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CHARACTERISATION OF HIGH PURITY RICE HUSK SILICA SYNTHESISED USING SOLVENT-THERMAL TREATMENT WITH DIFFERENT CONCENTRATION OF ACID LEACHING

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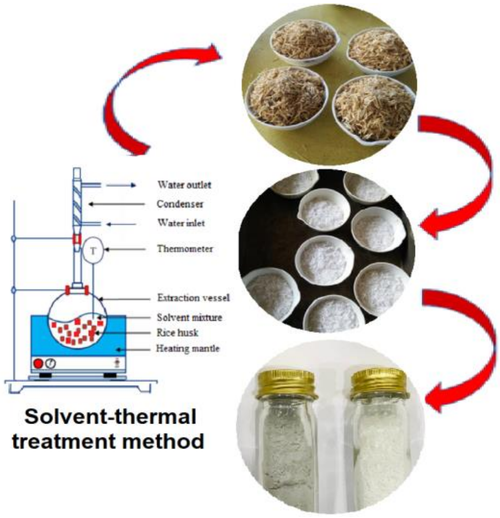
Graphical abstract



Abstract

In recent years, research on bio-based materials, such as rice husk is steadily gaining momentum. Despite their huge developmental potential, rice husks are often left unutilised following the harvesting season, wasting a natural wealth that could be explored. Their high silica content makes them potential fillers to replace commercial precipitated silica in the polymer industry, composites and building materials for construction. In this study, highly pure silica with small particle size and high surface area was extracted from rice husks via solvent-thermal treatment, followed by leaching with different concentrations of hydrochloric acid (HCl). This treatment method was modified from TAPPI T204 (2007) and TAPPI T264 (1997) standards, which are used for wood extraction in the pulp and papermaking industry. By using this method, rice husk silica (RHS) that was leached with 1.0 M HCl recorded the highest particle purity with 99.99% of SiO_2 content and the highest BET surface area of 234.25 m^2/g compared with RHS leached with 0.01 M, 0.1 M, 2.0 M, and 3.0 M HCl. All RHS samples were in the amorphous state following incineration at 700°C for 4 hours. This proved that RHS synthesised by solvent-thermal treatment method can be further developed as one of the alternatives to commercial silica in the market.

Keywords: Solvent-thermal treatment, rice husk silica, acid leaching, morphological study, surface analysis

Abstrak

Beberapa tahun kebelakangan ini, penyelidikan mengenai bahan berasaskan bio, seperti sekam padi semakin berkembang. Walaupun ia berpotensi untuk dimajukan, sekam padi sering dibiarkan selepas musim menuai, lalu membazirkan kekayaan semula jadi yang boleh diterokai. Kandungan silika yang tinggi di dalam sekam padi menjadikannya

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berpotensi sebagai pengisi untuk menggantikan mendakan silika komersial (precipitated silica) di dalam industri polimer, komposit, dan bahan binaan. Dalam kajian ini, silika yang sangat tulen dengan saiz zarah kecil dan luas permukaan yang tinggi diekstrak daripada sekam padi melalui pengekstrakan pelarut-terma, diikuti dengan proses larut-lesap dengan kepekatan asid hidroklorik (HCl) yang berbeza. Kaedah pengolahan ini diubahsuai daripada piawaian TAPPI T204 (2007) dan TAPPI T264 (1997) yang digunakan dalam pengekstrakan kayu di dalam industri pembuatan pulpa dan kertas. Dengan menggunakan kaedah ini, silika sekam padi (RHS) yang dilarut-lesap dengan 1.0 M HCl mencatatkan ketulenan zarah tertinggi dengan 99.99% SiO_2 dan luas permukaan BET tertinggi pada 234.25 m^2/g, berbanding dengan RHS yang dilarut-lesap dengan 0.01 M, 0.1 M, 2.0 M, dan 3.0 M HCl. Kesemua sampel RHS berada dalam keadaan amorfus selepas pembakaran pada 700°C selama 4 jam. Ini membuktikan bahawa pengekstrakan RHS dengan kaedah pelarut-terma boleh dibangunkan sebagai salah satu alternatif kepada silika komersial di pasaran.

Kata kunci: Kaedah perawatan pelarut-terma, silika sekam padi, larut-lesap asid, kajian morfologi, analisa permukaan

1.0 INTRODUCTION

Silica is a group of minerals comprised of silicon and oxygen which sources has been explored including sodium silicate from quartz, or sand, and from tetraethoxysilane and tetramethoxysilane. Silica is widely used in many industrial sectors including constructions, electronics, medical devices, ceramics, and polymeric materials [1]. However, the production of pure silica by smelting quartz and sand at 1300℃ is energy intensive [2], while tetraethoxysilane and tetramethoxysilane were reported to have high toxicity [3,4]. Therefore, researchers are seeking alternatives for silica from other natural sources including biomass wastes. Rice husk is one of the agricultural wastes that has inevitably attracted researchers [5]. Rice husk ash contains about 90-98% of silica [4]. By processing rice husks into synthesised silica, the greenhouse effect and pollutions due to out-dated disposal methods of field dumping and openly burning rice husks can be reduced [6]. Because of its greater availability, low cost, and non-toxicity, RHS is an appropriate alternative to replace commercial synthetic silica, to be used in a wide range of industrial applications.

Many studies have been conducted to synthesise silica from rice husks, considering that rice husk silica shows tremendous strength-related properties when incorporated in polymer composites and building materials for constructions [7,8]. To date, various processing methods have been developed to synthesise silica from rice husk, including precipitation method, sol-gel method , and calcination [9]. Among these methods, precipitation with acid and the dissolution of sodium silicate from rice husks is the preferred way to produce silica. Although high purity silica can be achieved using this method, the complicated process, large chemical consumption, and high costs prevent this method from undergoing further development. Silica obtained from sol-gel methods was also reported to have high purity and homogeneity. However, the synthesis process based on the low-temperature hydrolysis was time-consuming.

Therefore, a simple and practical method for producing high purity silica, with high surface area from rice husks, is vital since silica is on demand for many industrial applications, such as fillers to produce various rubber products. The main interest of this research was to synthesise high purity silica from rice husks using a simple solvent-thermal treatment, which was modified from a treatment method for wood in pulp and paper making industries. The limited knowledge and understanding of this method makes it a novel approach to explore.

In this study, silica with 99.9% purity was synthesised from rice husks using a solvent-thermal treatment method with different concentrations of acid for leaching. This method was adopted from Technical Association of the Pulp and Paper Industry (TAPPI) standard (T204 and T264), with some significant modifications. Hydrochloric acid (HCl) was used in the leaching process because HCl treatment could effectively remove metallic impurities in rice husks better than other acid treatments, such as nitric and sulphuric acids [10].

2.0 METHODOLOGY

2.1 Materials

Rice husks were obtained from a local mill in Kuala Selangor, Malaysia. Hydrochloric acid (37%) for leaching process and solvents for extraction, namely, toluene, ethanol, and acetone were purchased from Merck (M) Sdn. Bhd., Petaling Jaya, Selangor, Malaysia. The solvents were used as received from the suppliers.

2.2 Synthesis of High Purity Rice Husk Silica (RHS)

Rice husks were washed with distilled water to remove dirt and soluble particles. Then, the rice husks were dried in an oven at 110℃ for 24 hours before being subjected to the solvent-thermal treatment method.

The solvent mixture, which consisted of toluene, ethanol, and acetone (named as TEA solvents) with ratio of 3:2:1, with a total volume of 1,800 mL, was prepared in a beaker. The TEA solvent mixture was then poured into a 2 L glass reaction flask containing 180 g of cleaned rice husks. The extraction process was conducted for 45 minutes at 110℃. The extracted rice husks were then washed with distilled water before being subjected to the acid leaching process. The extraction set-up is showed in Figure 1.

Different concentrations of acid were used for leaching; 0.01, 0.1, 1.0, 2.0, and 3.0 M HCl. The rice husks were soaked in the acid solution for 24 hours. Then, the treated rice husks were washed thoroughly with distilled water to remove the remaining acid and then dried in an oven at 110℃ for 24 hours. The dried rice husks were incinerated in a furnace at 700℃ for 4 hours to obtain white ash silica. Finally, the rice husk ash was ground with an agate mortar until super fine white silica powder was obtained. Around 10-15% of RHS from the total weight of rice husk can be obtained in each cycle. The synthesized rice husk silica (RHS) is kept in a well closed container in a cool dry place for further analysis.

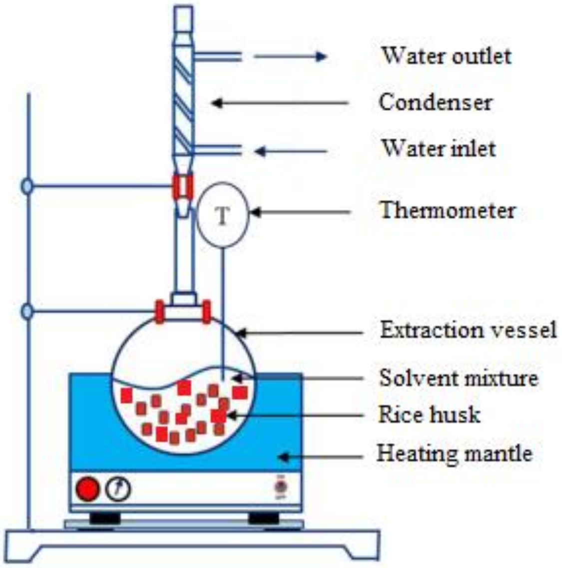

Figure 1 Extraction set-up

2.3 Characterisation of RHS

2.3.1 *Colour Analysis*

The colour of the untreated rice husk ash (RHA) and treated rice husk silica (RHS) powder were evaluated using chroma meter (model Konica Minolta CR-400; NJ, USA). Around 10 to 15 g of samples of untreated RHA and treated RHS were placed in different transparent zipper bags prior to measurement. The measuring head of the chroma meter was first calibrated with a white calibration plate. Three readings were obtained for each sample. The colour of the commercial precipitated silica (PS) was evaluated as a standard. The colour difference can be identified as the numerical comparison of a sample's colour to a standard by using Commission Internationale de l'Eclairage (CIE) L*a*b* coordinates, where L* indicates lightness, a* is the red/green coordinate, and b* is the yellow/blue coordinate. The total difference, delta E (ΔE*), was calculated according to the colour difference equation [11] in equation 1. The subscripts 1 and 2 represent the standard and the sample, respectively.

$$\Delta E^* = \sqrt{(L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)^2} \qquad (1)$$

Whiteness can also be measured using whiteness index (WI) which was originally proposed by Hunter [11], as in equation 2:

$$WI_{HUNTER} = L^* - 3b^* \qquad (2)$$

2.3.2 *XRF Elemental Analysis*

The elemental composition and purity of the RHS powder were measured using an X-ray fluorescence (XRF) spectrometer (model WDXRF; Shimadzu, Kyoto, Japan). Around 10 to 15 g of sample was placed into a plastic sample cup with a plastic support film. A flat surface of the support film to the X-ray analyser is important to ensure the sample was supported over the X-ray beam during analysis.

2.3.3 *Morphological Study and Surface Analysis*

The morphology and surface characterisations of RHS samples were conducted using a scanning electron microscope (SEM) (SUPRA 40VP; Carl Zeiss AG, Oberkochen, Germany) with a constant applied voltage of 10 kV. The powder samples were subjected to gold sputtering in a sputter coater (Type SCD 005; Bal-Tec Inc., Balzers, Switzerland) prior to the electron microscopy to prevent any electrostatic charges during the analysis.

A high-resolution transmission electron microscope (HRTEM) (model TECNAI G2 20 S-TWIN; FEI Company, Hillsboro, USA) was used to further investigate the structure and the average particle size of the synthesised RHS. The RHS sample (10 mg) was sonicated in acetone for 3 minutes to break the agglomerates. A little drop of the RHS suspension was taken using a micro-pipette and spread on the carbon coated copper grid and allowed to dry in room temperature. The copper grid was inserted into the HRTEM instrument and the sample was scanned along the path of the electron beam at the acceleration voltage of 200 kV.

To obtain the specific surface areas and average pore volumes of the RHS particles, the Brunauer-Emmett-Teller (BET) method was used. Surface area analysis was conducted using a micropore surface area analyser (model MIC271002 REV B; Micromeritics, Norcross, USA). After the powder samples have undergone the degassing procedure for 5 to 6 hours, measurements were taken under nitrogen adsorption at liquid nitrogen temperature. The average size of the RHS particles was measured using a Zetasizer Nanoseries (Malvern Instruments Ltd, Malvern, United Kingdom). The RHS powder was dispersed in water and then sonicated for 30 minutes prior to analysis.

2.3.4 XRD Analysis

The X-ray powder diffraction (XRD) data of the RHS samples were obtained from the XRD instrument (model Xpert Pro; Pan Analytical, Netherlands). It is a versatile, non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of the material. The RHS powder was pressed onto the metal holder to obtain a flat upper surface before being subjected to the analysis.

2.3.5 FTIR Analysis

Fourier transform infrared spectroscopy (FTIR) (model Spectrum One, PerkinElmer, Boston, USA) was used to determine the functional groups and chemical characteristics of the RHS through molecular absorption and transmission. The thin and translucent KBr pellets that were mixed with RHS samples were prepared prior to the analysis. The FTIR spectrometer was operated at a scanning range of 4,000 to 450 cm^{-1}.

3.0 RESULTS AND DISCUSSION

3.1 Colour Analysis

The colour of the rice husk ashes obtained after incineration could be the first indicator of the traces of carbon and metallic impurities in the rice husk. Figure 2 shows the appearance of the RHA and RHS after incineration at 700°C. The RHA from untreated rice husks was grey in colour, as shown in Figure 2(a), which indicated the presence of metallic impurities and unburnt carbon from the lignocellulosic components. However, the solvent-thermal-treated rice husks that were leached in 1.0 M HCl showed an incredible result, whereby the ash was completely white in colour after incineration, as shown in Figure 2(b). It shows that acid leaching followed by thermal treatment could induce the production of silica with the lowest carbon level.

Colour analysis was conducted to determine the whiteness index (*WI*) and the total colour difference (ΔE^*) of the untreated RHA and treated RHS with the standard (white commercial silica). As indicated in Table 1, RHS leached with 1.0 M HCl recorded the highest *WI* compared to untreated RHA, unleached RHS and RHS leached with lower concentration of HCl. The highest ΔE^* value recorded by untreated RHA. The colour changed drastically whiter after solvent-treatment and acid leaching process. The higher the concentration of HCl, the whiter the RHS became.

Figure 2 Appearance of RHA and RHS samples: (a) RHA extracted from untreated rice husks incinerated at 700°C; and (b) RHS extracted from solvent-thermal treated and leached rice husks in 1.0 M HCl, followed by incineration at 700°C

Table 1 Colour analysis of RHA and RHS

Sample	Whiteness index (*WI*)	Colour difference index (ΔE^*)
Untreated RHA	73.94	21.97
Unleached RHS (Solvent treated)	81.38	9.15
RHS leached with 0.10 M HCl	83.26	3.73
RHS leached with 1.0 M HCl	89.94	2.58

As reported by Della *et al*., the changes in colour of the treated rice husks were due to the complete combustion process, which can be associated with the structural conversion of the silica in the rice ash [12]. RHA usually contains incomplete combustion of organic residues and a mixture of amorphous and crystalline silica, whereas RHS generally contains low level of impurities compared to that of RHA [13].

The colour of ashes also depends on the temperature setting for the incineration. Ugheoke & Mamat had summarised that the transformation of grey raw rice husks to white is also critically dependent on the incineration temperature [14]. Temperatures between 300°C to 450°C would produce dark grey carbonised ash, while at higher temperatures of approximately 500°C to 650°C, the rice ash would become light grey and white ash. The disappearance of the grey colour in RHS indicated the effectiveness of the solvent-thermal treatment method in extracting undesirable organic extractives and heavy metal impurities that were interwoven within the lignocellulosic components. In addition, leaching the solvent-treated rice husk with 1.0 M HCl acid had effectively hydrolysed the lignocellulosic components contained in the rice husks, indirectly removing other traces of metal oxides residues that still existed. In consequence, high purity RHS was successfully obtained via this synthesis method, as reported further in XRF analysis.

3.2 XRF Elemental Analysis

The XRF elemental analysis was conducted to determine the percentage composition of the resulting RHS. The main objective of the treatment is to remove the metallic contaminants in RHS that affect surface area, reactivity and increase the crystallization rate of the silica. As indicated in Table 2, the untreated RHA contained 91.63% of SiO_2 and other metallic impurities, namely, K_2O, TiO_2, CaO, BaO, MnO, Fe_2O_3, and NiO. The content of the residual metallic impurities of the solvent-treated RHS showed a significant drop of K_2O and NiO, while TiO_2 and BaO were completely removed from the rice husk in comparison with the untreated RHA. After leaching with low concentration acid (0.01 M HCl), K_2O and MnO were totally removed, while CaO content showed a huge drop and had totally diminished after being leached with higher concentration of HCl (0.1 M). The highest content of SiO_2 was recorded at 99.99% after the solvent-treated rice husk was leached with 1.0 M HCl. All traces of metallic oxides residues were totally removed, except for a very small amount of Fe_2O_3. Leaching with HCl at higher concentrations of more than 1.0 M (2.0 M and 3.0 M) showed no linear relationship on the content of the SiO_2, however, the percentage of SiO_2 still recorded more than 99% for both. This finding is in conjunction with other claims made by other researchers. Most of the researchers reported that 1.0 M HCl is the ideal concentration molarity of the acid used for leaching, as molarity of more than 2.0 M HCl showed no significance improvement in the purities of the RHS produced [15, 16].

Table 2 XRF elemental analysis of RHA and RHS

Constituents (wt.%)	SiO_2	K_2O	TiO_2	CaO	BaO	MnO	Fe_2O_3	NiO
Untreated RHA	91.63	5.80	0.79	1.16	0.26	0.14	0.12	0.09
Unleached RHS (Solvent treated)	97.30	1.44	-	1.01	-	0.13	0.11	0.02
RHS leached with 0.01 M HCl	99.55	-	-	0.36	-	-	0.08	0.01
RHS leached with 0.10 M HCl	99.76	-	-	-	-	-	0.24	-
RHS leached with 1.0 M HCl	99.99	-	-	-	-	-	0.01	-
RHS leached with 2.0 M HCl	99.90	0.03	-	0.03	-	-	0.03	-
RHS leached with 3.0 M HCl	99.87	0.03	-	0.03	-	-	0.06	-

According to Chen *et al*., acid treatment for rice husks usually reacts in two distinct ways [17]. Firstly, it speeds up the hydrolysis of the lignocellulose to monosaccharides by removing extractives and hydrogen bonds. Soon after the polysaccharides are converted to monosaccharides, metal impurities that are bound in the lignocellulosic matters would be exposed and have the chelate reaction with acids, then would directly release to the acid leaching solutions. Metal impurities in rice husks can be categorised in three different forms; solvent and water-soluble form, the acid leachable form, and the residual. Based on Table 2, the composition of K_2O and NiO was dropped significantly after the solvent treatment, while BaO was fully removed. On the other hand, the percentage of CaO, MnO and Fe_2O_3 were not much affected during the solvent treatment, but gradually decreased after the acid leaching treatment. It shows that K_2O, NiO and BaO are mostly dissolved in the mixture of TEA solvents, while most of CaO, MnO and Fe_2O_3 are leached by the acid. This explains the difference in the solubility reactions and the distribution of those metal oxides in the rice husks. It can be deduced that K_2O, NiO and BaO were distributed at the edge of the lignocellulosic compounds or present in unbound state, while CaO, MnO and Fe_2O_3 were possibly bound inside the organic compounds, which might complicate the hydrolysis process. The addition of hydrogen ions accelerated the hydrolysis and the chelate reaction of the lignocellulosic components, especially lignin and hemicellulose, which are more unstable than cellulose.

It is known that TiO_2 is insoluble in organic solvents. However, Taku *et al*. have reported that Cl, TiO_2, Cr_2O_3, MnO, CuO, ZnO, BaO, and Fe_2O_3 (traced in untreated rice husks) were reduced and eliminated during the incineration process [18]. Even though elements like TiO_2 may not be affected by the solvents and HCl during leaching, the thermal treatment after the solvent extraction has, however, managed to improve the pozzolanic properties of RHS. The results showed that the purification through the solvent-thermal treatment method and leaching with 1.0 M HCl had successfully eliminated almost all the metallic impurities, except for Fe_2O_3 (0.01%). Therefore, the percentage of SiO_2 in the treated and leached RHS had increased to 99.99%.

3.3 Morphological Study and Surface Analysis

The SEM images of the untreated RHA and treated RHS samples are shown in Figure 3. Figure 3(a) shows untreated RHA with no clear boundaries between the particles. The irregularity in the shape of the untreated RHA was due to the presence of lignocellulosic components that is comprised of cellulose, hemicellulose and lignin. These carbon-based components bound not only the silica, but also other impurity particles together. The solvent-thermal treatment that was used in the synthesis of rice husk had modified the morphology of the RHS as in Figure 3(b). The spherical shape of RHS after solvent-thermal treatment was due to the decomposition of the lignocellulosic components. The lignocellulosic components of the rice husk tend to swell during the solvent extraction process, indirectly transforming the lignin from high to low molecular weight [19]. When the decomposition of the lignocellulosic components occurred, most of the metallic impurities and extractives bounding to them were easily exposed. The extractives and soluble impurities would dissolve in the TEA solvent mixture during the extraction process. This is aligned with the previous XRF result that clearly showed the decrement on the percentage of the metal impurities of the RHS after the solvent-thermal treatment as compared to the untreated RHA. The low molecular weight cellulose and lignin were then completely decomposed during incineration at 700°C.

The solvent-thermal treated RHS with acid leaching also shows a spherical shape, but smaller than unleached RHS in size, as in Figures 3(c) and (d). Other residual impurities that were insoluble in the solvent mixture would have the chelate reaction with HCl acid, then, released to the acid leaching solution. In terms of the morphological properties of the RHS, the concentrations of HCl acid at 0.01 M and 0.1 M for leaching did not show any major difference, except for the early formation of aggregates. After leaching with higher concentration of acid of 1.0 M HCl, the RHS particles became smaller because almost all metallic impurities have been removed, as previously reported in the XRF analysis.

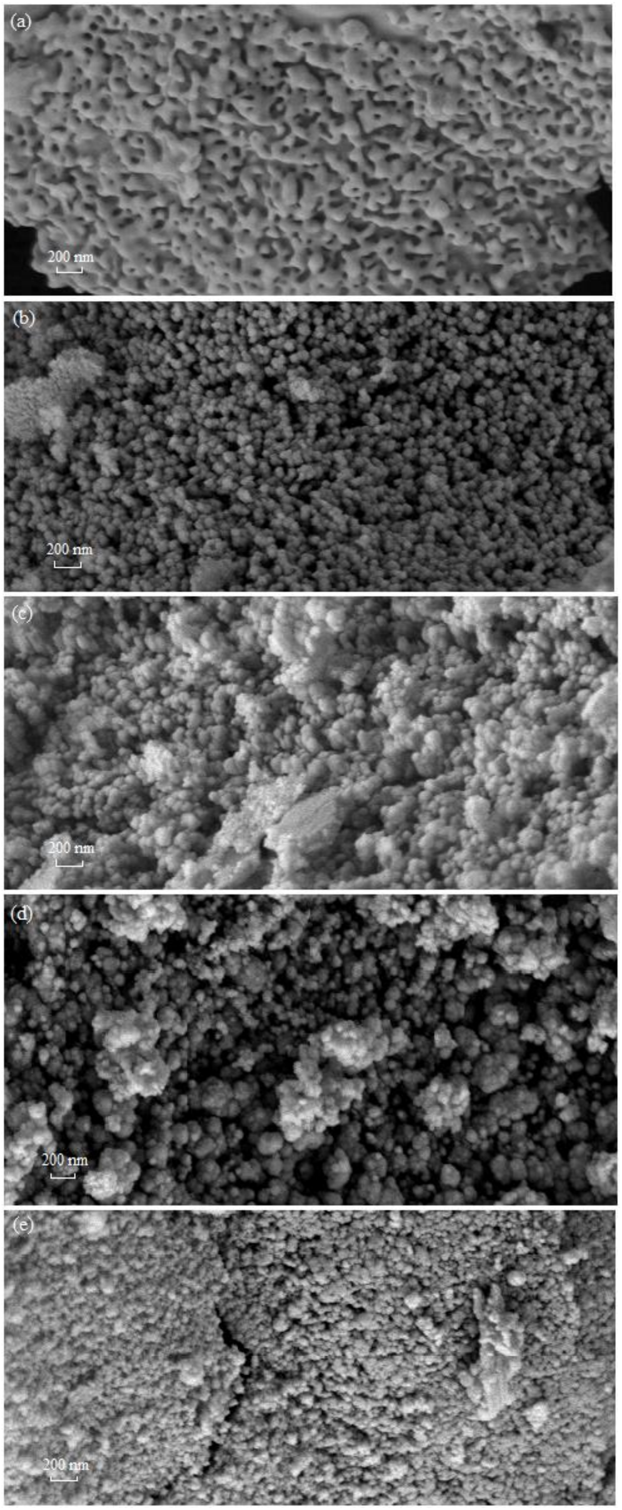

Figure 3 SEM images of RHA and RHS at 30.0k x magnification: (a) Untreated RHA; (b) Unleached RHS; (c) RHS leached with 0.01 M HCl; (d) RHS leached with 0.1 M HCl; and (e) RHS leached with 1.0 M HCl

This finding is in agreement with Faizul *et al*. [2]. Smaller particle size of RHS that at first was forming aggregates, had transform into agglomerates, as in Figure 3(e). The fast agglomeration was due to the large amount of bound water on the surface of the RHS, which resulted in strong interactions among the RHS particles. The presence of these hydroxyl groups will be discussed further based on the FTIR results.

Due to the fast agglomeration of RHS, the measurement of the exact primary particle size is complicated. From the Zetasizer analysis and SEM images, the size of the primary particles of solvent-thermal treated RHS before acid leaching was estimated around 80 to 100 nm (Figure 3b), while the size of solvent-thermal treated RHS leached with 1.0 M HCl acid was getting smaller, which was at approximately 50 nm. When compared to the particle size of the RHS leached with lower concentration of acid (0.01 M and 0.1 M), the particle size of the RHS leached with 1.0 M HCl acid was the smallest with a uniform narrow size distribution. This claim can also be supported by research conducted by Permatasari *et al*. and Xu *et al*. [20, 21].

The tendency of the treated RHS to form aggregates and agglomerates can be observed using TEM, as in Figure 4. Low and high magnification of TEM images of solvent-thermal treated RHS were captured. Figures 4(a) and (b) of RHS leached with 0.01 M HCl acid showed wide size distribution of the primary particles with an irregular geometry, causing difficulty in measuring the exact size. However, the TEM image of RHS leached with 0.1 M HCl acid shows a clearer picture of spherical shape of the primary particles. The average diameter of the RHS primary particles was observed at 80 nm, as in Figures 4(c) and (d). Aggregation had largely occurred to RHS leached with 1.0 M HCl. The primary particles were overlapping and adhering to one other, making it aggregated into clusters, as in Figure 4(e). At high magnification, agglomeration of the aggregates was clearly observed (Figure 4f). Agglomerates are clusters of loosely bound particles of aggregates, held together by weak van der Waals forces [22]. Smaller primary particle size of RHS leached with 1.0 M HCl acid provides larger surface area to adsorb more water molecules from the surrounding moisture, causing interconnection between the particles.

The analysis of the surface area was done by using BET instrument. The BET surface area and pore volume of the produced RHA and RHS leached in different concentrations of HCl acid are given in Table 3. From the table, the untreated RHA had a surface area of 11.41 m^2/g, while the unleached RHS was 93.76 m^2/g. The surface area of RHS had then gradually increased, as the concentration of the HCl acid for leaching also increased. The higher the concentration of the HCl acid used, the larger the surface area of the RHS. However, there was no significant difference on the surface area of the RHS leached with HCl at concentration higher than 1.0 M. RHS leached with 1.0 M HCl acid has recorded the highest BET surface area, which was at 234.25 m^2/g. It proved that 1.0 M is the most ideal concentration of HCl acid, which it had effectively purified the RHS by removing most of the undesired impurities, resulting in the highest surface area of the RHS. This result is consistent with SEM images analysis, as previously reported. Theoretically, a smaller particle size would result in a higher surface area that would perhaps yield a higher reinforcing effect on the rubber matrix [23].

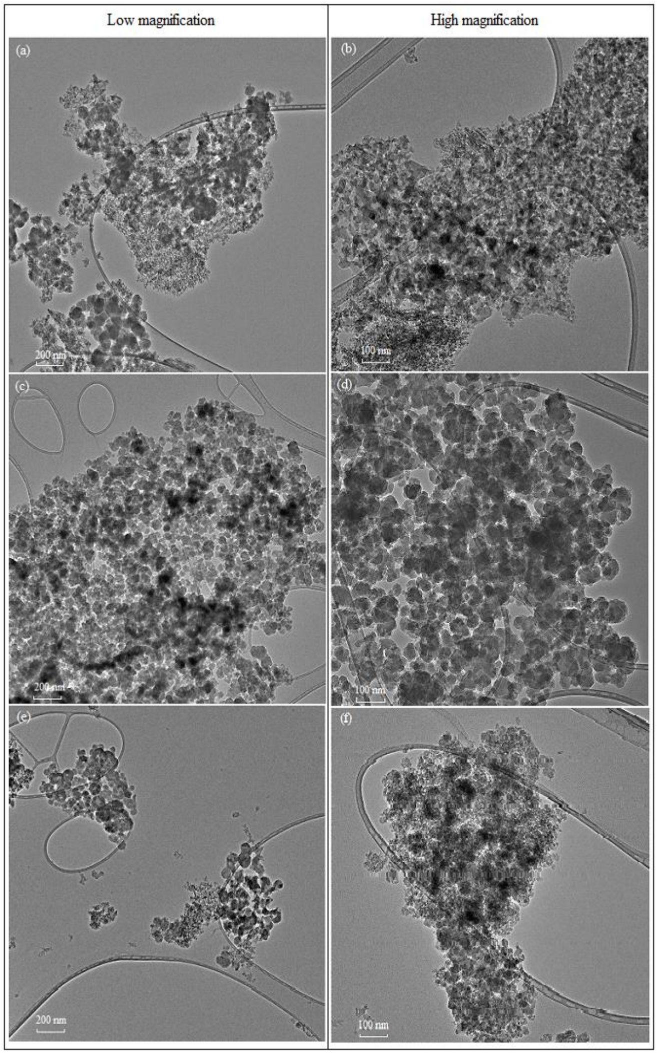

Figure Error! No text of specified style in document. TEM images of solvent-thermal treated RHS at low magnification (200 nm) and high magnification (100 nm): (a–b) RHS leached with 0.01 M HCl; (c–d) RHS leached with 0.1 M HCl; and (e–f) RHS leached with 1.0 M HCl

Table 3 BET surface area and pore volume of RHA and RHS

Sample	BET Surface Area (m²/g)	Pore Volume (cm³/g)
Untreated RHA	11.41	0.0786
Unleached RHS	93.76	0.1983
RHS leached with 0.01 M HCl	176.25	0.2605
RHS leached with 0.10 M HCl	227.93	0.3000
RHS leached with 1.0 M HCl	234.25	0.2957
RHS leached with 2.0 M HCl	229.57	0.3110
RHS leached with 3.0 M HCl	208.17	0.2743

As previously mentioned, smaller particles and fine particle size tend to form agglomeration due to the van der Waals attraction and hydrogen bonding. The formation of aggregates and agglomerates of the primary particles leads to the increment of pore volume, as indicated in Table 3. RHS leached with 0.1 M, 1.0 M, and 2.0 M HCl acid recorded the largest pore volume, which were 0.3000, 0.2957 and 0.3110 cm³/g, respectively. The pore volume of the untreated RHA and unleached RHS were 0.0786 and 0.1983 cm³/g, respectively, smaller than RHS leached with acid. Coarser particles of RHA and unleached RHS was due to the presence of metal impurities that were still attached to the particles. The decrement of pore volume of the untreated RHA and unleached RHS might be due to the high proportion of metal oxides and other residues that were blocking the pores. Although scarce, this claim can be supported by a similar research done by Liou & Yang [24].

3.4 XRD AND FTIR ANALYSIS

Incineration temperature and time are the two important factors to determine whether the silica particles remain amorphous or have transformed into crystalline phase. Crystallisation is avoided in most cases, as silica is inactive in crystalline form. Several studies have indicated that amorphous silica is formed at temperature below 700℃ and higher temperature would induce the formation of crystalline silica such as quartz, cristobalite and tridymite [25,26]. However, crystallisation may occur below 700℃ due to eutectic reaction of silica with other alkali metals that is present in the rice husk. The efficient treatment and leaching process of rice husk is crucial to eliminate most of the metal impurities to prevent this eutectic phenomenon that may lead to crystallisation formation at lower temperature [27,28]. To verify the amorphous phase of the silica produced after incineration at 700℃, XRD patterns of the untreated RHA and treated RHS are presented in Figure 5. The broad diffused peaks were displayed at 2θ = 22° for RHA and RHS, indicating the amorphous nature of silica. There is no sharp peak observed due to the absence of an ordered crystalline structure. It implies that the produced RHS is amorphous in nature and the eutectic phenomenon did not occur [26].

FTIR measurements were conducted to identify the functional groups present on the surface of the RHA and RHS. FTIR transmittance spectra were taken in the range of 4000 to 400 cm^{-1} and several peaks were detected, as in Figure 6. The broad band in the range of 3750 to 3250 cm^{-1} was detected in all of the treated RHS samples (Figure 6b–g), except for untreated RHA (Figure 6a). This broad peak is mainly corresponding to the O-H stretching vibration of surface hydroxyl (-OH) groups.

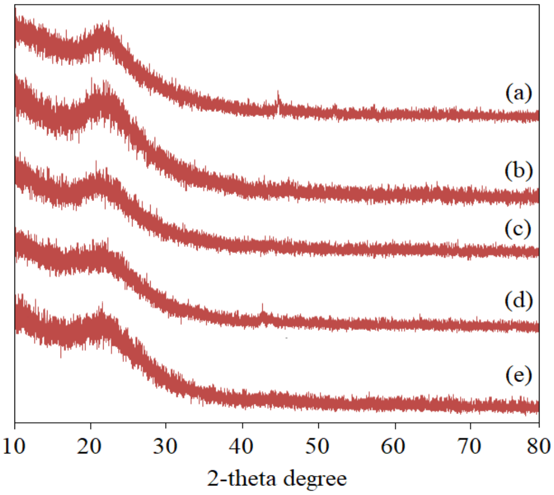

Figure 5 X-ray diffraction diagram of RHA and RHS: (a) Untreated RHA; (b) Unleached RHS; (c) RHS leached with 0.01 M HCl; (d) RHS leached with 0.1 M HCl; and (e) RHS leached with 1.0 M HCl

According to Premaratne *et al.* [29], the broadening of the -OH peak was due to the physically and chemically adsorbed water molecules on the silica surface. The medium peak had also appeared at 1640 cm^{-1} for all RHS samples due to the bending vibration of the O-H bonds from the adsorbed water molecule. No peak had appeared in the untreated RHA at these two points, 3750 to 3250 cm^{-1} and 1640 cm^{-1}, as in Figure 6(a), while only small bands were detected in the unleached RHS sample at these two points, as in Figure 6(b). These two O-H peaks became more intense as the concentration of acid used for leaching is higher. The higher the concentration of acid used for leaching, the deeper the slope of both peaks will be.

This result shows that lignin is still present in the untreated rice husk ash and is strongly attached to the silica. The presence of lignin in the rice husk not only prevents the fungal decomposition, but also resist water adsorption and penetration [30]. Therefore, there is no trace of O-H bond from the water molecules in the untreated RHA. After solvent-thermal treatment and leaching, the lignin in the rice husk was probably transformed to low molecular weight polymer and decomposed. Consequently, the silica particles were no longer protected by lignin, thus water molecules from surrounding may easily be adsorbed on the surface of the silica particles. This indirectly proved that the solvent-thermal treatment with acid leaching to be efficient in producing high purity RHS. The bands located at 1090 cm^{-1} and 800 cm^{-1} are related to the asymmetric stretching vibration and symmetric stretching vibration of the Si-O-Si bond, respectively. The small peak detected at 475 cm^{-1} is corresponding to the bending vibration of the Si-O elements [5,23,29]. There is no significant difference of Si-O element peaks that had appeared in all of the RHA and RHS samples, as shown in Figure 6.

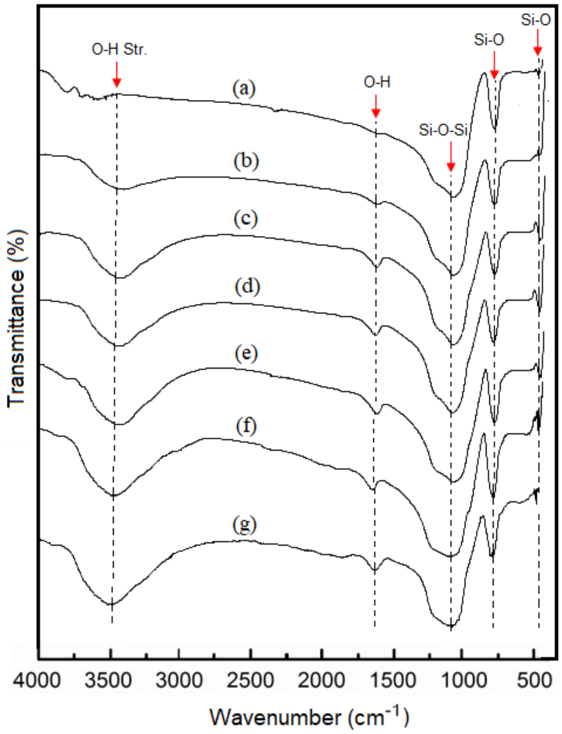

Figure 6 FTIR spectrum of RHA and RHS: (a) Untreated RHA; (b) Unleached RHS; (c) RHS leached with 0.01 M HCl; (d) RHS leached with 0.1 M HCl; (e) RHS leached with 1.0 M HCl; (f) RHS leached with 2.0 M HCl; and (g) RHS leached with 3.0 M HCl

4.0 CONCLUSION

In summary, the solvent-thermal treatment method with HCl leaching at 1.0 M concentration is the novel technique that effectively produced the highest purity of RHS with 99.9% of silica content and the largest BET surface area in amorphous state. These characteristics make RHS the right alternative for commercial precipitated silica used as filler in polymeric compounds, composites, and building materials.

Due to their low cost and low corrosive property, organic acids have recently gained more interest as substitutes for strong acids to pre-treat rice husks. Organic acids, such as acetic acid, oxalic acid, and citric acid have effectively removed metal impurities in rice husks to obtain amorphous silica with a purity ranging between 93.0% and 96.7%. These organic acids have not been proven to act as efficiently as HCl in removing metallic impurities in rice husks. However, further analysis on the effectiveness of different concentrations of organic acids, with the aid of solvent-thermal extraction method, the purity of the synthesised RHS might be improved. Then, these organic acids can be utilised as an alternative for strong acids like HCl.

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