PREPARATION OF MESOPOROUS ACTIVATED CARBON FROM JACKFRUIT PPI-1 WASTE AND DEVELOPMENT OF DIFFERENT SURFACE FUNCTIONAL GROUPS

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ABSTRACT. Jackfruit *PPI-1* variety was selected as source of lignocellulose material. Its rind and pulp waste was used as precursor for preparation of activated carbon. K_2CO_3 was selected as activating agent to prepare activated carbon. Various carbons were prepared by changing the impregnation ratio (IR) at different temperatures. Activated carbon prepared at $600^\circ C$ and at IR1 had good BET surface area ($987 m^2 g^{-1}$) and yield (61.97%). In order to introduce different functional groups, this carbon was divided into two parts. One part was subjected to liquid phase oxidation with 0.1N HNO_3 and the other part was soaked in 0.1N KOH for 3hours. SEM, FTIR, TPD, XRD and TGA analyses were done to identify surface morphological changes, nature of functional groups and thermal stability of activated carbons.

1. INTRODUCTION

Agricultural waste materials can be converted into useful activated carbon adsorbents. If not managed properly, agricultural wastes become an environmental problem and a hazard for human and animal health. Many researchers used different chemical activating agents like H_3PO_4 , H_2SO_4 , $ZnCl_2$ etc., to prepare activated carbon from lignocellulosic materials and applied them in removal of toxic substances from aqueous solution. But all these activating agents are toxic and cause secondary pollution. In the present study, the selected lignocellulosic agricultural waste was activated by K_2CO_3 which is not a hazardous chemical and not deleterious as it is frequently used for food additives. The aim of this study is to prepare activated carbon and to introduce different surface functional groups onto the prepared carbon. As surface functional groups play a vital role in attracting different types of toxic substances and give feasibility for their adsorptive removal [1].

2. MATERIALS AND METHODS

2.1 Material

Jackfruit *PPI-1* variety was collected from state horticulture mission, Paderu, Visakhapatnam, A.P., India. The rind and pulp waste of fruit was used as precursor for preparation of activated carbon. The waste was washed with hot distilled water to remove dirt and dehydrated at $105^\circ C$ until constant weight was obtained. This dried waste was then cut into small pieces and named as 'JWM'.

2.2 Preparation of activated carbon

JWM was mixed with K_2CO_3 solution in different impregnation ratios, 0.5, 1 and 1.5. Impregnation ratio (IR) was given by weight of K_2CO_3 (g) in solution/weight of JWM in g. These mixtures were dehydrated in an oven overnight at 105°C . The impregnated JWMs were carbonized in uniform nitrogen flow to different final temperatures, 500, 600 and 700°C . The heating was provided at rate of $10^\circ\text{C min}^{-1}$. The prepared activated carbons were cooled to room temperature and washed with hot distilled water to remove remaining chemical and filtered. The washing and filtration steps were repeated until the filtrate showed neutral pH. All activated carbons were sieved to 45mesh and were named in accordance with their activation temperatures JC_{500} , JC_{600} and JC_{700} . For comparative study of effect of activating agent on surface morphology, another sample of JWM is heated to 600°C under similar conditions without impregnation and it was named as $JC_{\text{Non-activated}}$.

In order to introduce different functional groups, JC_{600} (at IR 1) was divided into two parts. One part was subjected to liquid phase oxidation with 0.1N HNO_3 and the other part was soaked in 0.1N KOH for 3hours. Both carbons were filtered and washed with distilled water until filtrate showed neutral pH. These carbons were dehydrated in an oven overnight at 105°C and named as ' JC_{HNO_3} ' and ' JC_{KOH} ', indicating the chemical activating agent.

2.3 Characterization of prepared activated carbons

The pore structures of the resulting carbons were analyzed using N_2 adsorption, X-ray diffraction (XRD), scanning electron microscope (SEM). Surface area was calculated by Brunauer–Emmett–Teller (BET) equation. Thermal stability of carbons was analyzed by thermogravimetric analysis (TGA) and temperature programmed desorption (TPD) studies. Point of zero charge was determined for JC_{600} (at IR1), JC_{HNO_3} and JC_{KOH} .

2.4 Determination of point of zero charge (PZC)

Point of zero charge is the pH at which the external surface charge is zero [2]. 50 ml of 0.01N NaCl solution was placed in a closed Erlenmeyer flask. The pH was adjusted to a value between 2 and 12 by adding 0.1 N HCl or 0.1 N NaOH solutions. Then 0.15 g of carbon sample was added and the final pH measured after 48 h under agitation at room temperature. The PZC is the point where the curve $pH_{(\text{final})}$ vs. $pH_{(\text{initial})}$ crosses the line $pH_{(\text{final})} = pH_{(\text{initial})}$ taken as the PZC of the given carbon [3].

2.5 N_2 adsorption

The pore structure characteristics of prepared carbons were determined by nitrogen adsorption at -196°C by a Quanta chrome instrument (Nova 2200). Prior to gas adsorption measurements, the carbon was degassed at 150°C in a vacuum condition for 24 h. Nitrogen adsorption isotherms were measured over a relative pressure (P/P_0) range from approximately 0.03 to 0.995. The BET surface area was determined by means of the standard BET equation applied in the relative pressure range from 0.06 to 0.3. The total pore volume was calculated at a relative pressure of approximately 0.995 and at this relative pressure all pores were completely filled with nitrogen gas. The density functional theory (DFT) pore size distribution of all carbon samples were obtained based on nitrogen adsorption isotherms with medium regularization.

2.6 SEM analysis

A scanning electron microscope SEM Hitachi- S520 (OXFORD LINK-ISIS) was used to study the texture of the surface of activated carbons.

2.7 FTIR analysis

The surface chemistry characterization of each activated carbon was performed Fourier Transform Infrared Spectroscopy (FTIR) to identify its surface functional groups. FTIR spectra were recorded on Thermo Nicolet Nexus 670 spectrometer in the wavenumber range $400\text{--}4000\text{ cm}^{-1}$. To prepare pellets, samples were first ground to powder in an agate mortar and then

mixed with KBr at a mass ratio of 1:500. A hydraulic press was used to press the resulting mixtures to discs of 10 mm in diameter at 10 MPa for 5 min.

2.8 TPD analysis

TPD analysis was performed on MICROMERITICS CHEMISORB 2750 instrument. Activated carbon samples were kept in high pure Helium flow for 10 minutes. Gas changed to 10%NH₃ in Helium at a rate of 30ml min⁻¹ flow. NH₃ adsorbed for 30 minutes. Gas changed to pure Helium (30ml min⁻¹) and physisorbed ammonia was removed for stable baseline status.

2.9 TGA analysis

The thermogravimetric analysis (TGA) experiments were performed on a SDT Q 600 TGA analyzer (TA instrument). Each time, activated carbon sample was heated from room temperature to 900°C under nitrogen atmosphere at a heating rate of 10°C min⁻¹.

2.10 XRD analysis

Powder X-ray diffraction patterns were recorded on a Philips: PW1830 at 30 kV and 15mA (Cu K α radiation) at a step size of 0.01° and at a wavelength 0.154nm.

3. RESULTS AND DISCUSSION

Proximate analysis JWM was given in Table 1. This analysis indicated that the precursor used in this study has high carbon content; approximately 39% and low ash content about 2%. Hence JWM was used as activated carbon precursor.

Table1. Proximate analysis of JWM.

Material	Weight (%)
Moisture	6.82
Volatile	51.37
Ash	2.14
Fixed carbon	39.67

3.1 Yield of activated carbon

The yield of activated carbon is defined as the ratio of the weight of the resultant activated carbon to that of original precursor with both weights on a dry basis [4]. In every case, the yield of activated carbons obtained by K₂CO₃ activation was higher than fixed carbon content of proximate analysis. Jackfruit waste contains natural polymers like cellulose, lignin and hemicellulose [5]. During carbonization process these polymeric structures decompose and liberate hydrogen, oxygen, nitrogen and other elements in the form of tar and gases. The presence of K₂CO₃ in the interior of JWM might have restricted the formation of tar by forming cross-links and inhibited the shrinkage of precursor material by occupying certain substantial volumes [6]. K₂CO₃ will be reduced in inert atmosphere by carbon to give elemental potassium and carbon monoxide [7,8,9].

Hence potassium will be intercalated between the graphite layers or form graphite-potassium intercalation compounds [10]. The presence of intercalated potassium inhibited the shrinkage of carbon during activation process at elevated temperatures. In hot distilled water washing process of prepared activated carbon, potassium was removed and left micropores. As a result the surface area of impregnated activated carbons was also increased when compared with JCM_{Non-activated}.

3.2 Nitrogen adsorption

The effect of activation temperature and impregnation ratio on the BET surface area, micropore volume, and total pore volume were given in Table 2. The total pore volume, V_{total} , was calculated from nitrogen adsorption data as volume of liquid nitrogen at a relative pressure of 0.995. The micropore volume, V_{micro} , was determined by DFT method and the mesopore volume, V_{meso} , was obtained by subtraction of micropore volume from total pore volume.

Table2. Characteristics and yield of activated carbons prepared from JWM.

Sample	Impregnation ratio (IR)	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{micro} ($\text{cm}^3 \text{g}^{-1}$)	V_{meso} ($\text{cm}^3 \text{g}^{-1}$)	V_{total} ($\text{cm}^3 \text{g}^{-1}$)	Yield (%)
JC ₅₀₀	0.5	198	0.101	0.096	0.197	48.12
JC ₆₀₀	0.5	213	0.156	0.113	0.269	45.46
JC ₇₀₀	0.5	229	0.162	0.125	0.287	44.02
JC ₅₀₀	1.0	765	0.408	0.142	0.55	48.13
JC ₆₀₀	1.0	987	0.471	0.168	0.639	61.97
JC ₇₀₀	1.0	602	0.412	0.132	0.544	57.61
JC ₅₀₀	1.5	318	0.286	0.269	0.555	52.05
JC ₆₀₀	1.5	410	0.364	0.172	0.536	51.84
JC ₇₀₀	1.5	312	0.282	0.167	0.449	45.36
JC _{Non-activated}	-	114	-	0.106	0.106	43.07

Figure.1 (a) and 1(b) shows isotherms of JC_{Non-activated} and JC₅₀₀ at all impregnation ratios respectively. These fall under type III isotherms based on IUPAC classification. It indicates that these activated carbons had non-porous or macro porous surface. The corresponding DFT plots (shown in Figure. 2) also represented that these carbons do not contain micropores. Figure.1(c) depicts the isotherms of JC₆₀₀ at all impregnation ratios. These plots resembled type I isotherms. So these were microporous materials. However the plateau was not reached sharply. This indicates widening of pores. All these isotherms exhibit H4 hysteresis loop which is characteristic of slit shaped pores. As IR increases, these show combination of type I and type II isotherms. This indicates simultaneous presence of micro and mesopores. The DFT plot of JC₆₀₀ (shown in Figure 2(c)) specifies the presence of both micro and mesopores. The isotherm of JC₇₀₀ (shown in Figure.1 (d)) shows similar trend. However, DFT plot of JC₇₀₀ (shown in Figure.2 (d)) recorded the presence of macropores also. The reason for structural changes (with respect to pore development) could be explained as follows.

Figure 1. N₂ adsorption and desorption isotherms at 77K of JC_{Non-activated} and K₂CO₃ impregnated JWM.

When the ratio of impregnation of K₂CO₃ is 0.5, the activating agent is not sufficient to create required microporous structure in activated carbon to form graphite-potassium intercalation compounds. Hence for all activated carbons (JC₅₀₀ to JC₇₀₀ at IR 0.5), the surface area was lower than other impregnated carbons. However, for these carbons the S_{BET} surface area is greater than JC_{Non-activated}. In all activated carbons (JC₅₀₀ to JC₇₀₀ at IR 1), both micropores and mesopores were developed. Among all activated carbons JC₆₀₀ at IR1 showed larger surface area, 987 m² g⁻¹. At high temperature 700°C, some micropores might have combined to give large number of mesopores and macropores. As a result the surface area of prepared activated carbons decreased at this temperature. When the IR is 1.5, the surface area of all activated carbons was greatly decreased. It may be due to the excess activation made by substantial amount of impregnated K₂CO₃. In such a case, large number of micropores were combined to give pores with large diameter. The increased mesopores volume for IR 1.5 carbons and development of macropores (shown in Figure.2 (d)) supports conversion of micropores to large sized pores. Similar trend was observed in literature during preparation of activated carbon from K₂CO₃ impregnated straw pulp [11]. Hence JC₆₀₀ (at IR1) with higher surface area was selected for liquid phase activation in further studies.

Figure 2. DFT based pore size distribution of activated carbons produced at activation temperatures (a) 500°C, (b) 600°C, and (c) 700°C.

3.2 TPD analysis

Figure. 3(a) and 3(b) shows TPD analysis profile for CO₂&CO desorption from JC₆₀₀ (at IR1), JC_{HNO3} and JC_{KOH}. Surface oxygen groups present on these activated carbons decompose upon heating. They release CO₂ and CO at different temperatures. CO₂ peaks result from the decomposition of carboxylic acids [12] at low temperature or lactones at high temperature and anhydrides give both CO and CO₂. Groups like phenols, carbonyls, ethers and quinones originate CO peaks. Figure. 3(a) clearly shows nitric acid activation introduced sufficient number of oxygen functional groups on carbon surface. When compared with JC_{HNO3} (shown in Figure. 3(a)), JC_{KOH} had less number of oxygen functional groups, but much higher than JC₆₀₀. In both CO₂&CO desorption profiles, JC₆₀₀ showed less oxygen content. However, comparatively, JC₆₀₀ showed more oxygen content in CO profile than that of CO₂ desorption studies. It may be assumed that during preparation of activated carbon, heat treatments under inert atmosphere at high temperature effectively remove oxygen. But resulted activated carbon has active surface sites which are capable of re-adsorbing oxygen to form previously removed groups [13]. As a whole, JC₆₀₀ has very less oxygen content which in other words provide more hydrophobic surface. Activated carbons with more hydrophobic surface is one of the required properties for adsorption of disperse dyes from aqueous solution. As disperse dyes have low solubility, they have a tendency to occupy on hydrophobic solid surfaces [14]. In desorption studies of CO profile, JC_{KOH} showed release of CO at around 750°C. It evidenced that soaking the activated carbon in potassium hydroxide solution changed the surface chemistry of carbon by introducing different oxygen functional groups.

Figure 3. TPD analysis of JC₆₀₀ (at IR1), JC_{HNO₃} and JC_{KOH}; (a) Evolution profiles of CO₂ and (b) Evolution profiles of CO.

The PZC values of JC₆₀₀ (at IR1), JC_{HNO₃} and JC_{KOH} were tabulated in Table3. The PZC values of JC_{HNO₃} and JC_{KOH} were changed from 6.7 to 4 and 10 respectively. It may be due to the change in their surface functional groups generated by liquid phase activation.

Table 3. Point of zero charge values of selected activated carbons.

Activated carbon	PZC Value
JC ₆₀₀ (at IR1)	6.7
JC _{HNO₃}	4
JC _{KOH}	10

3.3 FTIR analysis

The FTIR spectra of JC₆₀₀ (at IR 1), JC_{HNO₃} and JC_{KOH} were shown in Figure.4. Bands observed in the range 1100-1450 cm⁻¹ are shown in Figure.4. due to C-O stretches in carboxylic acids, anhydrides, lactones, esters, ethers, phenols and epoxides [15,16]. Bands in this region are higher for JC_{HNO₃} and JC_{KOH} when compared with JC₆₀₀. This is in good agreement with TPD analysis results (shown in Figure.3). A distinct peak was observed at 1580 cm⁻¹ for JC₆₀₀ only. This is due to polyaromatic C=C stretching vibrations in sp²-hybridized carbons [17,18]. This indicates the non-polar (hydrophobic) nature of JC₆₀₀. Bands in the range 1350-1380 cm⁻¹ are due to C-N bond stretching vibrations of aryl amines. As the jackfruit is complex composite material formed of natural polymers, it may contain nitrogenous compounds like amino acids. Bands in the range 2364-2372 cm⁻¹ are attributed to C-H stretching due to presence of CH₂-CO-group. Bands around 2800-3000 cm⁻¹ are due to various C-H stretching modes [19]. Bands around 3400-3500 cm⁻¹ are due to -OH stretches in hydroxyl, carboxylic and phenolic groups.

Figure 4. FTIR analysis of activated carbon samples.

3.4 TGA analysis

TGA plots of JC₆₀₀ (at IR 1), JC_{HNO₃} and JC_{KOH} were shown in Figure.5. In all TGA plots before reaching 150°C temperature, there was little fall (8-10%) in weight of each carbon. In this region moisture content of carbon samples was removed. From this temperature, there was a gradual decrease in weight of each carbon sample. However, at 890°C, the fall is about 52% in JC_{HNO₃} and 43% in JC_{KOH}. It is may due to the difference in presence of surface oxygen functional groups in these two carbons. And these oxygen functional groups might have reacted with carbon to escape as CO₂ and CO gases. In JC₆₀₀, the fall is only 28% at this temperature. It may be due to the presence of less number of oxygen functional groups. This observation is also in good agreement with the FTIR analyses of corresponding activated carbons shown in Figure.4.

Figure 5. TGA of JC₆₀₀ (at IR1), JC_{HNO₃} and JC_{KOH}.

3.5 SEM analysis

SEM images of JC₅₀₀, JC₆₀₀ and JC₇₀₀ carbons of K₂CO₃ impregnation ratio 1 were shown in Figure.6. For comparison, SEM image of JC_{Non-activated} was also included. When compared with SEM images of impregnated activated carbons, pores are not observed in JC_{Non-activated}. Pore structure development was started in JC₅₀₀. But in JC₆₀₀ more number of pores was developed. When the temperature is reached to 700 °C (shown in Figure.6(d)), pores were ruptured and their size was increased. It supports the observation of conversion of micropores to meso- and macro pores in DFT analysis.

Figure 6. SEM Images of (a) $JC_{\text{Non-activated}}$; (b) JC_{500} (at IR1); (c) JC_{600} (at IR1) and (d) JC_{700} (at IR1).

3.6 X-Ray diffraction

The XRD pattern of JC_{600} (at IR 1), JC_{HNO_3} and JC_{KOH} was shown in Figure.7. The layer dimension L_a parallel to the basal plane of the graphite is calculated from the (100) reflection. The dimension perpendicular to the basal plane (L_c) was obtained from the (002) reflection.

Figure 7. XRD graph of JC_{600} (at IR1), JC_{HNO_3} and JC_{KOH} .

The interlayer spacing d_{002} is determined by using the Bragg's equation as follows:

$$d = \frac{\lambda}{2\sin\theta} \quad (1)$$

Where λ is the X-ray wavelength and θ is the scattering angle for the peak position.

$$L = \frac{K\lambda}{B\cos\theta} \quad (2)$$

Where L is L_c or L_a , B is the half-width of the peak in radians, and K is the shape factor. The shape factor K depends on the lattice dimension and the values $K = 0.9$ and $K = 1.84$ were used for calculation of L_c and L_a , respectively.

The values of d_{002} , L_c , and L_a of selected activated carbons were tabulated in Table 4. The XRD curves were shown in Figure. 7. For these activated carbons, the diffraction profiles exhibited broad peaks at around 27 and 48° which are assigned to the reflection from (0 0 2) and (1 0 0) planes, respectively. The occurrence of broad peaks at these 2θ indicates an increasing regularity of crystal structure and resulted in better layeral alignment [20].

Table. 4. XRD parameters of JC_{600} , JC_{HNO_3} and JC_{KOH} .

Sample	d_{002} (nm)	L_c (nm)	L_a (nm)
JC_{600}	0.319	1.85	2.25
JC_{HNO_3}	0.323	1.98	2.17
JC_{KOH}	0.313	1.98	2.39

From the XRD graph, it is clearly evident that JC_{600} (at IR1) structurally does not alter during liquid phase activation with HNO_3 and KOH . The L_a , L_c and d_{002} values of all the three carbons indicate that no appreciable change had happened to JC_{600} (at IR1) while introducing different functional groups upon carbon surface.

4. CONCLUSION

The selected JWM can be used as a precursor for preparation of activated carbon as it gave good yield. The presence of both micro and mesopores on JC_{600} (at IR1) may facilitate the adsorption of different types of pollutants with varying sizes. All the three activated carbons, viz., JC_{600} (at IR 1), JC_{HNO_3} and JC_{KOH} were found to contain nearly similar texture but have different functional groups and zero point charges. Hence these carbons can be used to adsorb different types of organic pollutants from water.

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