

Preparation of Potassium-Phosphate-embedded Amorphous Silicate Material from Rice Straw Waste

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Abstract. Rice straw is one of the agricultural wastes that increased every year. Since rice straw ash contains 74.6% of silica, this material is potentially used to produce silica. Thus, the purpose of this study was to investigate the possibility process for generating potassium-phosphate-embedded amorphous silica material. To extract silica from rice straw waste, we used potassium hydroxide solution followed by an acid precipitation treatment. Based on the experimental results, the proposed method is potential to be used as an alternative technique for getting silica material. In addition, the method has a positive impact on the environment because this is potential for reducing the amount of rice straw waste, whereas at the same time this provides an added value to the rice straw waste itself.

1. Introduction

Potassium, phosphate, and silicate are one of the main nutrients for plants, which have a great impact for the growth and development of plants. Potassium has impact for turning wood of cell walls of the spica plants and giving high resistance to against diseases and frost [1]. Phosphate is one of the elements that are required in large quantities (macronutrients) as an important component for building the key molecules, such as nucleic acids, phospholipids, and energy (as adenosine triphosphate). Indeed, the plants cannot grow without the supply of this nutrient [2]. Silica in plants is also important although it does not involve in the metabolic processes in the plant. Silica is necessary for making plants fresher and stronger [3]. Because of the importance of these elements for plant, study on the development of fertilizer containing silica, phosphate, and potassium is essential.

Although researches on the development of potassium silicate fertilizer have been reported [4], the study on the potassium silicate phosphate fertilizer production is still rare. In fact, these three elements can not be separated each other. Here, the purpose of this study was to investigate the possibility process for generating potassium-phosphate-embedded amorphous silica material, which can be applied as a fertilizer for plants. As a raw component of silica, we used rice straw waste [5,6]. This material was selected because rice straw waste is one of the largest agricultural wastes that are produced in large quantities and have not been used commercially. In fact, the components contained in the rice straw are



cellulose (32-47%), hemicellulose (19-27%), lignin (5-24%), and ash (13-20%) [7]. Some researchers also mentioned the rice straw containing high amount of silica [8]. For this reason, rice straw can be used as an alternative for source of silica which is cheap and largely available.

In short of our experimental procedure, rice straw waste was mixed with potassium hydroxide (KOH) solution followed by an phosphoric acid (H_3PO_4) precipitation treatment. Potassium hydroxide did not only act as a silica etching agent but also work as a source of potassium. Phosphoric acid can play as an important precipitating agent as well as a source of phosphor element. Based on the experimental results, the proposed method is prospective for an alternative technique for getting excellent fertilizer material: i.e. potassium-phosphate-embedded amorphous silicate material. In addition, this study also gave a positive impact on the environment because this can be an potential way for reducing the amount of rice straw waste, whereas at the same time this provides an added value to the rice straw waste itself.

2. Hypotetical Analysis

Silica contained in the rice straw can be extracted by an alkaline extraction. The solubility of silica increases in the pH of higher than 10. Interestingly, since dissolved silica can be precipitated when pH of lower than 10, the isolation of silica can be done by combining base and acid treatments of rice straw [9].

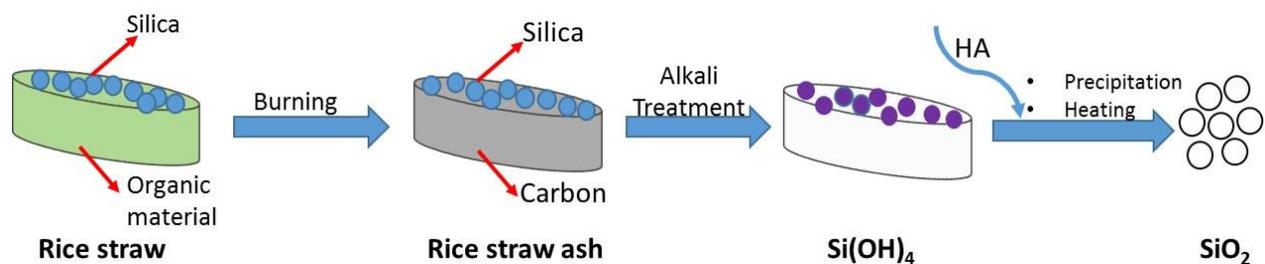
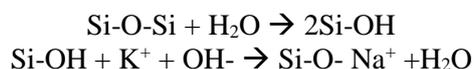


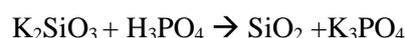
Figure 1. Illustration mechanism for the extraction of silica from rice straw

Figure 1 shows illustration mechanism for the extraction of silica from rice straw. The first step is a burning process of rice straw to convert organic material into carbon. This step is important for making further step easier because this step can make the burned material that has higher surface area and less volume. The second step is the additional alkaline solution. This step is used to obtain silicic acid ($Si(OH)_4$). The third step is the precipitation method using an acid solution followed by heat treatment to form a precipitated silica (SiO_2). In this study, we used KOH and H_3PO_4 as a source of potassium and phosphate. Thus, we expected that the resulting final product contained silica particles with potassium and phosphate. Detailed information about the involved reactions is as follow[10]:

1. Alkali treatment:



2. Acid precipitation:



3. Experimental Methode

3.1. Raw material

We used rice straw waste (rice field in Bandung, Indonesia), KOH (technical grade, PT. Bratachem, Indonesia), and H₃PO₄ (technical grade, PT. Bratachem, Indonesia). Rice straw was washed with an ion-exchange water, dried under sunlight for 5 days, and then cut with sizes of about 0.5 cm.

3.2. Synthesis of potassium-phosphate-embedded amorphous silica

Initially, rice straw was burned in furnace at 973 K for 5 hours to produce rice straw ash. Then, the rice straw ash was grinded to obtain 200-mesh powder and subsequently put into an alkali solution (KOH solution). The mixture was stirred (900 rpm) and heated at 338K for 2 hours. Next, the extracted solution was decanted for about one night. Then, the solution was precipitated by the addition of H₃PO₄ solution. The mixed was then aged for 24 hours, forming a white gel. Finally, the gel was filtered using a ashless filter paper (Whatman No. 41), washed with an ion-exchanged water, and then heated at 398K for 15 minutes.

3.3. Characterization

To obtain the characteristic of component in the rice straw ash, combination of an Atomic Absorption Spectroscopy (AAS) and gravimetry was conducted. The final powder was also analyzed using an X-ray Diffraction (XRD) and a Fourier Transform Infrared (FTIR) to obtain detailed chemical structure.

4. Results and Discussion

To confirm the content of silica and metal oxides in the rice straw ash, combination of gravimetric and AAS analysis was conducted (**Table 1**). The result showed that the rice straw ash contained 74.60% of silica and some an organic material. This result indicated that the rice straw is potential for a source of silica.

Table 1. Chemical content of rice straw ash.

<i>Composition</i>	<i>Quantity (%)</i>	<i>Method</i>
SiO ₂	74.6	Gravimetric
K ₂ O	9.06	AAS
CaO	1.87	AAS
MgO	1.48	AAS
Na ₂ O	0.45	AAS
Fe ₂ O ₃	0.35	AAS
Al ₂ O ₃	0.32	AAS

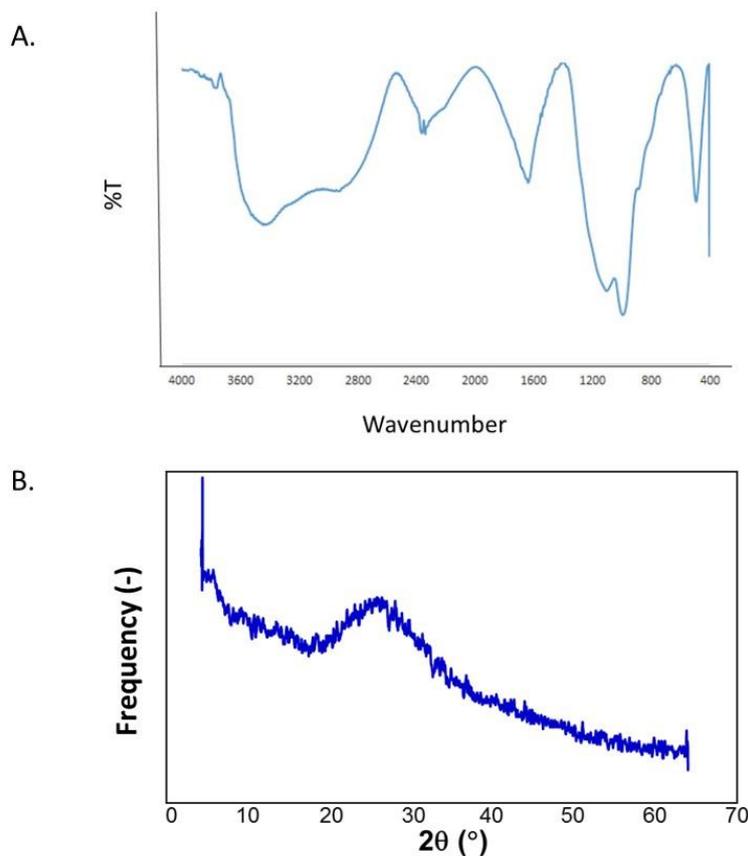


Figure 2. a). FTIR spectra b). XRD pattern of potassium-phosphate-embedded amorphous silica material

Figure 2a shows the FTIR result of our product. The infrared spectra shows peaks at 493.79 and 885.33 cm^{-1} , denoted to the Si-O-Si symmetric bending and Si-OH, respectively. The band located at 993.34 and 1105.21 cm^{-1} ascribed to the K_2HPO_4 and Si-O-Si asymmetric stretching, respectively. The peaks at 1639.49 cm^{-1} belonged to H-OH. The broad band at 3429.43 cm^{-1} was due to SiO-H stretching. To clarify the FTIR spectra, we compared our results with several references, as shown in **Table 2**.

Table 2. Comparison the peak absorption of particles synthesized with references

Functional Group	Wavenumber (obtained from experiment) (cm-1)	Wavenumber (from references) (cm-1)	References
Si-O-Si <i>symmetric bending</i>	493.78	461.34	[11]
Si-OH	885.33	803	[12]
K_2HPO_4	993.34	990	[13]
Si-O-Si <i>asymmetric vibration</i>	1105.21	1107	[14]
H-OH	1639.49	1635	[11]
SiO-H <i>stretching</i>	3429.43	2800 - 3750	[9]

Figure 2b shows the XRD analysis result of our product. XRD diffractogram shows peak with the highest intensity at about 25.15, which is a typical peak for amorphous silica. The amorphous form

obtained due to presence of water molecules in the samples analyzed. In the diffractogram, no peak for K_2HPO_4 was detected, in which this was due to the too low concentration of K_2HPO_4 .

5. Conclusion

Potassium-phosphate-embedded amorphous silica material has been synthesized from rice straw waste. The experimental results showed that the proposed method is an prospective technique for getting silica material. In addition, the method has a positive impact on the environment because this is potential for reducing the amount of rice straw waste, whereas at the same time this can provide an added value to the rice straw waste itself.

6. Acknowledgments

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References

- [1] Jančaitienė K and Šlinkšienė R 2014 Influence of the molar ratio of basic materials and temperature on production of potassium dihydrophosphate *Chemija* **25** (2) 89-95
- [2] Schachtman D P, Reid R J and Ayling S M 1998 Phosphorus uptake by plants: from soil to cell *Plant Physiol* **116** (2) 447-453
- [3] Rosmarkam A and Yuwono N W 2002 *Ilmu kesuburan tanah* (Yogyakarta: Kanisius)
- [4] Tokunaga Y 1991 Potassium silicate: a slow-release potassium fertilizer *Nutr Cycl Agroecosys* **30** (1) 55-59
- [5] Permatasari N, Suahya T N and Nandiyanto A B 2016 Review: Agricultural Wastes as a Source of Silica Material *Indones J Sci Technol* **1** (1) 82-106
- [6] Nandiyanto A B, Rahman T, Fadhlulloh M A, Abdullah A G, Hamidah I and Mulyanti B 2016 Synthesis of silica particles from rice straw waste using a simple extraction method *IOP Conf Series: Mater Sci Eng* **128** 012040
- [7] Zaky R R, Hessien M M, El-Midany A A, Khedr M H, Abdel-Aal E A and El-Barawy K A 2008 Preparation of silica nanoparticles from semi-burned rice straw ash. *Powder technol*, **185** (1) 31-35
- [8] Agbagla-Dohnani A, Nozière P, Clément G and Doreau M 2001 In sacco degradability, chemical and morphological composition of 15 varieties of European rice straw *Anim Feed Sci Technol* **94** (1) 15-27
- [9] Kalapathy U, Proctor A and Shultz J 2000 A simple method for production of pure silica from rice hull ash *Bioresource Technol* 257-62
- [10] Prezzi M, Monteiro P J and Sposito G 1997 The alkali-silica reaction: Part I. Use of the double-layer theory to explain the behavior of reaction-product gels *ACI Mater J* **94** (1) 10-17
- [11] Morsy F A, El-Sheikh S M and Barhoum A 2014 Nano-silica and $SiO_2/CaCO_3$ nanocomposite prepared from semi-burned rice straw ash as modified papermaking fillers *Arabian J Chem* in press
- [12] Noushad M, Ab Rahman I, Zulkifli N S C, Husein A and Mohamad D 2014 Low surface area nanosilica from an agricultural biomass for fabrication of dental nanocomposites *Ceram Int* **40**(3) 4163-71
- [13] Miller F A and Wilkins C H 1952 Infrared spectra and characteristic frequencies of inorganic ions *Anal Chem* **24** (8) 1253-94
- [14] Zulkifli N S, Rahman I A, Mohamad D and Husein A 2013 A green sol-gel route for the synthesis of structurally controlled silica particles from rice husk for dental composite filler *Ceram Int* **39** (4) 4559-67