ORIGINAL ARTICLE

Morphological and Compositional Changes Exhibited by Rice Husk When Subjected to Synergistic Thermochemical Treatments

Revathi Rajan[1,2], Yusmazura Zakaria[2], Shaharum Shamsuddin[2], Nik Fakhuruddin Nik Hassan[2]

[1] Department of Diagnostics and Allied Health Sciences, Faculty of Health and Life Sciences, Management & Science University, 40100 Shah Alam, Selangor, Malaysia.
[2] School of Health Sciences, Universiti Sains Malaysia, 16150 Kubang Kerian, Kelantan, Malaysia

ABSTRACT

Introduction: Rice husk has portrayed great potential in becoming a sustainable biomass source in producing silica, cellulose and carbon materials, which garnered widespread interest among researchers. The objective of the current study is to determine the morphological and compositional changes in rice husk due to the synergistic effects of thermochemical treatment. **Methods:** Washed and dried rice husk was blended into a fine powder and then subjected to step-wise heat treatment and acid digestion to produce white ash. The intermittent products, as well as the original rice husk and the final ash product, were characterised using analytical instruments to document the morphological and chemical composition changes. **Results:** This report highlights the production of pure rice husk ash using a step-wise treatment using a combination of thermochemical treatment and carbonisation. The results showed that a partial breakdown of the lignocellulose components was achieved using directed thermal treatment at low temperature. The ionic impurities were leached out in subsequent heated acid treatment. Thereafter, the carbonaceous organic matter was completely converted to carbon during the carbonisation of the sample and the remaining carbon residue was removed during calcination. High purity ash contained agglomerated and nanostructured silica in the dimensions of 20 to 50 nm in the amorphous form. **Conclusion:** The step-wise treatment allowed systematic removal of each compound while maintaining the amorphous mineral phase of silica and avoiding carbon fixation. Understanding the effect of each treatment offers insight to produce purer silica from rice husk.

Keywords: Rice husk, Thermochemical treatment, Morphology, Chemical composition, Characterisation, Purity

Corresponding Author:
Nik Fakhuruddin Nik Hassan, PhD
Email: nikf@usm.my
Tel: +609-767 7621

INTRODUCTION

Sustainable green chemistry advocates for environmentally friendly production of materials that have gained popularity in various fields encompassing medical, health and engineering sectors (1). Use of facile and low-cost precursors to meet the ever-growing customer demand allows for energy efficient material production without environmental compromisation (2). In line with this trend, extraction of various components such as silica, cellulose and hydro char from rice husk (RH) has become a popular undertaking among researchers (3–5). RH, an agricultural by-product of rice milling is generated in millions of tonnes in rice-producing countries (6). Safe disposal of this biomass is crucial to reduce the environmental impact that arises from burning this material in open air (7).

RH has been recognised as one of the most versatile biomass precursor for a variety of materials apart from palm trees. RH is rich in silica, hemicellulose, cellulose and lignin, which makes it an excellent source of amorphous silica and carbonaceous materials (8). Over the years, researchers have found application for crystalline and amorphous silica in numerous fields. Semiconductor, silicone synthesis and metallurgical industry often opt for the crystalline silica while the amorphous silica has found a widespread application in rubber and ceramic manufacturing, biomedical field, pharmaceutical and many other fields (6,9–12).

Conventional raw materials such as sand and quartz conversion into silicates or alkoxide followed by the secondary extraction of silica have several drawbacks (13). These drawbacks include the use of high energy, temperature and pressure intensive corrosive process (14–16). Alternatively, nanostructured amorphous silica can be extracted from RH with varying degree of purity. A wide range of research articles has covered various synthetic methods aimed at producing silica from RH with varied physicochemical properties (3,10,17). The physicochemical properties and the purity of the synthesised silica nanoparticle heavily rely on the type of thermochemical treatment the sample material is subjected to.

The easiest extraction of crude silica from RH can be performed using moderately high-temperature thermal treatment (13,17,18). Although this is the simplest extraction method, unwanted crystallisation, surface melting, carbon fixation and high amount extraneous impurities from the remnants of carbonised organic matters deems the method unsuitable for the various application (19,20). Additionally, this process also generates vaporised silica, which will become airborne and cause a health hazard to the surrounding population (21). The morphological and chemical composition of the silica such as the purity, crystallinity and colour, which plays an important role in determining their applicability is highly dependent on the conditions of pre-treatments, calcination temperature and rate of heating (20). In an effort to produce pure RHA, chemical pre-treatment using mineral acids, organic acids and ionic liquids have been suggested (22–24). Pre-treatment using hydrochloric acid (HCl) was proven to be relatively more efficient than its other mineral and organic counterparts (11,25).

The various changes that the RH undergoes during transformation into rice husk ash (RHA) can be closely monitored with the assistance of analytical instrument that records the morphology, chemical structure, elemental composition, state of solids as well as loss of mass and heat (26). Previously, the characteristics of the RHA has been studied to observe the effect of the thermochemical treatment on the final ash product. Investigating the morphology and interior structure of rice husk as a result of ashing at varied temperatures, revealed that particle size decreases and surface area increase with increasing ashing temperature (27). Thermogravimetric analysis revealed that rice husk thermal decomposition occurs in three stages, whereby the first stage signifies the lost moisture followed by decomposition of cellulose and hemicellulose. The final stages correspond to the breakdown of lignin (28,29) Studying the morphological and compositional changes that occur during every stage of thermochemical treatment can provide useful insight to better tailor each treatment to produce RHA with the desired physicochemical properties. This study reports a specific combination of thermal and chemical treatments in varying levels to extract pure RHA. Moreover, a comprehensive morphological and chemical compositional study of the RH and the intermediate sample material after each treatment prior to the production of RHA has been undertaken.

MATERIALS AND METHODS

Synergistic thermochemical treatment of RH
RH was subjected to stepwise thermal and chemical treatment, each step targeted to break-down or remove the specific component of the RH. RH obtained from a local rice mill nearby Peringat, Kelantan, Malaysia was thoroughly washed, dried and blended into a fine powder using counter-top blender before employment.

The experimental routine used in this study is synopsised in the flowchart presented in Figure 1. RH powder was heated in porcelain crucible on a hotplate to assist complete moisture removal and partial breakdown of the hard outer surface of RH. Subsequently, semi-charred rice husk (5 g RH to 100 mL acid) was refluxed in a solution of 1M HCl prepared from reagent grade HCl (37%) acquired from Merck Millipore, Darmstadt, Germany. Acid digestion, that was aimed to remove trace metal impurities, was conducted for an hour under vigorous magnetic stirring and constant heat. The solid residue was repeatedly rinsed to remove traces of acidic residues and dried. Dried treated rice husk (TRH) was heated on a hotplate at 80°C until full carbonisation was achieved. This step ensures easy removal of carbon when the sample material was subjected to sudden heating in the next phase of high-temperature calcination. Calcination of the carbonised rice husk (CRH) was performed for 5 hours using furnace (Carbolite CWF 1400, Keison Co, UK) at 700°C to obtain amorphous white RHA.
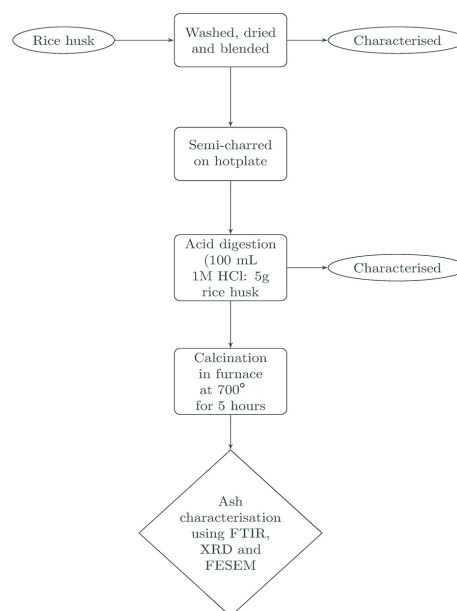

Figure 1: Flowchart for the synergistic thermochemical treatment on RH

Characterisation of RH before and after thermochemical treatment
The morphological, elemental composition, functional groups and solid state existence of RH, TRH, CRH and RHA were determined with the aid of analytical instrument to evaluate the changes that take place after each treatment. Inductively coupled plasma mass spectrometry (ICP-MS) analysis was conducted using by Agilent Technologies, Santa Clara, USA to determine the elemental composition of RH and TRH, pre and post acidic treatment. Field Emission Scanning Electron Microscope (FE-SEM) (Quanta FEG 450 manufactured by the FEI Czech Republic) was utilised to capture high-resolution images to study the morphological

changes exhibited by sample material after every stage of treatment. Samples were mounted on an aluminium stub with conductive carbon tape and gold coated under vacuum at 20 mA for 2 minutes using the Leica EM SCD005 Coating System. The working distance of observation was at ~9-10 mm while the sample was rastered using 5 kV electron beam acceleration voltage. Fourier Transform Infrared Spectroscopy (Tensor 27 FTIR, Bruker Corporations, UK) was operated over the range of 4000 to 400 cm-1 to collect the infrared (IR) spectra in the transmittance mode to ascertain the surface chemical bonding and functional groups of the sample materials. Traditional potassium bromide (KBr) pelleting method was employed by grinding the sample with KBr, which was pressed into transparent pellets. Elemental analysis of samples was conducted using Energy Dispersive X-Ray Spectroscopy (EDX), model Xmax 50mm2 (Oxford, UK) unit adjunct to the FESEM at an area size of ~ 0.25 to 1 mm^2 operated at 15.00kV. X-Ray diffraction (XRD) was utilized to determine the solid state of existence for all four samples. XRD patterns were recorded using a D8 Advance X-ray Diffractometer (Bruker Corporations, UK) with a 2θ angle ranging from 10° to 90° (40kV and 40 mA), using a graphite monochromator with Cu Kα radiation source (λ = 1.5406 Å) in the step scan mode of 0.04. The scanning rate was 1 s/step at an operating voltage of 40 kV and a filament current of 40 mA.

RESULTS

RH is a hard outer layer of the rice grain, primarily made up of lignocellulose and silica. RH is constructed using two main structure, palea and lemma, which are tightly interlocked with each other and shares similar morphology. Figure 2 displays the transformation of the RH when subjected to various thermochemical treatment. The surface glistening due to silica present on the RH surface became increasingly apparent after the initial two treatments. Complete charring left the sample in a totally blackened state, and subsequent calcination removed traces of carbon to produce white RHA. Figure 3 represents the levels of metals and trace metals present in sample material pre and post acid leaching process. Metallic impurities below 20 ppb concentration were classified under trace metal category. Significant decrease in levels of metallic impurities especially manganese, zinc, barium, calcium, copper and magnesium can be deduced from the analysis.

The cross-sectional and exterior surface micrographs of the RH, CRH and RHA are depicted in Figure 4. Thickly intertwined palea and lemma, both exhibiting similar morphology can be clearly visualised in the exterior view of the samples. Figure 4a shows the epidermal surface of the lemma is organised in linear crests interrupted with projecting conical protrusions with hair-like papillae (30). Double layers of thick-walled fibres can be observed beneath the external
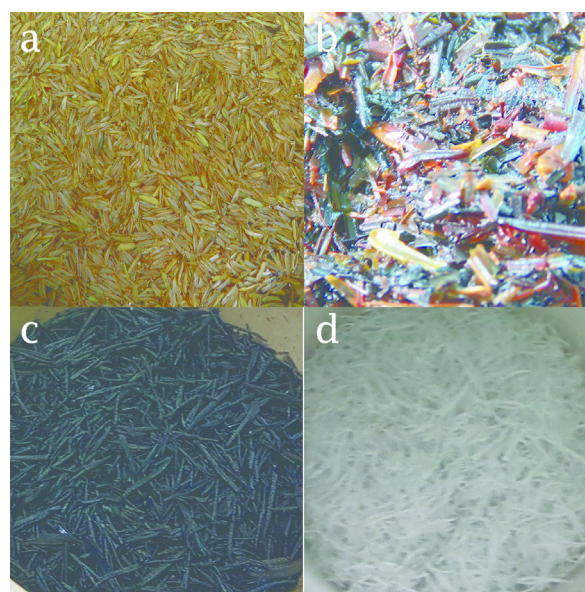

Figure 2: Visual examination of (a) RH, (b) TRH, (c) CRH and (d) RHA. The original RH appears shiny and light brown in colour that showed partial carbonisation upon initial low-temperature treatment. Complete blackening indicated completion of the carbonisation step, which was followed by calcination to produce bright white flaky RHA. Image captured using Canon Cybershort SX60, Canon Inc., Tokyo, Japan.
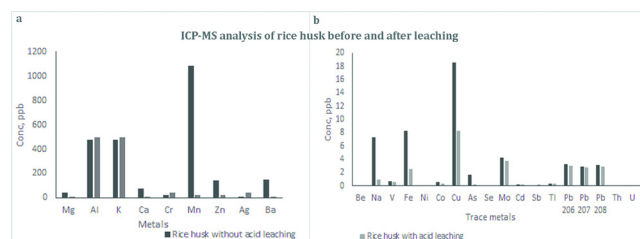

Figure 3: The pre- and post-acid treatment levels of trace metal impurities in RH a) metallic impurities and b) trace metal impurities. RH was subjected to acid pre-treatment to remove trace metal impurities. Thereafter, the ICP-MS analysis summarised in this bar chart represents the levels of each metals pre- and post-acid digestion. Trace metal impurities were present below 20 ppb concentration in the rice husk before acid leaching.
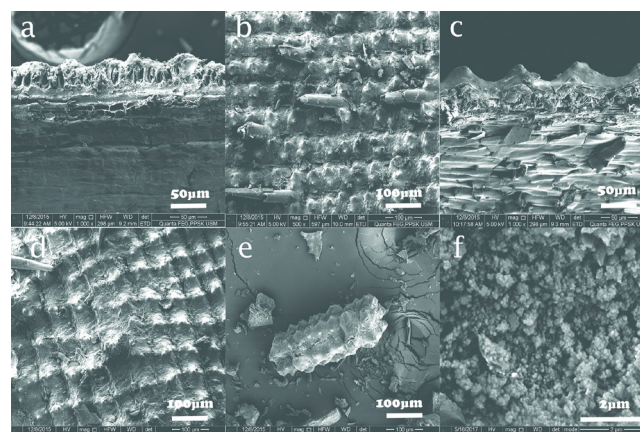

Figure 4: High-resolution micrographs of a) RH cross section b) RH external structure c) CRH cross section d) CRH external structure e) RHA f) nanostructured silica in RHA. The cross-section of RH consisting of double layered thick wall and the corrugated external surface appears crushed as well as smoothened out after pre-treatment stages. Examination of RHA revealed evidence of ash flakes retaining the original morphology of RH, which was evident that silica was homogenously distributed along the RH surface.

epidermal layer of the RH, viewed in cross-sectional micrographs of the RH (Fig. 4b) (31). Thick epidermal exterior layer appeared crushed and the internal surface was noticeably fractured, as observed in cross-sectional view of the CRH (Fig. 4c). Grainy deposits observed in micrograph 4b was absent in CRH (Fig. 4d) and instead aggregated clumps of silica was found scattered along the surface upon closer inspection. Smoothening along the linear crests and slight broadening of the parallel trenches were also perceived, in agreement with previous findings (32). RHA retained the original morphology of the individual rice grain even after the thermochemical treatments, indicating the presence of silica in the entirety of the RH (Fig. 4e). The delicate ash structure was reduced to coarse powder when a small amount of force is applied to it. Fig. 4f illustrates the nanostructured silica with particle size ranging from 20 to 50 nm revealed upon closer inspection of the RHA, in agreement with previous findings (32,33).

FTIR analysis was carried out on RH, TRH, CRH and RHA to observe the changes in functional groups present in the specimens. The IR spectra of all four samples in the range of 4000 to 400 cm-1 are shown in Figure 5. Characteristic bending and stretching of hydrocarbon, carbonyl, hydroxyl and alkene bonds were observed in the IR spectrum of RH. The –OH stretching vibration of the water molecules adsorbed on the surface of the RH corresponded to the wide-band at 3444 cm-1(20,34). Silanol peak was identified at 896 cm-1 exclusively in the RH sample, further proving the existence of RH silica in hydrated form. RH and TRH both exhibited intense peak aligning with bending vibrations of trapped water molecules and conversely, the intensity of this peak decreased significantly in CRH and RHA indicating loss of moisture from the sample. Low intensity stretching vibrations of C-O (~1384 cm-1) was present in TRH, CRH and RHA. The appearance of carbon-based bonds in TRH was evident of cellulose and lignin breakdown into simpler molecules. Subsequent, acid and heat treatment facilitated the further breakdown of C=C. The absence of C=C stretching and bending vibrations at 1707 cm-1 and 1515 cm-1 in RHA sample indicate removal of carbonaceous material from the sample. Deepening intensity of the peaks corresponding to siloxane and free Si-O bond stretching and bending at 1099 cm-1, 827.62 cm-1 and 465.05 cm-1 in TRH, CRH and RHA represented the increasing purity of the silica in sample materials (26,34).

Elemental analysis conducted on the RH (Fig. 6a) was evident of the presence of trace metal impurities in agreement with the ICPMS analysis. Metals detected in this stage included calcium, iron, zinc, magnesium, aluminium, sodium, potassium and manganese. Successive elemental examination of the CRH and RHA was indicative of trace metal removal from the sample material (Fig. 6b-c). XRD analysis of all the samples (Fig. 7) demonstrated that the amorphous nature of the
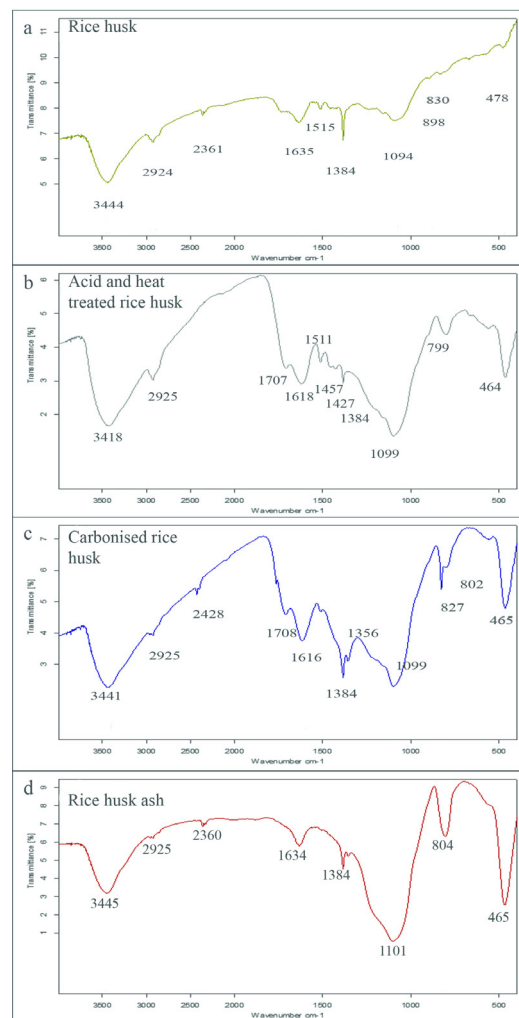

Figure 5: FTIR spectra of a) RH, b) TRH, c) CRH and d) RHA. The breakdown and removal of carbonaceous groups and moisture, as well as increase in the purity of silica in the sample material after each treatment, was observed through infrared analysis.

silica was maintained throughout the thermochemical treatment, presenting with characteristic amorphous silica broad peak between 17° and 38°, centred at 22.5° (26,35).

DISCUSSION

The composition of RH is primarily organic matter, silica and a trace amount of metals. In order to achieve pure silica extraction, each of the extraneous components has to be systematically removed. Hence, the extraction method used in this research illustrates a targeted approach that removes organic matter and purifies silica, while maintaining the amorphous nature of the RH silica. Extensive preliminary studies have been conducted to determine the optimal chemical pre-treatment conditions including the type and concentration of chemical as well as the duration of acid digestion (13,36). Primary findings of these researches were that acid was more effective in assisting the removal of the trace metals in comparison to alkaline solutions (37,38) and amongst various acids tested for this purpose, hydrochloric acid
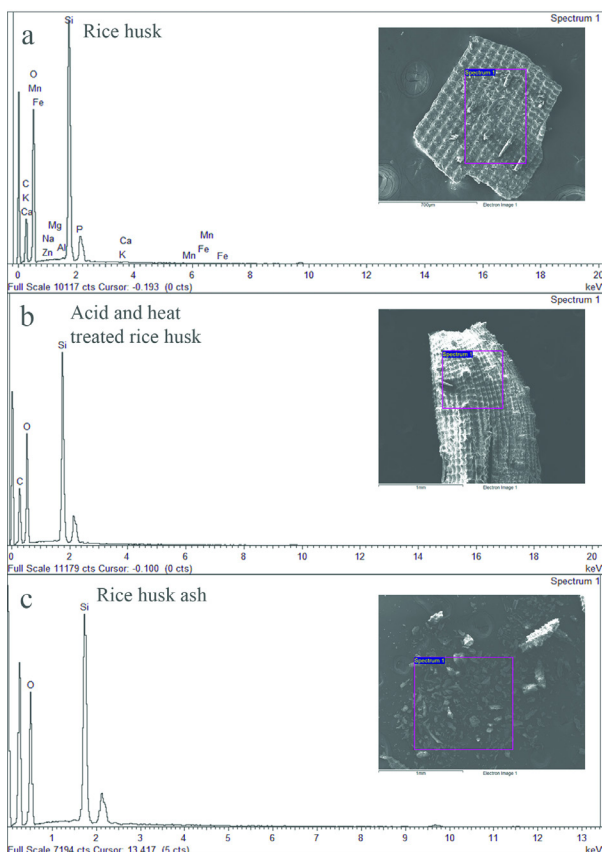
Figure 6: EDX spectra of a) RH, b) CRH and c) RHA. Elemental analysis conforms to the primary removal of trace metal impurities during the initial acid and low-temperature heat treatment.

Figure 7: XRD spectrum of a) RH, b) TRH, c) CRH and d) RHA. The presence of broad peak form 17° to 38° (2θ) with a centre of 22.5° indicated the amorphous nature of silica in all the sample materials, which remained unchanged throughout the thermochemical treatment.

showed the greatest promise in aiding improved metallic impurities removal (17,18). In this study, the efficiency of the acid pre-treatment on the RH was further enhanced by subjecting the RH to partial carbonisation prior to treatment. Darkening of the RH was observed after initial heat and acid treatment indicating initiation of carbonisation. Heat treatment assisting the breakdown of organic matter while the acid digestion removed metallic impurities by dissolution. ICP-MS analysis conducted on pre and post-acid treated RH indicated a significant decrease in metallic impurities, however, some impurities remain unchanged after the initial treatments. This observation could be attributed to the high water solubility of these metal chlorides, leading to retention in the analyte even after washing. In order, to remove them completely washing by centrifugation or sonication could be employed. Nevertheless, the multistep extraction procedure proven to have eliminated the compounds efficiently as reported in this research.

Quality of the final product was highly dependent on the removal of trace metal impurities, hence acid treatment was followed by heat treatment to assist further removal of the trace metals. Previous reports primarily utilised acidic pre-treatment, immediately followed by high-temperature calcination for the production of RHA (35,39). Nonetheless, sudden heating of the acid-treated
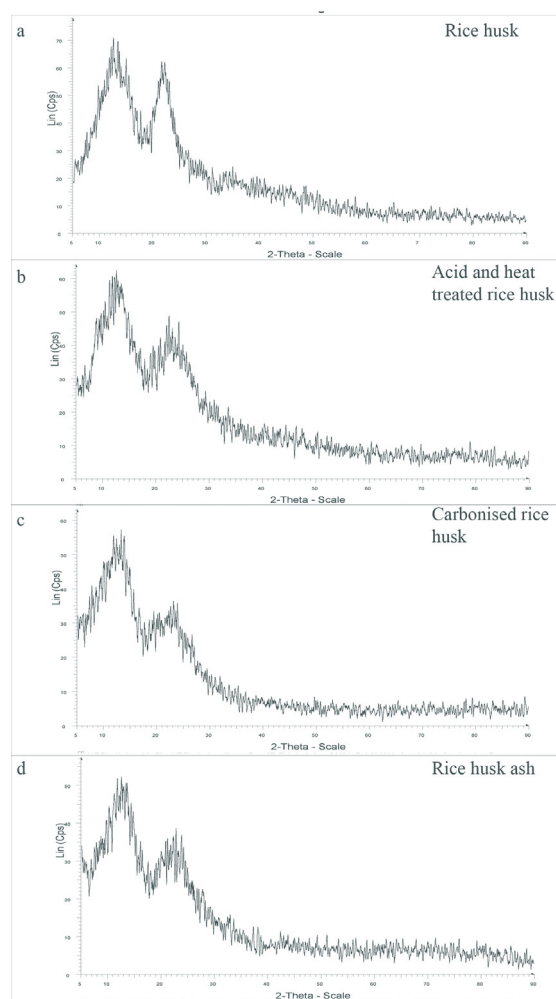
RH at high temperatures above 400°C results in the carbon particle trapping in the melted surface of the silica. Carbon fixation during calcination of the RH has posed several drawbacks in producing pure RHA (20,32). Hence, in this research RH was completely carbonised, to begin with, breaking down and converting the remaining complex organic compounds into carbon for easy removal during calcination. Carbonisation process involves the conversion of solid organic matter into carbon using thermal treatment (40). Carbonisation is a concurrent occurrence of several processes including dehydrogenation, condensation, hydrogen transfer and isomerisation (41). Degradation and removal or moisture as well as organic matter in the form of gaseous vapour during carbonisation. Finally, the remaining carbon was removed by high-temperature thermal treatment, leaving white amorphous silica. By inserting a low-temperature carbonisation process between the acidic pre-treatment and the calcination, the complex organic matter was reduced to simpler carbon forms that can be easily removed during calcination. This step became crucial in avoiding carbon fixation and deeming gradient

heating during calcination unnecessary. Calcination was conducted at 700°C for 5 hours to ensure fast and robust calcination while preserving the amorphous nature of the silica. Previous reports have indicated crystallization of silica when heated above 800°C (32). Ashing can also be conducted at 500°C for 7 hours to achieve complete carbon removal, nevertheless higher temperature was chosen to expedite carbon removal process.

CONCLUSION

This work shows the effects of efficient short time synergistic thermochemical treatment on the morphological, structural and chemical behaviour of RH. The synergistic heat and acid treatment facilitated the complete removal of metallic impurities and carbonaceous material. Carbon fixation, retainment of metallic impurities were avoided by inserting a carbonisation step prior to calcination. Analysis of the RH before and after treatments and the intermediates show a trend of decreasing impurities while retaining the amorphous nature of the silica. The results described herein will provide important clues on how to systematically remove each component to produce pure silica ash which in turn can be used in numerous applications.

ACKNOWLEDGEMENTS

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