



Extraction and Characterization of Bio-Silica from Sri Lankan Traditional Rice Husks and Evaluation to TLC Application

Sapna Poorni Fernando¹, Pahan I. Godakumbura², M.A.B. Prashantha³

^{1,2,3} Department of Chemistry, Faculty of Applied Sciences, University of Sri Jayewardenepura, Sri Lanka

ABSTRACT: Rice husk (RH) is one of the most abundant agricultural wastes, but can be identified as a useful bio resource. Gonabaru, Kahawanu, Patchaperumal, Dahanala and Suwandel are five emerging traditional rice varieties, competing with genetically improved rice in Sri Lankan rice market. Ash content of RHs of traditional rice varieties (>20.0%) was comparatively higher than genetically improved rice. It was identified that additional acid washing step was essential to improve the purity of bio silica. Mineral impurities such as Na, K, Ca, Fe and Mn were determined using atomic absorption spectrometer (AAS). High silica content was extracted from RHs of traditional rice varieties (>23.0%) than that of improved variety, BW 364 (~16.2%). The functional groups present in Rice husk ash (RHA) and rice husk silica (RHS) were determined using Fourier transform infrared (FTIR) analysis. The potential application of purified RHS was observed by preparing and analyzing the thin layer chromatography (TLC) in comparison with commercial TLC silica.

KEYWORDS: rice husk; rice husk ash; rice husk silica, thin layer chromatography.

INTRODUCTION

Rice husk (RH) is one of the most abundant agricultural wastes available in rice producing countries like Sri Lanka. Rice production of a country varies significantly with several factors, not only the rainfall, but also depends on the geographical areas, land availability, irrigation system, fertilizer usage and the variety. A developing trend for consuming the organically formed traditional rice is apparent in Sri Lanka, due to the medicinal and nutritional values compared to the genetically improved rice varieties [1]. It is believed that consumption of traditional rice is one of the alternative solutions to minimize the risk for non-communicable diseases. Gonabaru, Kahawanu, Patchaperumal, Dahanala and Suwandel are some of the examples for traditional rice varieties available in Sri Lankan rice market.

RH contains mainly 75% - 90% organic matter such as cellulose, hemicelluloses and lignin, while the rest is composed of silica, alkali and trace elements [2]. White rice husk ash (WRHA) is rich in silica and it contains small amount of trace elements such as Na, K, Ca, Fe and Mn [3]. Since the RH is a good alternative source of sustainable energy, conversion of RH through energy generation process into high purity silica is a cost-effective solution for the problem of accumulation of RH as agro waste in rice producing countries [2].

Literature has reported two step heat treatment processes to produce WRHA. It consists burning of RH to black rice husk ash (BRHA) followed by heating at 700°C temperature to produce WRHA. The yield of WRHA has varied in the range of 10% - 20% [4], [5]. RH can be considered as silica precursor for many laboratory and industrial works. Pure silica is heavily used in producing chips in electronic devices. Silica is also a useful material for thin layer chromatography or column chromatography techniques used in organic laboratory and it is used as filler in some industrial applications. Rice husk silica (RHS) is also tested for synthesizing zeolite NaY [6], zeolite Y [7] and zeolite LSX [8].

The focus of this study is to extract green silica from the selected RHs of Sri Lankan traditional rice varieties, and to characterize and evaluate its potential TLC applications. In addition, RH of genetically improved rice variety is also taken to compare with RHs of traditional rice varieties.

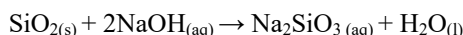
METHODOLOGY

A. Extraction of Silica

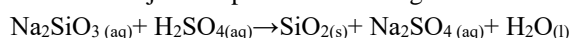
Five different traditional rice varieties (Gonabaru, Kahawanu, Patchaperumal, Dahanala and Suwandel) and one genetically improved rice variety (BW 364) were collected. Rice husks of all rice varieties were taken separately.



RH was burnt in air until it becomes BRHA and it was further burnt using a muffle furnace at 700°C until it becomes WRHA. A mixture of 10 g of WRHA and 100 ml of 2.0 moldm⁻³ HCl acid solution was stirred well for two hours. The acid insoluble fraction of WRHA was separated by suction filtration using the Whatman No.41 ashless filter paper. Acid insoluble fraction of WRHA was washed thoroughly with 100 ml of distilled water. Silica extraction from acid insoluble fraction of WRHA was carried out in a stainless-steel container using volume of 100 ml of 2.5 moldm⁻³ sodium hydroxide solution. The alkali mixture was boiled for three hours with continuous stirring. Sodium hydroxide converts silica into soluble sodium silicate.



The alkali solution was filtered using the Whatman No.41 ashless filter paper and the respective residue was washed with 50 ml of boiling water. The filtrate was allowed to reach room temperature. The pH of the filtrate was adjusted to 2 using 5.0 moldm⁻³ sulphuric acid and then ammonium hydroxide was added to adjust the pH to 8.5. Silica gel formation reaction is shown below.



The reaction was allowed to stand for three and half hours to yield a suspension of silica gel. The suspension of silica gel was separated and washed thoroughly. It was oven dried at 120°C for twelve hours to convert silica gel into high purity silica [9].

B. Proximate Analysis of RH Samples

Moisture content, ash content and volatile matter of RHs were determined in accordance with the ASTM D 1037 (1991), ASTM D 2017 (1998) and ASTM D 3175 standard methods respectively. The fixed carbon of RHs was calculated according to the ASTM 1992.

$$\text{FC}(\%) = 100 - (\% \text{VM} + \% \text{AC} + \% \text{MC})$$

Where: FC = Fixed Carbon; VM = Volatile Matter; AC = Ash Content; and MC = Moisture Content

C. Analysis of BRHA, WRHA and RHS

The HNO₃ digestion method was used to determine the mineral content of WRHA and acid insoluble fraction of WRHA by using thermo scientific iCE 3000 series atomic absorption spectrometer (AAS).

Attenuated Total Reflectance (ATR) mode of FTIR spectroscopy was used to identify major chemical groups present in BRHA, WRHA and RHS.

Weight to weight method was used to calculate the silica content of RH. Mass of RHS and mass of RHs used to produce RHS were used to calculate percentage of RHS with respect to the mass of RH.

Elemental Analysis was carried out by using Energy Dispersive X-ray (EDX) mode attached HITACHI SU 6600 SEM with an acceleration voltage of 12.0 kV.

D. Evaluation of TLC Application of Extracted RHS

RHS was used as an adsorbent material in thin layer chromatography (TLC) in order to study the possibility of using RHS in TLC application. A sample mixture containing 2-nitroaniline and 4-nitroaniline was analyzed using TLC plates prepared from RHS and they were compared with that of commercially available silica by calculating R_f values of TLC applications.

RESULTS AND DISCUSSION

A. Proximate Analysis of RHs

Table 1 shows the moisture content, ash content, volatile matter and fixed carbon of RHs of five different traditional rice varieties and one genetically improved rice variety (BW 364). Moisture content of RHs is not a constant value. It can be varied from one rice variety to the other rice variety. Because RH is a hygroscopic material as it can change its equilibrium moisture content depending on the temperature and relative humidity [10]. According to the results, moisture content of RHs of selected rice varieties has not been significantly varied and it is around 5.0%. Ash content of RHs is higher in traditional rice varieties (20.0%) compared to BW 364 (13.1%). Low ash content of BW 364 indicates the presence of high amount of combustible materials. High ash content of RHs of traditional rice varieties indicates the presence of high amount of silica compared to the RHs of genetically improved rice variety. Volatile matter of RHs is in a range of 18% - 21%. Fixed carbon in RH represents the non-volatile combustible organic substances. Fixed carbon content of RHs of traditional rice varieties is around 54% and it is less than approximately by 8% to the fixed carbon content of RHs of BW 364.



Table 1. Proximate Analysis of RH on Dry Basis

Type of RH	Mean ± SD			
	MC / %	AC / %	VM / %	FC / %
Gonabaru	5.5 ± 0.0	20.8 ± 0.0	20.2 ± 0.1	53.5 ± 0.0
Kahawanu	4.5 ± 0.2	21.2 ± 0.0	20.7 ± 0.1	53.6 ± 0.1
Patchaperumal	5.0 ± 0.1	20.0 ± 0.0	20.7 ± 0.1	54.3 ± 0.0
Dahanala	5.1 ± 0.1	20.4 ± 0.0	19.7 ± 0.0	54.8 ± 0.0
Suwandel	5.1 ± 0.2	21.9 ± 0.0	18.7 ± 0.0	54.3 ± 0.1
BW 364	4.9 ± 0.1	13.1 ± 0.0	20.3 ± 0.1	61.7 ± 0.0

B. Mineral Content of WRHA

WRHA contains minerals such as Na⁺, K⁺, Ca²⁺, Fe³⁺ and Mn²⁺ in its oxide forms [2]. Acid washing step refines WRHA in order to improve the purity of silica extracted from RHs. According to the Table 2, more than 87% of all the minerals (Na⁺, K⁺, Ca²⁺, Fe³⁺ and Mn²⁺) have been leached out as identified by AAS. It shows the significance of acid washing step to improve the purity of RHS by leaching out mineral impurities from WRHA.

Table 2. Percentage of Reduction of Mineral Content after Acid Washing Step

Type of RHA	PR / %				
	Na	K	Ca	Fe	Mn
Gonabaru	87.4	99.3	96.6	88.9	96.4
Kahawanu	93.9	99.4	96.1	95.0	100
Patchaperumal	90.3	99.8	97.5	89.5	97.7
Dahanala	88.7	99.8	97.3	90.9	96.9
Suwandel	92.0	99.7	95.7	87.5	100
BW 364	92.2	99.5	96.7	95.0	100

It indicated the effectiveness of acid washing to remove K by more than 99% of five traditional varieties and BW 364. Acid washing step for purification of Kahawanu and BW 364 is significantly effective for all metal ions.

C. Silica Content of RHs

According to the experimental readings, silica content of various RHs is given in Table 3. RHs of Sri Lankan traditional rice varieties contain higher silica content in a range of 24.0% - 27.0% compared to the genetically improved BW 364 (16.2%). As shown in Table 3, Kahawanu and Suwandel gave the highest yield of silica.

Table 3. Silica Content of Different Rice Husks

Type of RHs	Silica Content / %
	Mean ± SD
Gonabaru	24.9 ± 0.7
Kahawanu	26.4 ± 0.6
Patchaperumal	23.6 ± 0.5
Dahanala	25.4 ± 0.5
Suwandel	26.5 ± 0.5
BW 364	16.2 ± 0.3



According to the Table 2 and Table 3, RH of Kahawanu is more suitable one to obtain high yield of bio-silica. Kahawanu RHS sample was also analyzed using EDX to obtain the elemental analysis (shown in Table 4 & Figure 1). Results confirmed the RHS contains high amount of silicon (38.77%), oxygen (36.82%) and other elements such as carbon (22.78%), trace amounts of sodium (0.56%) and sulphur (1.07%).

Table 4. Elemental Analysis of RHS

Element	Net Counts	Net Counts Error	Weight %	Weight % Error	Atom %
C	4723	+/- 130	22.78	+/- 0.31	33.66
O	30881	+/- 372	36.82	+/- 0.22	40.83
Na	962	+/- 206	0.56	+/- 0.06	0.43
Si	104704	+/- 782	38.77	+/- 0.14	24.49
S	1916	+/- 324	1.07	+/- 0.09	0.59
Total	-	-	100.00	-	100.00

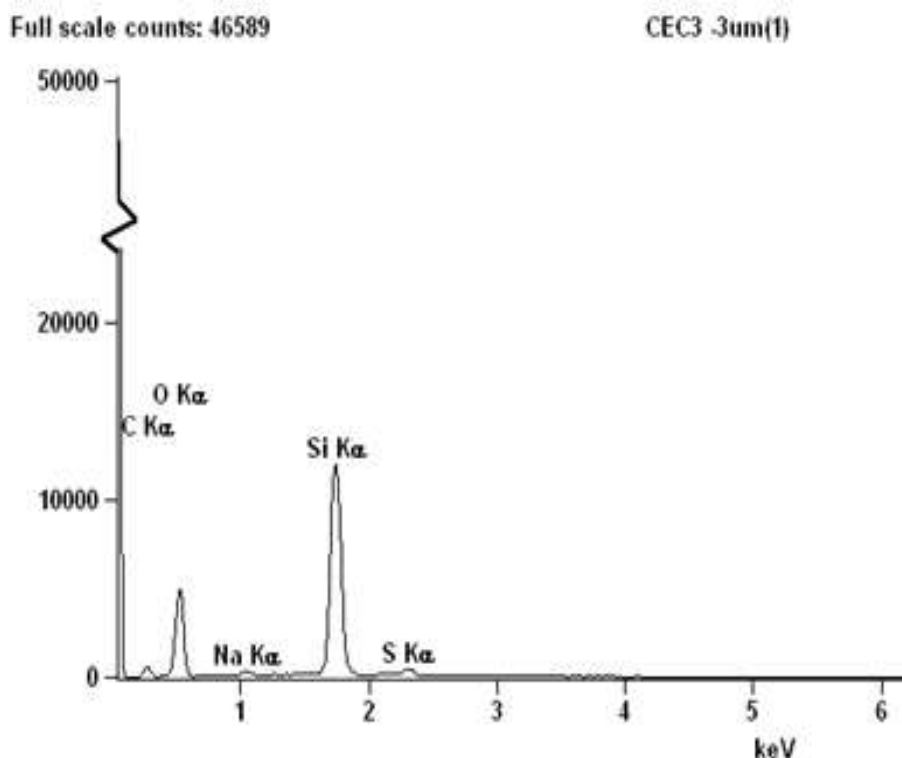


Figure 1. Elemental analysis of RHS using EDX spectroscopy

D. Fourier Transform Infrared (FTIR) Spectra of BRHA, WRHA and RHS

FTIR spectroscopy can be used to identify major chemical groups present in BRHA, WRHA and RHS. Figure 2 shows the FTIR spectra of BRHA, WRHA and RHS. According to the Figure 2, four major peaks (3309-3317 cm^{-1} , 1597-1604 cm^{-1} , 1050-1064 cm^{-1} and 793 cm^{-1}) have been appeared in BRHA. However, there is only two major peaks (1050-1064 cm^{-1} and 793 cm^{-1}) which are remained in the FTIR spectrum of WRHA after processing BRHA to WRHA. That means those two peaks (3309-3317 cm^{-1} and

1597-1604 cm^{-1}) which are only remaining in the BRHA have been mainly due to the non-removal organic matter. FTIR spectrum of WRHA contains only two peaks which are regarding to the asymmetric stretching of siloxane (Si-O-Si) bond (1050-1064 cm^{-1}) and symmetric stretching of siloxane (Si-O-Si) bond (793 cm^{-1}). Hence all the organic matter has been expelled during the ashing process. When proceeding to RHS, new peaks have been appeared due to the formation of new bonds.

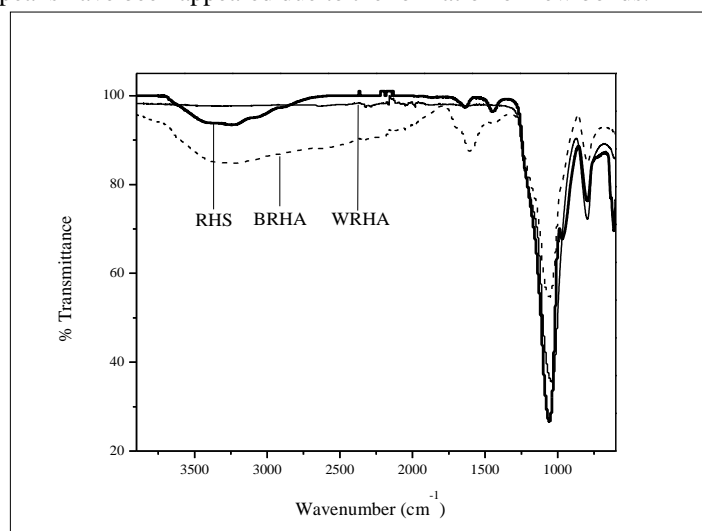


Figure 2. FTIR spectra of BRHA, WRHA and RHS

According to the FTIR spectra of RHS (Figure 3), five major peaks are presented. There is one broad peak at 3330-3450 cm^{-1} , one strong narrow peak at around 1056 cm^{-1} and three other peaks at around 1635 cm^{-1} , 966 cm^{-1} and 793 cm^{-1} . Those peaks are related to symmetric stretching vibrations of silanol O-H groups and O-H vibrations of H_2O molecules adsorbed on the silica surface (3330-3450 cm^{-1}), symmetric stretching vibrations of silanol O-H groups (966 cm^{-1}), bending vibrations of H_2O molecules bound to the silica matrix (1635 cm^{-1}), asymmetric stretching vibrations of the structural siloxane bond (1056 cm^{-1}) and symmetric stretching vibrations of siloxane bond (793 cm^{-1}).

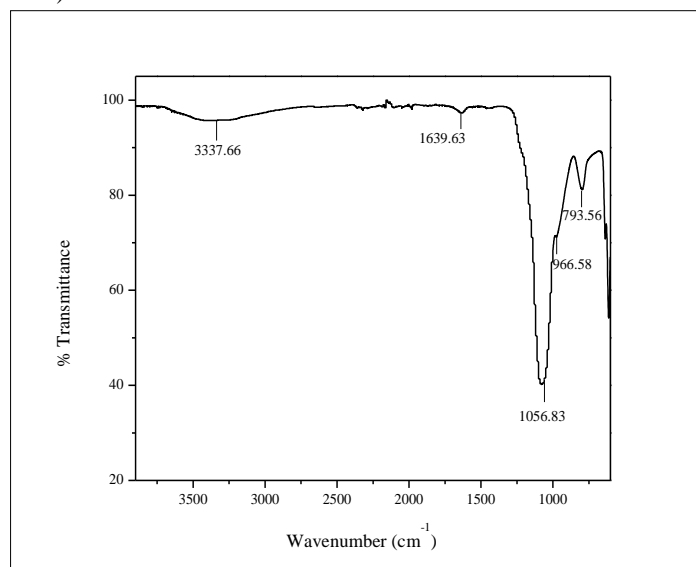


Figure 3. FTIR spectrum of RHS extracted from traditional rice variety (Kahawanu)

FTIR spectra of silica which is used for TLC and column chromatography, precipitated silica and RHS have been sketched in one FTIR spectrum (Figure 4) to compare RHS with commercially available silica.

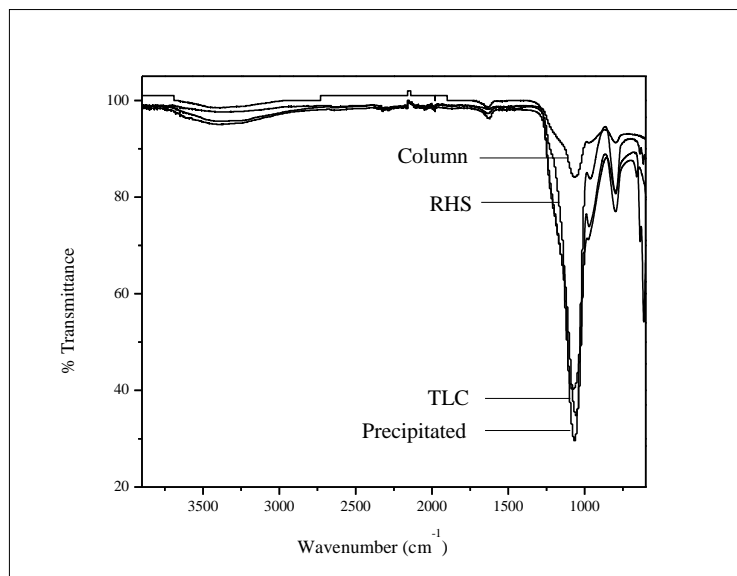


Figure 4. FTIR spectra of RHS compared with commercially available silica

According to the Figure 4, FTIR spectrum of RHS is almost same as the FTIR spectrum of silica which is used for TLC. Hence FTIR spectrum of precipitated silica is also matched with the FTIR spectrum of RHS. But FTIR spectrum of silica which is used for column chromatography is somewhat different from other spectra as it does not have sharp peaks. All FTIR spectra of RHS which is extracted from different RHs are identical.

E. Evaluation of TLC Application of Extracted RHS

As mentioned earlier, FTIR spectrum of RHS is almost similar to the FTIR spectrum of commercially available silica which is used for TLC. A mixture of 2-nitroaniline and 4-nitroaniline has been used to determine the prepared TLC plates are working properly. According to the retention factor (R_f) values shown in Table 5, it is proved that TLC plate which is prepared by RHS works properly as almost similar to the TLC plate which is prepared by commercially available silica.

Table 5. Determination of R_f Values Using Thin Layer Chromatography

Compound	R_f Values	
	RHS	Laboratory Silica
2-nitroaniline	0.61	0.60
4-nitroaniline	0.31	0.31

Therefore, RHS can be used to prepare TLC plates as they are very useful for a laboratory for several purposes. However, preparation of TLC plates is a potential application of RHS.

CONCLUSION

This research has been revealed that the utilization of RH to extract silica and their characterization. RH can be used as a fuel and as the silica source for other applications. Acid washing step is necessary to remove high content of mineral impurities. Silica content is higher in RHs of traditional rice varieties than that of BW 364. Prepared TLC plates using RHS have been working almost similar to the laboratory available TLC plates.

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