

# Production and Characterization of Activated Carbon from Banana Empty Fruit Bunch and *Delonix regia* Fruit Pod

P. Sugumaran<sup>1</sup>, V. Priya Susan<sup>2</sup>, P. Ravichandran<sup>1</sup> and S. Seshadri<sup>1,\*</sup>

<sup>1</sup>Shri AMM Murugappa Chettiar Research Centre (MCRC), Taramani, Chennai - 600 113, TamilNadu, India

<sup>2</sup>Department of Biotechnology, Karunya University, Coimbatore – 641 114, TamilNadu, India

\*Corresponding author: seshadris@mcrc.murugappa.org, Tel.: +91 44 22430937, Fax.: +91 44 22430369

**Abstract:** Activated carbon was produced from banana empty fruit bunch (BEFB) and *Delonix regia* fruit pod (DRFP) through single step chemical activation process. As both the lignocellulosic wastes showed maximum weight loss at temperatures lower than 500°C, they were carbonized at 450°C (BEFP) and 400°C (DRFP) respectively after impregnating with H<sub>3</sub>PO<sub>4</sub> and KOH. Highest yield of 41.09% was recorded in DRFP treated with H<sub>3</sub>PO<sub>4</sub> followed by other treatments. The KOH treated DRFP recorded maximum bulk density of 0.46 g/ml followed by H<sub>3</sub>PO<sub>4</sub> treated DRFP. The BEFP carbons displayed lower attrition values than DRFP carbons. While the H<sub>3</sub>PO<sub>4</sub> treated DRFP carbon sample showed higher surface area, the untreated DRFP registered higher pore volume. However BET surface area was comparatively low in both the substrates. FT-IR analysis of H<sub>3</sub>PO<sub>4</sub>, KOH and untreated carbon sample, though did not show much difference in surface functional groups, showed shifts in bands and changes in wave numbers and absorbance between the untreated and treated samples indicating chemical transformations during pyrolysis. While highest iodine removal was observed in KOH treated BEFP and DRFP samples, methylene blue reduction was high in H<sub>3</sub>PO<sub>4</sub>, KOH and untreated BEFP carbon samples.

**Keywords:** Activated carbon, ligno-cellulose, banana empty fruit bunch, *Delonix regia* fruit pod, BET, iodine adsorption, methylene blue reduction.

## 1. Introduction

Activated carbon (AC) a tasteless, solid, microcrystalline, non-graphitic form of black carbonaceous material with a porous structure [1-2], has been regarded as a unique and versatile adsorbent because of its extended surface area, microporous structure, high adsorption capacity, and high degree of surface reactivity [3-5]. AC is applied widely in a variety of fields such as food and chemical industries, wastewater treatment, solvent recovery, air pollution control and hydrometallurgy for the recovery of gold and silver.

AC obtained from agricultural by-products has the advantage of offering an effective, low cost replacement for non-renewable coal-based granular activated carbons (GACs) provided that they have similar or better adsorption efficiency [6]. The abundance and availability of agricultural by-products makes them good sources of raw materials for activated carbon production [7]. In recent years, this has promoted a growing research interest in the use of alternative waste materials from industry and agriculture for activated carbon production [8-10]. Biomass waste including corn cob [11], coconut shell [12], palm shell [13], apple pulp [14], chickpea husks [15], grain sorghum [16], pistachio nut shell [17], jute fiber [18], olive stones and walnut shell [19], cherry stones [20], coir pith [21], wild rose seeds [22], rice bran [23], gopher plant [24], jackfruit shell waste [9], oil palm shell [25], rubber tree seed coat [26], cotton stalk [27], flamboyant [28], beach casuarina, lantana weed, tea waste, sugarcane bagasse and empty oil palm fruit bunches [29], Palmyra tree leaves, inflorescence and fruit nutshell waste [30] have been found to be suitable precursors owing to their high carbon and low ash contents [31-36]. Chemical activation of AC has been reported as more advantageous over physical activation due to higher yields, more surface area and better development of porous structures in carbon [21,37-40]. In the present study, we report the production of AC from Banana empty fruit bunches (BEFB) and *Delonix regia* fruit pods (DRFP) using H<sub>3</sub>PO<sub>4</sub> and KOH by one step pyrolysis and its characterization for pore structure, surface area and surface chemistry and liquid adsorption capacity.

## 2. Experimental

### 2.1. Collection, processing and characterization

BEFB and DRFP were collected from Taramani, Chennai, Tamilnadu (Plate 1), processed [29] and subjected for proximate and biochemical properties such as moisture, volatile matter, fixed carbon, ash, cellulose, hemicelluloses and lignin [41-42]. After drying in a hot air oven at 110°C for 24 hrs, they were pulverized to fine powder, sieved to mesh size 40 and used for characterization and AC production.



A & B Fruit pod of *Delonix regia*; C & D Banana empty fruit bunch

**Plate 1.** Selected lignocellulosic wastes.

The air dried biomass samples were analyzed for proximate and biochemical properties using standard procedures. For elemental analysis, the samples were ground to fine powder (40 mesh size) and used for CHNS-O analysis (Perkin-Elmer 2400 Series). Thermal analysis (DTA/TGA) was carried out using NETZSCH (STA) 409 C/CD Simultaneous Thermal Analyzer and the devolatilisation rate of the biomass wastes was determined.

## 2.2. Activated carbon production

Activated carbon was prepared by following the one step pyrolysis method [21,43]. For this, the test samples were divided into three parts; the first part mixed with 10% phosphoric acid ( $H_3PO_4$ ) (100 g sample + 100 mL of  $H_3PO_4$ , wt/v) and the second part mixed with 10% potassium hydroxide (KOH) (100 g sample + 100 mL of KOH, wt/v) and the third part without any addition. Both the treated and untreated samples were pyrolyzed at 450°C (BEFP) and 400°C (DRFP) for 1 h in an electric muffle furnace. After activation, the mixture was removed from the furnace and allowed to cool to room temperature. The pyrolysed carbons were leached with 2% HCl (v/v) for 2 h and washed several times with de-ionized hot water until a neutral pH was achieved. Later the carbon paste was dried in an electric oven at 110°C for 24 h. The activated carbon yield was calculated by applying the formula [44].

$$X (\%) = m/m_o \times 100,$$

Where **X** is char or activated carbon yield (%), **m** is the char or activated carbon mass (g) and **m<sub>o</sub>** is the raw sample mass (g).

The carbon preparation experiments were carried out several times to obtain enough activated carbon samples for further analysis and characterization. Thus, X is an average value of all the effective experiments.

## 2.3. Physical and chemical characteristics

The pH, electrical conductivity (EC) and bulk density of the AC samples was determined by following standard methods [45]. For pH determination, 1% (w/w) suspension of activated carbon in de-ionized water was prepared and the suspension was heated to 90°C with stirring for 20 minutes. The suspension was then allowed to cool to room temperature and the pH was measured using pH meter (Ecoscan, Eutech, Singapore). For EC determination, 1% (wt/wt) solution of activated carbon in water was stirred at room temperature for 20 min and the electrical conductivity was measured using an Ecoscan conductivity meter (Eutech, Singapore) and values were presented in micro Siemens ( $\mu$ S).

### 2.3.1 Bulk density

For bulk density, a glass cylinder (25 ml) was filled to a specified volume with 40 mesh powder activated carbon and dried in an oven at 80°C overnight. The cylinder was tapped for 1-2 minutes to compact the carbon and the bulk density calculated and presented as  $g\ ml^{-1}$  following the formula:

$$\text{Weight of dry material (g) / Volume of Packed dry materials (ml)} \times 100$$

All the experiments were carried out in triplicate and the averages were presented.

### 2.3.2 Attrition

The attrition of activated carbon samples was determined using a wet attrition test [46]. One gram of activated carbon sample (40 mesh size) was added to 100 ml of acetate buffer (0.07 M sodium acetate and 0.03 M acetic acid (pH 4.8) in a 250 ml Erlenmeyer flask. The solution was stirred for 24 h at 25°C on magnetic stirrer (model. REMI, 2MLH) at 200 rpm using ½ inch stir bars. The samples were then poured onto a 40 mesh screen, and the retained carbon was washed with 250 ml of de-ionized water. After washing, the carbon was transferred to a pre-weighed silica crucible and dried at 90°C in a vacuum oven for 4 hrs. The samples were removed and allowed to cool in desiccators and weighed. The percentage of attrition was calculated using the formula:

$$\text{Weight of carbon retained by sieve (g)} \times 100 / \text{Initial sample weight (g)}$$

### 2.3.3 Scanning Electron Microscope (SEM)

The surface morphological changes of activated carbon

samples were investigated using a Scanning Electron Microscope (SEM, Make: JEOL, Japan) operated at 25kV. Oven dried, porous, carbon samples were mounted on an adhesive carbon tape attached to an aluminum-stub and subsequently sputter coated with platinum for 5 minutes in the JFC-1100 sputter coater. The SEM magnifications were selected as  $\times 1000$ ,  $\times 5000$  and  $\times 10000$ .

### 2.3.4 BET surface area

The surface areas measurements ( $m^2/g$ ) of the activated carbon samples were made by low temperature nitrogen adsorption, by BET equation [47] using Micromeritics (ASAP 2010) operated at 77 K.

### 2.3.5 FT-IR analysis

The surface chemistry of samples was analyzed through FTIR transmission spectra [48] recorded using a PERKIN ELMER Spectrum One FTIR spectrophotometer in the wave number range of 4000-450  $cm^{-1}$ . The carbon samples were ground with KBr (AR grade) at a ratio of roughly 1/1000. 500 mg of oven dried (110°C for 12 hrs) fine powder was made in to a pellet by continuously pressing at 5 ton/ $cm^2$  for 1 min. and 17 ton/ $cm^2$  for 2 min. using a Perkin-Elmer hydraulic pump. After preparation, the pellet was analyzed immediately, and the spectra were recorded to 1  $cm^{-1}$  resolution. A pellet prepared with an equivalent quantity of pure KBr powder was used as control.

## 2.4 Liquid adsorption studies

For liquid adsorption studies, both Iodine [45] and methylene blue adsorption [25] were performed.

### 2.4.1 Iodine removal

Different powdered activated carbon samples (0.2-1.0 g) were taken in a 250 mL flask and 10 mL of 5% HCl was added. The flask was swirled until the carbon became wet. Then 100 mL of stock iodine solution (2.7 g of Iodine (Merck) and 4.1 g of potassium iodide (Merck) in 1 L of de-ionized water) was added to it and the mixture was shaken for 5 minutes in an orbital shaker. All the samples were filtered through Whatman No.1 filter paper. Fifty mL of filtrate was titrated with 0.1 M sodium thiosulphate until the solution become pale yellow. Then 1 mL of starch indicator solution (1%) was added and titration was continued with sodium thiosulphate until the solution become colorless. A blank was prepared without adding carbon. The percent iodine removed by each carbon was calculated by applying the following formula:

$$(\text{mL of sodium thiosulphate used for blank} - \text{mL thiosulphate used for sample} \times 100) / \text{mL thiosulphate used for blank}$$

### 2.4.2 Methylene blue (Batch experiments)

For batch studies on methylene blue (MB) adsorption, 100 mL of MB solutions with initial concentrations of 50-200 mg/L were placed in Erlenmeyer flasks to which an equal mass of 0.1 g of the activated carbon of 40 mesh size was added and kept in a shaker at 30°C for 24 h to reach equilibrium. All samples were filtered prior to analysis in order to minimize interference of the carbon particles with the analysis. Each experiment was carried out in triplicate under identical conditions. The concentrations of MB in the supernatant solutions before and after adsorption were determined using a CARY Bio-300 UV-Visible Spectrophotometer (Varian) at 668 nm. The amount of adsorption at equilibrium,  $q_e$  (mg/g) was calculated by the formula:

$$q_e = (C_o - C_e)V / W$$

Where,  $C_o$  and  $C_e$  (mg/L) are the liquid-phase concentrations of the dye at initial and equilibrium state; V is the volume of the solution (L) and W is the mass of dry adsorbent used (g).

### 3. Results and Discussion

#### 3.1. Characterization of biomass wastes

The data on proximate, ultimate and biochemical analysis of the biomass samples are presented in Table 1. While the moisture and ash content were higher in Banana Empty Fruit Bunch (BEFB), fixed carbon had the same value for both wastes and volatile matter was high in *Delonix regia* fruit pods (DRFP) indicating the nature of the biomass where BEFB contained more water than the DRFP.

While the BEFB sample had more carbon and hydrogen content, the DRFP sample had more oxygen and nitrogen contents. However, sulphur content was very low in both the substrates. While the H/C ratio was 0.12% in BEFB it was 0.13% in the DRFP. Results obtained in this study are close to the earlier studies on C, H, N, O elemental analysis reporting their concentrations in different agricultural wastes of 43.8-58.30%, 2.6-7.0%, 0.4-6.8%, and 32.05-50.20%, respectively [49-53].

**Table 1.** Proximate, ultimate and biochemical analysis of lignocellulosic wastes.

Parameters	Lignocellulosic wastes (wt%) dry basis	
	Banana Empty Fruit Bunch (BEFB)	<i>Delonix regia</i> fruit pods (DRFP)
<b>Proximate analysis</b>		
Moisture	5.21 ± 0.16	0.22 ± 0.04
Ash	15.73 ± 1.66	2.80 ± 0.65
Fixed Carbon	5.95 ± 4.98	5.20 ± 3.81
Volatile matter	78.83 ± 5.58	92.03 ± 3.74
<b>*Ultimate (Elemental) analysis</b>		
Carbon	41.75	34.22
Hydrogen	5.10	4.50
Nitrogen	1.23	1.94
Sulphur	0.18	0.42
Oxygen	51.73	58.91
<b>*Biochemical properties</b>		
Cellulose	8.30	13.90
Hemi-cellulose	21.23	24.13
Lignin	19.06	23.36

Values are mean ± standard deviation of three replicates.

\*Results based on one time analysis

Cellulose, hemi-cellulose and lignin contents were higher in DRFP (13.31%, 24.13% and 23.36%, respectively) than BEFB (8.3%, 21.23% and 19.06%, respectively) (Table 1). Although the values are closer to the reports on other agro-wastes like silk cotton shell, oil palm fibre, oil palm nut shell and cashew nut shell (40-45% cellulose, 20-40% hemicellulose and 17-30% lignin, respectively) [43] the cellulose content observed in this study for the biomass samples were lower than in previous reports [54].

During the thermo gravimetric analysis (TGA) (Fig. 1), four weight loss stages were observed in BEFB and three stages in the DRFP. In the first stage (<150°C) a moisture content of 10.44% in BEFB and 7.53% in the DRFP were recorded. Maximum devolatilisation was observed in DRFP (52.45%) compared to BEFB (41.82%) in the second stage (150°C to 400°C) where there was a decomposition of hemicelluloses is followed by cellulose degradation. A considerable amount of decomposition was found in

the third stage (400°C to 650°C) with a decomposition rate of 30.59% in the BEFB and 32.94% in DRFP. Both the stages are signified by lignin degradation after the degradation of hemicelluloses and cellulose. The BEFB banana empty fruit bunch showed a degradation of 6.14% in the last stage (840°C). It is well known that the pyrolysis temperature plays an important role in product distribution, yield and characteristics of activated carbon [29,55]. Our TGA results showed that higher lignin content and higher char yield were obtained from DRFP. Lignin is found to be the main contributor to the final char weight [56].

#### 3.2 Activated carbon production

As maximum weight loss occurrence was observed at temperatures lower than 500°C in the present study, activated carbon production was carried out at 450°C for BEFB and 400°C for DRFP. The yield obtained is presented in Table 2. A higher yield of 41.09% was recorded in DRFP treated with H<sub>3</sub>PO<sub>4</sub> followed by KOH impregnated BEFB (38.86%) and untreated DRFP (38.6%), while the untreated BEFB registered a yield of 34.66% and the H<sub>3</sub>PO<sub>4</sub> treatment registered 36.10% yield. KOH treated DRFP registered 35.33% yield. Several activating agents have been reported for use in the chemical activation process. Among them H<sub>3</sub>PO<sub>4</sub> and KOH are widely used in the production of activated carbon because of low energy costs and high carbon yields as well as easy recovery of the activating agents [57-58]. While the general mechanism of the chemical activation are not so well understood as that of physical activation [59], the activation agents are reported to act as an acidic/alkaline catalyst to promote bond cleavage, hydrolysis, dehydration and condensation, accompanied by cross-linking reactions between acid/alkali and biopolymers [58].

**Table 2.** Carbon yield from lignocellulosic substrates at different activations.

Sample	Untreated (%)	H <sub>3</sub> PO <sub>4</sub> (%)	KOH (%)
BEFB (450°C)	34.66 ± 3.23	36.10 ± 1.07	38.86 ± 0.81
DRFP(400°C)	38.613 ± 1.02	41.09 ± 2.42	35.33 ± 1.89

Values are mean ± standard deviation of three replicates.

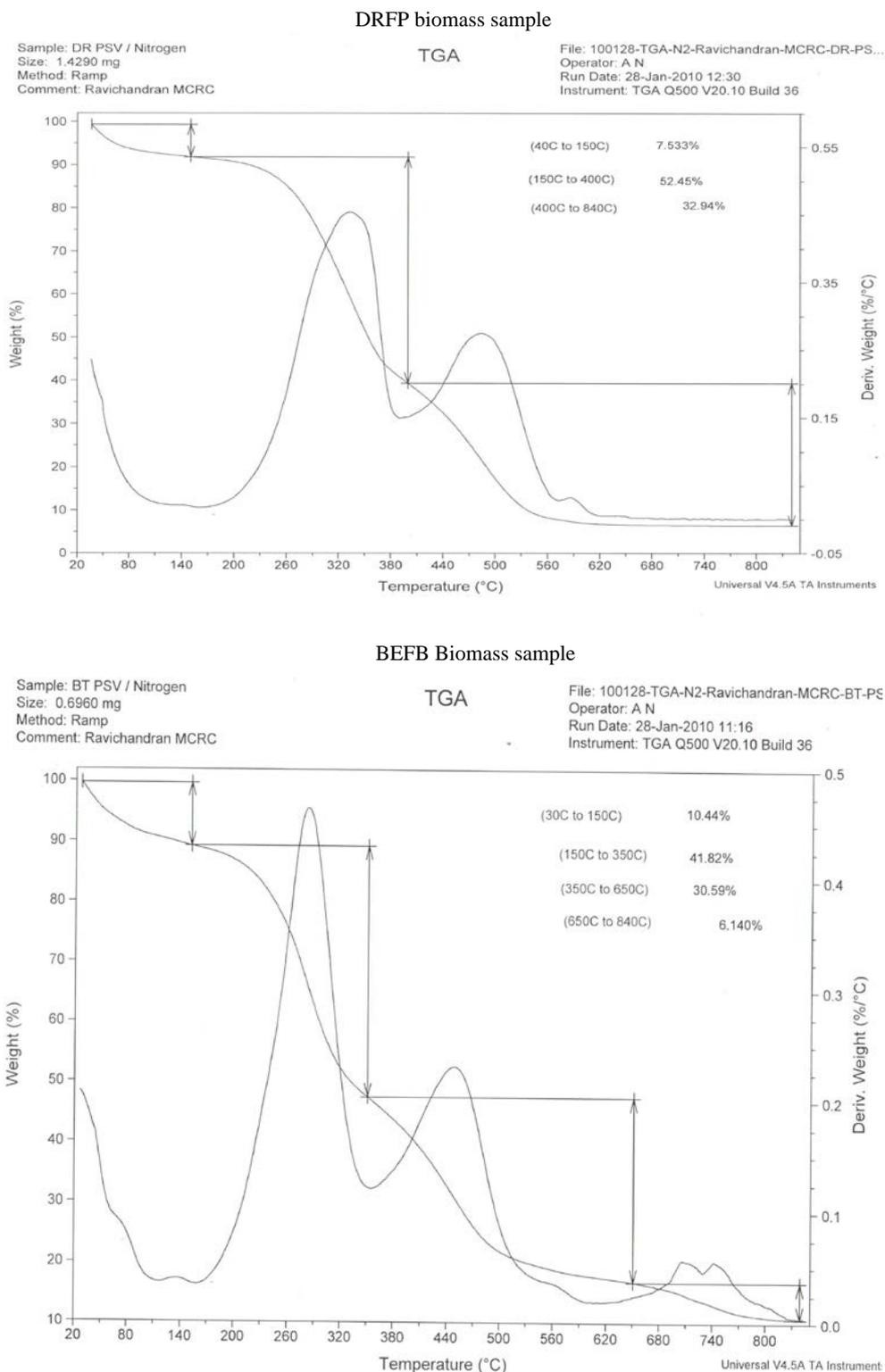
#### 3.3. Physico- chemical properties

The pH, EC, bulk density and hardness of the carbon samples were recorded and presented in Table 3. All the carbon samples recorded alkaline pH values except H<sub>3</sub>PO<sub>4</sub> treated DRFP (3.73±0.01). The untreated BEFB recorded the highest pH (10.23±0.01) followed by H<sub>3</sub>PO<sub>4</sub> and KOH treated carbon samples (9.78±0.0 and 9.04±0.01, respectively). Interestingly the KOH treated DRFP sample recorded a neutral pH (7.3±0.03) when compared to untreated carbon (8.72±0.08). The electrical conductivity of the BEFB samples was higher than for DRFP. Untreated BEFB had very high EC values (3040±0.03 μS) followed by H<sub>3</sub>PO<sub>4</sub> and KOH treated carbon samples (1227±2.43 μS and 1183±3.05 μS, respectively). A comparatively low EC value (353.66±3.51 μS) for H<sub>3</sub>PO<sub>4</sub> treated DRFP was obtained followed by untreated DRFP (321.33±1.52 μS) and KOH treated DRFP samples (189±3.86 μS), respectively. Bulk density is an important characteristic of the carbon and is invariably related to the starting material. In this study, KOH treated DRFP showed a higher bulk density (0.46 g/ml)

**Table 3.** Physical and chemical properties of activated carbon samples.

Name of the lignocellulosic waste	Activation method	pH	EC (μS)	Bulk density (g/ml)	Hardness (%)
BEFB	H <sub>3</sub> PO <sub>4</sub> treated	9.78 ± 0.00	1227 ± 2.43	0.33 ± 0.00	1.50 ± 1.02
	KOH treated	9.04 ± 0.10	1183 ± 3.05	0.34 ± 0.00	2.50 ± 1.45
	Untreated	10.23 ± 0.01	3040 ± 0.03	0.35 ± 0.00	1.90 ± 2.02
DRFP	H <sub>3</sub> PO <sub>4</sub> treated	3.73 ± 0.08	353.66 ± 3.51	0.45 ± 0.00	10.20 ± 1.56
	KOH treated	7.30 ± 0.04	189.0 ± 3.86	0.46 ± 0.00	7.40 ± 0.98
	Untreated	8.72 ± 0.08	321.33 ± 1.52	0.40 ± 0.00	10.30 ± 1.87

Values are mean ± standard deviation of three replicates.



**Figure 1.** Thermo gravimetric analysis (TGA/DTG) of biomass sample.

followed by  $H_3PO_4$  treated DRFP (0.45 g/ml). The  $H_3PO_4$  treated BEFP, however, showed lowest bulk density (0.33 g/ml) when compared to other experimental carbons. Hardness or attrition is a measure of the mechanical strength of the carbons and it is an important parameter for understanding its relative loss during the transportation, handling and regeneration. The results indicate that BEFP have lower attrition values than the DRFP (Table 3). The hardness was high in untreated (10.30%) and  $H_3PO_4$  activated (10.20%) DRFP. The  $H_3PO_4$  treated BEFP sample showed the

lowest attrition (1.5%) followed by untreated BEFP carbon (1.9%). The percentage of attrition observed in carbon, as the results indicate, depends upon the carbon density or starting materials of the attrition percentage is varied [60].

### 3.4. Surface Area analysis

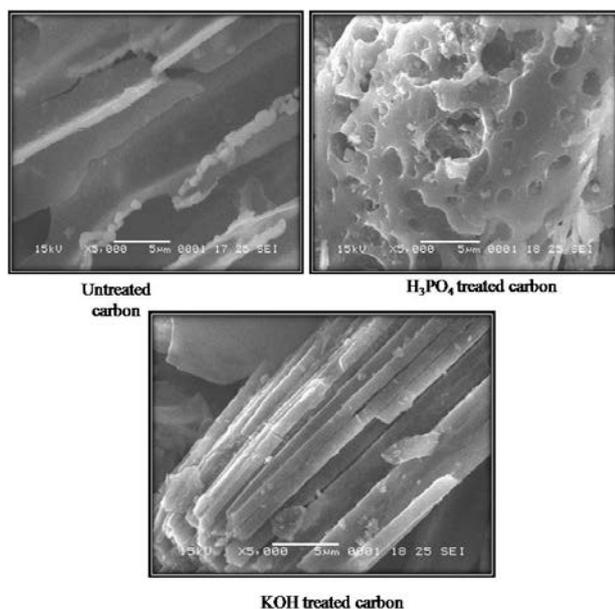
The results on BET surface area ( $m^2/g$ ) and pore volume data are presented in Table 4. Among the two different experimental carbons, the  $H_3PO_4$  treated DRFP carbon sample had the highest

surface area ( $22.29 \text{ m}^2/\text{g}$ ) followed by untreated carbon ( $17.54 \text{ m}^2/\text{g}$ ) and  $\text{H}_3\text{PO}_4$  treated BEFP carbon ( $15.37 \text{ m}^2/\text{g}$ ). The lowest surface area was observed in KOH treated DRFP ( $0.3242 \text{ m}^2/\text{g}$ ) followed by untreated BEFP carbon sample ( $1.04 \text{ m}^2/\text{g}$ ). While the pore volume was high in the  $\text{H}_3\text{PO}_4$  treated BEFP sample ( $0.456 \text{ cm}^3/\text{g}$ ) the KOH treated and untreated carbon samples showed only an insignificant pore volume. In DRFP the pore volume was very much distinct in all the samples with untreated samples registering a higher pore volume ( $0.6032 \text{ cm}^3/\text{g}$ ) than the KOH and  $\text{H}_3\text{PO}_4$  treated samples,  $0.3521$  and  $0.2598 \text{ cm}^3/\text{g}$ , respectively. However, the results on BET surface area and pore volume could not be compared with earlier reports. The BET surface area was comparatively low in both the substrates studied ( $0.2598$ - $22.2908 \text{ m}^2/\text{g}$ ). Earlier reports on DRFP found a lower surface ( $4.08 \text{ m}^2/\text{g}$ ) than our samples [28]. This could be attributed to the quality of substrates where both the samples were of a fibrous nature. This study derives support from an earlier study where the carbon obtained from coconut fibre treated with ammonium chloride solution and carbonized at  $400^\circ\text{C}$  for 1.5 hours was reported to have  $1.26 \text{ m}^2/\text{g}$  surface areas.

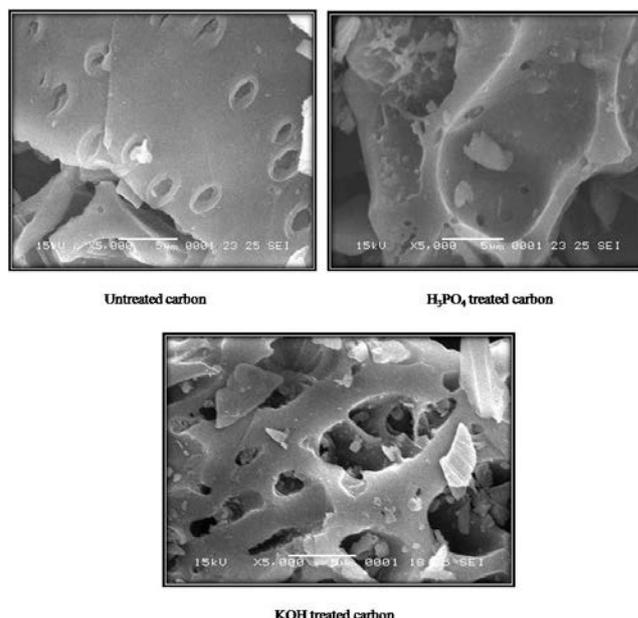
**Table 4.** The effect of different activation methods on BET surface area of activated carbon samples.

Name of Samples		Surface area ( $\text{m}^2/\text{g}$ )	Pore Volume ( $\text{g}/\text{cm}^3$ )	Pore size ( $\text{\AA}$ )
BEFB	Untreated	0.3242	---	-
	$\text{H}_3\text{PO}_4$	15.3757	0.4566	570.042
	KOH	1.0445	---	-
DRFP	Untreated	17.5457	0.6032	603.087
	$\text{H}_3\text{PO}_4$	22.2908	0.2598	617.503
	KOH	0.0139	0.3521	-

The SEM photographs of the untreated and treated BEFB samples showed rod like structures but while the untreated sample was bundled together the treated samples showed more spaced out structures (Plates 2a & 2b). The alkali treated BEFB sample showed porous structures. In the case of DRFP, the KOH and  $\text{H}_3\text{PO}_4$  treated samples showed open porous structures. The untreated sample showed holes that were spaced out on the surface with smooth edges. While the alkali treated samples showed many holes on the carbon surface with broken edges, the phosphoric acid treated samples showed larger pore structures than pore sizes.



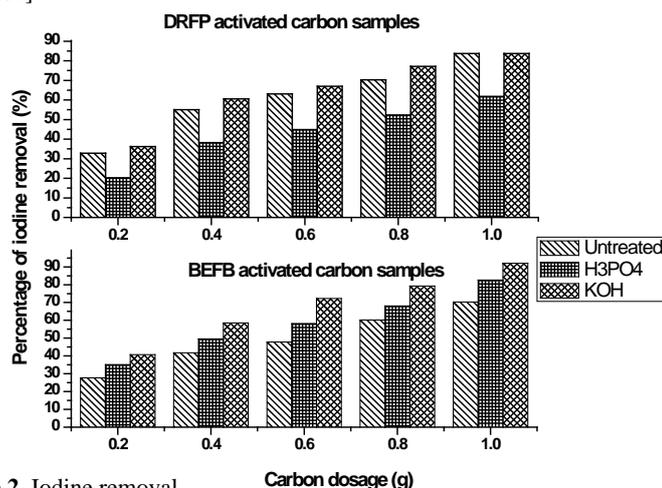
**Plate 2a:** SEM micrographs of carbon samples from *Delonix regia* pods (DRFP).



**Plate 2b:** SEM micrographs of carbon samples from Banana Empty Fruit Bunch (BEFB).

### 3.5 Liquid phase adsorption

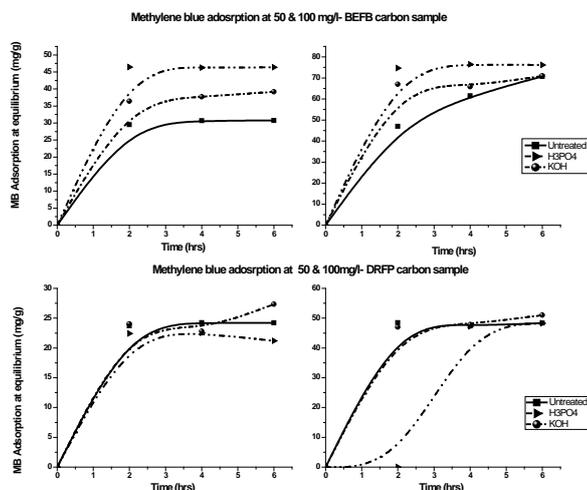
The results of iodine removal by different activated carbon samples at doses between 0.2-1.0 gms are presented in Fig. 2. The KOH treated carbon samples showed higher iodine removal than the  $\text{H}_3\text{PO}_4$  treated samples. While high iodine removal was registered in KOH treated BEFB and DRFP samples (92.0 and 83.69%) it was low in  $\text{H}_3\text{PO}_4$  treated DRFP (61.95%). Carbon from different agro-wastes was reported to remove iodine from aqueous solution in the range between 50 and 95% [45]. Higher degrees of iodine adsorption have been reported to indicate a higher surface area and the presence of largely micro and mesoporous structures [61]. Results observed in the present study indicate that there exist differences among the different carbons in iodine adsorption which could be attributed to the differences in their surface areas, porosity and activation methods [23,45,61].



**Figure 2.** Iodine removal.

The results of the methylene blue adsorption studies are presented in Fig.3. Adsorption at a concentration of  $200 \text{ mg}/\text{l}$  was found to be negligible. Among the two different activated carbon samples, adsorption was high in  $\text{H}_3\text{PO}_4$ , KOH and untreated BEFB,  $76.13$ ,  $71.06$ , and  $70.63 \text{ mg}/\text{g}$ , respectively in the  $100 \text{ mg}/\text{l}$  methylene blue concentration. When the carbon sample concentration was increased the methylene blue adsorption

also increased up to 50%. The adsorption values were 50.98, 48.28 and 48.36 mg/g in KOH treated, H<sub>3</sub>PO<sub>4</sub> treated and untreated carbon samples, respectively.



**Figure 3.** Methylene blue adsorption of activated carbon samples.

FTIR analysis of carbon samples from the wastes are presented in Fig. 4. The surface functional groups present in the DRFP derived activated carbon were the band corresponding to O-H group at 3834-3400 cm<sup>-1</sup>; a band at 2921-2853 cm<sup>-1</sup> corresponded to aliphatic C-H stretching; a band at 1560-1530 cm<sup>-1</sup> corresponded to secondary amide and N-H bending with C-N vibrations; a band around 1450-1430 cm<sup>-1</sup> was ascribed to an aromatic ring of P-C stretching vibration; the band around 1374-1330 cm<sup>-1</sup> was caused due to the presence of aromatic nitro compound NO<sub>2</sub> symmetric stretching; the peak around 1434-1375 cm<sup>-1</sup> corresponded to phenolic OH and C-N groups; an IR band around 1316-1200 cm<sup>-1</sup> corresponded to nitrate (NO<sub>2</sub>) symmetric stretching vibrations; a band from 1190-1120 cm<sup>-1</sup> ascribed to SO<sub>2</sub> symmetric stretching; an IR band around 850-750 cm<sup>-1</sup> corresponding to NH<sub>2</sub> amines group and a band from 700-600 cm<sup>-1</sup> attributed to C-H bending out of plane were observed. Similar results were recorded by Hu *et al.*, 2009 [28].

The main surface functional groups present in BEFB were the band between 3845-3800 cm<sup>-1</sup> corresponding to an O-H group; an IR band at 3399, 3196 cm<sup>-1</sup> due to O-H group of

carboxylic acids; a band from 2923-2800 cm<sup>-1</sup> ascribed to an aldehyde C-H group; an IR band at 1594-1500 cm<sup>-1</sup> corresponding to secondary amide N-H bending and C-N stretching; an IR band at 1395 cm<sup>-1</sup> related to aliphatic nitro (NO<sub>2</sub>) asymmetric stretching vibrations; a band from 1118-1000 ascribed Si-O-Si asymmetric stretching; an IR band between 870-840 cm<sup>-1</sup> ascribed to nitrate N-O stretching; a band between 765-750 cm<sup>-1</sup> corresponding to amide N-H wagging and a band at 700-600 cm<sup>-1</sup> assigned to C-S stretching.

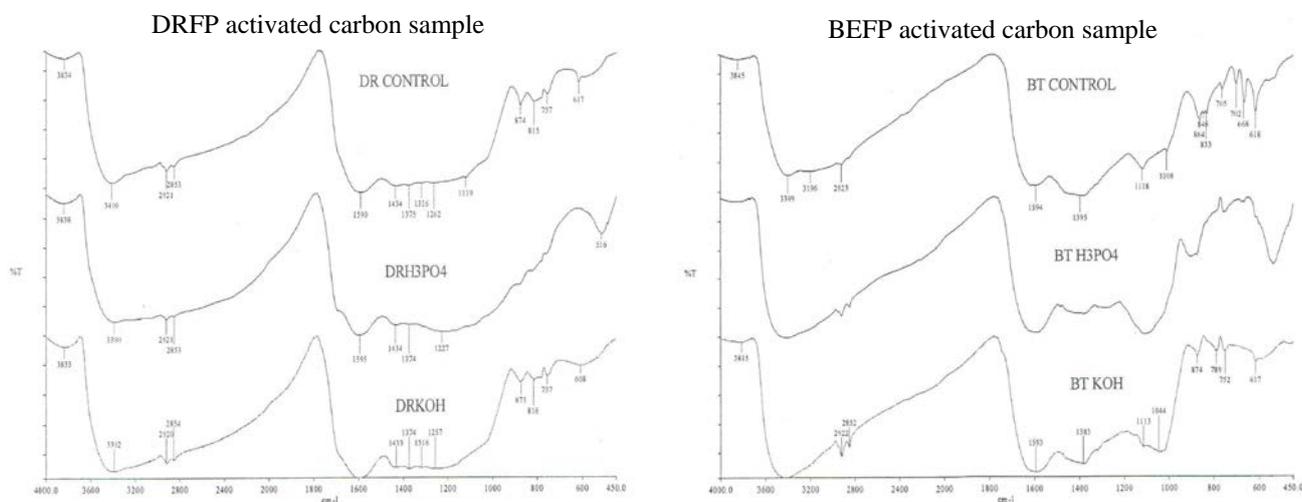
The FT-IR analysis results indicate that only minor differences between the samples could be established. However, shift in bands and changes in wavelength numbers and absorbance between the untreated and treated samples indicate that chemical transformation would have taken place during chemical treatment or during pyrolysis.

#### 4. Conclusion

Activated carbons were prepared from the pyrolysis of banana empty fruit bunch waste and fruit pods of *Delonix regia* at 450 and 400°C by chemical activation with H<sub>3</sub>PO<sub>4</sub> and KOH. The yields of the activated carbons produced by chemical activation were found to be higher than untreated carbon. The properties of the activated carbon produced in this experiment such as surface area, chemical functional groups and ability to remove iodine and methylene blue reveals that it had an improved adsorption behavior comparable to those of high performance adsorbents. Consequently, the activated carbons produced from lingo-cellulosic waste biomass can be used as adsorbents for various environmental applications including treatment of drinking water, removing colour from industrial effluents and removal of heavy metals.

#### Acknowledgements

The authors thank the Water Technology Initiative Programme, Technology Development, Department of Science and Technology (DST), Government of India, New Delhi for awarding a financial grant (Ref. No.DSTTDT/WTI/2K7/14) and Shri AMM Murugappa Chettiar Research Centre, Taramani, Chennai for providing necessary facilities to carry out this research work. The authors thank Mr. Narayanan and Mrs. Srividhya, Department of Chemistry, IIT Madras for BET surface area and CHNS-O elemental analysis and Mrs. Rama and Mr. Shankar, SAIF, IIT Madras for help in TGA and FTIR analysis.



**Figure 4.** FT-IR analysis of activated carbon samples.

## References

- [1] Smisek M, Cerney S, *Active Carbon Manufacture, Properties and Applications* (1970) Elsevier Pub., Comp., New York, 562-563.
- [2] Budavari S, *Merck Index* (1996) Whitehouse Station, NJ: Merck.1316.
- [3] Bansal R, Donnet J, Stoeckli F, *Active Carbon* (1988) Marcel Dekker Inc., New York, 1-163.
- [4] Nakagawa K, Mukai SR, Suzuki T, Tamon H, Gas adsorption on activated carbons from PET mixtures with a metal salt, *Carbon* 41 (2003) 823-831.
- [5] Williams PT, Reed AR, Development of activated carbon pore structure via physical and chemical activation of biomass fibre waste, *Biomass and Bioenergy* 30 (2006) 144-152.
- [6] Martin MJ, Artola A, Balaguer MD, Rigola M, Activated carbons developed from surplus sewage sludge for the removal of dyes from dilute aqueous solutions, *Chem. Eng. J.* 94 (2003) 231-239.
- [7] Malik R, Ramteke DS, Wate SR Adsorption of malachite green on groundnut shell waste based powdered activated carbon, *Waste Manag* 27/9 (2007) 1129-1138.
- [8] Kadirvelu K, Namasivayam C, Activated carbon from coconut coir pith as metal adsorbent: adsorption of Cd (II) from aqueous solution, *Adv. Environ. Res.* 7 (2003) 471-478.
- [9] Prahas D, Kartika Y, Indraswati N, Ismadji S, Activated carbon from jackfruit peel waste by H<sub>3</sub>PO<sub>4</sub> chemical activation: Pore structure and surface chemistry characterization, *Chem. Engin. J.* 140 (2008) 32-42.
- [10] Ioannidou O, Zabaniotou A, Agricultural residues as precursors for activated carbon production--A review, *Renew. Sustain. Ener. Revi.* 11 (2007) 1966-2005.
- [11] Tsai WT, Chang CY, Lee SL, Preparation and characterization of activated carbons from corn cob, *Carbon* 35 (1997) 1198-1200.
- [12] Hu Z, Srinivasan MP, Preparation of high-surface-area activated carbons from coconut shell, *Micropor. Mesopor. Mater.* 27 (1999) 11-18.
- [13] Daud WMAW, Ali WSW, Suleiman MZ, The effects of carbonization temperature on pore development in palm-shell-based activated carbon, *Carbon* 38 (2000) 1925-1932.
- [14] Sua'ez-García F, Martí'nez-Alonso A, Tascon JMD, Pyrolysis of apple pulp: chemical activation with phosphoric acid, *J.Analy. Appl. Pyrol.* 63 (2002) 283-301.
- [15] Hayashi J, Kazehaya A, Muroyama K, Watkinson AP, Preparation of activated carbon from lignin by chemical activation, *Carbon* 38 (2000) 1873-1878.
- [16] Diao Y, Walawender WP, Fan LP, Activated carbons prepared from phosphoric acid activation of grain sorghum, *Biores. Technol.* 81 (2002) 45-52.
- [17] Lua AC, Yang T, Guo J, Effects of pyrolysis conditions on the properties of activated carbons prepared from pistachio-nut shells, *J. Anal. Appl. Pyrol.* 72 (2004) 279-287.
- [18] Senthilkumaar S, Varadarajan PR, Porkodi K, Subbhuraam CV, Adsorption of methylene blue onto jute fiber carbon: kinetics and equilibrium studies, *J. Coll. Interface Sci.* 284 (2005) 78-82.
- [19] Martinez J, Norland S, Thingstad TF, Schroeder DC, Bratbak G, Wilson WH, Larsen A, Variability in microbial population dynamics between similarly perturbed mesocosms, *J. Plankton Res.* 28 (2006) 783-791.
- [20] Olivares-Marín M, Fernández-González C, Macías-García A, Gómez-Serrano V, Lillo-Rodenas MA, Carzrola-Ameros D, Linares-Solano A, Chemical reactions between carbons and NaOH and KOH -an insight into chemical activation mechanisms, *Carbon* 41 (2003) 265-267.
- [21] Ash B, Satapathy D, Mukherjee PS, Nanda B, Gumaste JL, Mishra BK, Characterization and application of activated carbon prepared from coir pith, *J.Sci.Ind.Res.* 65 (2006) 1008-1012.
- [22] Gürses A, Doğar C, Karaca S, Acikyildiz M, Bayrak R, Production of granular activated carbon from waste *Rosa canina* sp. seeds and its adsorption characteristics for dye, *J. Hazar. Mater.* B131 (2006) 254-259.
- [23] Suzuki RM, Andrade AD, Sousa JC, Rollemberg MC, Preparation and characterization of activated carbon from rice bran, *Biores. Technol.* 98 (2007) 1985-1991.
- [24] Ozgul G, Ozcan A, Ozcan AS, Gercel HF, Preparation of activated carbon from a renewable bio-plant of *Euphorbia rigida* by H<sub>2</sub>SO<sub>4</sub> activation and its adsorption behavior in aqueous solutions, *J. Appl. Surf. Sci.* 253 (2007) 4843-4852.
- [25] Tan IAW, Hameed BH, Ahmad AL, Equilibrium and kinetic studies on basic dye adsorption by oil palm fibre activated carbon, *Chem. Eng. J.* 127 (2007) 111-119.
- [26] Hameed BH, Daud FBM, Adsorption studies of basic dye on activated carbon derived from agricultural waste: *Hevea brasiliensis* seed coat, *J. Chem. Eng.* 139 (2008) 48-55.
- [27] Deng H, Yang L, Taota G, Daia J, Preparation and characterization of activated carbon from cotton stalk by microwave assisted chemical activation-Application in methylene blue adsorption from aqueous solution, *J. Hazar. Mater.* 166 (2009) 1514-1521.
- [28] Hu YS, Malarvizhi R, Sulochana N, Equilibrium Isotherm Studies of Methylene Blue Adsorption Activated Carbon Prepared from *Delonix regia* Pods, *J. Envi prpte. scin.* 3 (2009) 111-116
- [29] Sugumaran P, Seshadri S, Evaluation of selected biomass for charcoal production, *J.Sci.Indu.Res.* 68/8 (2009) 719-723.
- [30] Ravichandran P, Sugumaran P, Seshadri S, (2011) Preparation and Characterization of Activated Carbons Derived from Palmyra Waste of Coastal Region, *Proceedings of International conference on "Impact of Climate Change on Coastal Ecosystem" (ICC - ECO 2011)* (2011).
- [31] Banerjee SK, Mathew MD, Carbonization of Jute Stick, *Agro Waste.* 13 (1985) 217-227.
- [32] Wigmans T, Industrial aspects of production and use of activated carbon, *Carbon* 27 (1989) 13-22.
- [33] Gergova K, Petrov N, Eser S, Adsorption properties and microstructure of activated carbons produced from agricultural by-products by steam pyrolysis, *Carbon* 32 (1994) 693-702.
- [34] Pollard SGT, Thompson FE, McConnachie GL, Microporous carbons From *Moringa Oleifera* Husks for water purification in less developed countries, *Wat. Res.* 29 (1995) 337-347.
- [35] Namasivayan C, Kadirvelu K, Activated carbons prepared from coir pith by physical and chemical activation methods, *Biores. Technol.* 62 (1997) 123-127.
- [36] Kadirvelu K, Palanival M, Kalpana R, Rajeshwari S, Activated carbon from an agricultural by-product for the treatment of dyeing industry wastewater, *Biores.Technol.* 74 (2000) 263-265.
- [37] Lillo-Rodenas MA, Carzrola-Ameros D, Linares-Solano A, Chemical reactions between carbons and NaOH and KOH -an insight into chemical activation mechanisms, *Carbon* 41 (2003) 265-267.
- [38] Stavropoulos GG, Zabaniotou AA, Production and characterization of activated carbons from olive-seed waste residue, *Micropor. Mesopor. Mater.* 82 (2005) 79-85.
- [39] Guo Y, Rockstraw DA, Physical and chemical properties of carbons synthesized from 3 xylan, cellulose, and Kraft lignin by H<sub>3</sub>PO<sub>4</sub> activation. *Carbon* 44/8 (2006) 1464-1475.
- [40] Phan NH, Rio S, Faur C, Le Coq L, Le Cloirec P, Nguyen TH, Production of fibrous activated carbons from natural

- cellulose (jute, coconut) fibers for water treatment applications, *Carbon* 44 (2006) 269-277.
- [41] ASTM D-3172-89, *Standard Practice for proximate analysis of coal and coke* (2002) (ASTM, USA).
- [42] Goering HK, Van Soest PJ, *Forage Fibre Analyses (Apparatus, reagents, procedures and some applications)* (1975) Agricultural Handbook, United States Department of Agriculture.
- [43] Sugumaran P, *Production of activated carbon from agro-wastes for application in textile effluent treatment* (2009) Ph.D Thesis, Submitted to University of Madras.
- [44] Cui H, Cao Y, Pan WP, Preparation of activated carbon for mercury capture from chicken waste and coal, *Anal. Appl. Pyro.* 80 (2007) 319-324.
- [45] Ahmedna M, Clarke SJ, Rao RM, Marshall WE, Johns MM, Use of filtration and buffers in raw sugar color measurements, *J. Sci. Food. Agric.* 75 (1997) 109-116.
- [46] Toles CA, Marshall WE, Wartelle LH, McAloon A, Steam- or carbon dioxide-activated carbons from almond shells: physical, chemical and adsorptive properties and estimated cost of production, *Biores. Technol.* 75 (2000) 197-203.
- [47] Brunauer S, Emmett PH, Teller E, Adsorption of gases in multimolecular layer, *J. Amer. Chem. Soci.* 60/2 (1938) 309-319.
- [48] Gomez-Serrano V, Piriz-Almeida F, Duran-Valle CJ, Pastor-Villegas J, Formation of oxygen structures by air activation, A study by FT-IR spectroscopy, *Carbon* 37 (1999) 1517-1528.
- [49] Srikanth S, Das K, Ravikumar B, Rao DS, Nandakumar K, Vijayan P, Nature of fire deposits in a bagasse and groundnut shell fire 20 mw thermal boiler, *Biomass and Bioenergy* 75 (2004) 273-384.
- [50] Budinova T, Ekinici E, Yardim F, Grimm A, Björnbom E, Minkova V, Goranova M, Characterization and application of activated carbon produced by H<sub>3</sub>PO<sub>4</sub> and water vapor activation, *Fuel Process. Technol.* 87/10 (2006) 899-905.
- [51] Tsamba AJ, Yang W, Blasiak W, Pyrolysis characteristics and global kinetic of coconut and cashew nut shells, *Fuel Proce. Technol.* 87 (2006) 523-530.
- [52] Amaya A, Medero N, Tancredi N, Silva H, Deiana C, Activated carbon from biomass materials, *Biores. Technol.* 98 (2007) 1635-1641.
- [53] Rao MM, Rao GPC, Sessaiah K, Choudary NV, Wang MC, Activated carbon from *Ceiba pentandra* hulls, an agricultural waste, as an adsorbent in the removal of lead and zinc from aqueous solutions, *Waste Manage.* 28 (2007) 849-858.
- [54] Iyer PVR, Rao TR, Grover PD, Biomass-Thermo-chemical characterization (2002) 3<sup>rd</sup> edition, published by MNES, New Delhi, India.
- [55] Putun AE, Apaydin E, Putun E, Bio-oil production from pyrolysis and steam pyrolysis of soybean-cake: product yields and composition, *Energy* 27 (2002) 703-713.
- [56] Cagnon B, Py X, Guillot A, Stoeckli F, Contributions of hemicellulose, cellulose and lignin to the mass and the porous properties of chars and steam activated carbons from various lignocellulosic precursors, *Biores. Technol.* 100 (2009) 292-298.
- [57] Illingworth JM, Williams PT, Rand B, Novel activated carbon fibre matting from biomass fibre waste, *Waste and Resource Management* 165 (2012) 123-132.
- [58] Zuo S, Yang J, Liu J, Cai X, Significance of the carbonization of volatile pyrolytic products on the properties of activated carbons from phosphoric acid activation of lignocellulosic material, *Fuel Proce. Technol.* 90 (2009) 994-1001.
- [59] Lozano-Castello D, Lillo-Ródenas MA, Cazorla-Amoró's D, Linares-Solano A, Preparation of activated carbons from Spanish anthracite I. Activation by KOH, *Carbon* 39 (2001) 741-749.
- [60] Bansode RR, Losso JN, Marshall WE, Rao RM, Portier RJ, Adsorption of metal ions by pecan shell-based granular activated carbons, *Biores. Technol.* 89/2 (2003) 115-119.
- [61] Gergova K, Petrov N, Minkova V, Comparison of adsorption characteristics of various activated carbons, *J. Chem. Technol. Biotechnol.* 56 (1993) 77-82.