Yield and properties of nanobiosilica extracted from rice husk using technical grade chemicals: effect of extraction temperatures and times

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Abstract. Silica particles contained in rice husk (RH) are valuable materials with various industrial applications. However, simple and feasible techniques for large-scale production of silica nanoparticles from RH (nanobiosilica) remain challenging. This study aimed to investigate the influence of extraction temperatures and times on the yield and characteristics of nanobiosilica extracted from rice husk ash (RHA) using technical grade chemicals. The nanobiosilica was extracted from RHA using a simple sol-gel technique at three temperatures (25, 50, and 70 °C) for three extraction times (1, 2, and 3 h). The results showed that the extraction yield of nanobiosilica was significantly influenced by the extraction temperatures and times. The highest extraction yield (67.2%) was obtained at a temperature of 70 °C for 3 h. The use of technical grade chemicals affected the quality of nanobiosilica produced. The concentration of SiO2 in nanobiosilica from the best treatment was 86.21%. The presence of asymmetric Si-O-Si functional group was observed at 1101.68 cm⁻¹ wavelength. The nanobiosilica produced had particle sizes of 25.1-40.6 nm, bulk density of 0.67-0.81 g/mL, and averaged crystallinity degree of 58.50%. The best extraction technique developed may be used for large-production of nanobiosilica from RHA, depending on technical specifications required for further applications.

1. Introduction
Silica is a multifunctional material used in various industrial products, including glassware, chips, tires and rubber-based parts, cement, ceramics, cosmetics, electronics, paints, films, toothpaste, concrete, and fertilizers. Industrial applications and uses of silica are continuously increasing [1]. As industries and consumers are becoming aware of the importance of sustainable production and eco-friendly products, the use of silica from renewable sources is gaining more attention. Rice husk (RH) is rich in naturally occurring (biogenic) silica and this rice milling by-product is renewable, cheap, abundant, and underutilized in Indonesia.

Biogenic silica from RH is an excellent alternative to silica from non-renewable sources or synthetic processes. The biogenic silica is highly amorphous and reactive, exclusive in nanoporous layers, and could be produced at a relatively low cost [2-4]. Kalapathy [3] reported that the solubility
of silica from rice husk ash (RHA) was very low at pH <10, and increased significantly at pH> 10. Consequently, the extraction of silica from RHA is mostly carried out using alkaline solvent.

RH has a relatively high concentration of ash (14-25%) containing mostly silica (90-98%). Silica from RHA could be obtained through a sol-gel extraction process [5]. The extraction process is influenced by several factors, such as temperatures, extraction times, types of solvent (NaOH [3, 6-8], Na2CO3 [9], KOH [5]), solvent concentrations, RHA to solvent ratio [10], and stirring speed. These factors would determine the extraction yield and properties of silica particles produced. Extraction techniques of silica nanoparticles from RHA using analytical grade solvents have been well studied previously [9, 11-13]. However, those kinds of extraction techniques may result in a high production cost and thus they may not be suitable for large-scale production. Therefore, the use of technical grade chemicals in the extraction process could be a good solution to solve the problem. Nevertheless, the use of technical grade chemicals may lower the concentration of silica nanoparticles in the final product due to the presence of impurities [14]. The extraction techniques of silica nanoparticles from RHA using technical grade chemicals have not been reported widely and the extraction conditions should be optimized for the best possible results. The present study was the continuation of our previous study [10] and was aimed at investigating the yield and properties of silica nanoparticles extracted from RHA (nanobiosilica) using technical grade chemicals as influenced by the extraction temperatures and times.

2. Materials and Methods

2.1. Materials
Rice husk ash (RHA) was collected from a rice milling unit in Karawang District, West Java, Indonesia. The main chemicals used, including NaOH and HCl were of technical grade, purchased from PT Tjiwi Kimia and PT Brataco, respectively. Distilled water was used for all processes.

2.2. Silica extraction process
Nanobiosilica was extracted from RHA using the sol-gel method developed by Setyawan [10], Kalapathy [3, 8] and Handayani [15] with some modifications. RHA was soaked in hot water (80 °C) for 2 h, sieved and dried at 70 °C. About 25 g of dried RHA was mixed with 125 mL of 4% aqueous NaOH (w/v). RHA was extracted at three temperatures (25, 50, and 70 °C) for three times (1, 2, and 3 h). The sodium silicate solution was filtered and titrated with 3.65% aqueous HCl (w/v) under a constant stirring until pH 7 was achieved. The titration process produced silica gel, which was aged for 12 h and washed repeatedly with excessive amount of water to remove salts. The silica gel was dried at 70 °C for about 9 h, ground finely and the nanobiosilica particles produced were characterized.

2.3. Characterization
The quantitative expression of nanobiosilica color (Hunter L, a, and b values) were analyzed with a chromameter (Minolta, CR-3000). The values were used to calculate the whiteness index (WI) using the following equation reported by Mawarni [16].

\[
WI = 100 - ((100 - L)^2 + a^2 + b^2)^{1/2}
\]  

where \(L\), \(a\), and \(b\) are the hunter \(L\), \(a\), and \(b\) values.

Density measurement of nanobiosilica followed the method developed by Apriliani [17]. Moisture content was determined by the gravimetric method (AOAC) [18]. The morphological structures of nanobiosilica particles were analyzed by a scanning electron microscopy equipped with energy dispersive X-ray spectroscopy (SEM-EDX, EVO MA10, ZEISS, Germany). The X-ray diffraction (XRD) patterns were observed with a D8 Advance Discovery X-ray Diffractometer (Bruker, Germany) using Cu anode, LynxEye detector operated at 20 between 5° to 80°. Chemical composition of nanobiosilica was analyzed by an Axios mAX WDXRF X-Ray Fluorescence (XRF) Spectrometer.

Consequently, the extraction of silica from RHA is mostly carried out using alkaline solvent.
Identification of specific functional groups present in the product was examined with an IR Prestige-21 FTIR (Shimadzu, Japan).

2.4. Statistical analyses
The present study was conducted in a completely randomized design with three replicates. The differences among means were analyzed by Analysis of Variance (ANOVA). The least significant difference (LSD) test was performed to identify the populations whose means are statistically different. The statistical analyses were carried out using SPSS version 21.

3. Results and Discussions

3.1. Extraction yield of silica
Figure 1 shows the yields of silica extracted from RHA as influenced by extraction temperatures and times. It is shown that silica yield increased drastically when the extraction was conducted at temperature of above 50 °C for more than 2h. The highest yield of silica (67.2%) was obtained at an extraction temperature of 70 °C for 3 h. The result implies that high solubility of silica from RHA during the extraction process resulted in a high concentration of sodium silicate.

Production of silica from sodium silicate through the sol-gel method could be described by the following reactions as reported by Mittal [19]. The reaction of SiO\(_2\) in RHA with alkali solution is as follows:

\[
\text{SiO}_2 + 2\text{NaOH} \rightarrow \text{Na}_2\text{SiO}_3 + \text{H}_2\text{O}
\]

Then, the addition of HCl (acidification process) converted the sol solution into the gel form. This process occurred at pH 7 through the following reaction:

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

Sodium silicate solution adjusted to pH 7 could produce silica particles with a relatively high yield and large surface area as reported by Ayu [20].

![Figure 1](image-url)

**Figure 1.** Yields of silica extracted from RHA as influenced by extraction temperatures and times. *Different letters show significant differences among means (p<0.05).

3.2. Physicochemical properties of silica
Whiteness Index (WI) and moisture content of silica produced are shown in Figure 2. Silica color is classified as white when the WI more than 80 [17]. Figure 2a shows that silica produced from RHA by the extraction process with various extraction temperatures and times possessed high WI values (>90).
Silica with the highest WI value (97.86) was obtained following extraction at 70°C for 1 h. The result showed that longer extraction times produced lower WI values.

![Graph](image1)

**Figure 2.** Whiteness index (a) and moisture content (b) of silica extracted from RHA as influenced by extraction temperatures and times. *Different letters show significant differences among means (p<0.05).

The results showed that moisture content was significantly influenced by extraction temperatures and times (Figure 2b). In this case, moisture content increased with extraction temperatures and times. The correlation between Figure 2b and 2a implies that higher moisture content produced lower WI values. In other words, silica with a lower moisture content showed a brighter color. A relatively high moisture content could be due to a large amount of Si content in the silica powder binding more –OH and O during absorption of water vapor [21].

Figure 3 shows the density of silica extracted from RHA. Based on the density values, the obtained silica was categorized as amorphous silica. Japanese Industrial Standard [22] has classified that silica with density of 0.72 g/mL is considered as amorphous silica. On the other hand, Smallman [23] reported that crystalline silica has density between 2.23 and 2.65 g/mL. The density values of silica produced in the present study were 0.67-0.81 g/mL.

![Graph](image2)

**Figure 3.** Density of silica extracted from RHA as influenced by extraction temperatures and times. *Different letters show significant differences among means (p<0.05).

### 3.3. Structural features and composition of silica powders

Figure 4 presents SEM image and EDX spectrum of silica from RHA extracted at 70 °C for 3 h (the highest yield). It is observed that silica particles had spherical shapes and agglomerated structures with...
particle sizes of approximately 25.1–40.6 nm, which is then called nanobiosilica (Figure 4a). The spherical shape of silica was in agreement with the previous study reported by Ghorbani [24]. The EDX spectrum shows the elemental composition of nanobiosilica particles (Figure 4b). It is shown that Si was the major element contained in nanobiosilica. However, several impurities such as Na, K, Cl, and C was also observed in the EDX spectrum. The presence of impurities might come from the technical grade chemicals or might be due to insufficient washing process prior to drying.

![SEM image and EDX spectrum of silica extracted from RHA.](image)

**Figure 4.** SEM image (a) and EDX spectrum (b) of silica extracted from RHA.

Table 1 shows the chemical composition of nanobiosilica from the best extraction treatment analyzed by XRF. The SiO$_2$ content of nanobiosilica powder produced from RHA was 86.21 %. Na and Cl were the highest contaminants in the silica powder (7.24 % and 4.47 %, respectively). The result was in line with the EDX spectrum above and the previous study reported by Setyawan [10]. For fertilizer application, the presence of Na and Cl in silica products is not expected because they may reduce the ability of plant roots to absorb potassium [25].

| Compounds | Composition (%) |
|-----------|-----------------|
| SiO$_2$   | 86.21           |
| Na$_2$O   | 7.24            |
| K$_2$O    | 1.33            |
| CaO       | 0.26            |
| MgO       | 0.05            |
| Fe$_2$O$_3$| 0.04            |
| Cl        | 4.47            |

The XRD pattern of nanobiosilica is shown in Figure 5. A typical amorphous silica structure was observed. This was indicated with the presence of a broad peak at $2\theta = 22^\circ$ and crystallinity degree of 58.50%. The similar XRD pattern of nanobiosilica was also reported by Setyawan [10] and Rafiee [26]. Production of the typical amorphous silica from RHA was also in agreement with the previous study reported by Bakar [27]. The RHA used in this study was ashed at 600 °C. Generally, the crystallization process of silica starts to occur at 900 °C. The high sharp peak at $2\theta = 32^\circ$ could represent impurities, mainly Na, as confirmed by the chemical composition shown in Table 1.
Figure 5. The XRD pattern of nanobiosilica extracted from RHA.

Figure 6 depicts FTIR spectrum of nanobiosilica extracted from RHA. The result showed the presence of several functional groups in the sample. Si-O-Si bonds in silica were around 1095 to 474 cm\(^{-1}\) absorption band. The absorption bands at 3427.5 and 1639.45 cm\(^{-1}\) could be due to the –OH stretching vibration of the silanol or adsorbed water molecules and bending vibration of the trapped water, respectively (Figure 5). The peaks at 1101.68; 797.42; and 468.25 cm\(^{-1}\) could be due to the asymmetric (siloxane), symmetric (silanol) and the bending modes of SiO\(_2\), respectively. The results were in agreement with the previous study reported by Adam et al. [11].

4. Conclusion
In this study, an attempt has been made to use rice husk, a cheap, plentiful, by-product material, to produce silica nanoparticles, called nanobiosilica. The technical grade chemicals used and the best sol–gel method developed were able to produce a relatively high yield amorphous nanobiosilica powder (67.2%) with purity reaching 86.21%, particle sizes ranging from 25.1-40.6 nm, and crystallinity degree of 58.50%. The nanobiosilica obtained from RHA had high WI values (>90) and density values of 0.67-0.81 g/mL. The presence of asymmetric Si-O-Si functional group in the nanobiosilica product was confirmed at 1101.68 cm\(^{-1}\) wavelength.
Acknowledgments
Authors appreciate Aniva Rizkia Dewi from Bogor Agricultural University for her technical contribution to this research work. We thank Indonesian Agency for Agricultural Research and Development for the provision of research fund supporting this work.

References
[1] Chun J and Lee J H 2020 Sustainability, 12, 24. p. 10683.
[2] Athinarayanan J Periasamy V S Alhazmi M Alatiah K A and Alshatwi A A 2015 Ceram. Int. 41 1, Part A p 275–281.
[3] Kalapathy U Proctor a. and Shultz J 2002 Bioresour Technol. 85 3 p 285–289.
[4] Fernandes I J et al., 2017 Mater. Res. 20 p 512–518.
[5] Sembiring S Simanjuntak W Manurung P Asmi D and Low I M 2014 Ceram. Int. 40 5 p. 7067–7072.
[6] Qu Y et al., 2010 Bioresour Technol 101 21 p 8402–8405.
[7] Premaratne W A P J Priyadarshana M G I Gunawardena S H P and De Alwis A A P 2013 J. Sci. Univ. Kelaniya 8 p 33–48.
[8] Kalapathy U Proctor A and Shultz J 2000 Bioresour Technol 73 p. 257–262.
[9] An D Guo Y Zhu Y and Wang Z, 2010 Chem Eng J.162 2 p 509–514.
[10] Setyawan N Hoerudin and Wulanawati A,2019 Conf Ser Earth Environ Sci. 309, 1.
[11] Adam F Chew T S and Andas J 2011 J. Sol-Gel Sci. Technol 59, 3 p. 580–583.
[12] Gu S Zhou J Luo Z Wang Q and Ni M 2013 Ind Crops Prod 50 p 540–549.
[13] Ma X et al., 2012 Powder Technol 217 p. 497–501.
[14] Umeda J Imai H and Kondoh K 2009 JWRI 38, 2 p. 13–18.
[15] Handayani P A Nurjanah E and Rengga W D P 2014 J. Bahan Alam Terbarukan 3, 2 p. 55–59.
[16] Mawarni R T and Widjanarko S B 2015 J. Pangan dan Agroindustri 3, 2 p. 571–581.
[17] Apriliani N 2016 Bogor (ID): Bogor Agricultural University.
[18] AOAC 2007 Official methods of analysis of AOAC International 18th ed. Gaithersburg, Md.: AOAC International.
[19] Mittal D, 1997 Silica from ash Resonance 2, 7 p. 64–66.
[20] Ayu A M Wardhani S and Darjito D 2013 J. Ilmu Kim. Univ. Brawijaya 2, 2 p. pp.517-523.
[21] Fahmi H and Nurfalah A L 2016 J. Iptek Terap. 10, 3 p. 176–182.
[22] [JIS] Japanese Industrial Standard, 1977, Silicagel Desiccants for Packaging (Foreign Standard). Japan (JP) : Japanese Standards Association.
[23] Smallman R E and Bishop R J 2003 Metalurgi fisik modern dan rekayasa material Jakarta: Erlangga.
[24] Ghorbani F Sanati A M and Maleki M 2015 Environ. Stud. Persian Gulf 2, 1 p. 56–65.
[25] Giri B Kapoor R and Mukerji K G, 2007 Microb. Ecol. 54, 4 p. 753–760.
[26] Rafiee E Shahebrahimi S Fayzi M and Shaterzadeh M 2012 Int. Nano Lett. 2, 1 p. 29.
[27] Bakar R A Yahya R and Gun S N 2016 Procedia Chem. 19 p. 189–195.