Engineering Data for Optimization of Preparation of Activated Carbon from an Economically Viable Material

Y. C. Sharma,* Uma,[†] and F. Gode[‡]

Department of Applied Chemistry, Banaras Hindu University, Varanasi 221 005, India, and Department of Chemistry, Suleman Demierl University, Isparta, Turkey

Activated carbon has been a fascinating material, especially for the removal of different pollutant species from gaseous and aqueous phases. Activated carbons can be prepared from a variety of cellulosic materials. This study is an effort to investigate the characteristics of activated carbon prepared from an agricultural waste material, coconut coir. The surface area and porosity of the activated carbon were determined by nitrogen adsorption isotherms at 77 K. The pore size distribution was determined by a N_2 adsorption isotherm that shows the pore width, surface area, and total pore volume of the activated carbon. The BET surface area of synthesized activated carbon was found to be 205.27 $m^2 \cdot g^{-1}$. After activation, both micropores and a small volume of mesopores are formed in the product. Thermogravimetric analysis was used to monitor the course of pyrolysis of coconut coir and $ZnCl_2$-impregnated coconut coir. Important physicochemical properties of the activated carbon were confirmed by Fourier transform IR spectroscopy and X-ray diffractometry.

1. Introduction

Coconut (*Cocos nucifera*) coir is a biomass that is abandoned near coconut processing plants. It has been used for preparing ropes, nets, cushions, mattresses, and canvas and has the potential to add an economic input in water treatment as a low-cost material for development of a novel adsorbent for removal of pollutants.[1,2] Coconut coir activated carbon (CCAC) was prepared through physical activation of the basic carbon obtained from pyrolysis of coconut coir under an inert nitrogen atmosphere. The primary carbon was treated with an activating agent, $ZnCl_2$, and then thermally treated to produce an activated carbon.[3] The surface area analysis by nitrogen adsorption isotherm and the porosity characteristics of the activated carbon were determined to observe the development of the pores, and thermogravimetric analysis (TGA) and X-ray diffraction (XRD) analysis were used to visually observe the course of the pyrolysis phase present on the surface of the prepared CCAC. The groups attached to the derived activated carbon and the chemical composition of the CCAC were characterized by Fourier transform IR (FTIR) spectroscopy.[4] The final product was found to have both micropores and mesopores. On the basis of the characterization results, CCAC seems to be an ideal material for treatment of effluents in treatment plants and pollution abatement applications.[5,6]

2. Materials and Methods

2.1. Preparation of Activated Carbon. Activated carbons are mostly prepared by pyrolysis of lignocellulosic materials that are freely available in large quantities. Prior to preparation of carbon and its activation, coconut coir was dried in sunlight. The dried coir pith was cut into small pieces having the desired mesh size and then carbonized at 700 °C under purified nitrogen (99.99 %). The heating rate was fixed at 10 $°C \cdot min^{-1}$ to reach a final temperature of 700 °C for 1 h using a tubular muffle furnace under an inert atmosphere. A constant nitrogen flow of 150 $mL \cdot min^{-1}$ was maintained throughout the process of carbonization. The carbon so formed was cooled to room temperature under the same nitrogen atmosphere and washed with hot distilled water [(70 to 100) °C] and 0.5 N HCl until the pH of the sample reached 7.0. The HCl was added at room temperature. The product was then dried in a hot air oven at 110 °C overnight.

The carbonization process was conducted by heating the raw material in absence of air at high temperatures. Chemicals such as $ZnCl_2$, KOH, or H_3PO_4 were thoroughly mixed with the primary carbon prior to its activation. In this study, coconut coir was used as a precursor of activated carbon. The mechanism for $ZnCl_2$ activation tends to produce a well-developed porous (meso- and microporous) activated carbon, and $ZnCl_2$ acts as a catalyst and dehydrating agent, allowing more carbon to be kept fixed.[7]

Activation of primary carbon was carried out by using a physicochemical activation method in the presence of $ZnCl_2$ by applying the optimum operating conditions. The mixture was then dehydrated in an oven for 1 h to remove moisture and subsequently activated under the same conditions as for carbonization but to a final temperature of 700 °C for 2 h. The activated product was then cooled under a nitrogen gas flow to room temperature and washed with hot distilled water and 0.1 M HCl until the pH of the washing solution reached neutral.[8,9] In all of the experiments, the heating rate and nitrogen flow were kept constant. The detailed experimental procedure was as reported elsewhere.[8]

3. Characterization of Coconut Coir Activated Carbon

3.1. Porosity and Surface Area Determination. Prior to nitrogen adsorption experiments to determine the surface area and pore size distribution, the activated carbon sample was

---

* Corresponding author. E-mail: ysharma.apc@itbhu.ac.in. Tel: +91 542 6702865. Fax: +91 542 2306428.

[†] Banaras Hindu University.

[‡] Suleman Demierl University.

10.1021/je100041x

Table 1. Physical Characteristics of Coconut Coir Activated Carbon

BET surface area/$m^2 \cdot g^{-1}$	205.27
single-point surface area/$m^2 \cdot g^{-1}$	231.73
BJH adsorption cumulative surface area of pores/$m^2 \cdot g^{-1}$	23.90
micropore surface area s_{mic}/$m^2 \cdot g^{-1}$	181.37
mesopore surface area s_{mes}/$m^2 \cdot g^{-1}$	23.90
single-point total pore volume of pores/$cm^3 \cdot g^{-1}$	0.1279
total pore volume, V_p/$cm^3 \cdot g^{-1}$	0.0246
BET adsorption average pore width/Å	22.09
mean pore diameter, D/Å	41.24
100 w_{carbon}	72.02
100 $w_{hydrogen}$	0.02
100 $w_{nitrogen}$	0.24
100 w_{others}	27.72

degassed at 350 °C under vacuum for 12 h. The N_2 adsorption data were obtained using a Micromeritics ASAP 2020 surface area analyzer.

The calculations of surface area, microporosity, mesoporosity, and pore volume were carried out using standard methods on the basis of volumetric adsorption of nitrogen on the activated carbons at 77 K using the Brunauer−Emmett−Teller (BET) method.[10] The pore size distribution was calculated using Barrett−Joyner−Halenda (BJH) method. The BET surface area was calculated from the isotherm using the BET equation. After the physical and chemical characteristics of CCAC were determined, elemental analysis was also carried out. The determination of the mass fractions (w) of carbon, hydrogen, nitrogen (by difference), and oxygen in CCAC were investigated using an elemental analysis instrument (PerkinElmer 2400), as shown in Table 1. The system provided data for the determination of the monolayer adsorbed amount, the apparent specific surface area, the pore volume, and the pore size distribution.

The $ZnCl_2$ activation solution produced micropores and mesopores in CCAC. The surface area, pore volume, and pore size of the carbon can be controlled by changing the activation conditions. The pore analysis of CCAC showed the dominance of micropores. It displayed a surface area of 181.37 $m^2 \cdot g^{-1}$ out of a total BET surface area of 205.27 $m^2 \cdot g^{-1}$. The BJH pore area was found to be 23.90 $m^2 \cdot g^{-1}$ for pore size range of (17 to 3000) Å. The adsorption average pore width was 22.09 Å, whereas the BJH average pore diameter was found to be 41.24 Å. The single-point total pore volume of pores (< 2529.5 Å) was $12.80 \cdot 10^{-2}$ $cm^3 \cdot g^{-1}$, whereas the cumulative pore volume of the pores (17 Å < d < 3000 Å) was $24.64 \cdot 10^{-3}$ $cm^3 \cdot g^{-1}$. The BJH adsorption average pore diameter was found to be 41.24 Å. Micropores (d < 20 Å) accounted for 88.35 % (181.37 $m^2 \cdot g^{-1}$) of the pore surface area and mesopores (20 Å < d < 500 Å) for 11.64 % (23.90 $m^2 \cdot g^{-1}$). The single-point surface area of CCAC was found to be 231.74 $m^2 \cdot g^{-1}$, and the single-point total pore volume of pores (< 3394.24 Å) was 12.80 $cm^3 \cdot g^{-1}$, whereas the cumulative pore volume of pores (17 Å < d < 3000 Å) was $12.3 \cdot 10^{-2}$ $cm^3 \cdot g^{-1}$. The details of the characteristics of CCAC are given in Table 2.

3.2. Determination of pH_{zpc}. The point of zero charge (pH_{zpc}) of CCAC was determined by a titration method. NaCl solution (50 mL) was transferred to a series of six stoppered 250 mL Erlenmeyer flasks. The pH values of the NaCl solution samples were adjusted to pH in the range 2 to 12 by addition of 0.1 M HCl or 0.1 M NaOH solution. CCAC (0.20 g) was added to each flask, after which the flasks were shaken well and their contents allowed to equilibrate for 48 h. The pH_{pzc} value is the point where the plots of pH_{final} and $pH_{initial}$ intersect each other, and subsequently that point was recorded as pH_{zpc} of the surface of CCAC. The pH_{zpc} of CCAC was found to be 5.1.

Surface characteristics (either acidic or basic) of the adsorbent can be displayed by the following two expressions:

$$\mathrm{CCAC{-}OH} + \mathrm{H}^+ \rightarrow \mathrm{CCAC{-}OH_2}^+ \qquad (1)$$

and

$$\mathrm{CCAC{-}OH} \rightarrow \mathrm{CCAC{-}O}^- + \mathrm{H}^+ \qquad (2)$$

3.3. FTIR Analysis. An FTIR spectrometer (Shimadzu 8400S) was used to determine the presence of functional groups on the surface of CCAC. For analysis, the pellets were prepared by mixing the adsorbent with KBr. The spectral wavelength was covered from (4500 to 500) cm^{-1}. The FTIR spectrum of CCAC is shown in Figure 1. The band appearing with a maximum at about 3471.40 cm^{-1} indicates the existence of hydroxyl groups in the product. The peak at 2916.60 cm^{-1} can be attributed to either the stretching vibrations of C−H bonds in alkanes or carbon bonded with hydrogen bonds. The band at 2291.69 cm^{-1} corresponds to vibrations in alkyl groups, whereas the band near 1583.39 cm^{-1} is attributed to vibrations in the aromatic groups. The band at 1083.04 cm^{-1} is a less intense band and is related to the C−O stretching vibration of the bonds in esters, ethers, or phenol groups. A weak absorption band was observed at 777.28 cm^{-1}, and this is related to γ(C−H) vibration in a benzene derivative.[11]

3.4. XRD Analysis. The phase characterization of CCAC was carried out using an X-ray diffractometer (Scifert and Co., Model ID-3000), and the XRD pattern is shown in Figure 2. The XRD of CCAC after thermal degradation in nitrogen or in an air medium was carried out. Copper was used as the target and nickel as the filter medium for the XRD. The powder sample for XRD was prepared by smearing a thin layer of powder over a glass plate. The goniometer speed was maintained at 1 $deg \cdot min^{-1}$, and its orientation was varied from 0° to 100°. A quartz standard slide was run to check the instrument drift and obtain the accurate location of 2θ peaks. Broad, diffused peaks of the sample were observed, and these indicate the amorphous nature of the CCAC sample. At the angles $2\theta = 20.5°$ and $2\theta = 23.7°$, the peaks indicate the presence of an amorphous form of carbon with minor components such as quartz, calcium orthosilicate, and alumina, while the major components are wollastonite, calcium silicate, and silicon oxide. A diffraction peak of crystalline carbon was not observed. It was seen by the X-ray diffractrograms that the activated carbon has a heterogeneous surface.[12]

3.5. TGA and DTA Analysis. TGA curves were obtained using a thermal analyzer (Figure 3). The samples (initial or exhausted) were exposed to an increase in temperature of 10 $°C \cdot min^{-1}$ and a constant nitrogen flow rate of 100 $mL \cdot min^{-1}$. TGA was used to monitor the course of carbonization. The TGA and differential thermal analysis (DTA) curves of the tested sample indicate a significant weight loss due to release of volatiles from (250 to 400) °C. In the TGA curve, only one sharp peak was observed, and a low weight loss in the last stage from (400 to 800) °C was also observed (Figure 3). The DTA and TGA profiles suggest that the weight loss of raw coconut coir can be described (approximately) by volatile lumps. In the carbonization process, tar is probably an intermediate product, and it indicated a significant weight loss (60 % by weight) in the temperature range (250 to 400) °C. The total weight loss is due to the loss of both the water either physically adsorbed or occluded inside the channels in addition to partial dehydroxylation of some

Table 2. BJH Adsorption Pore Distribution Report for Coconut Coir Activated Carbon

pore diameter range	average diameter	incremental pore volume	cumulative pore volume	incremental pore area	cumulative pore area
Å	Å	$10^{-3}\cdot cm^3\cdot g^{-1}$	$10^{-3}\cdot cm^3\cdot g^{-1}$	$m^2\cdot g^{-1}$	$m^2\cdot g^{-1}$
399.0 to 178.0[a]	211.1	4.81	4.81	0.91	0.91
178.0 to 115.2	132.6	2.45	7.26	0.74	1.65
115.2 to 84.5	94.7	1.64	8.91	0.69	2.35
84.5 to 66.5	73.1	1.44	10.35	0.79	3.14
66.5 to 54.3	59.0	1.22	11.57	0.83	3.97
54.3 to 45.4	48.9	1.53	13.11	1.25	5.22
45.4 to 38.6	41.4	1.17	14.29	1.14	6.36
38.6 to 33.2	35.4	1.40	15.69	1.58	7.94
33.2 to 28.7	30.5	1.70	17.39	2.23	10.17
28.7 to 24.8	26.4	2.08	19.48	3.16	13.33
24.8 to 21.4	22.8	2.24	21.72	3.94	17.28
21.4 to 18.1	19.4	3.63	25.36	7.50	24.78

[a] The values of the incremental pore volume, cumulative pore volume, incremental pore area, and cumulative pore area at an average diameter of 211.1 Å were found to be constant.

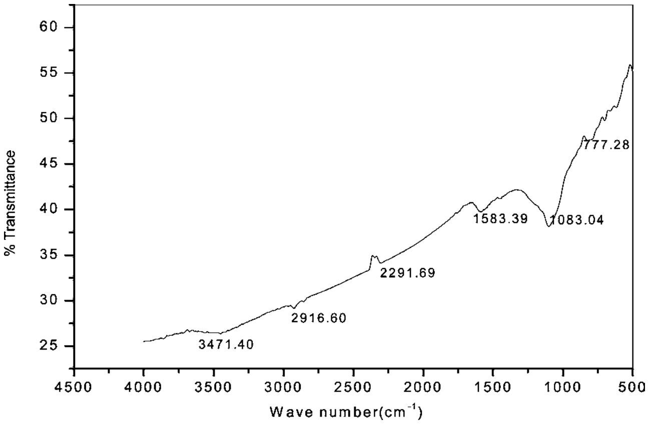

Figure 1. FTIR spectrum of coconut coir activated carbon.

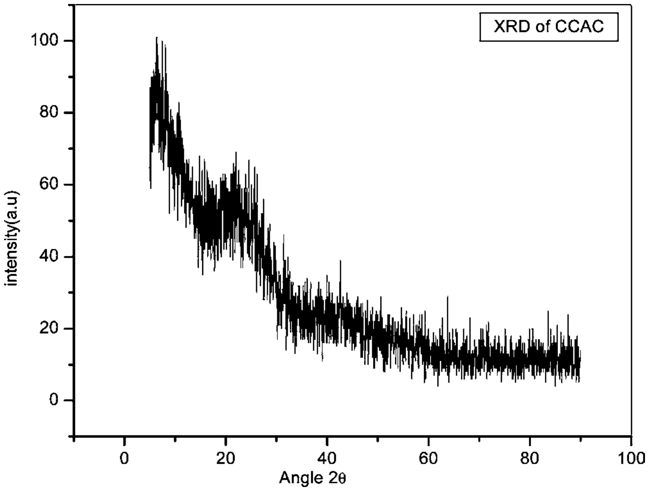

Figure 2. XRD pattern of coconut coir activated carbon.

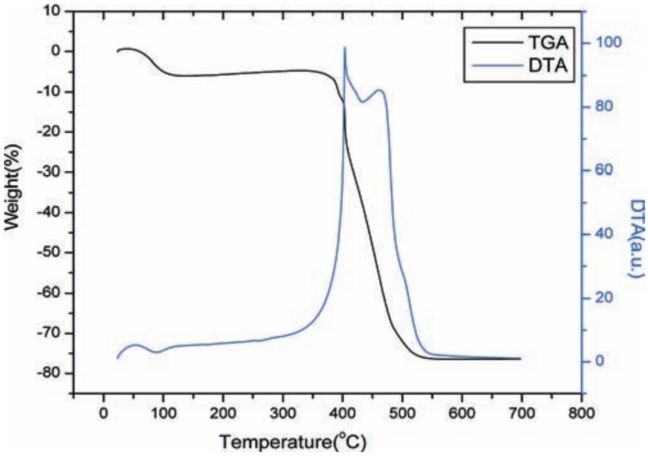

Figure 3. Thermograms of coconut coir activated carbon.

hydroxyl groups and formation of tar as well. This is because calcinations at 800 °C help complete the decomposition of intact surfactant molecules interacting with the framework.[13]

TGA indicated that the sample initially decomposes into an intermediate of smaller molar mass, after which the reaction releases various oxides (gaseous) as intermediate products and volatile matter. Thus, the reaction mechanism can be expressed as

$$\text{coconut coir} \rightarrow \text{intermediate} + \text{volatiles} \tag{3}$$

At higher temperatures, the surface groups decompose and produce CO [(150 to 600) °C], CO_2 (350 °C and above), water vapor, and free hydrogen. At higher temperature, the intermediates further decompose to form other volatile species, tar, and char. Thus, the reaction mechanism can be expressed as

$$\text{intermediate} \rightarrow \text{tar} + \text{char} + \text{volatiles} \tag{4}$$

The peak intensity of CCAC did not obviously change as the temperature was increased from (100 to 350) °C. This temperature zone is quite constant.

4. Conclusions

This study has shown that the agricultural raw material coconut coir can be successfully used to synthesize activated carbon. Various sophisticated methods, including FTIR, XRD, DTA, and TGA have been used to characterize the activated carbon. The data can be used to synthesize activated carbons from different precursors.

Literature Cited

(1) Krishnan, K. A.; Haridas, A. Removal of phosphate from aqueous solutions and sewage using natural and surface modified coir pith. *J. Hazard. Mater.* **2008**, *152*, 527–535.

(2) Namasivayam, C.; Kumar, M. D.; Selvi, K.; Begum, R. A.; Vanathi, T.; Yamuna, R. T. Waste coir pith—a potential biomass for the treatment of dyeing wastewaters. *Biomass Bioenergy* **2001**, *21*, 477–483.

(3) Namasivayam, C.; Sangeetha, D. Kinetic studies of adsorption of thiocyanate onto $ZnCl_2$ activated carbon from coir pith, an agricultural solid waste. *Chemosphere* **2005**, *60*, 1616–1623.

(4) Namasivayam, C.; Kavitha, D. IR, XRD and SEM studies on the mechanism of adsorption of dyes and phenols by coir pith carbon from aqueous phase. *Microchem. J.* **2006**, *82*, 43–48.

(5) Suksabye, P.; Nakajima, A.; Thiravetyan, P.; Baba, Y.; Nakbanpote, W. Mechanism of Cr(VI) adsorption by coir pith studied by ESR and adsorption kinetics. *J. Hazard. Mater.* **2009**, *161*, 1103–1108.

(6) Kavitha, D.; Namasivayam, C. Recycling coir pith, an agricultural solid waste, for the removal of procion orange from wastewater. *Dyes Pigm.* **2007**, *74*, 237–248.

(7) Sharma, Y. C.; Uma; Upadhyay, S. N. Removal of a Cationic Dye from Wastewaters by Adsorption on Activated Carbon Developed from Coconut Coir. *Energy Fuels* **2009**, *23*, 2983–2988.

(8) Tan, I. A. W.; Ahmad, A. L.; Hameed, B. H. Optimization of preparation conditions for activated carbons from coconut husk using response surface methodology. *Chem. Eng. J.* **2008**, *137*, 462–470.

(9) Uğurlu, M.; Gürses, A.; Açıkyıldız, M. Comparison of textile dyeing effluent adsorption on commercial activated carbon and activated carbon prepared from olive stone by $ZnCl_2$ activation. *Microporous Mesoporous Mater.* **2008**, *111*, 228–235.

(10) Barret, E. P.; Joyner, L. G.; Halenda, P. P. The determination of pore volume and area distributions in porous substances. I: Computations from nitrogen isotherms. *J. Am. Chem. Soc.* **1951**, *73*, 373–380.

(11) Sujirote, K.; Leangsuwan, P. Silicon carbide formation from pretreated rice husks. *J. Mater. Sci.* **2003**, *38*, 4739–4745.

(12) Liou, T.-H.; Wu, S.-J. Characteristics of microporous/mesoporous carbons prepared from rice husk under base- and acid-treated conditions. *J. Hazard. Mater.* **2009**, *171*, 693–70.

(13) Mall, I. D.; Srivastva, V. C.; Agarwal, N. K. Removal of orange-G and methyl violet dyes by adsorption onto bagasse fly ash—Kinetic study and equilibrium isotherm analyses. *Dyes Pigm.* **2006**, *69*, 210–223.

Received for review January 13, 2010. Accepted July 2, 2010. The authors are thankful to AICTE, Government of India, for funding this study through the RPS Scheme to Y.C.S.

JE100041X