

Synthesis and Characterization of Ricehusk Activated Carbon by Torrefaction, Desilication and Alkalies Based Approach

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Received: 07 July 2023; Accepted: 01 August 2023

Challenges have come from global warming and environmental pollution, which has led to the requirement of sustainable carbon-rich precursors for the synthesis of carbon materials. This study has been carried out to demonstrate the attempt of utilizing agricultural bio waste as Rice Husk (RH) as it is abundantly available, environmentally friendly, and low cost and a kind of renewable precursor material for the production of activated carbon. Activated rice husk-based porous carbon with honeycomb-shaped porosity was synthesized by torrefaction of finely powdered rice husk in a tubular furnace. Pyrolyzed rice husk carbon (RHC) has been desilicated by reflux method by mixing sodium carbonate solution with RHC to remove the silica layer so as to enhance the porosity of rice husk carbon. Desilicated RHC has been mixed with mixed alkaline metal base hydroxides at a specific heating rate. The effect of saturating the carbon with mixed activating agents at different mass ratios has been also studied. The confirmation of rice husk activated carbon (RHAC) has been confirmed by different techniques such as Scanning Electron Microscopy (SEM), X-ray diffraction analysis (XRD), Energy Dispersive X-Ray Analysis (EDX). The interlayer spacing (d_{002}) of the RHAC1 and RHAC2 samples are 0.39 nm and 0.34 nm. These values are greater than the interlayer spacing for graphite (0.335 nm). This shows the distorted structure with low graphitization level for both samples. It has been recognized that apparently amorphous-shaped RHAC was obtained along with meso-micro hierarchical porosity in topography. The ash yield of rice husk carbon obtained after Pyrolysis has been found to be 43.8% which was obtained by weighing rice husk samples once it was cooled down in a few hours. The use of this activated rice husk carbon can be used in the fabrication of energy storage devices featuring the concepts of green energy.

Keywords: Rice husk, X-ray diffraction, Activated carbon, Impregnation, Yield

1 Introduction

Activated carbons (ACs) are commonly referred to the carbon materials with high specific surface area, hierarchical pore size distribution as well as wide-ranging spectra of oxygenated functional groups. AC has good absorption capacity as well as high surface reactivity due to high specific surface area and hierarchical pore size. They have wide area of applications such as purification of water, air and gas purification, energy storage/conversion fields^{1,2}

Activated carbon can be derived from a wide variety of raw materials such as biomass shells (coconut, peanut, palm kernel and watermelon), waste tea leaves, sugarcane bagasse, tree products (flowers, fruits, leaves), corncob, plastic waste, rice and onion husks, soybean pods, orange fruits peel etc.³⁻⁶ Preparation of activated carbon from lignocellulosic and biomass waste precursors have countless benefits in terms of their synthesis, cost effectiveness,

diversity, abundance and renewability. Lignocellulosic mostly composed of cellulose and hemicellulose carbohydrate polymers and a lignin aromatic polymer⁷. There are two main stages for the production of activated carbon one is torrefaction (also known as pyrolysis) and another is activation. Pyrolysis is the technique of carbonization that has been generally employed before the activation. It is accomplished by maintaining the temperature in the range of 600-1000 °C with vacuum in the oxygen deficient environment to ensure the high surface area and to develop porous structures. Activated carbon⁷ produced by this method has higher surface area of 969.08 m²g⁻¹.

Generally, activated carbon is produced by the physical and chemical activations processes. Though, thermal process in the presence of nitrogen gas and microwave (MW) radiation has suggested as efficient methods to obtain ACs⁸. MW heating is the fast and uniform, which makes it a promising technique. Also, it results in the enhancement of carbon yield and

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improves the AC quality⁹. Besides, this combined activation i.e. physicochemical activation is also used as another alternative to achieve high surface area and porous structures. In the chemical activation process frequently the raw biomass precursors are directly impregnated with particular chemical agent such as H_3PO_4 , H_2SO_4 , NaOH and KOH. The commonly used acid salts for chemical activation are H_2O_2 , K_2CO_3 and $CaCl_2$ etc¹⁰⁻¹². The subsequent mixture is afterward heat-treated usually at temperatures in between 400 - 1000 °C in the controlled atmosphere. Chemical activation is commonly favoured as it gives high yield with good porous structure at low temperature. Pandey et al., revealed the improvement in BET specific surface area from 584 to 826 m^2g^{-1} and pore size from 1.32 to 2.15 nm at 1:3 ratio of NaOH with peanut biomass waste by using chemical activation method¹³. A. Jain et al., in 2015 shows in their work that the high specific surface area and mesopore area of $\sim 2440 m^2g^{-1}$ and $\sim 1121 m^2g^{-1}$, respectively have been achieved by using hydrothermal pre-treatment technique. And when this porous carbon was studied for the energy storage performance then it shows excellent storage capacity with energy density of 7.6 Wh kg^{-1} at a power density¹⁴ of $\sim 4.5 kW kg^{-1}$.

Recently, a lot of work is done on the rice husks (RHs) agricultural biomass for making activated carbon. RHs are a proper and generally used biomass waste for activated carbon preparation as it is majorly available by-product from rice mills. The main reason for using RHs to prepare activated carbon is the presence of high major contents of the cellulose that is up to 38%¹⁵. D. Kalderis et al., demonstrated that specific surface areas for rice husk and bagasse were achieved up to 750 m^2g^{-1} and 674 m^2g^{-1} for the ratio of activation salt $ZnCl_2$ with rice husk and bagasse as 1:1 and 0.75:1 by a single-stage chemical activation method. Also, the highly porous structure was confirmed from the SEM analysis¹⁶. L. Muniandy et al., obtained the activated carbon from RHs by via alkali (NaOH and KOH) leaching of rice husk at room temperature. The results of BET analysis showed the maximum specific surface area of 2696 m^2g^{-1} at 850 °C with ratio of rice husk with KOH as 1:5 in the presence of nitrogen¹⁷. Accordingly, the high specific surface area of carbon prepared from RHs leads to its utilization for Supercapacitors. H. Xu et al. studied the energy storage properties of RHs derived porous carbon, which exhibited an excellent capacitance¹⁵ of 250 F g^{-1} at 1 A g^{-1} .

In this work, mixed NaOH and KOH based activation was done to prepare rice husk derived activated carbon. It was seen that mixed alkalies, NaOH-KOH activation produced honeycomb like porous structures with hierarchical micro-meso and macro pores size distribution. In present work, the porous activated carbon was derived from RHs by firstly following torrefaction at 550°C for 20 minutes in nitrogen atmosphere, which was then followed by desilication treatment at 110 °C by reflux method by mixing the obtained desilicated rice husk carbon with sodium carbonate solution and at last mixed alkalies carbon activation at 80 °C. The novelty of this work lies in the fact that eco-friendly agrobased bio waste. RHs has been utilized to synthesize activated carbon which has superior characteristics of being renewable, abundance in earth. In order to increase the carbon yield, de-silication process has been followed that again attributes significance to this method for obtaining high purity carbon effectively and selectively.

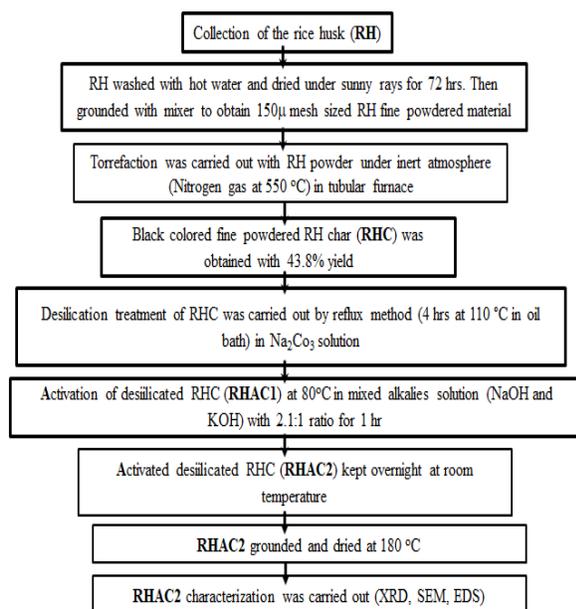
2 Materials and Methods

2.1 Materials

Bio-waste Rice husk obtained from local area (Rice mill) of Kurukshetra, Haryana (iInsi. NaOH (with 90.0% purity), KOH (with 90.0% purity) obtained from Sigma Aldrich (USA) , Na_2CO_3 procured from Loba (India), Deionized water, double distilled water from Merck, ASTM Test Sieve, Alumina boat (99.7% alumina), glass bottles, stirrer , Liquid scintillation vials volume 20 mL, clear glass vial, mortar pastel, magnetic beads, Magnetic heat stirrer and glassware brought from Borosil (India). G-4 crucible brought from antsLABS, Tube furnace (NANO TEC, Nitrogen cylinder, Oven, UltraSonicator, Ground Mouth Reflux Condenser with Coiled Inner Tube(Ningbo Sintrue medical Instruments Co., Ltd). All reagents were used without any further purification.

2.2 Synthesis of activated carbon from Rice Husk

Synthesis of activated carbon from agro based bio waste rice husk was carried out as per method demonstrated in Scheme 1 & Fig. 1. Rice Husk (RH) were taken from rice mill in Kurukshetra, India. The activated carbon was synthesized according to the torrefaction method¹⁸, but with several modifications. Varying molar ratio of activating agents (KOH/NaOH) in proportion of (51.5/48.5) and weight ratio in which activating agents were impregnated



Scheme 1 — Flow chart for the synthesis of activated carbon (RHAC2) from rice husk.

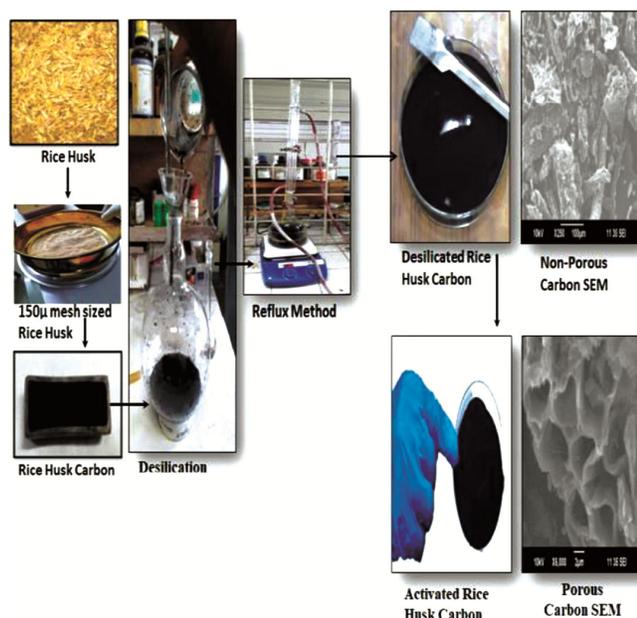


Fig. 1 — Photographic presentation of Desilicated Rice husk carbon (RHAC1) and Activated carbon (RHAC2).

with rice husk carbon are 1:2.1 and 1:3.2 were taken. The RH was initially washed with boiling water, and then dried under the sun-light for 72 hours. Then RHs were grounded in mixer and strained via test sieve up to mesh size of 150 μ horizontal long tube furnace is used to carry out torrefaction the process of converting rice husk (RH) into pyrolyzed rice husk carbon (RHC) In order to ensure a non-reacting atmosphere, two hundred milliliters of nitrogen gas

were injected into it for 20 minutes. As the pyrolysis temperature (200 $^{\circ}$ C, 400 $^{\circ}$ C, and 550 $^{\circ}$ C) stabilized over time, three different alumina boats were placed in the tubular furnace with rice husk powder (49.37g). Temperatures were estimated to rise at a rate of 5 $^{\circ}$ C/minute. Here in this study rice husk was held for 20 min at 550 $^{\circ}$ C under stabilized fast pyrolytic conditions. As soon as the furnace temperature returned to normal, the sample feeders were removed. After pyrolysis, obtained RHC showed 43.8 % yield. This was obtained by weighing rice husk samples once they had cooled down in a few hours.

$$\% \text{ Yield (RHC)} = \frac{S_b}{S_a} \times 100 = \frac{21.5}{49.37} \times 100 = 43.8 \%$$

where S_b = rice husk carbon remaining after torrefaction; S_a = rice husk powder original weight taken before torrefaction.

The obtained, finely black powdered RHC was demonstrated with Desilication treatment using ground mouth reflux condenser tube to remove the huge amount of silica. By assessing the final analysis of rice husk biomass that was obtained after pyrolysis, Ravindran & coworkers studied the presence of silica in rice husk carbon¹⁹. As pyrolytic temperature of 550 $^{\circ}$ C was maintained within the furnace, silica, which had a high melting point of (1710 $^{\circ}$ C)¹⁹, remained anchored inside the ash of the RHC, making it difficult to activate rice husk carbon by producing a silica peridium. 18 grams of RHC was combined with a 15 wt % (390 ml), softly made sodium carbonate solution using the sonication method. The mixture underwent a process known as desilication treatment of RHC generated after pyrolysis, which consisted of refluxing the mixture at 110 $^{\circ}$ C for 4.5 hours. Following desilication, solid desired slags filtration was carried out on the leftovers using a vacuum pump in the G-4 Crucible. The final filtrate was cleaned with deionized water, and the Desilicated rice husk carbon (RHAC1) was then dried for 24 hours at 105 $^{\circ}$ C. Fixed molar ratio of KOH/NaOH prepared in deionized water was stirred with RHAC1 at a restricted mass ratio of 1/2.1 and 1/3.2. Both mass ratio varied alkali impregnated RHAC1 mixtures received various heating treatments on an 80 $^{\circ}$ hot plate, one for an hour and the other for half an hour while being rotated at a moderate frequency on a magnetic stand up. The solutions were then rinsed with 0.1M HCl and demineralized water to achieve a pH of 7, followed by desiccating at 120 $^{\circ}$ C to weigh the final biomass-collected porous carbons. The

obtained RHAC2 was found to be highly porous carbon can be seen in Fig.1.

3 Results and Discussion

With the help of X-ray diffractometer (XRD, RIGAKU, MINIFLEX II SWITZERLAND) via Cu K α radiation of 1.54 Å with a scan rate (2 θ) of 5o/min between 10° to 90°, structural analysis of synthesized activated carbons was done. Morphological analysis was being demonstrated by electron microscopy (SEM, JEOL JSM-6390LV, 20 kV) accompanied with X-Ray energy dispersive analyzer to study the elemental composition of synthesized samples (EDS, OXFORD INCA X-ACT, US).

Figure 2 shows the XRD pattern of Desilicated Rice husk carbon (RHAC1) and activated carbon (RHAC2) after NaOH and KOH treatment. For the RHAC1 there was formation of a strong diffraction peak at 2 θ = 22.8° and a weak diffraction peak at 2 θ = 44° that can be credited to the (0 0 2) and (0 0 1) planes²⁰ which compares to diffuse impression of pyrolytic nature and low graphitization level of carbon system. XRD pattern for activated carbon (RHAC2) shows diffraction peak at 2 θ = 26.28° confirms to the graphitic structure of the activated carbon. Also the XRD pattern is well matched to the JCPDS No. 75-1621 for activated carbon. After activation of Desilicated RH the peaks of (0 0 2) weakened and shifted to 26.28° .It suggests the increment in the stacking thickness of the graphitic layers due to the activation treatment process. The interlayer spacing (d002) of the of the RHAC1 and RHAC2 sample calculated using Bragg's equation²¹

$$d_{002} = \frac{\lambda}{2 \sin \theta}$$

where wavelength (λ = 0.154 nm), and θ is the angle of the peak position are 0.39 nm and 0.34 nm. These values are greater than the interlayer spacing for graphite (0.335 nm). This shows the distorted structure with low graphitization level for both the samples²¹.

Scanning electron microscopy was done so as to ascertain the morphology of the prepared activated carbon after the samples were first prepared and then analyzed under electron microscope at an accelerating voltage of 10 KV at high magnification levels. The SEM image of sample of RHC obtained after torrefaction exhibited a fabric like structure with cylindrical geometry is shown in Fig 3(a), however, first desilication and then activation of the same resulted in a honeycomb like porous geometric structures as observed in electron micrographs of the final prepared products (Fig. 3.)

SiO₂, Al₂O₃, CaO, MgO, K₂O, SO₃, P₂O₅, C, H, N, O, Si, S etc. are present in the ash of RHC²². Fig. 3(b) represents a composite type morphology whose peculiarity is seen from the evacuation and annihilation of SiO₂ protective layer of RHC, opening piece of the pores of RHC which is denoted as RHAC1. Figure 3(c-d) show the activated carbon micrographs as we change the impregnation Molar mass ratio from 1:3.2 to 1:2.1 Average pore size increases from 3.52 μ m to 4.13 μ m. For this reason, the cross-sectional SEM image of the larger pore size in Figure 3(d) makes the mixed activated carbon a considerably good material for when stored on graphite sheet as also demonstrated by the Activated carbon (RHAC2). This improves the porosity, providing a large number of dynamic pores for adsorption/desorption and generally increasing the electrical conductivity of the synthesized electrode. Therefore this high porosity carbon can be used to create future energy storage devices, such as various (asymmetric, symmetric and hybrid) super capacitors ,batteries and also can show excellent performance in multiple applications, including water pollutant absorption , ionic liquid concentration , carbon dioxide capture²³.It can be seen in the Micrographs that usage of mixed alkalis allowed the RHAC2 to exhibit a significant more graded mesoporous microstructures and larger pore sizes than the Non activated RHAC1 . Potassium has a boiling point of 758 °C, which is lower than the boiling point of

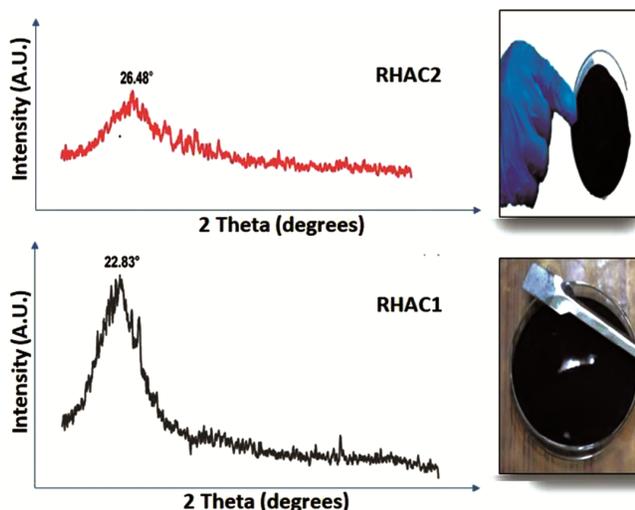


Fig. 2 — XRD template of Desilicated (RHAC1) and activated carbon (RHAC2).

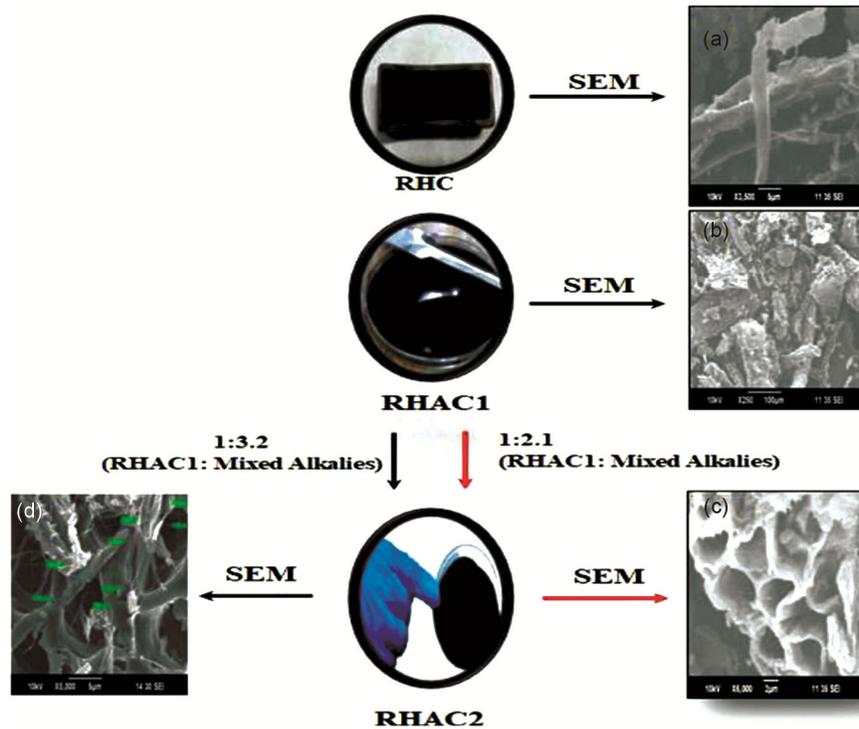


Fig. 3 — Images of (a) RHC, b) RHAC1, c) RHAC2 in molar ratio (1:3.2), & (d) RHAC2 in molar ratio (1:2.1).

sodium (883°C)²². In this way, potassium ions have the capability to diffuse inside the internal cervices of porous RHAC1, while sodium ions enter in the outer pores through which it can adsorbed inside pores. As a result, different porosities are produced, resulting in variations in surface morphology.

The composition of elements is exhibited by energy dispersive X-ray spectroscopy as displayed in Figure 4. The mean atomic and weight % of the respective peaks of different elements can also be visualized. The inset shows the elemental composition ratio of each sample. Figure 4 (a& b) represent the energy dispersive spectroscopy (EDS) of non-activated RHC and RHAC with silica abundances of 2.80 and 1.45 (atomic %), respectively. This indicates that the protective SiO₂ layer is removed from the RHC by the combined effect of the desilication and mixed alkali activation reaction. Rice husk has excellent properties of being renewable, its abundant availability at no cost and its constituents cellulose and hemicellulose are interconnected to form a very rigid tissue in which abundant silica is present. It enters rice roots as orthosilicic acid (H₄O₄Si). Another component of rice husk is lignin which is present as main fraction and its decomposition is very slow as lignin structurally involves the cross-linking

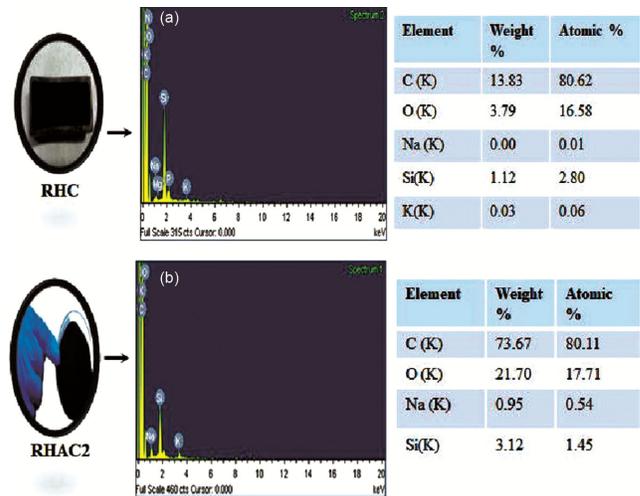


Fig.4 — EDX of (a) the elemental analysis of (RHC), & (b) activated carbon (RHAC2).

of different types of monolignols, latter are anchored with cellulose and hemicellulose. Second, orthosilicic acid also forms strong ester bonds with monolignols, a phenolic monomer, finally all these strong bondings lead to a decrease in carbon yield²⁴. Therefore, and this is a new method to efficiently and selectively obtain high-purity carbon by adopting the desilication method to increase the carbon yield.

4 Conclusion

It has been effectively concluded that the pyrolyzed porous carbon has been successfully synthesised from agro biowaste rice husk using desilication and activation treatments where raw rice husk has been treated with chemicals such as Na₂CO₃, NaOH and KOH. From the activated carbon micrographs, it has been observed that as we change the impregnation molar weight ratio from 1:3.2 to 1:2.1, average pore diameter has increased from 3.52 μm to 4.13 μm resulting into the expansion in pore size, which has a direct impact on electrochemical double layer capacitance performance.

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