

## FT-IR, TG, XRD and SEM Studies of Activated Carbons Prepared From Agricultural Waste

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Activated carbon adsorbents were made from *Phaseolus trilobus*, *Leucena leucocephala* and *Casuarina* which are waste bio-mass materials collected from agricultural fields. These raw materials were carbonized under the protection of an inert gas flow with subsequent nitric acid treatment and the resulted carbons surface properties were investigated. X-ray diffraction (XRD) analysis indicated characteristics of graphitic crystallites. Surface chemical groups were detected by absorption bands assigned to carbonyl, phenolic, ethers and surface hydroxyl groups by the Fourier transform infrared spectroscopy (FTIR). Surface morphological studies given by scanning electron microscope (SEM) showed the random arrangement of slant flakes with roughened.

**Key Words:** Activated carbons, Agricultural wastes.

### INTRODUCTION

The industrial use of activated carbons goes back many years. Activated carbon is widely used as adsorbent in drinking water and wastewater treatment, odour control and various chemical processes<sup>1-3</sup>. The adsorption capacity as one of the most important properties is directly determined by the surface structure of the activated carbon. Activated carbon is usually obtained from a biopolymer material, which is carbonized first and activated in second step. It has been reported that pyrolysis process produced a richer carbon content material with a more ordered structure and the heat treatment caused the development of the porosity<sup>4</sup>, by burning out graphene layers from the crystallites, slit-like micropores are formed. Extensive preparation methods have been studied to reveal the surface structure in an effort of developing high performance activated carbon and chemical activation as one of the most important steps during the preparation has attracted extensive attention<sup>5,6</sup>. The advantages of chemical activation include low activation temperature, reduced activation time, high surface area, high yield and an important reduction of the mineral content<sup>7</sup>.

Not only active sites but also micro graphite crystallites may have great effect on the chemical activation process. Activated carbons are not composed of well

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crystalline graphite, but disorderly micro graphite crystallites<sup>8</sup>. A small crystallite thickness and short range ordering between crystallites is necessary for the achievement of the high surface area of the activated carbons.

Recently, much attention has been focused on activated carbon adsorbents prepared from low cost materials due to the benefits from their utilization in various fields and as an alternative to commercially available activated carbons. For many applications it is desirable to investigate their surface characteristics which were discussed in several papers. Our objective was to prepare activated carbons from low-cost materials and to characterize by using TG, FTIR, XRD and SEM techniques which provide an insight into surface properties of these newly synthesized carbons.

### EXPERIMENTAL

Three carbons were prepared from parts of three different bio-materials viz., *Phaseolus trilobus*, *Leucena leucocephala* and *Casuarina* collected from agricultural field. *Phaseolus trilobus* is a grass material and branches of *Leucena leucocephala* and *Casuarina* are used. Raw materials crushed, dried and carbonized at 500 °C in a uniform nitrogen flow. These carbons were subjected to liquid phase oxidation with 0.1 N HNO<sub>3</sub> (analytical reagent grade). After that the carbons were washed with double-distilled water to remove the excess acid and dried at 150 °C for 12 h. The carbons were named as NPTC, NLLC and NCC obtained from *Phaseolus trilobus*, *Leucena leucocephala* and *Casuarina* after the acid activation, respectively.

The prepared carbons were examined using FT-IR spectroscopy. The sample discs are prepared by mixing of 2 mg of powdered carbon with 200 mg of KBr (Merck; for spectroscopy) in an agate mortar, then pressing the resulting mixture successively under a pressure of 5 tones. cm<sup>-2</sup> for about 5 min and at 10 tones. cm<sup>-2</sup> for 5 min under vacuum. The spectra measured from 4000 to 400 cm<sup>-1</sup> and recorded on a Spectrum GX model spectrometer (Perkin-Elmer). The instrument used was a ZEISS scanning electron microscope with energy dispersive Si-Li detector for X-ray detection forming an integral part of the system. X-ray diffraction (XRD) experiments were performed using a Philips PW 1840, X-ray diffractometer with a copper target (Cu-K<sub>α</sub>) at a scanning rate of 0.050 2θ/s, chart speed 10 mm/2θ, in the range 2-50° and a slit of 0.2 mm, applying 40 kV, 20 mA. Thermogravimetric analysis was carried out on Mettler Toledo 851e system with a heating rate of 10 °C/min. The samples were analyzed in the temperature range 25 to 1000 °C under nitrogen atmosphere with a flow rate of 30 mL/min.

### RESULTS AND DISCUSSION

The FTIR results of these carbons are given in Table-1. The O-H stretching vibrations bands were observed in all carbon samples around 3600-3200 cm<sup>-1</sup> due to the existence of surface hydroxyl groups. The band of asymmetric stretching at lower wave numbers indicates the presence of strong hydrogen bonds<sup>9</sup>. Band at

TABLE-1  
SURFACE FUNCTIONAL GROUPS OF NPTC, NLLC AND NCC  
OBSERVED BY FT-IR SPECTROSCOPY

Wave number (cm <sup>-1</sup> )			Bonds indicative of
NPTC	NLLC	NCC	
3376	3368	3372	O-H stretch
2928	2923	2928	Carboxylic/phenolic
2340	–	2340	Combination or overtone bands
–	1702	–	C=O in carboxylic and lactones
1597	1590	1583	C=C in aromatics or C=O stretch
1383	–	1383	C-H deformation in alkane
1263	1246	1240	CH <sub>3</sub> -CO-O-, Esters or epoxides, <i>etc.</i>
1166	1165	1165	C-O stretch in phenols, ethers lactones, <i>etc.</i>
1033	1033	1033	Alcoholic C-O stretch
Below 913	Below 889	Below 841	Plane deformation

2925 cm<sup>-1</sup> may be due to the stretching modes carboxylic or phenolic structures<sup>10</sup>. Bands around 2854 cm<sup>-1</sup> are C-H stretching vibrations of aliphatic groups. The band appearing at 1580 cm<sup>-1</sup> for carbon samples has been interpreted unequivocally. This has been assigned to aromatic ring stretching coupled to highly conjugated carbonyl groups<sup>11</sup> or attributed to the stretching vibrations of C=O moieties of conjugated systems such as diketone, keto ester and keto-enol structures<sup>12-16</sup>. Bands around 1260 cm<sup>-1</sup> are observed in NPTC, NLLC and NCC and may be assigned to esters (*e.g.*, CH<sub>3</sub>-CO-O-) and with epoxides<sup>17</sup> or lactones, phenols and carboxylic anhydrides<sup>18</sup>. Bands around 1160 cm<sup>-1</sup> are clearly observed and attributed due to the C-O stretching bonds in phenols, ethers, lactones and hydroxyl groups<sup>19</sup>. Bands at 1033 cm<sup>-1</sup> correspond to alcoholic C-O stretching vibration. Bands observed below 950 cm<sup>-1</sup> are characteristic of out of plane deformation vibrations of C-H group in aromatic structures.

**Thermo gravimetric studies:** The NLLC and NCC samples exhibited a slight weight loss of *ca.* 8 % and NPTC showed 10 % from 30 to 100 °C, attributed to the release of moisture. Carbons are stable from 100 up to 200 °C observed by the plateau. Slow degradation was noted up to 420 °C, after that a cumulative weight change was identified up to 850 °C for NLLC and NCC and 900 °C for NPTC as shown by the curved portion in the graph. From 200 to 850 °C, a weight loss of 60.95, 32.52 and 45.76 % of NPTC, NLLC and NCC was observed. The later weight loss could be due to the decompositions of volatiles and the wide temperature range may due to the overlap of thermal decomposition of multi unstable species on the surface of the sample, implying the presence of various structures in the samples.

Hence the weight loss shown in the thermograms is distributed over a wide temperature range and the rate becomes slower only at a much higher temperature. These results corroborate the above observations concerning the effect of oxidation by HNO<sub>3</sub> on the surface chemical nature of active carbon. It can also be deduced

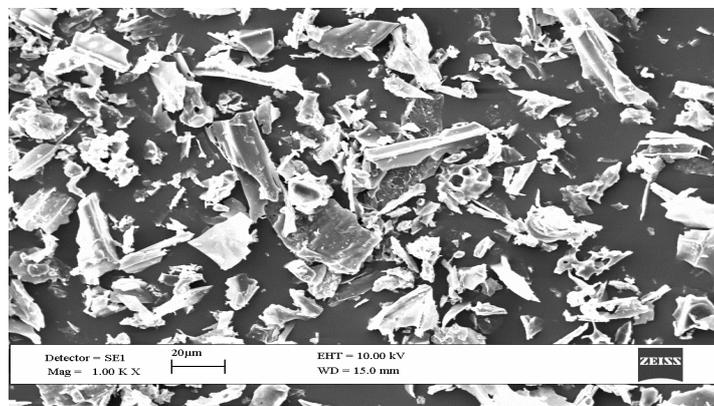
that activated carbons are easily ignited under oxidizing conditions starting from 430 upto 700 °C and showing more gradual weight loss that extends up to 900 °C. It can be concluded from TG analysis that the weight changes monitored in flowing N<sub>2</sub> up to 1000 °C mainly reflect the presence of functional groups on the oxidized carbon surface and at the same time their successive decomposition or desorption. Moreover, it also reflects the relative thermal stability of the oxidized sample by preserving its carbon matrix and spreading the weight loss shown in the thermo gram to much higher temperature.

**X-ray diffraction studies:** The structure of the activated carbons studied in terms of crystalline order with respect to graphite structure by analyzing their X-ray diffractograms. By observing the diffractograms, all carbons exhibit structural parameters typical highly disordered solid carbons as would expected for activated carbons as reported in earlier studies<sup>20</sup>. Diffraction peaks corresponding to  $2\theta \sim 23^\circ$  and  $\sim 42^\circ$  are assigned to disordered graphite 002 plane and 10 plane, respectively and can often be this disordered structure was termed as 'turbostratic structure' as reported by Biscoe *et al.*<sup>21</sup> 002 peak is due to stacking structure of aromatic structure of aromatic layers and broadness of it can be interpreted in terms of small dimensions of crystallite perpendicular to aromatic layers. Each sample has a different full width at half maximum of the 002 peak, indicating the presence of a different micropore wall structural unit<sup>22</sup>. All samples show very broad 002 diffraction peaks, indicating that these are typical low-temperature carbon materials.

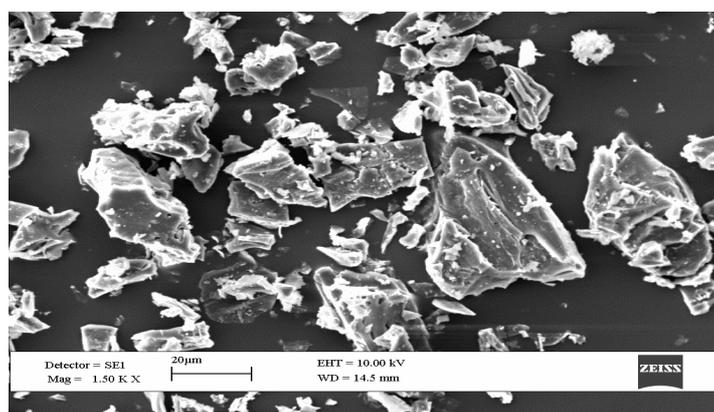
This result is expected since the treatments are limited only to moderate temperatures up to 500 °C. Very high treatment temperature, around 2227 °C, will affect the crystalline structure because at that temperature the micropores will completely disappear<sup>23</sup>. Furthermore, the weaker broad peak at 42°, indicating that the (100) and (101) peaks have merged to yield a single (10) reflection, stems from the hexagonal ring structure of the carbon sheets and also demonstrates a relatively higher degree of randomness of the scattering carbon atoms. The disorder is probably more pronounced in the sheets of the activated carbon and the more disordered the higher is its reactivity<sup>20</sup>.

**SEM:** SEM micrographs of the smooth and rough areas of the surfaces of activated carbons are analyzed at different magnification. The images are given in Fig. 1(a-c). Smooth areas are characterized by a roughness structure. A few macro pores are clearly identifiable. The rough surface micrographs showed a distinct roughness with oval patterns. Within each oval section, presence of the macro pores is clearly noticeable.

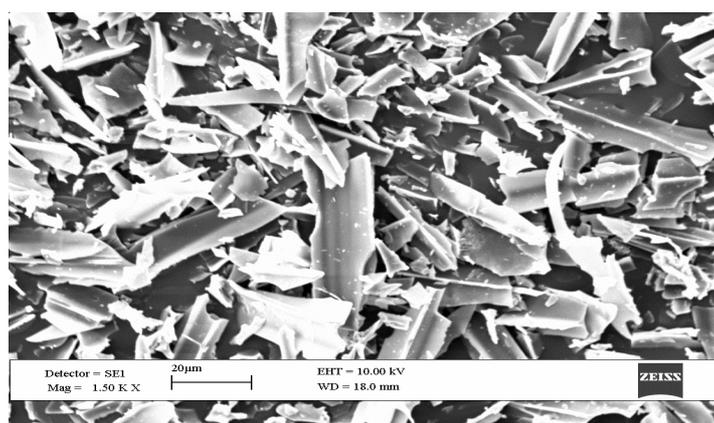
The effectiveness of the activated carbon to remove specific contaminants depends on the presence of the functional groups on the carbon surface, which strongly influences the adsorption. In addition, it is possible that the defects due to missing units in the carbon-hexagon networks are also responsible for adsorption of certain contaminants<sup>24</sup>. The dislocation of groups with large number of carbons such as C60, C70 and higher fullerenes create significant number of gaps within the carbon



(a)



(b)



(c)

Fig. 1. SEM micrographs of (a) NPTC, (b) NLLC and (c) NCC

matrix. Although the activated carbons have high porosities and large internal surface area, the characteristics of the exterior surface play a significant role in defining the effectiveness of the activated carbon particles in removing specific contaminants. The reactive groups on the exterior surface of the carbon particles are easily accessible. Also the molecular size of the contaminants, contact time for adsorption as well as the tortuosity characteristics of the pores may limit the accessibility of the interior surface.

By observing the figures slant flakes are found in the three carbons which are associated with micro and meso pores. In NCC long steep line planes are completely smooth and the sides of most of them are rough and sharp. Corrugation of the planes is observed in morphology of the surfaces of three carbon samples which may be due to the action of nitric acid<sup>19</sup>. Random arrangement of the flake crystallites which are graphite crystallites<sup>25</sup> noticed in three images of carbon samples supporting the presence of turbostratic static structure given by the XRD studies.

### Conclusion

FT-IR studies revealed that NPTC, NLLC and NCC have different surface functional groups which play a key role in adsorption like removing toxic dyestuffs from water and other processes. Weight loss shown by thermogravimetric curves concluded that wet oxidation of activated carbon with HNO<sub>3</sub> to an appreciable degree of functionality formation on carbon surface. These functionalities become attached to a high degree that their desorption primarily as CO<sub>2</sub> and/or CO, requires high energy. Besides having the turbostratic structure these carbons have good porous surface morphology. Obviously the activated carbons prepared from the bio-materials collected from agricultural fields have good surface characteristics.

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