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Improvement High Purity Biogenic Amorphous SiO_2 Derived from Rice Husk Ash: Synthesis and Its Characterization

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Abstract. In this work a simple process for the production of high purity biogenic amorphous SiO_2 derived from rice husk ash have been studied. Rice husk ash obtained from heat treatment of rice husk and citric acid leaching of rice husk at 700 ° C for 6 h. Improvement of purity SiO_2 from rice husk ash conducted by precipitation technique. The precipitated SiO_2 particles obtained were characterized by x-ray fluorescence (XRF) analysis, Fourier transform infrared (FTIR) spectroscopy, and x-ray diffraction analysis (XRD). The XRF result shows that the high purity of biogenic amorphous SiO_2 obtained is 99.258 %. The XRD result shows the silica have amorphous phase and for the FTIR results shows bending and stretching vibration of Si-O and Si-O-Si.

Introduction

Indonesia is the third-largest producer of rice in the world and the estimated total paddy production in 2018 is 56.54 million tons [1], which intended approximately 11.31 tons of rice husk (RH). RH is by-product from rice mills industries and it will cause a pollution problem if not manage properly [2-3]. Therefore, recycling RH into a high value added material is a great challenge, not only beneficial for the environment but also as a promising resource.

The primary constituents in RH are cellulose, hemicellulose, lignin, and ash [4-5]. When RH is heat treated, it produces approximately 20 wt % rice husk ash (RHA) rich in silica [6]. Uncontrolled heat treated RH such as in open land produces crystalline RHA with high emissions [7], however controlled heat treatment temperature below 800 ^oC produce biogenic silica mainly in amorphous form [8].

The chemical composition of RHA is varying which is depending of some factors such as type of paddy and soil, harvesting season and geographical conditions [9-11]. In addition, in order to be used in the advanced materials, the biogenic silica obtained should have high purity and also be amorphous [12-13].

There are many studies have been conducted to improve the purity of biogenic silica such as by combustion of RH [14-15], pre-treatment of RH [9,16,17], and post-treatment of RHA [18]. However, there are still have different results in the purity of silica and other constituents obtained. Therefore, the effort to study the characteristic of biogenic amorphous silica derived RHA from different region especially in Indonesia is challenge. In this paper, the combination citric acid leaching and precipitated technique to synthesize and evaluate the characteristic of high purity biogenic amorphous silica powder obtained from RHA in order to add the currently existing data's on biogenic amorphous silica materials was presented.

Experimental Method

Preparation of Rice Husk Ash (RHA) and Citric-Acid Rice Husk ash (CA-RHA)

Raw material rice husk (RH) used for preparation of rice husk ash was collected from a local milling factory around of Pringsewu Regency Lampung, Indonesia. RH was first washed thoroughly with tap water to remove the adhering soil and dust. It was then dried under sunlight for 24 h and followed by oven dried at 100 ºC for 10 h. The dried RH then was grinded by using laboratory blender for 20 minutes to become fine powder. 30 g RH powder was magnetic stirred in 500 ml 5% citric acid solution at 80 ºC for 60 minutes. Subsequently the mixture citric acid RH (ca-RH) was filtered and rinsed using deionized water 5 times in order to remove citric acid from RH, then dried in oven at 100 ºC for 10 h. The dried of RH and ca-RH powder then heat treated in muffle furnace at 700 ºC for 6 h with heating rate 5 ºC/minutes. The ash powder obtained then denoted as RHA and CA-RHA, respectively.

Preparation of High Purity Biogenic Amorphous SiO_2

The preparation of high purity biogenic amorphous SiO_2 derived from RHA and CA-RHA by precipitation was adopted from the procedure described by Yufakumar *et al.* [19] with modifications. 7.51 g RHA or CA-RHA powder first was washed with 250 ml deionized water to neutralizes the pH and removes the adhered impurities on the surface of silica and then refluxed with 6 N HCL for 2h at 100 ºC. The mixture then filtered and washed with 250 ml hot deionized water to make it acid free. It was then dissolved in 2.5 N NaOH at 80 ºC by continuous stirring on magnetic stirrer for 2 h and then filtered to obtain sodium silicate (Na_2SiO_3) solution. The reaction is as follows:

$$SiO_2\,(Ash) + 2\,NaOH \rightarrow Na_2SiO_3 + H_2O \quad (1)$$

The concentrated H_2SO_4 was then added drop wise to the solution in order to lower the pH of the solution to 2. The reaction is as follows:

$$Na_2SiO_3 + H_2SO_4 \rightarrow SiO_2 + Na_2SO_4 + H_2O \quad (2)$$

The precipitated silica was then washed repeatedly with boiling deionized water until the filtrate became alkali free, dried in oven at 100 ºC for 24 h, then calcined at 700 ºC for 6 h with heating rate 5 ºC/minutes. The biogenic SiO_2 powder obtained then denoted as P-RHA and PCA-RHA, respectively.

Characterization of Biogenic Amorphous SiO_2

The chemical compositions of biogenic amorphous SiO_2 (RHA, P-RHA, CA-RHA, and PCA-RHA) samples were analysed using X-ray Flourescence (XRF- PAN analytical). The crystal structure analysis of all samples were monitored by using x-ray diffractometer (PW3040/60 Xpert Pro) using CuKα radiation, 40 kV and 30 mA in 2 theta range of 5-80 degrees. The compositional of functional group in the samples were conducted by using FTIR spectrophotometer (Perkin Elmer Optima 100).

Results and Discussion

Table 1 shows the chemical compositions of RHA, CA-RHA, P-RHA, and PCA-RHA samples. The silica contents in ashes are 94.143, 97,587, 98.847 and 99.258 wt % respectively. By citric acid leaching the silica substance expanded from 94.143 to 97.587 wt %, it implies that the use of citric acid leaching treatment caused the reduction of the overall substance of metal oxide impurities and resulted a high purity of silica. An increase about 3.529 wt % was achieved in this experiment. The use of the citric acid solution is effective for the chelate reaction [20] between carboxyl groups (–COOH) and metallic impurities contained in RH, and results in the removal of such impurities as

metal complexes from RH during the leaching treatment. The presence of metallic impurity especially K_2O in RH causes the difficulty to obtain silica with high purity above 97 wt% by direct combustion technique [21], however pre-treatment RH by citric acid and post treatment by precipitation technique increased the content of silica and decreased the impurities in these samples. Post-treatment of RHA and CA-RHA by precipitation technique increased the content of silica in these samples of 98.847 and 99.258 wt % respectively.

Table 1. Chemical compositions of biogenic amorphous SiO_2.

Constituents	wt %			
	RHA	CA-RHA	P-RHA	PCA-RHA
SiO_2	94.143	98.847	97.587	99.258
P_2O_5	3.140	0.376	0.827	0.198
K_2O	1.119	0.011	0.012	0.009
MgO	0.114	0.021	0.731	0.032
Al_2O_3	0.677	0.456	0.653	0.419
CaO	0.612	0.243	0.151	0.082
Fe_2O_3	0.075	0.003	0.025	0.002
Cl	0.015	0	0	0
Others	0.105	0.043	0.014	0

The XRD pattern for the RHA, CA-RHA, P-RHA and PCA-RHA samples is shown in Fig. 1. The absence of sharp peaks in the XRD pattern of all samples indicated the amorphous nature of the materials. RHA has been reported to be amorphous at ashing temperatures of 500 ºC -700 ºC with crystalline silica forming at temperatures equal to or greater than 800 ºC [22].

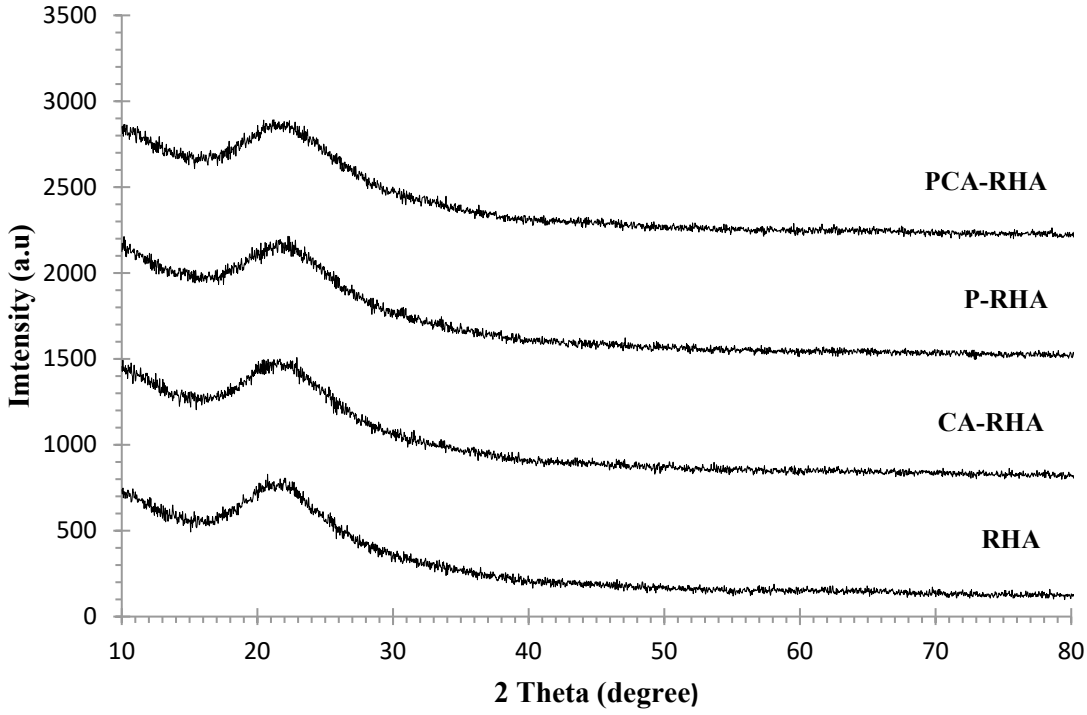

Figure 1. XRD pattern of RHA, CA-RHA, P-RHA, and PCA-RHA samples heat treated at 700 ºC for 6 h.

The FTIR spectra of RHA, CA-RHA, P-RHA, and PCA-RHA samples are shown in Fig. 2 and the transmittance spectra is summarized in Table 2. The band peaks were observed at 468 cm^{-1} is

attributed to the rocking bond and the band peaks at 802 cm^{-1}, 803 cm^{-1} and 808 cm^{-1} are corresponding to the symmetric bond vibration of the Si-O elements. The band at 1096 cm^{-1}, 1098 cm^{-1}, and 1107 cm^{-1} are related to vibration stretching of asymmetric of Si-O-Si element. The broad band were also detected at 3438 cm^{-1}, 3439 cm^{-1}, 3343 cm^{-1}, and 3445 cm^{-1} which is ascribed to the stretching vibration of the O-H bond in Si-OH and HO-H vibration of the water molecules absorbed on the silica surface [23].

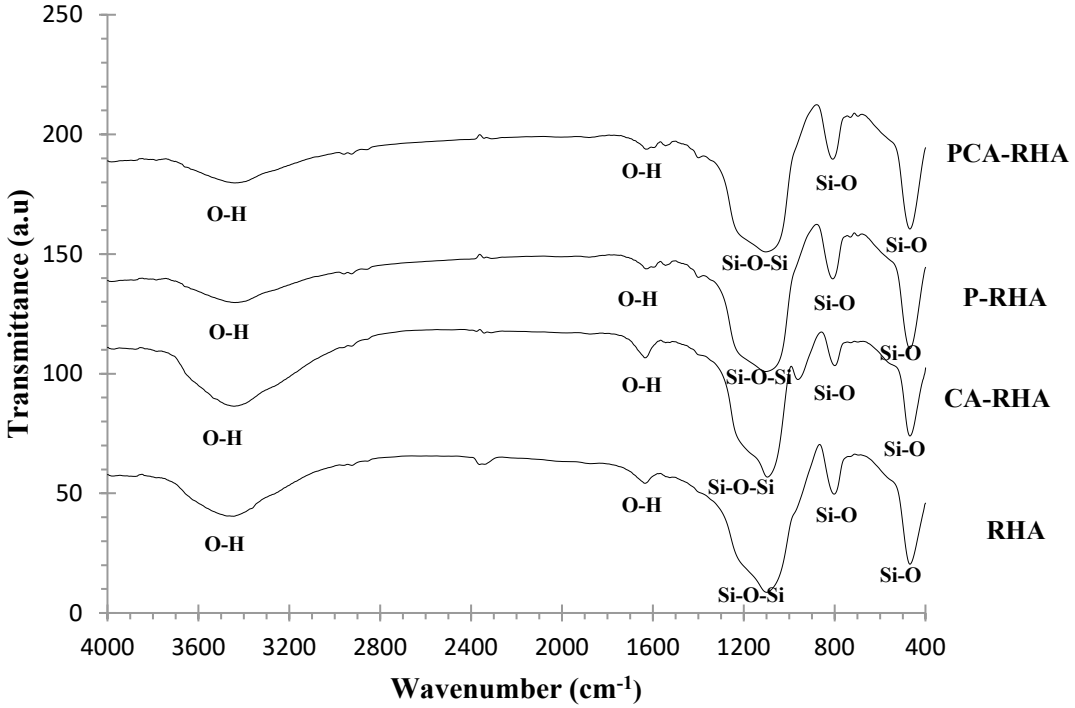

Figure 2. FTIR spectra of RHA, CA-RHA, P-RHA, and PCA-RHA samples heat treated at 700ºC for 6 h.

Table 2. Assignment of the bands in the FTIR of RHA, ca-RHA, P-RHA, and Pca-RHA samples.

Band Assignment	Wavenumber (cm^{-1})				Literature value of wavenumber (cm^{-1})	References
	RHA	ca-RHA	P-RHA	Pca-RHA		
Si-O bond rocking	468	468	468	468	465-475	[24]
Symmetric Si-O bending (silanol)	802	800	803	803	790-805	[25-27]
Asymmetric Si-O-Si	1098	1096	1107	1107	1050-1115	[28]
O-H bending	1632	1632	1631	1631	1630	[23-24]
O-H stretching and absorbed water	3445	3443	3439	3438	3000-3800	[23,25]

Conclusion

This study revealed that improvement of purity biogenic amorphous silica produced from rice husk ash has been demonstrated. The purity of silica increased from 94.143 to 97.587 wt% for RHA sample and from 98.847 to 99.258 wt% for CA-RHA sample. The XRD profiles showed that the overall rice husk ashes have amorphous diffraction patterns, due to the presence of biogenic amorphous silica. Based on the high purity of silica obtained, the product biogenic amorphous silica can be potential used as filler and absorbents materials.

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