The impact of solvent concentration on the characteristic of silica from rice husk ash using sol gel method

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Abstract. Synthesis of silica particle was conducted using the sol gel method from Aceh Besar rice husk ash. Sol gel method is an environmental-friendly and easy process to extract silica particles (SiO₂) that consists of two stages of hydrolysis and polycondensation. The aim of this research was to analyse the influence of variations in the solvent concentration (1 N, 1.5 N, 2 N, 2.5 N and 3 N) using the sol gel method on the characteristics of silica particle. The rice husk ash was refluxed using sodium hydroxide and the acidification process was using hydrochloric acid (HCl). The result of this study indicated that the highest yield in treatment was using 3 N NaOH, which was 39.66 percent. Based on XRD result, the silica was in the crystalline phase and had a particle size of 13,59-41,56 nm and functional groups of silanol (Si-OH) and siloxane (Si-O-Si). Based on the result of SEM characterization, uneven and agglomerated particle shapes were obtained.

1. Introduction
The nanotechnology expands continuously, and inspires researchers to put more effort in the nanotechnology field. The new technology is to use rice husk waste produced from rice milling. Rice husk ash is an agricultural residue that is abundant, cheap and able to produce silica and nano-silica when it was processed [1]. The properties of rice husks are more unique compared to other agricultural waste due to the high content of silica as well as the high porosity and high surface area which make them valuable for industrial use [2].

There are two methods in synthesizing rice husk ash silica, namely thermal treatment at a temperature of 500-1400 °C, which involves high temperatures and leaching using an acid or base solution, and being neutralized using an acid to make silica. The second method is an environmental-friendly method since it uses low energy and costs, CO₂ emissions from the Na₂CO₃ and SiO₂ reaction can be minimized more compared to the smelting method obtained during the process of making sodium silicate [3].

Due to their low price and simple process, nano-silica particles are used as raw materials in chemical processing, thickening fluids, improving surfactant efficiency, drug delivery systems, and fillers [4]. Nano-silica from palm kernel ash (PKSA) was extracted using the sol gel process [5].

Sol-gel technology has been used to manufacture biopolymer-silica hybrid materials with potential properties, stability of living matter and applicability in biomimetic processes. Preparation of this hybrid material is started by a regulated process of hydrolysis and condensation through the use of alkoxyisilane such as tetraethoxyisilane in alcohol and other polar solvents such as solution or colloid polymer suspension [6]. The sol-gel system consists of a silica hydrolysis process followed by a
polycondensation reaction cycle [7]. Rice husk ash (RHA) pre-treatment with acids or alkali raises SiO_2 (>98 percent). Alkali extraction is an economical method that is capable of synthesizing nano-silica or high-purity silica and can be commonly used [8]. The aim of this research was to investigate the impact of variations in the alkaline solvents concentration using the sol gel process on the yield and structure of silica.

2. Materials and methods
2.1. Materials
Rice husk ash was obtained from rice mills in Aceh Besar and the residue of burning rice husk was used as raw material. Rice husk ash was crushed with mortar and sieved with 80 mesh sieves. The materials used are hydrochloric acid (HCl) p.a, sodium hydroxide (NaOH), distillate water, whatman filter paper and pH meter.

2.2. Extraction of silica
Twenty grams of rice husk ash was added to a three-cock flask and 200 mL of NaOH was added with the concentration of 1 N, 1.5 N, 2 N, 2.5 N and 3 N respectively. The solution was refluxed for 1 hour at 80 °C and was stirred continuously. Silica dissolves and produces sodium silicate solution (Na_2SiO_3) at this point. The solution was filtered using the filter paper Whatman No. 41 and the solution was cooled down at room temperature. The filtrate was then titrated using 3 N HCl with regular stirring up to pH 7. Silica gel starts to settle when the pH is < 10 and white silica gel is obtained. The silica gel shaped was set aside for 18 hours, then filtered and heated in the oven at a temperature of 120 °C for 12 hours to extract moisture and create xerogel. The xerogel obtained washed using 100 ml of distilled water and stirred for 15 minutes at temperature of 80 °C. The next step was to filter the mixture and heat the precipitate obtained in the oven for 4 hours at a temperature of 120 °C. Silica was crushed with a mortar and then placed in a jar for the Fourier Transform Infrared (FTIR) test to analyse the functional groups and the X-ray diffraction (XRD) to determine the structure of the silica. Figure 1 Shows the process of extracting silica using the Sol gel method.

![Figure 1. Sol gel process.](image)

3. Results and discussion
3.1. Impact of NaOH concentration on silica extraction
Rice husk ash has been dissolved using NaOH solvent with different concentrations of 1 N, 1.5 N, 2 N, 2.5 N and 3 N. A compound formed between silica ash and NaOH becomes a solution of sodium silicate. The sodium silicate solution is reacted with HCl to produce silica gel. Extraction of silica from rice husk ash using the sol gel method was achieved as the following reaction.

\[
\text{Na}_2\text{SiO}_3 + 2 \text{HCl} \rightarrow \text{SiO}_2 + 2 \text{NaCl} + \text{H}_2\text{O} \quad (1)
\]

\[
\text{SiO}_2 + 2 \text{NaOH} \rightarrow \text{Na}_2\text{SiO}_3 + \text{H}_2\text{O} \quad (2)
\]
Reaction 1 shows that NaOH reacts with silica from rice husk ash and forms sodium silicate. Furthermore, sodium silicate forms silica acid when the pH becomes <10. The precipitate obtained is dried in an oven and the dry silica gel is crushed with a mortar. The yield of silica obtained from rice husk ash to silica powder following a chemical processes can be seen in Table 1. Treatment of variations in solvent concentration has been given in order to obtain the highest yield. It can be seen that there is an increase in yield at each degree of NaOH concentration. This is because more silica decays as the NaOH concentration increases [9].

| No. | Solvent (N) | Rice husk ash (gr) | Silica (gr) | Yield (%) |
|-----|-------------|--------------------|-------------|-----------|
| 1   | 1           | 20                 | 0.761       | 3.805     |
| 2   | 1.5         | 20                 | 0.879       | 4.395     |
| 3   | 2           | 20                 | 2.010       | 10.050    |
| 4   | 2.5         | 20                 | 4.999       | 24.999    |
| 5   | 3           | 20                 | 7.932       | 39.660    |

3.2. Characterisation of silica

3.2.1. Silica particle structure analysis using XRD (X-Ray Diffractometer). The x-ray diffractometer pattern results in Figure 2. illustrate the diffraction pattern of rice husk ash from Aceh Besar rice mills. The diffraction pattern formed at an angle indicated that the peaks of $2\theta = 21-23^\circ$ were indicated by the presence of silica compounds [10]. The diffraction pattern shows a broad, gently sloping hill. Sloping hills are silica with an amorphous structure and crystalline.

![Figure 2](image)

**Figure 2.** XRD diffraction pattern for rice husk ash.

XRD analysis was chosen to obtain a diffraction pattern that is useful for analysing the changes in crystal structure. Figure 3 shows the diffraction pattern of SiO$_2$ particle powder extracted using the sol gel process using different of NaOH concentrations.
Figures 3a, b, c, d, and e display the diffraction pattern coordinates about 20.93 °, 21.93 °, 28.54 °, 31.62 °, and 45.41 ° respectively. By using the Debye equation, the silica particle size was between 13.59 nm and 41.56 nm. From this figure, it can be seen that the higher the concentration of NaOH, the higher the diffraction pattern, and silica contains the crystal phase. Peak in the XRD pattern was caused in the chemical pre-treatment process, which was involved in the extraction process and was deposited in the gelatine phase [11]. Due to the small SiO$_2$ particle size, the XRD peaks are large, suggesting that a high percentage of these particles are formless in all samples and are in the crystal phase according to XRD data [12]. Based on the XRD characterization, it can be inferred that the concentration variance significantly affects the diffraction peaks and size silica.

3.2.2. Silica functional group analysis by Fourier Transfer Infra Red (FTIR). Silica of rice husk ash was analyzed in the 500-4000 cm$^{-1}$ wavelength range. The FTIR spectrum of rice husk ash is shown in Figure 4. The flexural vibration of the O–Si–O bond appeared at 474.49 cm$^{-1}$. The wide band about 3618.46 cm$^{-1}$ belongs to the vibrational stretching of O-H bonds in water molecules, bound by hydrogen bonds or O-H groups expressed in organic compounds [13].

Figure 5 shows the FTIR spectrum of industrial silica and rice husk ash added with the differences of NaOH concentration. The results show that chemical compositions of silica products obtained from various NaOH concentration was similar to each other, namely the silanol (Si-OH) and siloxane (Si-O-Si) groups. The FTIR spectrum in Figure 5 shows that the siloxane (Si-O-Si) group is present at wave numbers 457.29 cm$^{-1}$ and 1074.76 cm$^{-1}$. The wave number 806.87 reflects the formation of the Si-O group, and the wave band 3650.08 cm$^{-1}$ is the O-H silanol group due to the presence of water molecules adsorbed to silica, and part (a) indicates that industrial silica has the same functional group as silica particles from rice husk ash. The addition of NaOH concentration causes the range of O-H groups to be wider, where the higher the NaOH concentration the more OH groups found in the silica. The increase in O-H groups can affect the number silanol (Si-OH) groups in silica. As the silanol (Si-OH) increases the number of silica particles, it is easier to react with other substances [14].
3.2.3. Scanning electronic microscope analysis (SEM). Figure 6 shows the morphology of rice husk ash formed like hill. Rice husk ash, which had been burned at a temperature of 600 °C and had a structure that resembled hills without chemically impregnating [15]. The morphological characteristics of silica with different solvents are shown in Figure 7. Figure 7a-b reveals an irregular particle shape consisting of grouping and clustering patterns in Figure 7c-e to form clusters. The differences of solvent concentration did not affect the morphology of silica particles. Size of spherical silica nanoparticles varies between 10 nm and 60 nm, even after calcination and purification, the morphology of nano-silica remained unchanged [16]. This is due to the hygroscopic nature of silica (easy to absorb water) and the presence of a fairly diverse grain size with uneven surface distribution.
4. Conclusion
The NaOH concentration impacts the yield of silica particles which can be synthesized from rice husk ash. The higher solvent concentration, the higher the yield produced. The highest yield for dissolving 3 N NaOH solution was 39.66 percent. Silica was in the crystalline phase and has a particle size of 13.59-41.56 nm. The result of the FTIR analysis showed that functional groups of silanol (Si-OH) and siloxane (Si-O-Si) continued to increase with the NaOH concentration, making it easier for the silica particles to react with other substances. The general results of the particle shapes were uneven and consisted of spherical or agglomerated and structural clusters.

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