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Research Article

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Preparation and Characterization of Silica Nanoparticles from Rice Straw Ash and its Application as Fertilizer

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ABSTRACT

This study was carried out to investigate the characteristics of silica extracted from rice straw obtained from rice farming region of Pekalongan. The silica was obtained using sol-gel method, which involves extraction of silica using alkalis solution and gelation of the silica using acid solution. It was found that the highest yield was obtained from the extraction using 5% KOH solution with the extraction time of 60 minutes, and gelation pH of 7.0. The SiO_2 chemical composition was confirmed by EDS and FTIR and the amorphous by XRD. SEM analysis indicates the existence of various particle sizes distributed irregularly, which reflects that homogeneous sample has not been achieved in this study. Nanosilica powders with a 45,3869 nm average poresize and have specific surface (94,761 m^2/g). Silica nanoparticle fertilizer applied to various plants such as peanuts, tomato and soybean. Based on the research can be seen that the plant height and number of leaves of plants with nanosilica fertilizers more show very rapid growth.

Keywords: Rice straw; Silica nanoparticles; Fertilizer

INTRODUCTION

Nutrient is needed by plants and nitrogen, phosphorus and potassium (NPK) are included in the soil nutrient. If the nutrient deficiency, especially NPK, occurred to the plant, and then the quality and quantity of peanuts decreased. NPK in the soil were limited and they would decrease gradually because of plant growth, harvesting, washing, vaporization and erosion. Fertilization was needed to fulfill the deficiency of NPK. The suitable fertilizer to fulfill those nutrient was Phonska that contain 15% N, 15% P and 15% K [1]. Silica was included nutrient that never added to soil. The best solution could be done to produce silica nanoparticle was the reuse of agricultural waste i.e., rice straw. Rice straw is torched after the rice product is collected, which is due to the increase in soil nutrition elements for the next year of cultivation, as well as removing the necessity for straw storage. In the developed countries however, in the developed countries the concept of "waste material" is no longer valid, as all waste materials are considered as sources for the production of new products and increasing added value. Studies have proven that rice straw, the waste material of agricultural processes, may be a potential candidate. But a major problem is the pile up of rice straw ash (RSA) which is rich in silica. The content of silica collected in rice straw is much greater than other plants as the organic constitutes of rice straw as follows: Cellulose: 32-47%, Hemi cellulose:1927%, Lignin: 5-24%, Ash: 13-20% [2]. Rice straw ash has around 60% of silica. Santos et al. which, of course, is reported to be different in different climatic conditions, depending on the type of soil, the season of rice cultivation, weather conditions and geography [3].

The advantages of silica source from agricultural waste than mined source silica were (1) value added to agricultural waste, (2) its structure were amorph, reactive and easy to transformed to cristobalite, so it was suitable to used as starting material in silica production and (3) easy to separated from impurities; from the separation we got silica with high purity.The use of nanoparticle silica were expected to have significant advantages than a regular silica.

This research could give information about nanotechnology application especially silica nanoparticle in Indonesian agriculture.

EXPERIMENTAL METHODS

Materials

Rice straw from Pekalongan City were used as silica sources. Potassium hydroxide, hydrochloric acid, sulfuric acid, ammonium hydroxide and aquadest were used in this research. Hot plate, stirer, burner, laboratory glassware, oven, XRD, FTIR, SAA, TGA, and SEM-EDX were instruments that we were used.

Rice Straw Preparation

Rice straw were cleaned from impurities and dried under the sunlight. After dried, rice straw were heated at 700°C for 4 hours until the ash formed. Rice straw ash crushed and sifted 200 mesh.

Silica Extraction from Rice Straw Ash

About 20 g of rice straw ash were dissolved in 160 mL potassium hydroxide 3 M; 3.5 M and 4 M. The solution were covered then be heated; stired at 85°C for 3 h. Solution were filtered. Residu were washed with 40 ml aquadest. After it was cold at room temperature, the solution were added hydrochloric acid 1 M slowly while it were stirred; til neutral. The result were kept at room temperature for 3.5 h. Solution were filtered and got residu. Residu were dried [4]. Pure silica reflucted using hydrochloric acid 6 M for 4 h then washed until neutral. Solution were disolved in sodium hydroxide 2.5 N then stired for 6 h. Sulfuric acid was added until pH 8. Residu were washed until neutral. The result were dried [5].

Characterization

To determine the structure, X-ray diffraction (XRD) experiments were performedusing Phillips PW1800 diffractometer. Phillips PW1480 apparatus was also used to determine the chemical composition of RSA and purity of silica synthesized through Energy-dispersive X-ray spectroscopy (EDS). In order to study the morphology of silica with scanning electron microscopy (SEM). To study stability thermal of silica use a thermogravimetric analyzer (TGA-50, Shimadzu, Japan), respectively. Samples were heated at a ramping rate of 10°C/min from 30 to 600°C in air flowing at a 30 mL/min rate. Finally, BET test was performed to determine the specific surface area.

RESULTS AND DISCUSSION

Characterization with FTIR

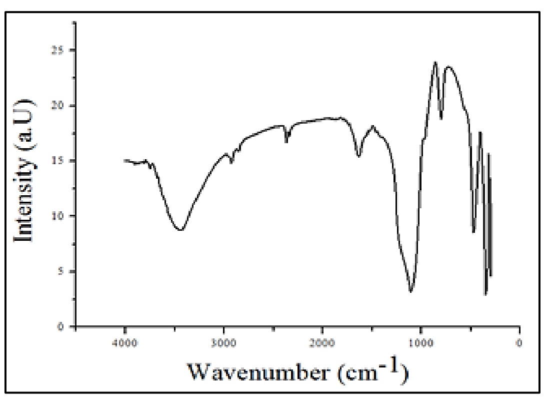

Figure 1: Silica FTIR spectrum were got from rice straw

Silica were got from rice straw with extraction, were analized with FTIR and Figure 1 had shown the spectrum. Main peak at wave number 3448.72 cm^{-1} were showed the typical for stretching vibration for –OH (Hydroxyl group). Therefore, silica were used as sample, had hydroxyl group. It showed Si-OH bond or silanol [6-8]. Although the vibration were not only silanol bond but also –OH from water which could not be ignored [9]. Second peak at 1103.28 cm^{-1} showed silica group. It showed siloxane group Si-O-Si. Siloxane group were made sure with peak at 470.63 cm^{-1} [6,10] and deformation of Si-O bond for SiO_4 [11,12]. Other peak with high intensity was shown at 1635.64 cm^{-1}. It showed carbonyl vibrational stretch from hemicellulose. It might be disolved when extractrion process and adsorbed by silica also H-O-H bond. Other weak peak were shown at 972.12 cm^{-1}, that showed bond between Si-O and metal [13,14].

Characterization with XRD (X-Ray Diffraction)

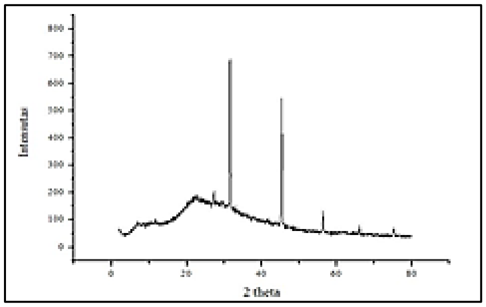

Figure 2: Silica from rice

Silica crystal structure analysis were done by using X-ray difraction method. Detected phase in next chromatogram were identified by ploting method using Origin software. Figure 2 showed the spectrum. The resulting pattern showed amorphous silica, with additional phase at 2θ=31.46 and 50.16. There was no phase that appeared at 2θ=22. Based on the table, main peak from the cristobalite difractogram and quartz polymorphy appeared as companion phase and polymorph tridimit did not appear. This result was similar with previous research. Standard nanosilica in Figure 3 showed strong board peaks at 22.14 which is characteristic of amorphous silica [4,15]. Crystal size of silica nanoparticle- based the equation was 45,3869 nm.

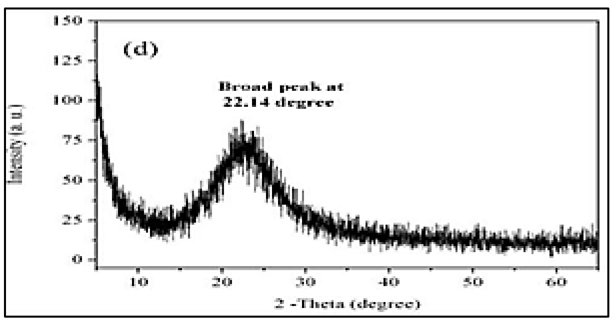

Figure 3: Nanosilica standard straw straw

Morphology and Chemical Components

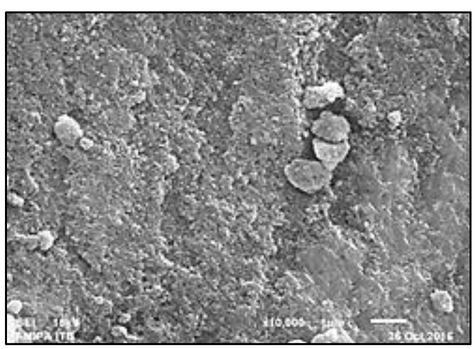

Figure 4: Silica morphology magnifications 10000x

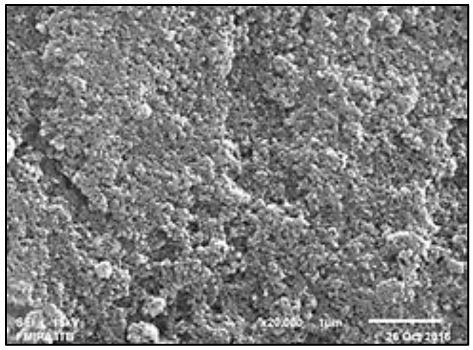

Figure 5: Silica morphology magnifications 20000x

Silica surface structure characteristic was shown in Figures 4 and 5. Figure 4 showed unregulated surface and the structural characteristics of the silica surface studied and addressed by the SEM results in Figure 4 for magnification of 10000x and Figure 5 for magnification 20000x. From Figure 4 it was clear that the sample surface is uneven and consists of clumps (clusters), which indicates the grain size is quite diverse with an uneven distribution on the surface. The separation between the clumps were also seen quite clearly, namely in the form of micro-cracking that occur between clusters. Analyses with greater magnification (Figure 5) shows that the cluster is actually made up of particles with a size relatively similar to the relatively even distribution as well, but was interrupted by microcracking fairly wide and deep.

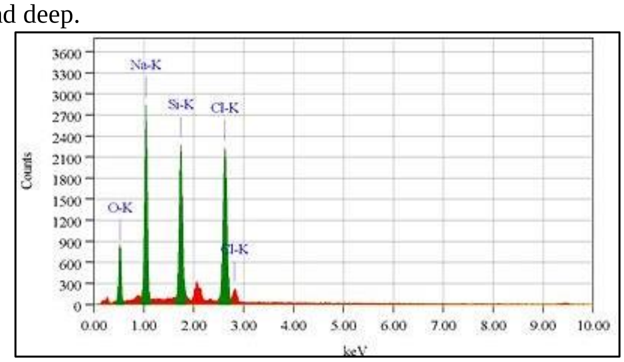

Figure 6: EDS spectrum and chemical components

The chemical composition of silica was confirmed by EDS (Figure 6) that showed Si and O at a calculated 1:2 atomic ratio. The absence of other elements, such as C, K, Na, Cl, reported in rice straw, also confirmed that extensive washing of the ground rice straw powders with water before heating was effective in removing these earth metals. Metal impurities have also been reported to be carried away with the volatiles during thermal decomposition of rice straw. Strategic pausing at these critical temperatures and lengthening the heating process may have enhanced this efficacy.

Surface Area and Thermal Decomposition

The Brunauer–Emmett–Teller (BET) surface area of silica powders is 94,761 m^2/g. These specific surfaces are much lower than the 326.9 m^2/g for the commercial silica.

Table 1: Surface area of as-prepared silica powders by BET from nitrogen adsorption isotherm, the data of commercial silica is also provided for comparison

Sample	BET surface area (m^2/g)
Silica from rice straw	94,761
Commercial silica	326.9

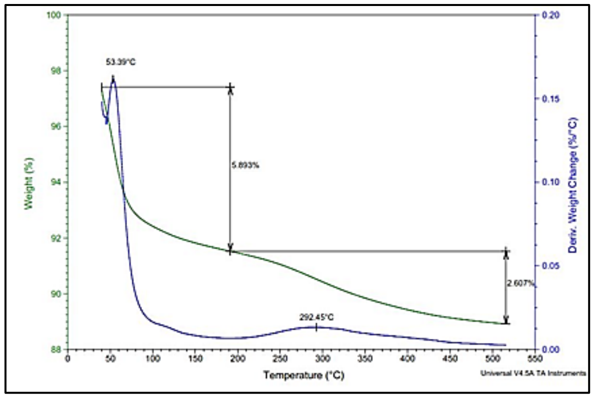

Figure 7: Thermal decomposition of silica from rice straw

The thermal characteristics of rice straw were studied first to determine the heating process to generate ash without affecting the amorphous state of silica (Figure 7). There are two significant oxidative decomposition exotherms between 260 and 500°C, and the completion of thermal decomposition in the 500°C region. The exothermic peak at 200°C coincided with the end of a sharp 5,893% mass loss from 50 to 200°C while the second exothermic peak at 500°C happened in the latter part of a more gradual 2,607% mass loss between 200 to 500°C. The residues from TGA analyses appeared gray in color, indicating the presence of carbon from incomplete oxidative decomposition of the organics and possibly over-heating. This observation suggests heating in stages according to these thermal transitions may be beneficial.

Application Nanosilica to Grow the Variety of Plant

Based on the results of research influence nanoslilia use of fertilizers, compost, fertilizers ZA, and without fertilizer to the growth of peanut plants (*Arachis hypogaea* L.), soybean, and tomatoes which data is retrieved plant height and number of leaves for 14 days. This research was conducted with by watering every day for 14 days. In general, with the addition of fertilizer, the plants will be faster growing and rather than plants that are not fertilized at all. Provision of fertilizer makes plants grow faster.

Table 2: Data of observation various types of fertilizers on crop growth peanuts

Days	Fertilizer SiO_2		Fertilizer ZA		Fertilizer Compost		Nothing Fertilizer Compost	
	Height (cm)	Leaves	Height (cm)	Leaves	Height (cm)	Leaves	Height (cm)	Leaves
1	-	-	-	-	-	-	-	-
4	3.8	-	3.2	-	0.7	-	-	-
7	8.5	8	8	8	4.2	-	2	-
11	17.5	12	12	12	16.3	12	13.5	8
14	23	16	16	-	21	16	19	16

Table 3: Data observations of various types of fertilizer on plant growth of tomatoes

Days	Fertilizer SiO_2		Fertilizer ZA		FertilizerCompost		Nothing Fertilizer	
	Height (cm)	Leaves	Height (cm)	Leaves	Height (cm)	Leaves	Height (cm)	Leaves
1	-	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-	-
7	4	2	3.75	2	5	2	3	1
11	4.5	3	5	2	5	3	3	2
14	5.3	5	5	2	5.3	3	5	2

Table 4: Data observations of various types of fertilizer on plant growth of soybean

Days	Fertilizer SiO_2		Fertilizer ZA		FertilizerCompost		Nothing Fertilizer	
	Height (cm)	Leaves	Height (cm)	Leaves	Height (cm)	Leaves	Height (cm))	Leaves
1	-	-	-	-	-	-	-	-
4	7.0	2	4.0	2	5.5	2	3.5	2
7	16.4	2	14.1	2	13.6	2	11.5	2
11	20.0	4	18.0	2	19.5	5	18.1	2
14	22.9	5	19.1	2	21.0	5	19.0	2

According to Tables 1-3 can be seen that the plant height and number of leaves of plants with fertilizers nanosilika more show very rapid growth. This is in accordance with the opinion which states that the use of manure fertilizer nano has advantages compared to regular size because it is more reactive which can directly reach the target or targets because the size is very smooth and is only required in smaller amounts. Needs fewer very helpful in the application use of silica in the field while doing cultivation. Some studies explain that the influence monosilikat acid on soil properties focused in its interaction with the elements of phosphate (P). According Sudibyo award Andisol Si on the ground can significantly increase the availability of soil P dama. The addition of Si in the soil will go through two processes. The first process is the increase of acid concentration monosilicate on the ground which will result in the conversion of P does not dissolve into the P available to plants. Phosphorus is not available for plants to stop on the side of the pin causes the P pinned becomes available to plants (Table 4). This is because SiO_4^{4-}has electronegativity take more thanPO_4^{3-}so as SiO_4^{4-}iO (4-) can replace PO_4^{3-}. The second process is Si can bind P So leaching P reduced by about 40-90% [16]. The equation is as follows:

$$CaHPO_4 + Si(OH)_4 \longrightarrow CaSiO_3 + H_2O + H_3PO_4$$
$$2\,Al(H_2PO_4)_3 + 2Si\,(OH)_4 + 5H^+ \longrightarrow Al_2Si_2O_5 + 5H_3PO_4 + 5H_2O$$
$$2FePO_4 + Si\,(OH)_4 + 2H+ \longrightarrow Fe_2SiO_4 + 2H_3PO_4$$

Silva suggests that the mechanism of land by Si in improving plant growth is by increasing the solubility of P from P terfikasai, lowering the binder P by components of the soil such as Al and Fe, improve soil CEC and lower concentrations of Al, Fe, and Mn in the soil. The use of nano-sized Si will lead to uniformity in the spread of Si into the soil and plant tissue is more secure because of the very small size [17]. This is in accordance with the opinion of Ranjbar and Shams which states that the nano fertilizer is more easily absorbed by plants and more efficient than conventional chemical fertilizers [18].

CONCLUSION

Pure amorphous silica was successfully extracted through base dissolution-acid precipitation of rice straw ash, EDS analysis confirmed that the as derived product contained Si and O. The FTIR of as-derived silica matched that of pure silica available commercially. Furthermore, the amorphous nature of the silica was affirmed by XRD. These freeze-dried amorphous silica powders with an average pore size of 45,3869 nm.

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