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Effect of Different Acids on Rice Husk Calcination and Extraction of Bio-Silica

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Silica is an essential material which has many applications in various fields such as construction, catalyst, optical fibers and raw material of metallurgical industry. This work observed the recent trends in silica extraction from agro and natural wastes for high-tech applications. Hence, this work approached in new way for the bio-silica extraction from waste rice husk using HCl, H_2SO_4 and CH_3COOH for the calcination. The results revealed that the effect of pH on ash nature and silica purity. The purity of silica was differed based on metal ions, rice husk ash color and non-combusted carbon. The results were compared with treatment in absence of acid ash using FT-IR, SEM, EDAX and XRD analysis to measure the effect of pH on the bio-silica purity. This work observed the lower carbon content in acid treated ash when compare to water washed rice husk.

Keywords: Rice husk ash, Acid treatment, Bio-silica, pH.

INTRODUCTION

Rice husks are the outer shells of paddy, made up of organic starch molecules with some inorganic salts. These are protecting rice grains and removed by milling process of paddy which consists 95% of silica in 20% of rice husks ash [1]. Rice husk is one of the agriculture milling byproducts of rice [2]. It is reported that about 29 million tons of rice husk per annum produced in India and it is creating pollution issues while disposal [3]. Many studies have exposed that the rice husks having 15-28 wt.% of silica based on the climate, variety, origin, geographic location and about 72-85 wt.% of lignocellulose, which includes cellulose (35-40 wt.%), hemicellulose (15-20 wt.%), lignin (20-25 wt.%), respectively. Rice husks highly pose environmental problem causing damage to the land and the surrounding area, wherever it is dumped due to the shells hard nature.

Rice husk is a fine source for silica production. Several researchers have reported silica production from rice husk by inorganic acid treatment [4,5]. Silica exists in different forms such as gel, crystalline and amorphous states in nature. Naturally, rice husk contains silica in the form of hydrated amorphous state like silica gel which is harmful to soil [6-8]. The rice husk is combusted at moderate temperature and converted to silica containing ash with some metallic impurities. These kinds of metallic impurities can be removed by acid-leaching treatment [9]. Hence, this work referred the synthesis of silica from rice husk related reports for the further investigations [10-13]. From the reports, this work observed that the effect of pH on the rice husk and its calcination was not explained in details. In addition, characterizations of each process with the chemical compositions were not clear. So, the present research work is now endeavored to investigate the effect of acids such as inorganic and organic acids on rice husk. After the heat treatment process, pure silica was synthesized from rice husk using different acid treatments, followed by maintaining the neutral pH and then calcinated at different temperatures. This is compared with untreated rice husk results.

EXPERIMENTAL

The rice husk was collected from the local rice mill from Tirupati, India. Hydrochloric acid, sulfuric acid, acetic acid and sodium hydroxide (GR grade Chemicals) were purchased from Merck India Limited, India. Distilled water purified by using the Milli Q apparatus (Millipore Bedford, USA). Reaction mixture acidity was examined by pH meter, Hanna instruments, India. Vibrational spectroscopy of the calcinated product was analyzed by Fourier transform infrared spectroscopy, Shimadzu, Japan. X-Ray diffractometer supplied by Shimadzu Japan. In addition, the product surface morphology was analyzed using scanning electron microscopy with energy-dispersive X-ray supplied by JSM-LT- 500 RUSA. As per the reported procedures, EDAX and surface morphology were measured to identify the compositions and SiO_2 nature.

Acid treatment and calcination of rice husk: The collected rice husk was cleaned with water to remove adhered soil and dust, and then dried at 110 ºC for 12 h. Dried rice husk (20 g) were leached with 3 mol/L HCl, 3 mol/L H_2SO_4 and 3 mol/L CH_3COOH, respectively in a three separate round bottomed flasks for 24 h at 90 ºC with constant stirring. After 24 h, the masses were cooled and washed with plenty of distilled water then pH was measured. The reaction masses have shown the pH of HCl = 4.1, H_2SO_4 = 4.5, CH_3COOH = 3.9, respectively. The acid treated rice husk (about pH-4) was air dried at 100 ºC for 4 h. The dried rice husk was calcined at high temperature 600 ºC for 4 h in the muffle furnace along with untreated rice husk (water wash). But, the samples were not combusted at 600 ºC and the temperature was increased to 700 ºC, which was main-tained for 4 h in the muffle furnace. The samples were not combusted suitably at 700 ºC also when compared with untreated rice husk which was combusted 100% with whitish colour. The acid treated rice husk was not combusted properly at pH 4 due to more acidity effect. Same experiment repeated at pH = 7.02 (HCl), 7.05 (H_2SO_4), 7.01 (CH_3COOH), respectively. The acid treated rice husk (about pH 7.00) was air dried at 100 ºC for 4 h. The dried rice husk was heated at 600 ºC for 4 h in the muffle furnace and observed the incomplete combustion. Hence, the complete combustion achieved at 700 ºC for 4 h. Finally, it is in the form of white colour rice husk ash contains silica with increased purity as atom percentage. Then, obtained white colour 100% complete combustion products were carried for the characterization. All the samples were characterized by Fourier transform infrared spectroscopy, Scanning Electron microscopy with Energy dispersive X-ray.

Purification of silica: Sodium silicate solution was prepared by treating 5 g of HCl washed rice husk ash with 2.0 M aqueous NaOH solutions at 80 ºC for 5 h with continuous stirring to form gel then cool to room temperature (eqn. 1). The solution was filtered under vacuum to separate it from insoluble.

$$\text{Rice husk ash } (SiO_2) + 2NaOH \xrightarrow{80\ °C \text{ for } 5\ h} Na_2SiO_3 + H_2O \quad (1)$$

The prepared sodium silicate solution was titrated against 1N HCl with constant stirring up to complete precipitation at pH = 7 (eqn. 2). The silica gels formed were aged for 18 h and added with deionized water to form gels. Then, the slurry was centrifuged at 2500 rpm and the precipitates were separated. The products were dried at 100 ºC for 12 h.

$$Na_2SiO_3 + HCl \rightarrow SiO_2 + NaCl + H_2O \quad (2)$$

RESULTS AND DISCUSSION

This work successfully investigated the optimized pH and calcination temperature for the bio-silica extraction. Initially, higher acidic condition pH 4 and temperature 700 ºC treated rice husk products are shown in Figs. 1 and 2. The results showed that the incomplete combustion will affect the purity of silica. Hence, this work extended to optimize the pH and calcination temperature.

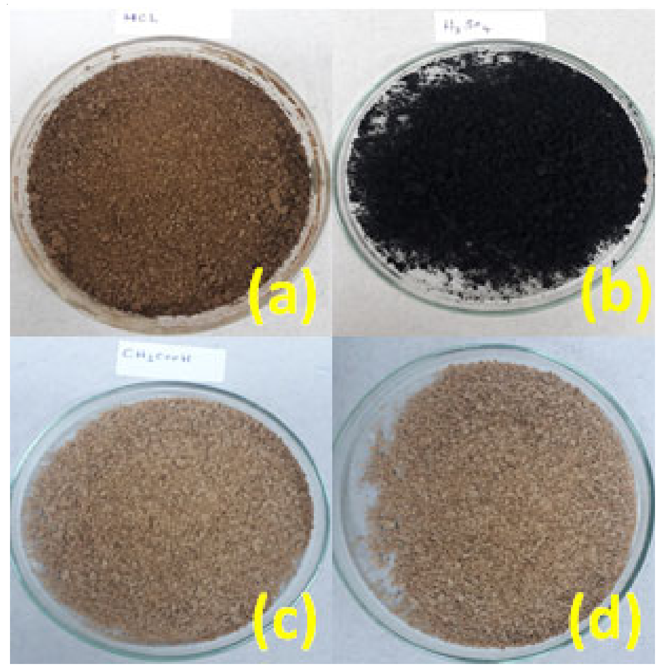

Fig. 1. Rice husk treated with acids at pH = 4.0 (a) HCl treated rice husk, (b) H_2SO_4 treated rice husk, (c) acetic acid treated rice husk, (d) water treated rice husk

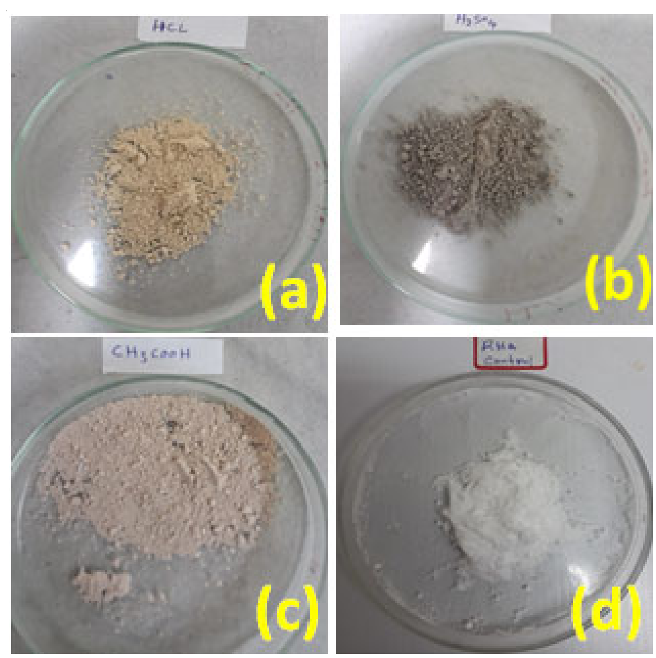

Fig. 2. Calcination conducted at 700 °C at pH = 4.0 (a) HCl treated rice husk, (b) H_2SO_4 treated rice husk, (c) acetic acid treated rice husk, (d) water treated rice husk at pH = 7.0

EDAX studies: The pH was increased to 7.2 and heated at 700 ºC process exposed the good white colour change in rice husk which is required for the silica extraction. The obtained calcined products are shown in Fig. 3. Then, the acid treated samples ashes were tested for their combustion products compositions using EDAX spectra. The resultant combustion products percentages of three acids are presented in Table-1. Resultant compositions exposed the difference between inorganic and organic acid treated compositions. The results were almost coincidence with the reported values [14,15].

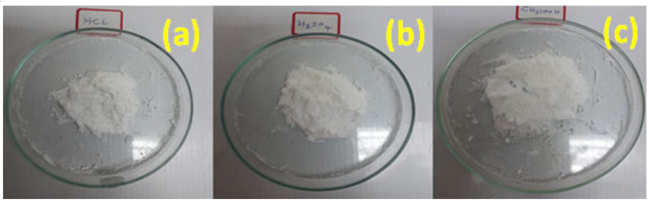

Fig. 3. Calcination conducted at 700 ºC at pH = 7.2 (a) HCl treated rice husk, (b) H_2SO_4 treated rice husk, (c) acetic acid treated rice husk

The results showed that the control and the organic acids are exhibiting similar chemicals with different percentages. Inorganic acid treated samples consist of similar compositions with different percentages. Apart from all four samples, HCl acid treated product showed good purity of silica (99.58%). These values were confirmed by EDAX spectra (Fig. 4) and this work proposed that neutral pH with water produced the white colour ash at 600 ºC, while the acid treated samples required to be washed plenty of water and calcination completed at 700 ºC. Most of the reports exposed the acid treated process, but they didn't clearly explain the impact of the acid pH and neutral pH. This work proposed the optimized pH and calcination temperature for the silica extraction from rice husk.

TABLE-1
CHEMICAL COMPOSITIONS OF
EACH ACID TREATED RICE HUSK

Composition	Percentage after the acid treatment			
	Control	HCl	H_2SO_4	CH_3-COOH
Na_2O	0.30	0.01	0.05	0.13
MgO	0.13	0.05	0.06	0.18
Al_2O_3	0.14	0.06	0.33	5.86
SiO_2	89.86	99.58	99.08	91.82
P_2O_5	0.26	0.03	0.04	0.03
SO_3	0.09	–	0.04	0.06
ClO_3	0.12	0.02	0.01	0.03
K_2O	0.05	0.02	0.01	0.01
CaO	0.09	0.02	0.15	0.13
MnO	0.03	0.01	0.03	0.02
Fe_2O_3	0.01	0.01	0.01	0.02
CuO	0.01	–	–	0.03
ZnO	0.02	0.01	0.01	0.01
C	8.89	0.17	0.18	1.67
Hf	–	0.01	–	–

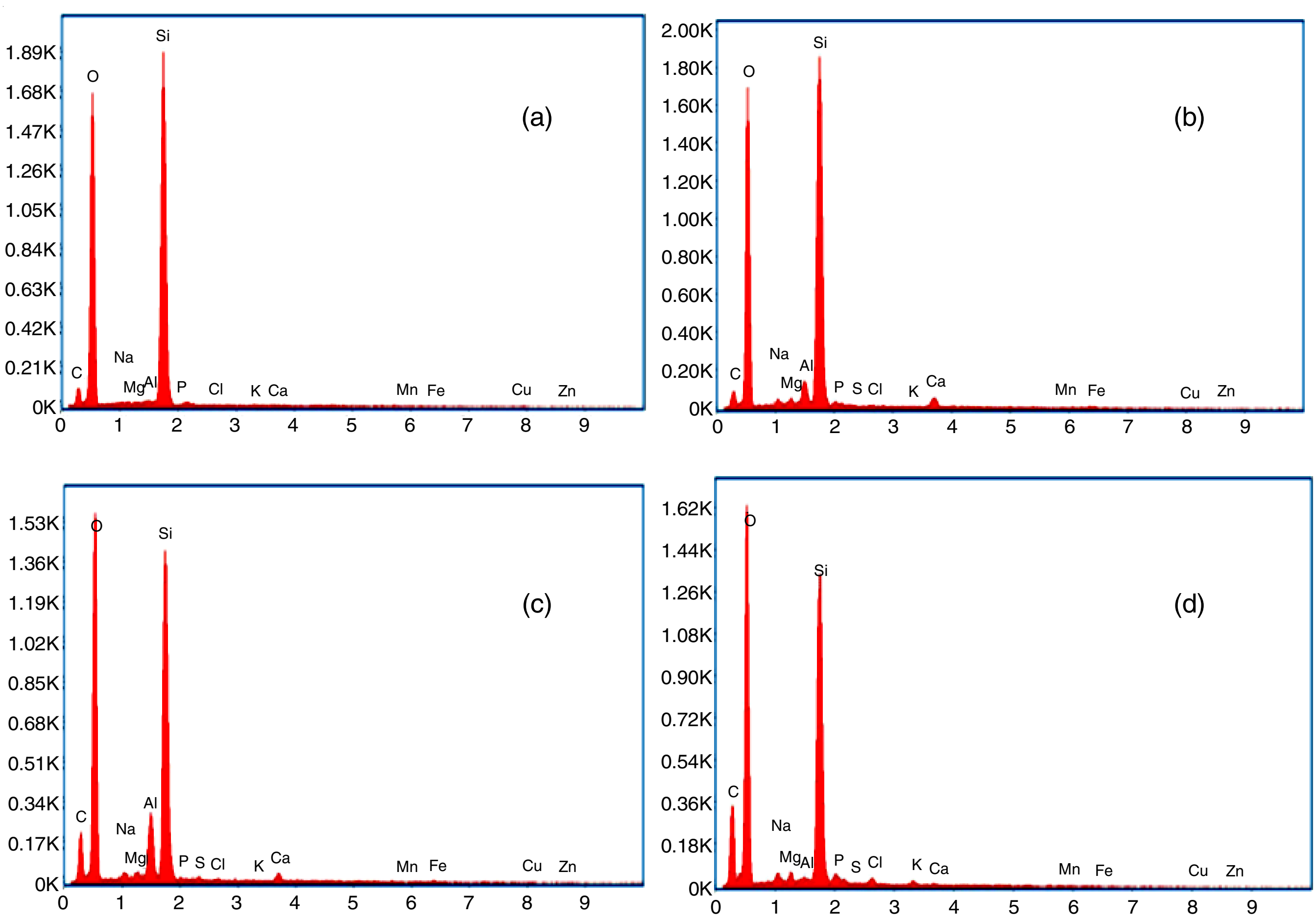

Fig. 4. Calcination conducted at 700 ºC at pH = 7.2 EDAX results (a) HCl treated rice husk, (b) H_2SO_4 treated rice husk, (c) acetic acid treated rice husk, (d) water treated rice husk

SEM studies: All the rice husk ashes were characterized by SEM technique to confirm the rice husk structures which are shown in Fig. 5. The surface morphology confirmed the porous nature of the bio-silica, which is coincidence with the reported values [15]. When compared the surface morphologies of all the samples, sulphuric acid shows hard amorphous nature and remaining samples are soft porous samples.

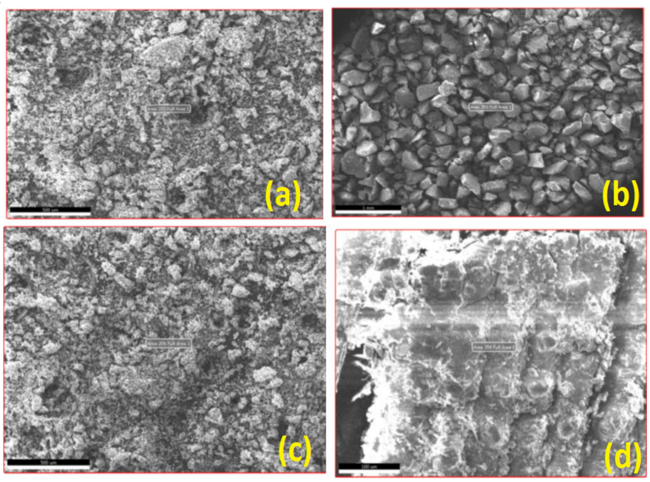

Fig. 5. SEM images of the samples (a) HCl treated rice husk, (b) H_2SO_4 treated rice husk, (c) acetic acid treated rice husk, and (d) water treated rice husk

FTIR studies: FTIR vibrational spectra of the derived silica samples are shown in Fig. 6. In washed rice husk sample, no peak of Si-O-Si stretching approximately at 1072 cm^{-1} for non-calcinated rice husk was observed. The rice husk control shows a typical band around 1072 cm^{-1}, which indicates the asymmetrical stretching vibration of the Si-O-Si. Similarly, hydrochloric acid, sulphuric acid and acetic acid samples have shown IR typical band around 1072 cm^{-1} and confirmed the pure rice husk. The vibrational spectra also exposed the temperature effect on the silica purity. A typical band at 1078 cm^{-1} in obtained silica corresponds to the asymmetrical stretching vibration of the Si-O-Si. No other additional bands in FT-IR confirmed the purity silica material.

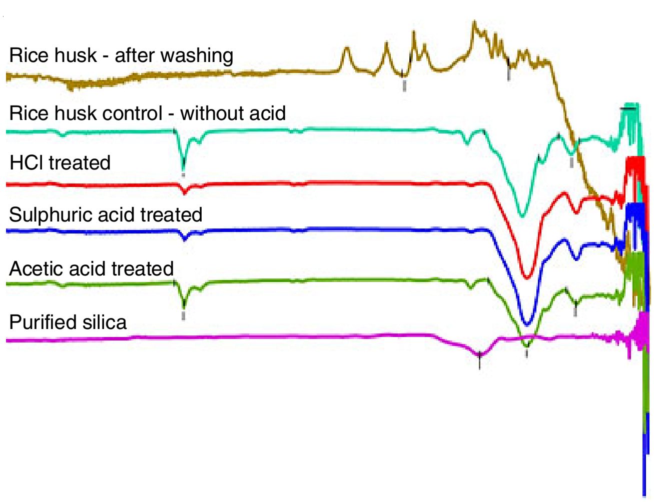

Fig. 6. FTIR spectra of the source, control and aid treated silica samples

After the preliminary acid treatment, the samples were treated with alkali and characterized by SEM and EDAX. The purified sample, SEM and EDAX results are shown in Fig. 7. Fig. 8 shows the XRD pattern of the 99.58% pure silica sample, which confirmed the amorphous state of silica. The percentage of silica (SiO_2) was 99.58% and other percentage of elements was very minor but carbon formation was reduced to 0.17% as atom compared with untreated control. The SEM result of purified silica sample showed the amorphous nature and also represents the silicon dioxide is made up linear triatomic molecules. The EDAX result confirmed the purity and maximum chemical compositions were removed during the alkali treatment. The sample showed the highest purity of 99.58%, which can be applicable in various application fields.

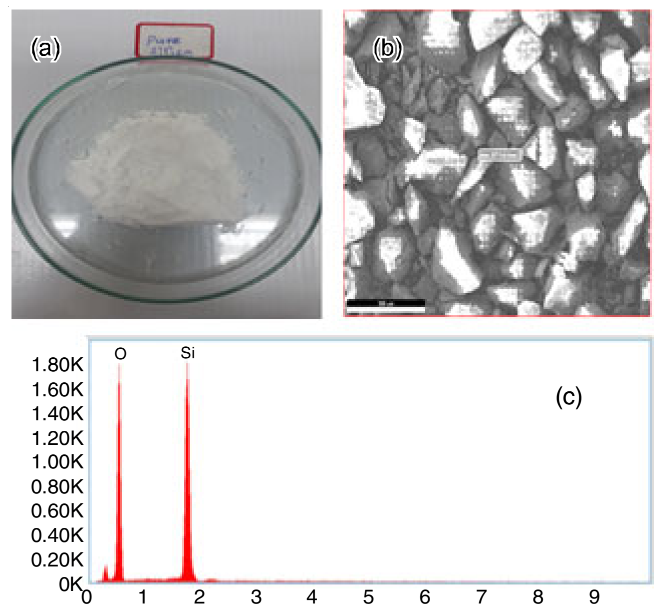

Fig. 7. (a) Pure silica isolated from rice husk by alkali treatment, (b) SEM image of pure silica by alkali treatment, (c) EDAX result of purified silica

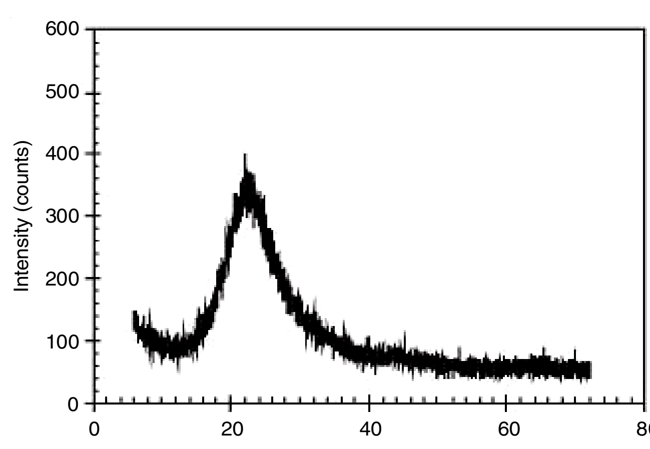

Fig. 8. XRD pattern of 99.58% pure silica samples

The rice husk is very dissolute with mineral acids (HCl, H_2SO_4), then the carbon formation was very less in rice husk ash compared with control rice husk (without acid wash). The silica ash was increased in the acid leached (HCl, H_2SO_4) rice husk ash and the silica were not increased much more in the acid leached (CH_3COOH) rice husk ash compared the control rice husk ash. Since strong acids were more dissoluted with rice husk than weak acids, accordingly the silica percentage was increased. The weak acids was not more dissolute with rice husk, accordingly the silica percentage was not increased. Finally the silica percentage was increased up to 99.58% with leached hydrochloric acid rice husk ash compared to sulfuric acid and acetic acid and control. The results of silica percentage were mostly same as compared between HCl and H_2SO_4. The percentage of silica was 99.58% with HCl leached rice hush ash and the percentage of silica was 99.08% with H_2SO_4 leached rice hush ash. Finally, it is in the form of rice husk ash contains pure silica.

Conclusion

The untreated rice husk and acid treated rice husk were not combusted at 600 ºC and the right temperature of rice husk was 700 ºC with maintained neutral pH to become fully converted to ash contains silica when it compared the acid wash rice husk with maintained pH about 4, when the rice husk leached with acids then washed with plenty of water to maintained neutral pH otherwise rice husk was not combusted properly accordingly silica purity was not increased due to more acidity effect of rice husk. The rice husk was leached with inorganic acids (HCl, H_2SO_4) and organic acids (CH_3COOH), the rice husk ash contains silica purity is very high with inorganic acid treatment of rice husk than organic acid treatment of rice husk and the rice husk ash contains silica purity was increased with inorganic acid treatment of rice husk than control of rice husk (water wash). Hence the percentage of silica increases as atomic wise of with hydrochloric acid treatment of rice husk than sulfuric acid treatment of rice husk. The rice husk is very dissolute with mineral acids (HCl, H_2SO_4), then the carbon formation was very less in rice husk ash compare with control rice husk (without acid wash). The silica was very increased in the acid leached (HCl, H_2SO_4) rice husk ash and The silica was not increased much more in the acid leached (CH_3COOH) rice husk ash compare the control rice husk ash. The reason is the strong acids was more dissoluted with rice husk than weak acids, accordingly the silica percentage was increased as % atomic size. The weak acid is less dissoluted with rice husk, accordingly the silica percentage was not increased as % atomic size. Finally, the silica percentage as atomic size was increased up to 99.58% with leached HCl rice husk ash compared to H_2SO_4 and CH_3COOH and control as unleached with acids. The results of silica percentage was mostly same as compared between HCl and H_2SO_4. The percentage of silica was 99.58% as atom with HCl leached rice hush ash and The percentage of silica was 99.08% as atom with H_2SO_4 leached rice hush ash. It is concluded that the some factors such as pH, temperature and acid dissolution on the rice husk played the very important role to achieving the best rice husk ash containing pure silica. Finally, the high purity of silica was obtained from the dissolute of rice husk with HCl. Finally, silica produced in the form of amorphous state with high purity 99.58% as atom.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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