

**PREPARATION OF ACTIVATED KAZA'S CARBONS FROM BIO-MATERIALS AND THEIR CHARACTERIZATION**

M.Nageswara Rao<sup>2</sup>, Ch.Chakrapani<sup>3</sup>, B.V.Rajeswara Reddy<sup>3</sup>, Ch.Suresh Babu<sup>3</sup>, Y.Hanumantha Rao<sup>4</sup>, Kaza Somasekhara Rao<sup>1</sup>, and Kaza Rajesh<sup>5</sup>

<sup>1</sup>Dept. of Chemistry, Nagaland University, LUMAMI-798627, Nagaland. <sup>2</sup>Dept. of Chemistry, Sri Chaitanya Mahila Kalasala, Vijayawada, A.P

<sup>3</sup>Dept. of Chemistry, ANU- NUZVID Campus, Nuzvid, A.P

<sup>4</sup>Dept. of Chemistry, Andhra Lyola College, Vijayawada, A.P

<sup>5</sup>Dept. of Pharmacy, Sri Vidyaniketan College, Tirupati, A.P

Mail- [sr\\_kaza1947@yahoo.com](mailto:sr_kaza1947@yahoo.com)

**ABSTRACT:** Prepared three different activated carbons from parts of three different bio-materials viz., *Phaseolus trilobus*, *Leucena leucocephala* and *Casuarina* collected from agricultural field. In the present study physico-chemical and surface characteristics of these prepared carbons have been discussed. For surface characterization FT-IR and EDAX methods were used.

**Key words :** Activated Kaza's carbons, Characterization by FT-IR and EDAX

**INTRODUCTION**

The study of activated carbons, or carbon adsorbents, is included in what is commonly called Science and Technology of Carbon Materials, where a variety of carbon based materials are employed. The adsorption capacity as one of the most important properties is directly determined by the surface structure of the activated carbon. 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>1</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>2,3</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>4</sup>. 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 numerous papers.

We prepared three different activated carbons 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 and studied physico-chemical and surface characteristics of these prepared carbons.

## MATERIALS AND METHODS

The raw materials collected and their particulars are

### i) *Phaseolus trilobus*

Botanical name	: <i>Phaseolus trilobus</i>
Common name	: African gram, Jungle mat bean and <i>Vignatrilobata</i> (L.)
Genus	: <i>Phaseolus</i>
Family	: Fabaceae
Distribution	: A regenerating annual herb, with reddish glbrous or rarely pubescent stems, prostrate, trailing (rarely weakly twining to 50 cm. Cultivated in many places in India

The plant is shown in figure1.



**Figure 1. *Phaseolus trilobus***

### ii ) *Leucena leucocephala*

Botanical name	: <i>Leucena leucocephala</i>
Common name	: <i>Leucena glauca</i> , <i>Mimosa glauca</i> and <i>Acacia glauca</i>
Genus	: <i>Leucena</i>
Family	: Fabaceae
Distribution	: This tree is a small Mimoid tropical tree native to Mexico. Cultivated in many places in India. It is used for a variety of purposes, such as firewood, fiber and livestock feed.

The plant is shown in figure 2.



**Figure 2. *Leucena leucocephala***

## iii) Casuarina

Botanical name	: Casuarina
Common name	: Australian beefwood, Australian pine, casuarina, fire oak and river she-oak.
Genus	: Casuarina
Family	: Casuarinaceae
Distribution	: This tree is native to Australia. Cultivated in many places in India. It is used for a variety of purposes, such as firewood, and valued for protecting riverbanks.

The plant is shown in figure 3.



**Figure 3. Casuarina**

The raw materials were collected, crushed into small pieces, washed with water and dried under sunlight for two days. The dried materials were carbonized in uniform nitrogen flow in a horizontal tube furnace electrically heated at 500°C for 4 h, cooled to room temperature and ground to 45 mesh. These powdered carbons were subjected to liquid phase oxidation with 1N HNO<sub>3</sub>. After that the carbons were washed with double-distilled water to remove the excess acid and dried at 150°C for 12h. These activated carbons which are prepared from *Phaseolus trilobus*, *Leucena leucocephala* and *Casuarina* are named as NPTC, NLLC and NCC respectively. These are also collectively named as **Kaza's carbons** after the name of **Kaza Somasekhara Rao**.

The Apparent density, Moisture content, Volatile matter, Acid insoluble matter, Water soluble matter, Ash content, pH, pH<sub>zpc</sub><sup>5,6</sup>, oxygenated surface groups<sup>7</sup>, internal surface area<sup>8</sup>, and decolorizing power<sup>9,10</sup>, were determined by standard methods. Surface characteristics for the prepared carbons were determined by FT-IR analysis and EDAX analysis (Energy dispersive x-ray analysis).

## RESULTS AND DISCUSSION

Physico-chemical characteristics:

The results of physico- chemical parameters of the prepared activated carbons were presented in Table.1.

Table 1. Physico-chemical characteristics of NCC, NPTC and NLLC

Parameter	Value		
	NCC	NPTC	NLLC
Apparent density, g ml <sup>-1</sup>	1.18	1.14	0.98
Moisture content, %	8.6	7.9	6.85
Volatile matter, %	43.5	48.4	31.35
Ash, %	2.6	2.1	2.25
Fixed carbon, %	47.3	43.2	60.95
Matter soluble HCl, %	0.75	0.81	0.65
Matter soluble in H <sub>2</sub> O, %	0.65	0.53	0.51
Decolorizing power, mg g <sup>-1</sup>	196.5	204.4	215.35
pH	7.4	7.6	7.5
pH <sub>ZPC</sub>	8.6	8.1	8.65
Surface acid groups, meq g <sup>-1</sup>			
I Carboxyl	0.88	1.09	0.83
II Lactonic	1.14	1.57	1.21
III Phenolic	1.36	1.29	0.95
IV Carbonyl	1.08	0.85	1.31
Total basic groups, meq g <sup>-1</sup>	6.27	5.79	6.5
Iodine number, m <sup>2</sup> g <sup>-1</sup>	632	675	738

The apparent density is very useful for the estimation of the packing volume or to determine the grade of carbon needed for an existing system. The observed apparent densities of NCC, NPTC and NLLC are of low value, i.e., 1.18, 1.14 and 0.98 g ml<sup>-1</sup> respectively. According to literature review, activated carbons with a random arrangement of micro-crystallites and with strong cross-linking between them have a porous structure and relatively low density.

The moisture content for NCC, NPTC and NLLC are found to be 8.6, 7.9 and 6.85 %. If the moisture content of the adsorbent is more it may dilute the action of activated carbon and it necessitates utilizing some extra-load of carbon. Since the moisture content for all the three activated carbons is low, it may not influence the adsorption power of activated carbon<sup>11</sup>. The volatile matter of NCC, NPTC and NLLC are 43.5, 48.4 and 31.35 % respectively. The observed values are comparable with the activated carbon prepared from coir-pith<sup>12</sup>.

The ash content of NCC, NPTC and NLLC are 2.6, 2.1 and 2.25 % respectively. The ash content increases in direct proportion to the degree of activation and it can be used to determine the raw material used to produce an activated carbon. For instance, coconut shell carbons contain 1-3 % ash<sup>5</sup>. Since observed values are also within the range, the raw materials used for the preparation of these activated carbons can be considered as good sources.

Matter soluble in HCl is 0.75, 0.81 and 0.65 % for NCC, NPTC and NLLC respectively. These low values indicate that the carbons are almost insoluble in acid; hence these may be used in treating water with acidic nature<sup>13</sup>.

Matter soluble in water is 0.65, 0.53 and 0.51 % for NCC, NPTC and NLLC respectively. These low values indicate that the prepared activated carbon adsorbents are well suited for ground water analysis since it may not much alter the physical properties of water. This is also confirmed by their pH values 7.4, 7.6 and 7.5 for NCC, NPTC and NLLC respectively, which are in optimum neutral medium range 6.4 to 7.2 for pure water.

The  $pH_{zpc}$  values of NCC, NPTC and NLLC are 8.6, 8.1 and 8.65 respectively. If the  $pH > pH_{zpc}$ , acidic functionalities will dissociate, releasing protons into the medium and leaving a negatively charged surface on the carbon. On the other hand, if the  $pH < pH_{zpc}$ , basic sites combine with protons from the medium to leave a positively charged surface<sup>15</sup>. In the present study, for every carbon, the pH value is less than its corresponding  $pH_{zpc}$  value. This indicates that the surface is positively charged.

From Table 1, it is clear that for each carbon, the total basic groups are slightly greater than the total acidic groups (due to carboxylic, lactonic, phenolic and carbonyl groups). Boehm states that the chemisorption of oxygen suggests that the basicity may be due to oxygen functional groups, and the existence of pyrone-type structures on the edges of the polyaromatic layers has been suggested. Support for the hypothesis of pyrone-type structures came from theoretical calculations, which showed that the base strength increases strongly when the carbonyl group and the ring oxygen of a pyrone-type structure are distributed on polycyclic aromatic compounds<sup>7</sup> the results are in harmony with the activated carbon prepared from rice straw<sup>14</sup>. It has been established that iodine number (in  $\text{mg g}^{-1}$ ) gives an estimate of the surface area (in  $\text{m}^2 \text{g}^{-1}$ )<sup>18,19</sup>. Iodine numbers of NCC, NPTC and NLLC are 632, 675 and 738  $\text{m}^2 \text{g}^{-1}$  respectively. The decolorizing power of NCC, NPTC and NLLC are 196.5, 204.4 and 215.35  $\text{mg g}^{-1}$  respectively. The results are comparable with the activated carbon prepared from coir pith<sup>17</sup>.

## Surface characteristics

### FT-IR analysis

The presence of oxygen and aromatic structures were identified in prepared activated carbons by FT-IR analysis. Surface chemical groups were detected by absorption bands assigned to carboxyl, carbonyl, phenolic, ethers and surface hydroxyl groups. Figures 4,5 and 6 are the FT-IR graphs of NPTC and NLLC NCC and the results are given in Table 2.

Table 2. Bonds assigned to functional groups of NPTC, NLLC and NCC in FT-IR study

Wave number ( $\text{cm}^{-1}$ )			Bonds indicative of
NPTC	NLLC	NCC	
3376	3368	3372	O-H stretch
2928	2923	2928	Carboxylic/phenolic
2340	-	2340	Ketene or alkyne or nitrogen double bond
-	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 etc.,
1166	1165	1165	C-O stretch in phenols, ethers lactones etc.,
1033	1033	1033	Alcoholic C-O stretch
Below 913	Below 889	Below 841	Plane deformation

Band of O-H stretching vibrations were observed in all carbon samples around 3600 - 3200  $\text{cm}^{-1}$  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>18-22</sup>. Band at 2925  $\text{cm}^{-1}$  may be due to the stretching modes carboxylic or phenolic structures<sup>23</sup>. Bands around 2928  $\text{cm}^{-1}$  are C-H stretching vibrations of aliphatic groups. A weak band centered near 2340  $\text{cm}^{-1}$  is can be seen, such bands have been observed in earlier IR studies of carbon<sup>24</sup> but assignments have been difficult to make because of the limited number of bonds that absorb in these regions. Carbon-oxygen bands have been proposed to give bands around 2350  $\text{cm}^{-1}$ , perhaps due to ketene<sup>25</sup> or result of alkynes (acetylenic) groups, transition metal carbonyl and nitrogen double bond<sup>26</sup>.

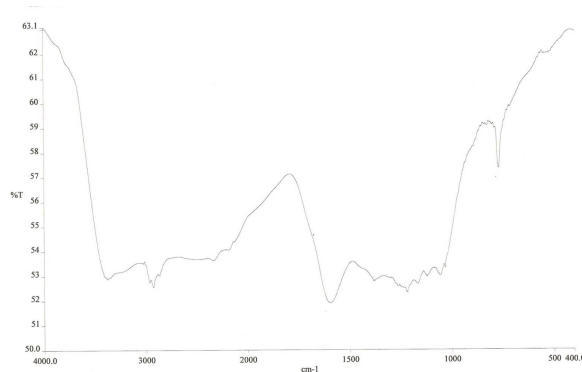


Figure 4. FT-IR of NPTC

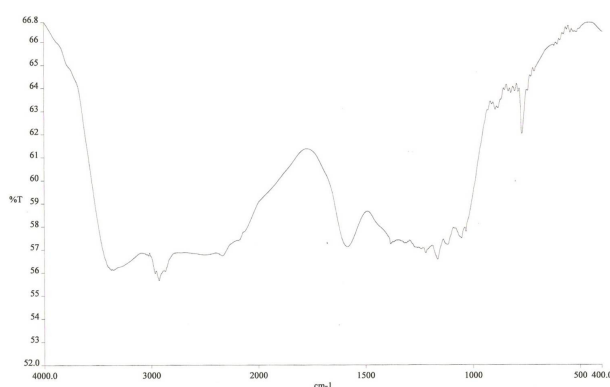


Figure 5. FT-IR of NLLC

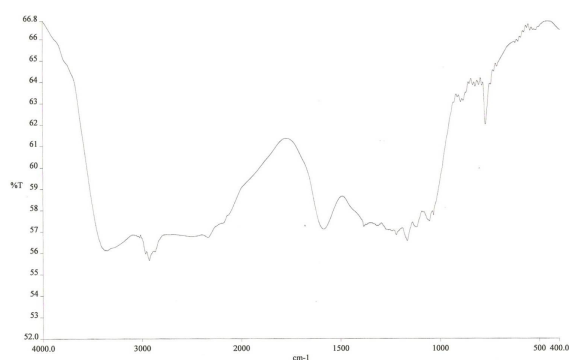


Figure 6. FT-IR of NCC

The band observed at  $1702 \text{ cm}^{-1}$  in NLLC is due to from C=O stretch in carboxylic and lactonic structures.

The band appearing nearly at  $1590 \text{ cm}^{-1}$  for carbon samples has been interpreted unequivocally. This has been assigned to aromatic ring stretching coupled to highly conjugated carbonyl groups 21 or attributed to the stretching vibrations of C=O moieties of conjugated systems such as diketone, keto ester and keto-enol structures<sup>21-22,27,28</sup>. The band observed  $1383 \text{ cm}^{-1}$  in NPTC and NCC may attribute to the C-H deformation in alkane. Bands around  $1260 \text{ cm}^{-1}$  are observed in NPTC, NLLC and NCC and it may be assigned to esters (e.g. CH<sub>3</sub>-CO-O-) and with epoxides as well as with acyclic C-O-C in olefinic or aromatic structures (e.g. ethers such as -OCH<sub>3</sub>) 21 or lactones, phenols and carboxylic anhydrides<sup>29</sup>.



Bands around  $1165\text{ cm}^{-1}$  are clearly observed and attributed due to the C-O stretching bonds in phenols, ethers, lactones and hydroxyl groups<sup>30</sup>. Bands at  $1033\text{ cm}^{-1}$  correspond to alcoholic C-O stretching vibration. Bands observed below  $950\text{ cm}^{-1}$  are characteristic of out of plane deformation vibrations of C-H group in aromatic structures.

The results of EDAX analysis are compiled in Tables 3,4 and 5 and the corresponding spectra are shown in Figures 7,8 and 9 for NPTC, NLLC and NCC respectively. The carbon content is 87.4, 83.7 and 87.8 % and the oxygen content is 12.6, 16.3 and 12.2 % for NPTC, NLLC and NCC respectively.

Table 3. Elemental composition (from EDAX) of NPTC

Elem	Wt %	At %
C K	87.40	87.60
O K	12.60	12.40
Total	100.00	100.00

Table 4. Elemental composition (from EDAX) of NLLC

Elem	Wt %	At %
C K	83.70	84.40
O K	16.30	15.60
Total	100.00	100.00

Table 5. Elemental composition (from EDAX) of NCC

Elem	Wt %	At %
C K	87.80	87.40
O K	12.20	12.60
Total	100.00	100.00

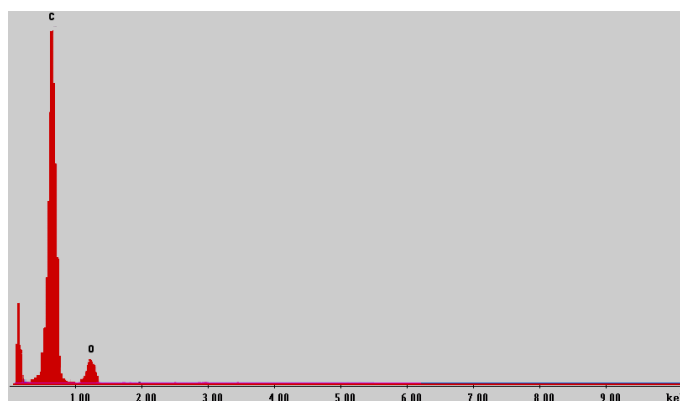


Figure 7.EDAX Spectra of NPTC

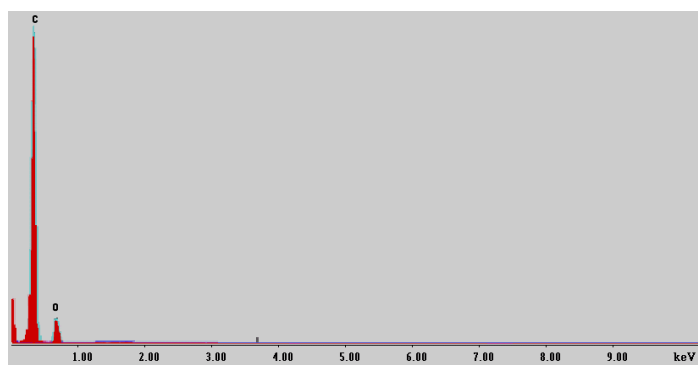


Figure 8.EDAX spectra of NLLC

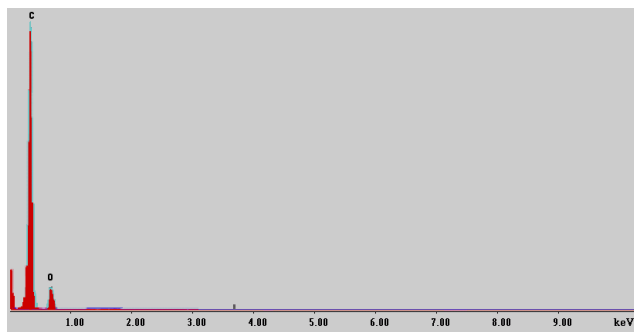


Figure 9. EDAX Spectra of NCC

## CONCLUSION

The prepared carbons named as NPTC, NLLC and NCC after preparation from bio materials *Phaseolus trilobus*, *Leucena leucocephala* and *Casuarina* respectively and collectively named as Kaza's carbons which were collected as waste from agricultural field. In the study of physico-chemical characteristics, observations of Boehm titration indicated that presence of basic groups is more when compared to acidic group in these carbons and for every carbon, the pH value is less than its corresponding  $pH_{zpc}$  value. This indicates that the surface is positively charged which favors the adsorption of anions.

Surface chemical groups were detected by absorption bands assigned to carbonyl, phenolic, ethers and surface hydroxyl groups by the FT-IR. Carbon and oxygen elements composition is given by the EDAX technique. Among the three adsorbents, NLLC has the best characters in comparison with others in properties like moisture content, the loss on ignition, the amount of acid soluble matter, water soluble matter, pH, and surface area (as iodine number). The order is NLLC>NPTC>NCC. In the further work these carbons were used for defluoridation and decolorization in aqueous solutions. These materials are cheaper than commercial activated charcoal.

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