Surface Area and Pore Size Distribution of Activated Carbon Produced from Low Cost Precursors

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(Received on 24th April 2008, accepted in revised form 31st March 2009)

Summary: Fast growing wood (*Paulownia tomentosa-PT, Ailanthus altissima-AA, Salvadora oleoides-SO*) and animal bones were utilized for the preparation of activated carbon. The carbon samples were activated by thermal means (400-1000°C). The samples were characterized by surface area (Langmuir and BJH) with micropore and mesopores volume (BJH). The surface area of other carbon samples activated at 800 °C was found in the sequence: 654.9 for *Salvadora oleoides* > 615.8 for *Ailanthus altissima* > 346.3 for *Paulownia tomentosa* > 300.0 for animal bones. BJH surface area (m^2g^{-1}) analysis of the carbon samples activated at 800 °C was found in the sequence: 274.6 for *Salvadora oleoides* > 261.76 for animal bones > 224.8 for *Paulownia tomentosa* > 200.2 for *Ailanthus altissima*. The micropore volume (BJH method) of 800 °C activated carbon samples were in the sequence: 0.15 for *Ailanthus altissima* > 0.13 for *Salvadora oleoides* > 0.08 for animal bones.

Introduction

Precursors like wood of fast growing trees, coconut shell, apricot stones, corncobs, bamboo, plum kernels were used for conversion into activated carbon [1-3]. Amongst the adsorbents, activated carbon is more efficient for the removal of pollutants from wastewater [4]. The effectiveness of activated carbon adsorption for wastewater treatment has made it an ideal alternative to other expensive treatment options [5]. During preparation, the raw material is carbonized first and then activated at 400 °C-800 °C to yield a highly porous product of surface area ranging from 300-1400m^2/g. Chemical activation proceeds under conditions that prevent the deposition of hydrocarbons on the surface. The raw material is mixed with the chemical agent, dried and calcined at temperatures up to 800 °C. Activated carbon particles have micropores (< 20Å), mesopores (20-500Å) and macropores (> 500Å). The macropores provide a passageway to the particle interior and to the micropores but do not contribute substantially to the particle surface area. The micropores on the other hand are responsible for the specific surface area of activated carbon particles. Bangash [6-8] prepared activated carbon at different carbonization temperature (400 - 800 °C) using different precursors. The results showed that the low carbonization temperature yield a poor porosity while high carbonization temperature (800 °C) enhanced the porosity. Evans [9] studied the preparation of activated carbon from macadamia nut shells. Initially the precursors were subjected to elevated temperatures (400-900 °C). Pore size distribution studies (micropore volumes exceeding 1.0 cm^3 g^{-1}) were also carried out for 750 and 800 °C activated samples. A high yield of microporous carbon was obtained at 540 °C activation temperature. Guzel [10] prepared activated carbons from sour cherry pits and was chemically activated. From the results it was found that four hours activation time was suitable for the production of porous structure. They also found a greater removal efficiency of the prepared activated carbon towards dyes. Ismadji [11] prepare activated carbon from sawdust by vacuum pyrolysis. The effects of temperature and activation time on the pore structure of activated carbons were investigated. High surface area (1150°m^2/g) and pore volume (0.43°cm^3/g) were obtained from the conditions applied for the preparation of activated carbon.

The aim of this work is to study the effect of activation temperatures (400 °C-800 °C) on the pore development and surface area of activated carbon by BJH and Langmuir's methods.

Approach

BJH Model

When the initial relative pressure $(P/Po)_1$ is close to unity, all pores are filled with adsorbate. The

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largest pore of radius $r\rho_1$ has a physically adsorbed layer of nitrogen molecules of thickness t_1. Inside this thickness is an inner capillary with radius r_K from which evaporation takes place as P/Po is lowered. The relationship between the pore volume $V\rho_1$ and the inner capillary (Kelvin) volume V_K is given by;

$$V\rho l = \frac{VKlr^2}{r^2kl} \quad (1)$$

When the relative pressure is lowered from $(P/P_o)_1$ to $(P/P_o)_2$ a volume V_1 will desorbs from the surface. This volume V_1 represent not only emptying of the largest pore of its condensate but also a reduction in the thickness of its physically adsorbed layer by an amount Δt_1. Across this relative pressure decrement the average change in thickness is $\Delta t/2$. The pore volume of the largest pore may now be expressed as:

$$V\rho\, l = V_l\left(\frac{r_{\rho l}}{rKl + \Delta t1/2}\right) \quad (2)$$

When the relative pressure is again lowered to $(P/P_o)_3$ the volume of adsorbate desorbed includes not only the condensate from the next larger size pores but also the volume from a second thinning of the physically adsorbed layer left behind in the pores of the largest size. The volume $V\rho_2$ desorbed from pores of the smaller size is given by:

$$V\rho_2 = \left(\frac{r_{\rho 2}}{rK2 + \Delta t2/2}\right)\left(V_2 - V_{\Delta t2}\right) \quad (3)$$

$$V_{\Delta 2} = \Delta t_2 Acl \quad (4)$$

where Ac_l is the area exposed by the previously emptied pores from which the physically adsorbed gas is desorbed. Substituting the general values for $V_{\Delta t\,2}$ into equation (5) results in an exact expression for calculating pore volumes at various relative pressures.

$$V\rho n = \left(\frac{r\rho n}{r_{K\,n} + \Delta t_n/2}\right)^2\left(\Delta V_n - \Delta t_n \sum_{j=l}^{n-1} Acj\right) \quad (5)$$

Equation (5) can be used for computation of pore size distributions [12].

Results and Discussion

SEM

SEM micrographs both in 1000x and 3500x magnification (plate-1-4) of all carbon samples

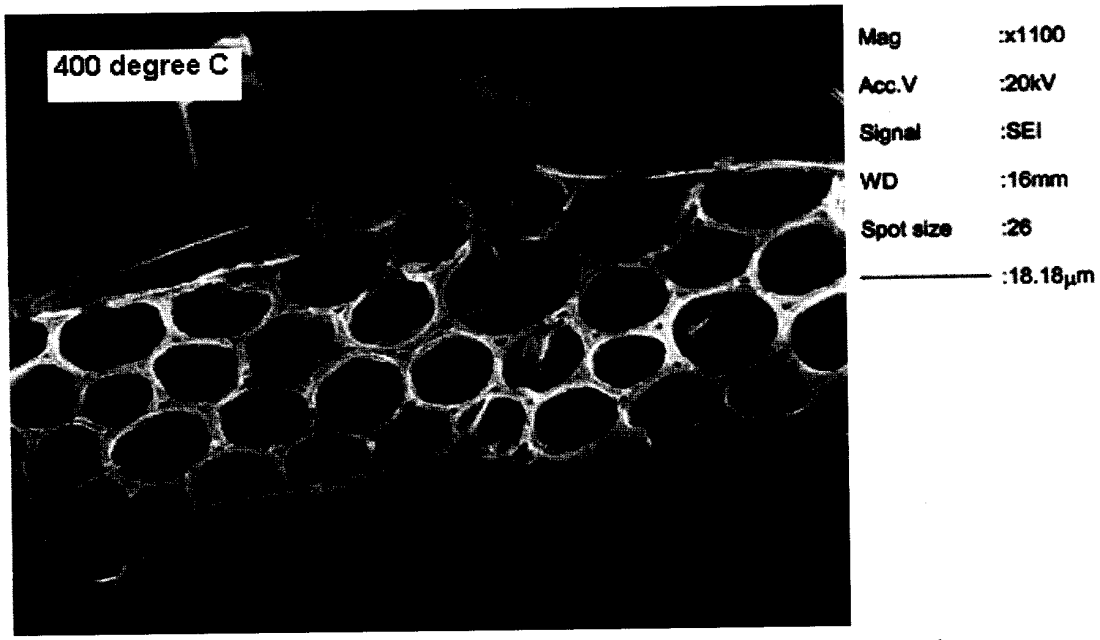

Plate-1: SEM micrographs of *Paulownia tomentosa* (PT) activated carbon sample.

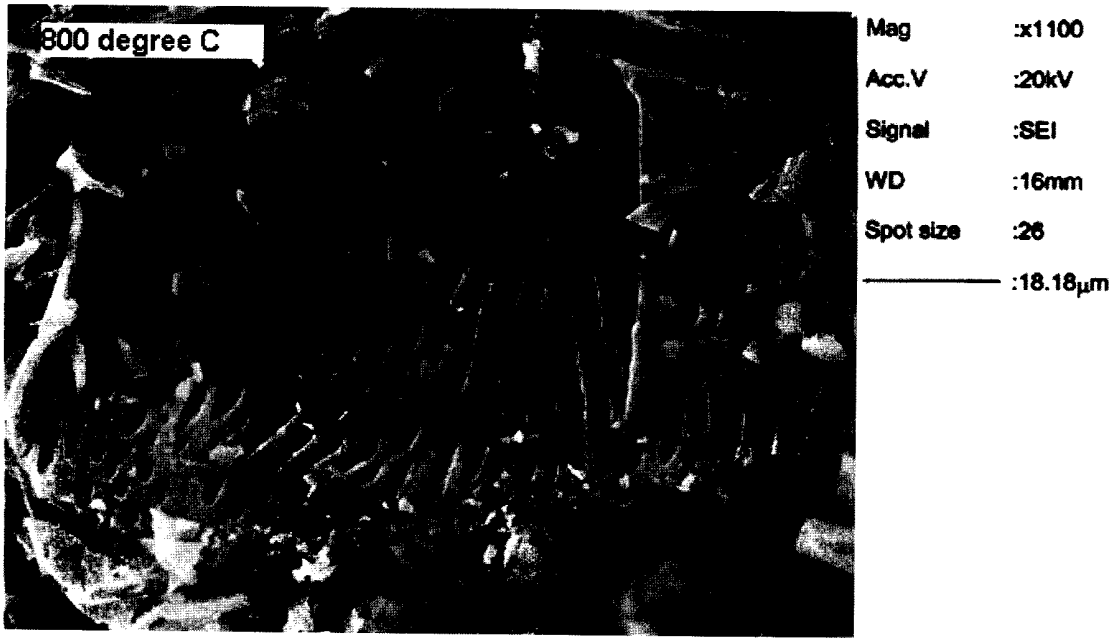

Plate-2: SEM micrographs of *Ailanthus altissima* (AA) carbon sample.

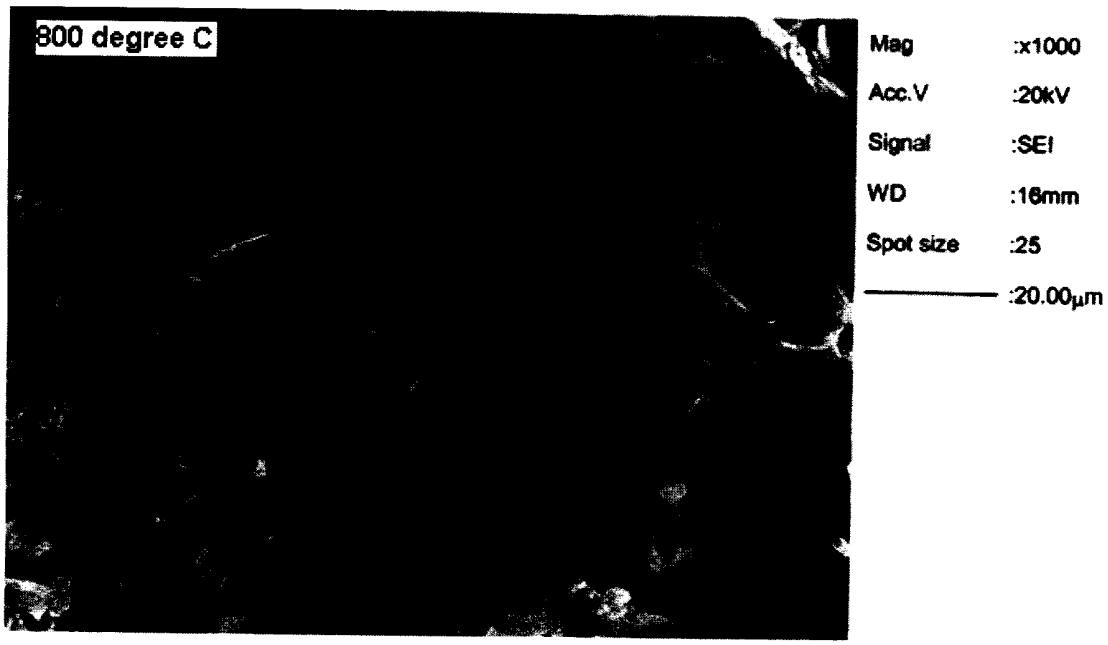

Plate-3: SEM micrographs of *Salvadora oleoides* (SO) carbon sample.

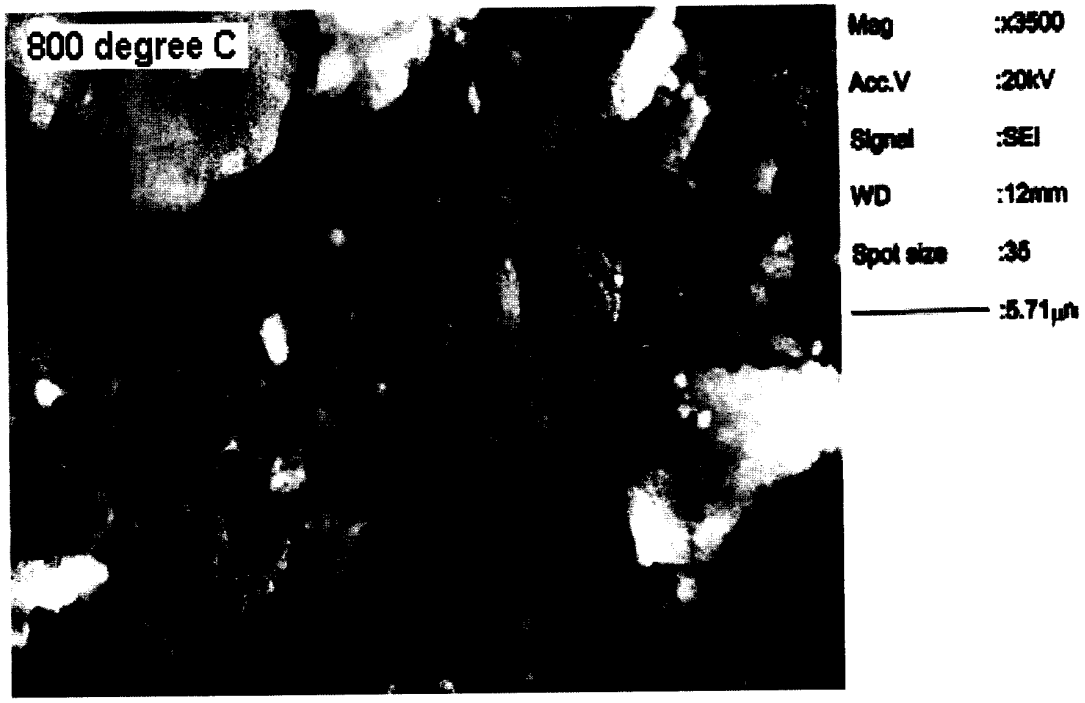

Plate-4: SEM micrographs of animal bones charcoal (ABC) sample.

showed smooth areas as well as roughness with oval and hexagonal pore patterns. Within each oval/hexagonal pore, presences of the macropores are clearly noticeable. It was observed that with increase in activation temperature the porosity increases with the emission of volatile matters trapped the pores. Thus increase the porosity of the samples.

Surface Area

The surface area of the carbon samples was determined by Langmuir and BJH methods and is given in Table-1. The nitrogen adsorption isotherms for all carbon samples are provided in Figs. 1-4. All curves exhibit type-I isotherm which are characterized by unimolecular adsorption and applies to microporous adsorbent with small pore sizes [13].

Langmuir's [14] surface area of the all carbon samples were obtained by plotting $(P/P_o)/W$ against P/P_o of the N_2 adsorption are shown in Fig. 1-4 and the values are given in Table-1. As indicated by the results, the PC has greatest surface area of 688, activated at 800 °C. The surface area ($m^2.g^{-1}$) of other carbon samples activated at 800 °C was found in the sequence: 654.9 for SO > 577.8 for AA > 346.4 for PT > 300.0 for ABC. These values were compared with the Langmuir surface area of China GA commercial carbon (806.2 $m^2.g^{-1}$) and found that the surface area of our carbon samples were lower than the commercial China-GA as, PT (402.2 $m^2.g^{-1}$), AA carbon (407.9$m^2.g^{-1}$) and ABC (506.2$m^2.g^{-1}$). The surface area of the samples was found to increase with the increase in activation temperature (Table-1). During activation at high temperature the blind pores become opene, which in turn increased the porosity and surface area of the samples. A high non-polar surface at high temperature is another reason for high surface area which may be due to the fact that polar functional groups situated at the pore opening emit and leaving the surface with wide pore volume [15]

The surface area of carbon samples were also determined by applying the BJH equation [12] and the results are given in Table-1. BJH surface area (m^2g^{-1}) analysis of the carbon samples activated at 800 °C was found in the sequence: 274.64 for SO > 244.25 for ABC > 224.89 for PT > 200.24 for AA. The surface area of each sample was compared with BJH surface area ($m^2.g^{-1}$) of china-GA commercial

Table-1: Surface area and pore size distribution of carbon samples.

Carbon sample	Raw/ Degassing	Surface area (m^2/g)		Micropore size distribution (BJH method)	
		BJH method	Langmuir method	Micropore volume (cc/g)	Average pore width (Å)
Paulownia tomentosa (PT)	Raw	97.8	234.9	0.02	2.95
	400 °C	107.3	252.57	0.05	13.9
	800 °C	224.9	346.4	0.100	18.7
Ailanthus altissima (AA)	Raw	50.3	111.5	0.02	2.36
	400 °C	247.8	516.6	0.11	3.74
	800 °C	200.2	577.9	0.14	6.76
Salvadora oleoides (SO)	Raw	0.58	3.18	0.00	3.4
	400 °C	45.5	149.7	0.02	4.5
	800 °C	274.6	654.9	0.13	14.2
	1000 °C	452.1	897.6	0.21	19.5
Animal bones charcoal *(ABC)*	600 °C	40.9	135.1	0.02	13.9
	800 °C	244.3	300.0	0.04	18.6
	1000 °C	360.5	400.2	0.05	21.3
Commercial China GA carbon		560.4	806.2	0.29	51.0
Data reduction parameters		Analysis gas = Nitrogen, Molecular Wt = 28.013, Cross section = 16.200 *Å/mol*, Liquid Density = 0.808 *g/cc*, Surface tension = 8.850 *erg/cm²*, Eff. Mol. Diameter (D) = 3.5400 Å, Eff. Cell stem Diameter (d) = 4.00 *mm*, Po override = 760.00 *mmHg*, Bath Temp = 74K, Press tolerance = 0.100/0.100 (ads/des), Equi. time = 60/60 *sec* (ads/des).			

activated carbon (560.4) and found that the surface area of our samples are lower than China-GA carbon as, SO (285.8), AA (360.2) and ABC (316.2).

Porosity can also be predicted from the N_2 adsorption isotherms. Type-I isotherms were obtained for all carbon samples (Fig. 1-4). Such types of isotherms are concave to the P/P_o axis and N_2 uptake is governed by accessible micropores volume rather than the internal surface area. Such a behavior was observed for all the samples indicating the porous structures (SEM plat 1-4). The results in Table-1 show that activation temperature has a significant effect on pore volume and increases with the increase in activation temperature. The micropore volume (BJH method) of 800 °C activated carbon samples

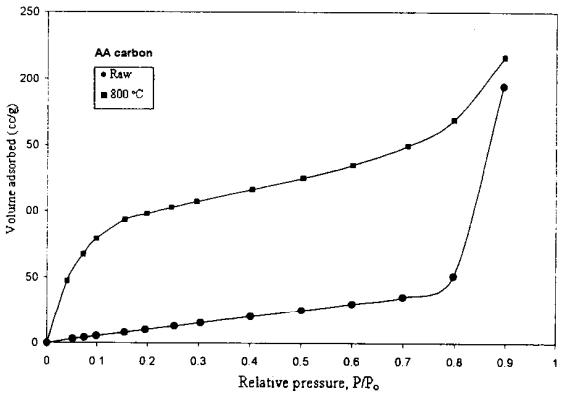

Fig. 2: Nitrogen adsorption isotherms of AA carbon samples.

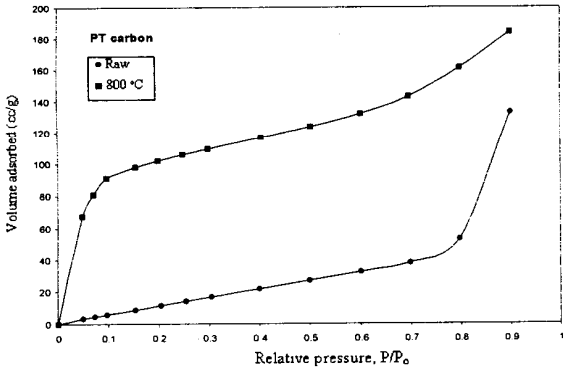

Fig. 1: Nitrogen adsorption isotherms of PT carbon samples.

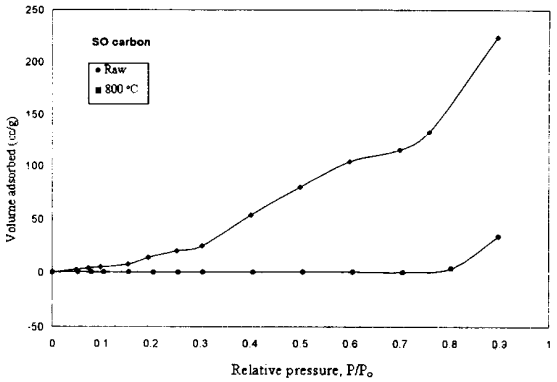

Fig. 3: Nitrogen adsorption isotherms of SO carbon samples.

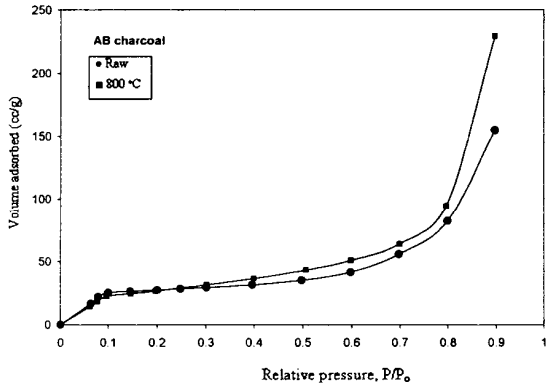

Fig. 4: Nitrogen adsorption isotherms of animal bones carbon samples.

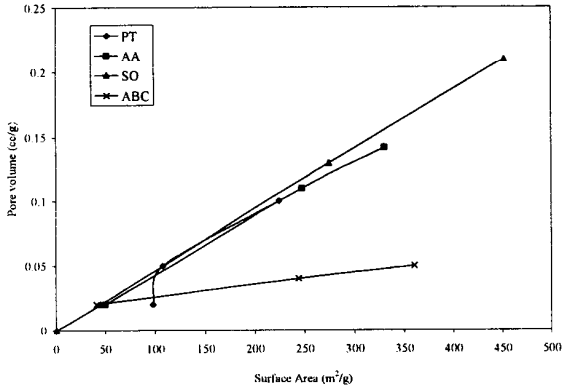

Fig. 5: Change in pore size with respect to surface area of the carbon samples.

were in the sequence: 0.15 for AA > 0.13 for SO > 0.1 for PT > 0.08 for ABC.

The mesopores volumes ($cm^3.g^{-1}$) of carbon samples determined by BJH method and were found in the sequence: 0.37for SO > 0.36 for ABC > 0.32 for AA > 0.21 for PT.

Experimental

Preparation of carbon

Low cost material of fast growing wood (*Paulownia tomentosa-PT, Ailanthus altissima-AA, Salvadora oleoides-SO*) and animal bones were collected and heated continuously for 8 hours on a flame burner in an iron container with an outlet for the emission of volatile matter. Carbon obtained was cooled in the container and ground with the help of mortar and pestle and screened with US standards mesh 150-180 μ m. It was then treated with 0.5 M aqueous solution of KOH for 24 hours with occasional stirring. The mixture was then filtered and washed with double distilled water for the complete removal of base. The carbon was then leached with 0.2N solution of HNO_3 : HCl (1:1) and allowed to stand for 24 hours at room temperature with regular mixing. It was then filtered and washed with double distilled water until free from Cl^- and NO_3^- ions. The carbon thus obtained was then air-dried in an oven at 105 ± 2 °C. This treated carbon was then extracted with n-hexane for two hours in a soxhlet extractor and allowed to dry for 8 hours in a vacuum oven. The sample was then degassed by placing in silica (SiO_2) tubes and heated at 400 and 800 °C in a tube furnace (FS. 215 Gallenkamp England) with a vacuum facility. The samples thus obtained were allowed to cool and stored under nitrogen atmosphere.

Surface Area

Nitrogen adsorption experiments were carried out manometrically at -196 °C using Quantachrome NOVA 2200 surface area and pore size analyzer. Surface area was obtained by applying the standard Langmuir and BJH equations to the adsorption data in the relative pressure (P/P_o) range: 0.05 - 0.99. The values of 0.81 g cm^{-3} and 16.2 × 10^{-20} m^2 were used for the density of liquid nitrogen and the molecular area of adsorbate nitrogen at -196 °C, respectively. The pore size distribution was determined by BJH method using the NOVAWin2 data analysis software.

SEM

Scanning electron micrographs of the samples were obtained by mounting the sample on aluminum discs (1 cm × 0.25 cm) and by using scanning electron microscope (SEM-Model-JSM-5910, Japan JEOL).

Acknowledgements

Institute of Chemical Sciences (ICS), University of Peshawar and Centralized Resource Laboratory, University of Peshawar are acknowledged for providing the research facilities.

Nomenclature

PT	=	*Paulownia tomentosa*
AA	=	*Ailanthus altissima*
SO	=	*Salvadora oleoides*
ABC	=	Animal bones
SEM	=	Scanning electron microscope
μm	=	Micrometer
P/P_o	=	Relative pressure
BJH	=	Barrett, Joyner and Holenda

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