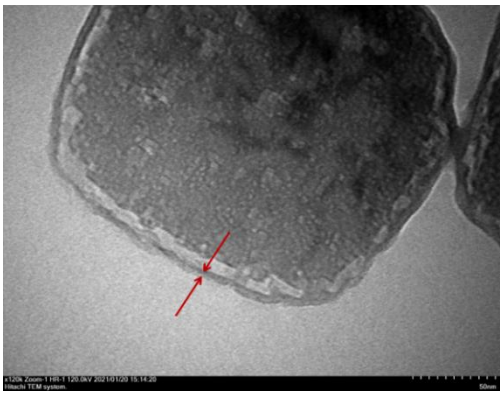

(c)

Figure 9. Surfactant template on nano silica formed with surfactant (a) ABS, (b) CTAB, and (c) SDS

The formation of these salts inevitably occurs in both the nano silica synthesis without and with surfactants. However, when seen in Figs. 7 and 8, the NaCl was not found in the nano silica product without surfactant. It happens because of the washing process that will dissolve the salt completely. The washing process with the same procedure was also carried out on the other four nano silica products (with surfactants). However, this washing process cannot completely dissolve the salt impurities. The salt is still trapped in the solid because there is still a template (miscellaneous) that surrounds the surface of the solid. The presence of this template makes it very difficult for water to diffuse into the solid and dissolve the salt.

The micelle formation of this surfactant causes the outer part of the template to be more hydrophobic due to the influence of the tail portion of the surfactant. It causes water, as a washing medium, to be retained on the outside of the template and form a thin layer [25], [39]. This concept applies to this study because it is supported by the results of characterization using the TEM (transmission electron microscope) instrument to show the morphology of the product and the template that is still left behind. The characterization results are presented in Fig. 9, and the template in question is indicated by arrows.

This study also characterize the size distribution of the formed particles and the results are presented in Fig. 10. Based on that figure, there are two peaks in the product produced using ABS and PVP surfactants (see Figs. 10(b) and 10€) and indicates that there are two different particle size distributions. One of the peaks proves that SiO_2 particles have a particle size (in bulk) in the range of 100-300 nm. When compared with the product without surfactant (see Fig. 10(a)), both surfactants were able to reduce the formation of agglomerates. Based on the tests carried out with PSA, quantitatively, the average diameter of the nano silica product particles changed from 4,822.9 nm (without surfactant) to 1,256.6 nm (for ABS) and 1,625.1 nm (for PVP). This shows that in this study, the use of the two surfactants was able to reduce the particle size between 66.30-73.95%.

Morphologically, the nano silica products synthesized with four types of surfactants were characterized using a TEM instrument. The characterization results are presented in Fig. 11. When compared to the nano silica product without surfactant (Fig. 4), the particle shape of the nano silica with surfactant also resembles a spherical shape. However, if seen in Figs. 11(a) to 11(c) (ABS, CTAB, and SDS surfactants), the interparticles formed are still agglomerated even though each particle is nanometer in size. However, the use of PVP (Fig. 10(d)) showed its success in preventing agglomeration between particles. The size of the nano silica synthesized

with PVP surfactant ranged from 2.01-3.65 nm (measurements were made using ImageJ software). The results obtained in this study are in line with the study conducted by Stanley and Nesaraj [26] where in their study, the use of PVP in the synthesis of nano silica from TEOS resulted in the smallest mean particle diameter compared to CTAB and SDS surfactants.

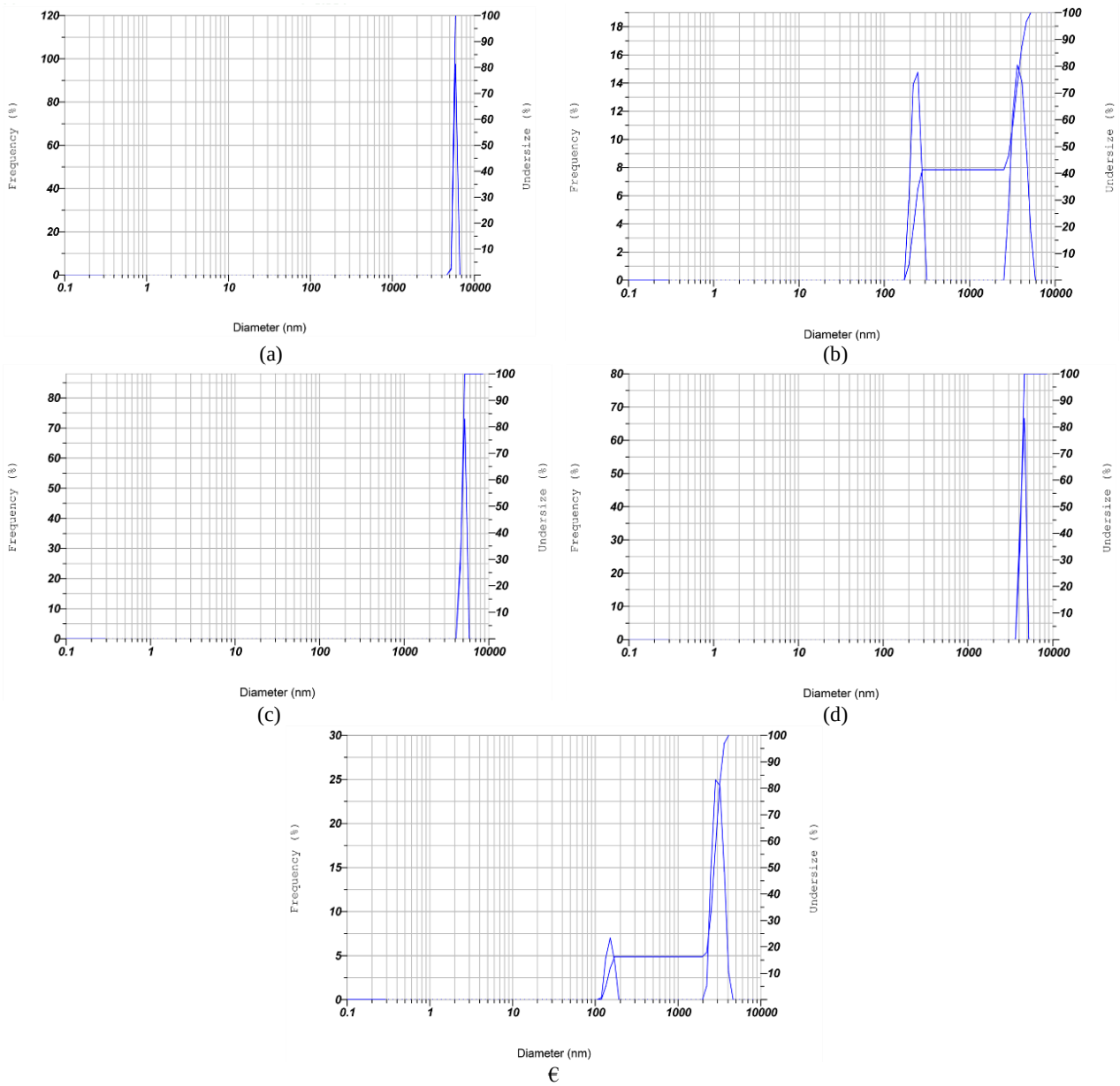

Figure 10. Size distribution of nano silica formed (a) without surfactant, with (b) ABS, (c) CTAB, (d) SDS, and (e) PVP

Based on particle size and degree of agglomeration, nano silica synthesized with PVP surfactant was the best product. However, based on the product composition, nano silica with PVP is the worst product due to salt impurities that cannot be removed entirely due to the presence of the template. It indicates that to get the best results, the template removal from the surfactant must be removed so that the product formed is not only small but also pure. This template can be removed using the calcination method [41].

To prove this point, this study tried to remove this PVP surfactant from the nano silica product through the calcination method. The calcination process was carried out at 400 °C for 3 hours. Then, the nano silica was characterized using the FTIR (fourier transform infrared spectroscopy) instrument to determine whether the surfactant functional groups were missing from the nano silica. The results of the characterization are presented in Fig. 12.

Figure 12 shows that the calcination process can reduce the PVP surfactant present in the nano silica product. It is indicated by a change in the functional groups of PVP surfactants such as CH_2 groups at 2,339.1 and 2,367.4 cm^{-1}; group C=N at 1,667.1 cm^{-1}; NH_2 group at 1,637.3 cm^{-1}; and the $N(CH_3)_2$ group at 517 and 805 cm^{-1}.

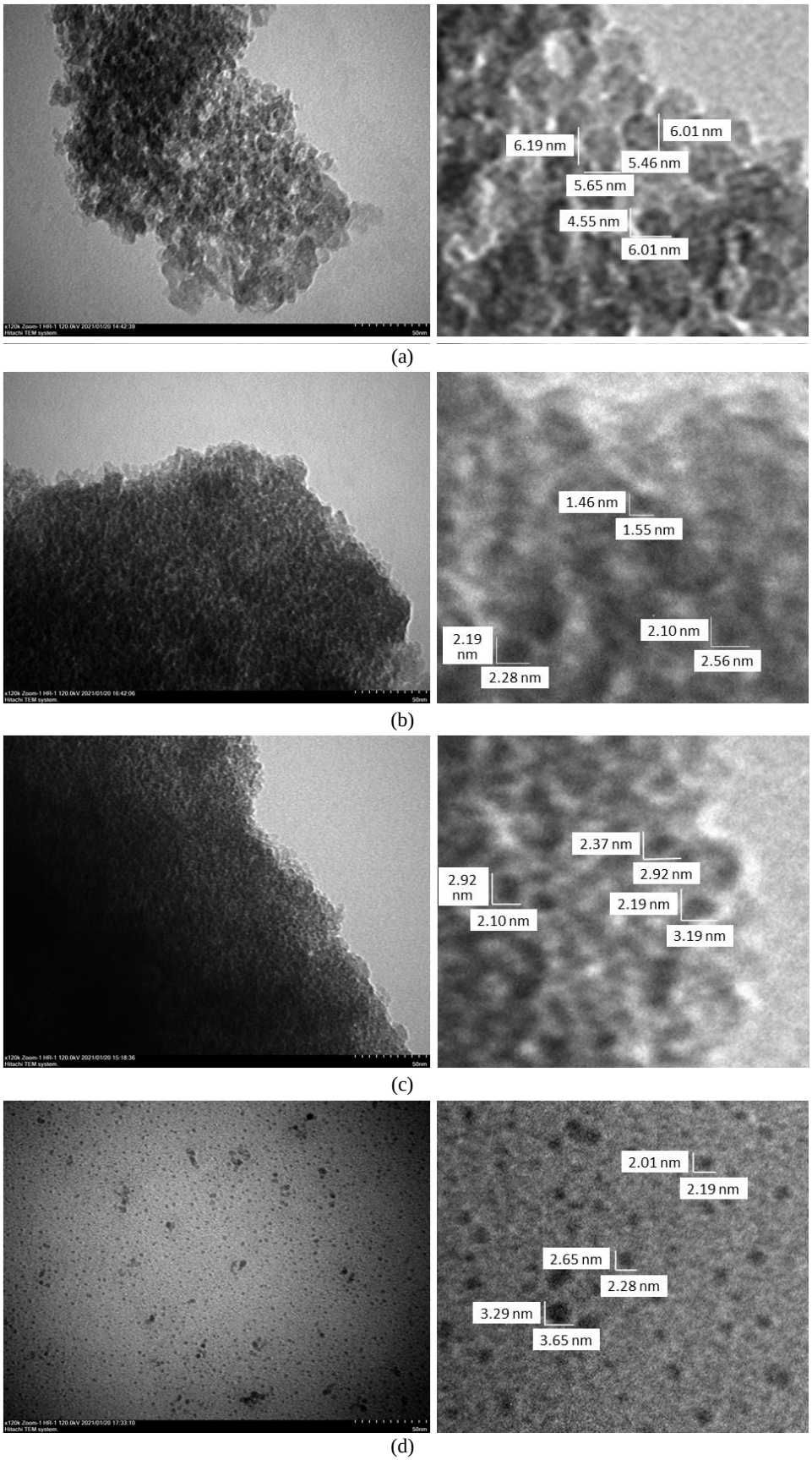

Figure 11. Morphology (left) and the size (right) of nano silica formed with (a) ABS, (b) CTAB, (c) SDS, and (d) PVP

Although in this study, the surfactant had not been completely removed, the results of the calcination process gave a positive pattern.

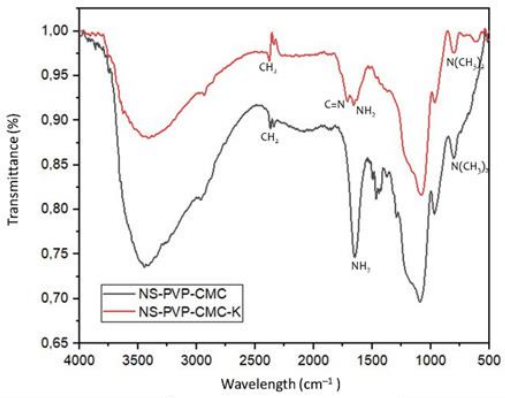

Figure 12. Results of FTIR characterization of PVP nano silica without calcination (black) and with calcination (red)

By changing the operating conditions of the calcination process, this PVP surfactant can be removed entirely.

4. CONCLUSION

This type of surfactant was studied in nano silica synthesis from geothermal sludge. Surfactants can prevent agglomeration between particles when it is used at the right surfactant concentration or usually called CMC (critical micelle concentration). This study showed that the CMC values of each surfactant studied were 0.15, 0.05, 0.50, and 1.00 wt% for ABS, CTAB, SDS, and PVP, respectively. Based on the characterization results of the nano silica composition, the product that gives the purest purity is nano silica without surfactant, where the purity of this product is 98.03%. Surfactants has been shown to reduce the possibility of agglomerated interparticle. A reduction in particle size prove it, and in this study, nano silica produced using PVP surfactant was able to reduce up to 66%. However, the product purity also decreased because the NaCl salt impurities were trapped in the surfactant template and made this salt challenging to remove. The results also showed that the type of surfactant that gave the best quality of nano silica products was PVP. The use of PVP resulted in the least agglomerated product, with particle sizes ranging from 2.01-3.65 nm.

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