Simple extraction of silica nanoparticles from rice husk using technical grade solvent: effect of volume and concentration

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Abstract. One of the main components of rice husk ash (RHA) is silica, which can be used as raw material for fertilizer. The study examined influences of various volume and concentration on silica extraction. The silica was extracted using a technical alkaline grade solvent (NaOH) with a variation in volume/ the ratio of RHA to the amount of solvents (1: 4, 1: 5, and 1: 6) and the solvent concentration (0.50, 0.75 and 1 N). The highest average yield was found in the concentration of 1 N solvent with the ratio of RHA to the number of solvents 1: 6 is 62.83%. Based on the physical characteristics of silica from RHA which include whiteness (93.24-96.66%), moisture content (0.49-2.81%), and density (0.56-0.95 g / mL) indicates that the use of technical alkaline solvents tends to decrease the purity of the proven silica also with the presence of major contaminants such as Na and Cl and other elements through SEM-EDX, XRF, and XRD test. In saline soils, the presence of contaminants in silica with an amorphous phase (2θ = 22.29°) especially Na and Cl may have a negative effect if used as raw material for fertilizers.

1. Introduction
Paddy is one of the main staple food plants in Indonesia which besides producing rice also resulting in rice husk (RH) as by-product. This agricultural by-product reaches 20% of the weight of unhulled rice [1]. In 2017, Indonesia produced 80 million tons of dry-mill rice/year and there were approximately 16 million tons/ year of RH. The composition of RH depends on geographical conditions, rice varieties, and the type of fertilizer [2]. The burning of rice husks will convert all organic components into 20% carbon dioxide, air, and ash. The main component in rice husk ash (RHA) is silica as much as 90-98% [3] and Indonesia is able to produce 3.2 million tonnes/ year of silica from RHA.

Naturally, silica in rice husk ash is amorphous and has a large surface area, but when combustion above 650 °C will change the silica phase to crystalline [4]. Amorphous silica can be used as fertilizer [5]. Various types of silica fertilizers are potassium silicate slag, calcium silicate hydrate, liquid potassium silicate, and silica gel [6]. The use of silica-based materials in industrial fields is adsorbents, filter media, glass industry, refractory industry, ceramic materials and raw materials for the production of silicates, silicones and alloys [7]. Therefore, RH can be used as raw materials of bio-silica that are very useful and can increase the added value.
Silica from rice husk ash can be obtained easily and at a relatively low cost by the extraction process. The solubility of silica increases sharply at pH more than ten [8]. Therefore, the extraction of silica from rice husk ash (RHA) is carried out using alkaline solvents. In addition, the use of alkaline solvents has advantages such as making it easy, can be stored for a long time, has good adsorption and ion exchange properties, and its characteristics can be adjusted depending on the combustion temperature (amorphous, quartz, cristobalite, and tridimite) [9]. Commonly used alkaline solutions are potassium hydroxide (KOH) and sodium hydroxide (NaOH).

The extraction process is affected by several factors such as solvent concentration and the ratio of the solvent to the RHA. Supitcha et al. [10] reported that silica extraction with a ratio of RHA and 0.5 N NaOH (analytical grade) of 1 : 6, at 60ºC resulted in a yield of 54.95%. The same ratio of RHA and 1 N NaOH (analytical grade) at 80 ºC produced a result of 91.59% as reported by Handayani et al. [11]. It can be concluded that the higher NaOH concentration and extraction temperature, the more silica will be obtained.

The use of NaOH analytical grade solvent and high concentration in the silica extraction process will have an impact on the high cost of silica production. Therefore, an alternative solution is needed to reduce the cost of silica production by using technical grade solvents. However, the use of this solvent will directly reduce the level of purity of silica. Thus, optimization process by reducing of concentration and amount of solvents against RHA to increase the purity of silica is needed. The study aimed to examine the influences of various volume and concentration on silica extraction as raw material for fertilizer.

2. Materials and methods

2.1. Materials
The rice husk asks (RHA) was from Karawang District, West Java, Indonesia. All chemicals included sodium hydroxide (NaOH) and hydrochloric acid (HCl) were technical grade solvent purchased from PT Tjiwi Kimia and PT Brataco respectively. Distilled water was applied for all extraction and treatment process.

2.2. Silica extraction
Silica nanoparticle was extracted from RHA adapting the method of Kalapathy [12] and Handayani et al. [11]. 25 g of the RHA was mixed with 0.50 N, 0.75 N, and 1 N NaOH solution in the various ratio: 1:4, 1:5, and 1:6. The mixture was then heated at 80ºC with constant stirring for 1 h to dissolve the silica and produce a sodium silicate solution. Solutions were filtered through Whatman no. 41 ash less filter paper. The filtrate was allowed to cool to room temperature and titrated with 1 N HCl with constant stirring to pH 7. The silica gels formed were aged for 24 h. Distilled water was added to gels and then the gels were broken to make a slurry. Slurries were then washed repeatedly (4 times). The gels were transferred into a beaker and dried at 70ºC for 22 h to produce xerogels. Selected silica xerogel samples were ground and characterized.

2.3. Characterization
The moisture content of the silica was determined using an air oven method (AOAC, 2007). Colour profiles (Hunter L, a, and b values) were measured using a Chroma meter (Minolta, CR-3000). Whiteness index (WI) was calculated following equation reported by Mawarni and Widjanarko (2015) [13]. The density of silica was measured by the method of Apriliani [14]. The highest yield of silica was then further analyzed included Fourier Transform Infrared (FTIR), scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX), X-ray diffraction (XRD), and X-ray fluorescence (XRF).
2.4. Statistical analyses

All the treatments were performed in triplicate in a completely randomized design. Data were analyzed by ANOVA and means were separated by the least significant difference when significant F (P<0.05) values were observed (SPSS version 22).

3. Results and discussion

3.1. Composition of RHA

The composition of minerals in RHA is shown in Table 1. The gross weight of silicon dioxide (SiO$_2$) in the RHA was 73.85 %, and the residual was other impurities. RHA was produced by burning at 600° C to produce amorphous silica followed procedure developed by Ghorbani et al. [15]. This process obtained a yield of RHA 21.14%. The combustion changed rice husk became silicon dioxide followed chemical reaction below.

$$\text{C, H, Si, O}_2 \rightarrow \text{CO}_2 (g) + \text{H}_2\text{O} (g) + \text{SiO}_2 (s)$$ [9]

| Composition | Value (%) |
|-------------|-----------|
| SiO$_2$     | 73.85     |
| Na$_2$O     | 0.07      |
| K$_2$O      | 2.78      |
| CaO         | 0.61      |
| MgO         | 0.64      |
| Fe$_2$O$_3$ | 0.40      |
| Cl          | 0.29      |
| Al$_2$O$_3$ | 0.53      |
| MnO$_2$     | 0.14      |
| P$_2$O$_5$  | 1.72      |

3.2. Silica extraction yield

The yield of silica was shown in Figure 1. Consistent with the report of Rhevi et al. (2014) [1], the result showed that the yield of silica increased with increasing concentration and amount of alkaline solvents. The amount of NaOH also affected the contact area between the RHA and the solvent. The more solvent, the higher contact area, so that distribution of solvents to rice husk ash will be even higher. The even distribution of solvents to RHA will increase the formation of Na$_2$SiO$_3$ and the yield of obtained silica.

![Figure 1. Yield of silica. Values are mean ± SD (n=3).](image-url)
The highest yield of silica (62.83%) was obtained from the extraction process using 1N alkali technical grade solvent with a ratio of RHA and solvent of 1: 6. The percentage of yield decreased of 28.76% compared to yield of silica which carried out from the extraction process using pure solvents at the same concentration and ratio as reported by Handayani et al. [11]. The use of technical solvents effected decreasing the yield of silica.

3.3. Physicochemical properties of silica

The highest whiteness index of silica (96.66) was produced from the extraction process using 1 N NaOH with ratio RHA and solvent of 1: 6 (Figure 2). The higher concentration and amount of solvent caused the higher whiteness index. This is contrary to the facts related to the use of technical grade solvents. The higher concentration and amount of technical alkali solvents increase contaminants present in silica caused the lower whiteness index. The result showed increasing in concentration and the amount of alkaline solvents were not directly proportional to the amount of contaminant in silica.

![Figure 2. Whiteness index of silica. *Different letters showed significant differences (p=0.05). Values are mean ± SD (n=3).](image)

Moisture content of silica obtained from all treatments was between 0.49-2.81 % (Figure 3). The moisture content in the treatment of 0.50 N NaOH for all ratios did not meet the JIS Z0701 standard [16] for commercial silica (max 2%). An increasing in whiteness index of silica was also followed by a decreasing in moisture content (Figure 3). The use of lower solvent concentration caused increasing of the moisture content of silica. This parameter was also caused by the breaking of a bond of water and silanol groups and the results of condensation of silanol groups. The process of water release in silica followed reaction below [17].

![Figure 3. Water release in silica](image)

The moisture content of silica must be in low level because high value can reduce adsorption strength of silica to phosphorus. Silica will bind the phosphorus in the soil so leaching of this element decreases approximately 40-90% [18].
Whiteness index and moisture content affected density of silica. The parameter of silica produced in this study was 0.56-0.95 g/mL (Figure 4). The results were higher than the density of silica obtained by Apriliani [14] which extracted from RHA using analytical grade solvent (0.49-0.59 g/mL). Following the JIS Z0701 standard [16] for commercial silica (max 0.7200 g/mL), there were only three silica densities meet, namely silica produce using 0.50 N NaOH with a ratio RHA and solvent of 1:6 and 1 N NaOH with a ratio RHA and solvent of 1:4 and 1:5 (Figure 4). This result showed that the use of technical grade solvent producing contaminant effected to the density of silica.

3.4. Structural features of silica from RHA
Extraction process using 1 N NaOH with ratio RHA and solvent of 1:6 produced the highest yield of silica powder. This sample product was then further analyzed included Fourier Transform Infrared (FTIR), scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX), X-ray diffraction (XRD), and X-ray fluorescence (XRF).

Table 2. Mineral content of silica powders prepared from RHA

| Composition | Value (%) |
|-------------|-----------|
| SiO₂        | 86.17     |
| Na₂O        | 5.82      |
| K₂O         | 0.22      |
| CaO         | 0.62      |
| MgO         | 0.10      |
| Fe₂O₃       | 0.09      |
| Cl           | 6.43      |
| Al₂O₃       | 0.17      |
| P₂O₅        | 0.03      |

Data in Table 2 showed that the metal composition of the as-obtained silica powders by XRF measurement. The silica content of the powders produced from RHA was 86.17%. Two highest contaminants were contained in the silica (Na and Cl). The presence of contaminants in silica especially Na and Cl can reduce the ability of plant root to absorb potassium [19].

The X-ray diffraction pattern of silica powders was shown in Figure 5. It was a typical amorphous structure, and the absence of any ordered crystalline structure indicated relative high disordered structure of silica. The XRD patterns from this study showed similar patterns as silica produced by Apriliani (2016) [14], Abu Bakar et al. [20] and Rafiee et al. [21]. The broad diffused peaks with maximum intensity at 2θ = 22.29° are observed, indicating the amorphous nature of silica. Abu Bakar et al. [20] reported that the crystallization transformation of silica starts to occur at 900°C.
Amorphous silica properties are suitable for fertilizer because it is more easily absorbed by plants (90% absorbed) and then will accumulate in the cell wall and cuticle forms the structure of Si-cellulose (silica layer). The silica layer will increase leaves strength and absorption of sunlight and the rate of photosynthesis [22, 23].

Figure 6. X-ray diffraction pattern of silica produced from RHA

The silica powders were confirmed by FT-IR examination in Figure 6. The absorption bands at 3441.08 and 1649 cm\(^{-1}\) were due to the H–O–H stretching and bending modes of the adsorbed water, respectively. The peaks at 1086.10; 779.49; and 468.41 cm\(^{-1}\) were due to the asymmetric, symmetric and the bending modes of SiO\(_2\) respectively.

Figure 7. Fourier transform infrared spectra of silica produced from RHA

Figure 7. showed morphology and particle size of silica extracted from RHA. The results described an uniform and slight agglomerated structure with the size of approximately 49-91 nm. Silica which is nanometer size has advantages as fertilizer because it will be more easily absorbed by plant roots, more reactive, and more efficient to increase productivity [24].
4. Conclusions
   a. The highest yield of silica (62.83%) resulted in an extraction process using 1N NaOH technical grade solvent with a ratio RHA and solvent of 1:6.
   b. Silica produced from RHA had whiteness index 93.24-96.66, water content 0.49-2.81%, and density 0.56-0.95 g/mL.
   c. Obtained silica was categorized as a typical amorphous structure. In saline soils, contaminants in the amorphous phase of silica (2θ = 22.29°), especially Na and Cl may have negative impacts if used as raw materials of fertilizer.

5. References

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Acknowledgments
Authors appreciate to Sintya Dico Fabriciany from Bogor Agricultural University for assisting the work at the laboratory of ICAPRD. We also thanks to IAARD for budgeting the research year 2017.