



COMPOSITE ACTIVATED CARBON FROM PLASTIC WASTE AND LIGNOCELLULOSIC WASTE MATERIALS

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ABSTRACT

Composite activated carbons were prepared by physical activation methods from both synthetic polymer and lignocellulosic waste materials. The precursors were first carbonized at 600 °C in N₂ atmosphere and then activated with steam at 850 °C. Carbons obtained were then subjected to physical and structural analysis. The results indicated that the composite activated carbons obtained had micropores which were narrower and as such showed higher adsorption capacities of iodine and methylene blue as compared to activated carbons from oil palm shells and synthetic polymer prepared under the same conditions. All the samples had large surface areas (800 to 1500 m²/g) and pore sizes in the range of 0.4 – 0.9 nm, characteristic of microporous solids. Infrared (IR) investigations showed enough hydroxyl and carboxylic functional groups on the surfaces. Scanning Electron Microscopy (SEM) showed that the composites activated carbons pore walls were thinner and smoother compared to the activated carbon from lignocellulosic material. Finally Raman spectra exhibited a D-band at 1350 cm⁻¹ and G-band at 1600 cm⁻¹ showing further disorder into graphene layers. However, the main characteristic of the obtained activated carbon was the

increase in yield of composite activated carbon compared to that obtained exclusively from synthetic polymer.

Key words: lignocellulosic waste and plastic waste; composite activated carbon; micropores.

I. INTRODUCTION

Synthetic polymers are among the main products that result from the transformation of petroleum. They are very much used in daily life as plastic bags, plastic floor tiles and window and door frames in the construction industry. This is because they are portable, light, cheap, and non-toxic and have a very high tensile strength compared to their adversaries [1]. Because they are cheap and not recycled in most countries, plastics are always dumped as wastes. Since they are very stable, non-degradable, and very light to be carried by wind and deposited just everywhere (rivers, streams, fields, mountains and even in the sea), they as such stand out to be a major environmental pollutant [2]. Despite their various advantages, post-consumer plastics by nature are very voluminous compared to their weight. It is indisputable then that plastics are real source of pollution which need attention [3-5].

Recycling, everything being equal stands to be the most acceptable solution to the management of post-consumer plastics, but it is not the case since recycling processes from research stands out to be more expensive than its production [6]. This justifies why alternative methods are needed to solve the ever growing canker worm of environmental pollution resulting from post-consumer plastics. The transformation of plastic wastes to Activated Carbon (AC), which is of growing need, stands out to solve the problem of plastic waste pollution. Transforming plastic wastes to (AC) is a concrete and immediate contribution to harnessing environmental pollution. This is because non-biodegradable plastic wastes are transformed to biodegradable AC which is also very much needed in the fight against pollution.

ACs are widely used as adsorbents of gases and vapours, in medicine as anti-toxin and in research as a catalyst and support to catalysts [7]. From recent findings [5-10], ACs of plastic origin stands out to have a better adsorption capacity as compared to that from plant origin which is mostly used [4]. But there exists a big problem of output since too much plastic is needed to produce very little activated carbon and as such very expensive as compared to that from plant origin which has a relatively good output.

The goal of the present work is to produce AC having high adsorption capacity as the commercial AC which is widely used with an equally good output from the mixture of

lignocellulosic material and post-consumer plastics; as well as compare it with AC prepared within the same condition from each of the pure raw material.

II. Methods

The raw materials for the preparation of ACs are Polyethylenterephthalate (PET) as synthetic plastic and Oil Palm Shell (OPS) as lignocellulosic materials. The composite ACs were obtained by mixing both PET and OPS in the ratios 2:1 and 1:1 respectively before carbonization.

II.1 Preparation of Activated Carbon

The OPS samples were grinded into small particle sizes ranging between 0.5 to 1.5 mm in diameter and PET samples were cut down to desirable particle sizes also. The OPS sample were dried at 110°C for 24hrs in the oven to remove all the moisture content weight, and PET sample in sunlight for 5hrs. OPS and PET were mixed in the ratio 1:1 and 2:1 and were then subjected to carbonization using a cylindrical furnace. The heating started from room temperature with a temperature increment rate of 10 °C/min up to a final temperature of 600 °C. The heating process was stabilized with nitrogen at a flow rate of about 100 mL/min. The residence time of the samples at the final stabilized temperature of 600°C was 3hrs. After heat treatment, the nitrogen flow was stopped and the charcoals were cooled down to room temperature.

In the activation step, 5–6 g of the carbonized samples (charcoal) were activated with steam (0,13 mL/min) in a furnace by heating the reactor from room temperature to 850 °C at a heating rate of 10 °C/min, with a residence time of 2 hrs. The percentage of weight loss, % burn-off, is defined by Equation 1:

$$\text{Burn - off (\%)} = \frac{w_i - w_f}{w_i} \times 100 \quad (1)$$

Where, w_i and w_f were the weight of char and the weight of the obtained AC, respectively.

For comparison studies, ACs from the pure raw materials (PET and OPS) were also prepared under the same conditions in the cylindrical furnace.

II.2 Characterization of Activated Carbon

II.2.1 Nitrogen adsorption isotherms

N₂ physisorption experiments were performed by MICROMERITICS TRISTAR 3000 at 77 K after outgassing during 24 h at 373K under vacuum. BET specific surface areas

of the samples were determined from these data, in the range of relative pressures 0.01–0.30. Micropore volumes were calculated by applying t-plot method of Harkins and Jura. Barrett, Joyner and Halenda (BJH) method was used for the estimation of pore size distribution (PSD).

II.2.2 Adsorptions tests

- **Adsorption of iodine**

The iodine number (I_2) of activated carbon was obtained on the basis of the Standard Test Method by titration with sodium thiosulphate.

The concentration of iodine solution adsorbed was thus calculated from total volume of sodium thiosulphate used and volume dilution factor.

- **Adsorption of methylene blue**

By batch experiment, methylene blue (MB) solution was mixed with activated carbon and shaken at the rate of 200 rpm at room temperature. After the completed reaction, the solutions were filtered and the residual concentrations of methylene blue solutions were then determined by using a spectrophotometer at 660 nm. The equilibrium adsorption capacities (q_e) of the AC were determined based on the adsorbate mass balance using Equation 2:

$$q_e = \frac{(c_0 - c_e)V}{m} \quad (2)$$

where c_0 and c_e are the initial and equilibrium concentrations of the dye (mg/L) respectively, V is the volume of the aqueous solution (L), and m (g) is the mass of activated carbon used.

II.3 Scanning Electron Microscopy, Fourier Transform Infra-Red and Thermogravimetric analysis

Raman spectroscopy is one of the most powerful tools for characterizing carbon materials, because the spectra shape exhibits wide variety corresponding to the forms of carbon, revealing fine structural information. In this work Raman spectra were obtained with a T6400 Raman Spectrometer (JOBIN/YVON). The 5145 Å line was used on occasion.

Thermal analysis (TGA, DTA) is performed in air using a PERKIN-ELMER DTA–TGA analyzer. A JEM 100s, an FEI Tecnai G2 Spirit and an FEI Tecnai F20 X-Twin at 200 kV FEG with an Oxford EDS system were used for transmission of electron microscopy (TEM) studies. All samples were ultrasonically suspended in methanol and a drop of the suspension was transferred to a copper grid and allowed to dry before TEM analysis.

III. Results and discussion

The ACs obtained by mixing synthetic polymer and lignocellulosic material (composite) or the pure of both components prepared under the same conditions presented different burn-offs. Actually, the burn-off increases with the amount of lignocellulosic material in the mixture. ACs from lignocellulosic material is named OPS, PETA from polyethyleneterephthalate, COM1 and COM2 are composite ACs from the ratios 1:1 and 2:1 respectively. Table1 presents the characteristics of the different ACs obtained. The burn-off values of COM1, COM2 and OPS ranged between 50 and 75 %, indicating that the product has a mixed porous structure and contains all types of pores.

III.1 Adsorption in aqueous solution

The methylene blue (MB) test was used to estimate the adsorption capacity of carbon to organic compounds from aqueous solution. The four samples obtained showed good adsorption capacity for MB (Table1). This indicated that all the samples were effective adsorbents and also accentuating the use of ACs in the elimination of large molecules in aqueous media particularly certain colorants. The adsorption values of MB obtained for the samples showed the presence of mesopores. Effectively, mesopores serve as gateway to micropores.

For adsorption of I₂, important values were also obtained, which showed high micropores contained in the ACs samples (Table1). The adsorption values for I₂ for all the samples (PETA, COM1, COM2 and OPS) were between 930 and 1237 mol.g⁻¹ expressing the high adsorption capacities of the samples to smaller molecules indicating the presence of micropores. It can be noticed in Table 2 that composites AC have highest indices number; this is an unexpectable observation obtained from the preparation, which reveals that the addition of lignocellulosique material in the mixture of raw material increases the microporosity of adsorbent materials [14].

Table 1: Characteristics of different ACs obtained and their adsorptions test capacities.

Activated carbons	Raw materials	Yields%		Burn-off	Q _(ads) I ₂ (mol/g)	Q _(ads) MB
		Carbonization	Activation			
OPS	<i>Oil palm Shell(OPS)</i>	30	45.6	61.4	930,2	386.7
PETA	PET (post consumer	15	61.4	38.6	1110,4	272.8
COM1	OPS +PET; Ratio 1/1	24	32	67.6	1237,3	386.0
COM2	OPS +PET; Ratio 2/1	21	40	59.3	1181.8	276 .0

III.2 Porous structure analysis

Nitrogen adsorption/desorption is a standard procedure for the determination of porosity of carbonaceous adsorbents. The forms of isotherms and hysteresis loops were found to be type II with H₃ hysteresis according to the BDDT (Brunauer-Deming-Deming-Teller) classification (Figure 1). These observations clearly reveal a greater microporosity development in each sample, which is indicated by the higher nitrogen volume adsorbed at low relative pressure. The knee shape at relative pressures close to unity shows the presence of mesopores and eventually the macropores. This can be attributed both to the structure of raw material and to the use of steam within the activation process, steam was observed to generate a narrow but more extensive microporosity [15]. Pore evaporation therefore occurs by a receding meniscus at a pressure which is less than the pore condensation pressure showing the formation of hysteresis, the pressure where the hysteresis closes corresponds again to the situation of an adsorbed multilayer film which is in equilibrium with a vapour in the core of the pore and the bulk phase. For all the samples the pronounced intensity of hysteresis imply the presence of a more extensively developed pore network wherein the fraction of larger pores trapped within the network of smaller pores is much higher [16].

Table 2: BET surface area (S_{BET}), Micropore area (S_{mic}), External surface (S_e), micropore volume (V_{micro}), Cumulate volume (V_{cum}), and mean BJH pores sizes of AC prepared from oil palm shell OPS, post-consumer plastics PETA, and their mixtures COM1 and COM2 by physical activation.

samples	S_{BET}	S_{mic}	S_e	% S_{mic}	Pores		Pores sizes (nm)		
					V_{micro}	V_{cum}	BET_{ads}	BJH_{des}	BJH_{ads}
OPS	1500.5	1000.4	500.1	66,67	0.498	0.864	2.397	4.778	4.455
PETA	1063.5	753.9	309.6	70,89	0.335	0.595	2.238	4.190	3.874
COM1	800.8	632.2	168.6	78,14	0.251	0.389	1.984	3.076	2.944
COM2	1000.9	759.4	241.5	75,87	0.315	0.491	2.055	3.889	3.705

S_{BET} : BET surface, S_{mi} : micropore surface, S_e : External surface

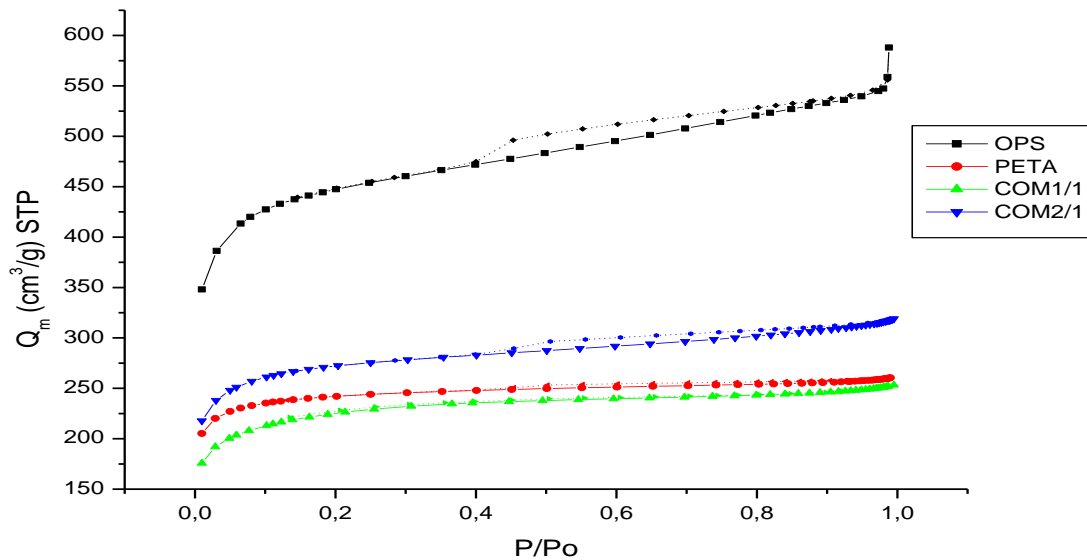


Figure1: Typical Nitrogen Adsorption/desorption Isotherm of the Four samples of Activated Carbon Prepared by Physical Activation.

Surface area and porosity values of the activated carbons are presented in Table 2. It shows that the activated carbons had remarkable BET surface area, due to the high micropore content [10, 14]. Porosimetry parameters such as micropore area, micropore volume, cumulate volume and pore diameter were also compiled in Tables 2. It can be seen that the ACs had remarkable BET surface area in agreement with micropores content. The micropore area contribution is more than 75% for composite AC and around 70% for AC obtained for pure precursors. This was expected because the existing mesopores help micropores to communicate to the external surface area. In Figure.2, the transmission electron microscopy (TEM) images of Composite ACs COM1 show external pores open to the framework of the carbon materials which is mainly microporous. The average pore diameters were between 1.9 nm and 2.4 nm, indicative of its microporous character. It can be noticed that the minimum and the maximum pore diameters belong respectively to PETA and OPS and then the average pore diameter are from composite (2.0 and 2.1 respectively from COM1 and COM2).

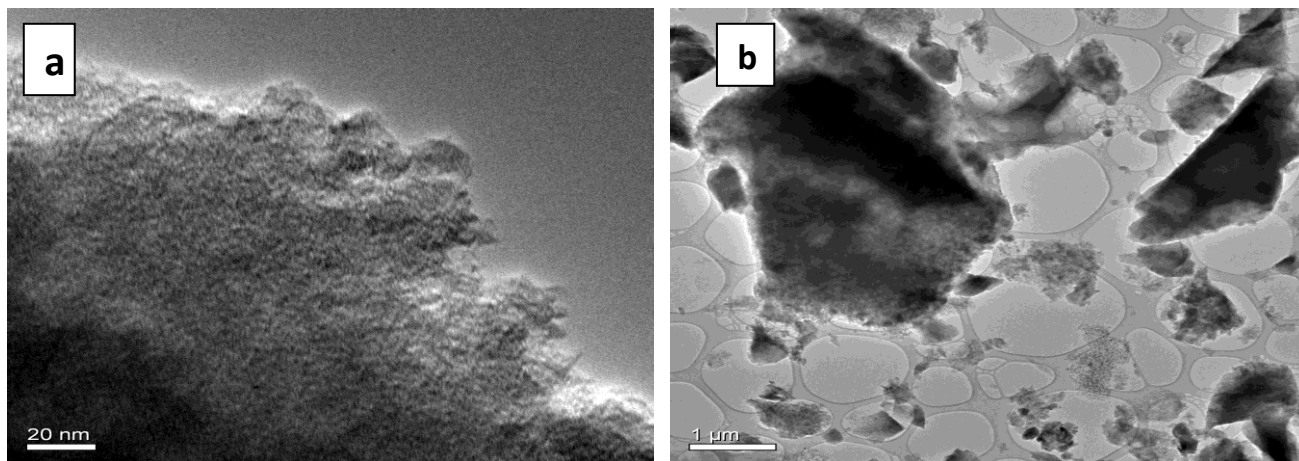


Figure 2. High resolution transmission electron micrograph of COM1: (a) at 20nm (b) at 1 μ m

The FTIR spectra can provide valuable information about the chemical compositions of the materials. Figure 3 shows that the spectra of ACs obtained from lignocellulosic material and composite AC (COM1) are identical and contain bands which are more intense than those of other samples. All spectra show a wide absorption band at 3200–3600 cm^{-1} with a maximum at about 3425 cm^{-1} . This band can be assigned to the O–H stretching mode of hydroxyl groups and adsorbed water. The absorption band between 1600 and 1675 cm^{-1} can be attributed to C=C aromatics cycles stretching vibration. The bands located at about 1638 cm^{-1} , attributing to carbonyl C=O stretching vibration. The absorption peak around 1120 cm^{-1} indicated the existence of C=O bond stretch. The region between 900 and 400 cm^{-1} are due to deformation vibrations out of the aromatic C-H bonds. This zone permits the justification of benzene rings and evaluates the degree of condensation of the aromatic nucleus. This zone is subdivided into five domains, each characterized by a degree of substitution or condensation of aromatic rings as follows: 900-860 cm^{-1} : 1H isolated; 860-800 cm^{-1} : 2H adjacent to each other; 810-750 cm^{-1} : 3H adjacent to each other; 860-735 cm^{-1} : 4H adjacent to each other.

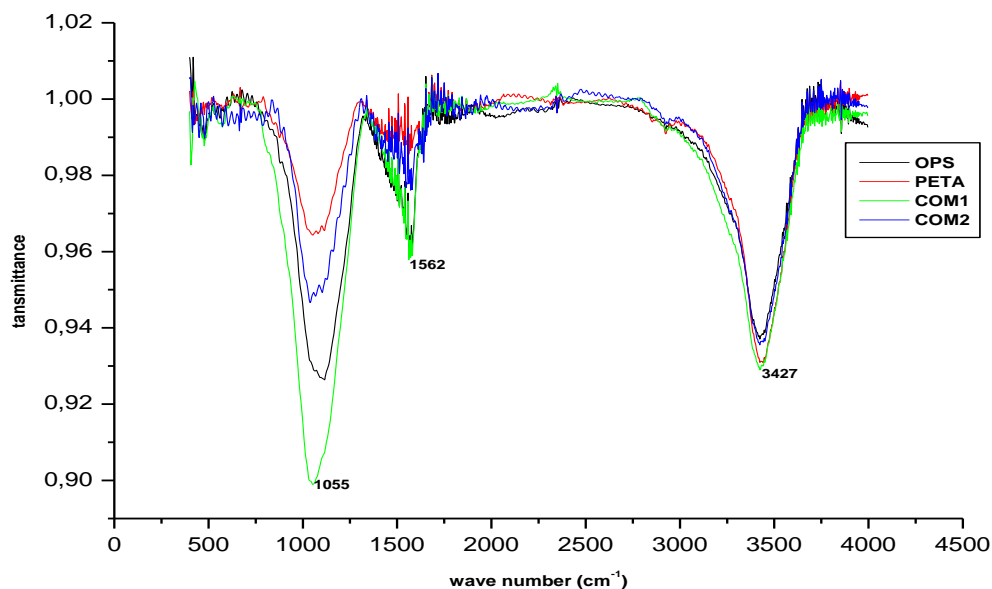


Figure3: FTIR spectra of Four Activated Carbons obtained by Physical Activation.

Scanning Electron Microscopy is used for imaging the morphologies of ACs. These carbons (Figure 4) exhibit independently of the composition of raw material, a cellular fibrous morphology. The prepared carbons are constituted by an interconnected channel framework in concordance with the fact that the precursor is constituted by a fibrous structure. For ACs obtained from vegetal material and mixture, SEM images show some white dots that have been associated with the inorganic composition of precursor [12].

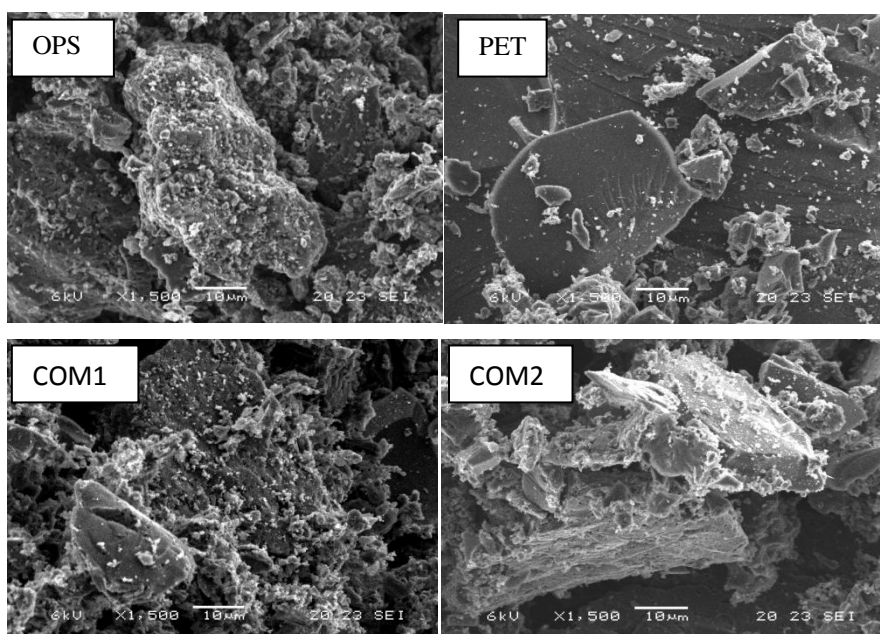


Figure 4: SEM Photographs of the Four Activated Carbons Prepared.

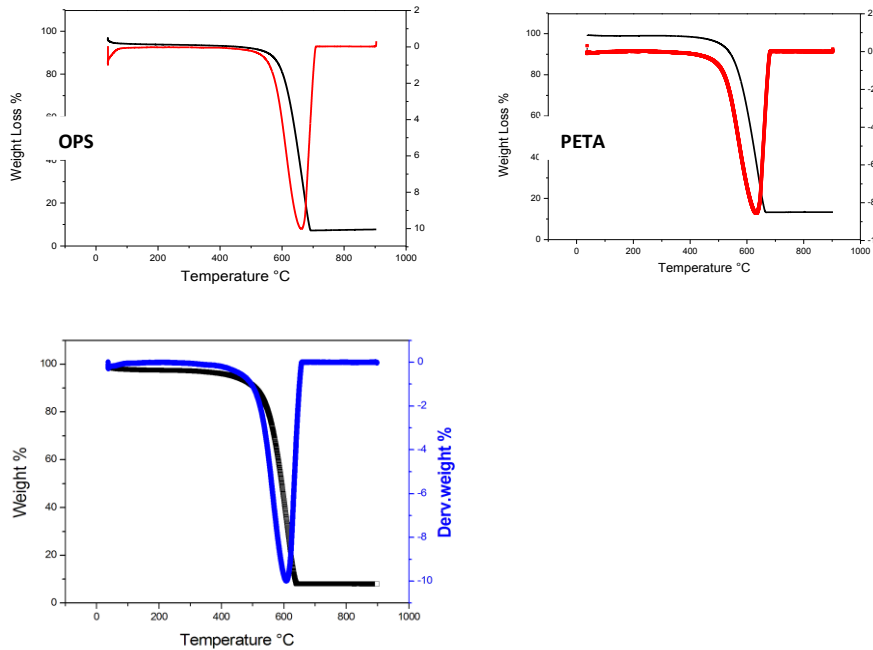


Figure 5: DSC-TGA Thermogram of Oil Palm Shell (OPS), Polyethyleneterephthalate (PETA) and composite activated carbon (COM2/1).

Thermogravimetric analysis is studied in order to confirm the external surface functions of ACs (Figure 5). It shows that the weight loss occurred in the range of 558-689 °C indicating the higher stability of samples. This decomposition is attributed to CO₂, CO and water vapour evolved from the decomposition of carboxyls, phenols or to the recombination of evolved hydrogen atoms as a result of splitting of C-H bonds [12].

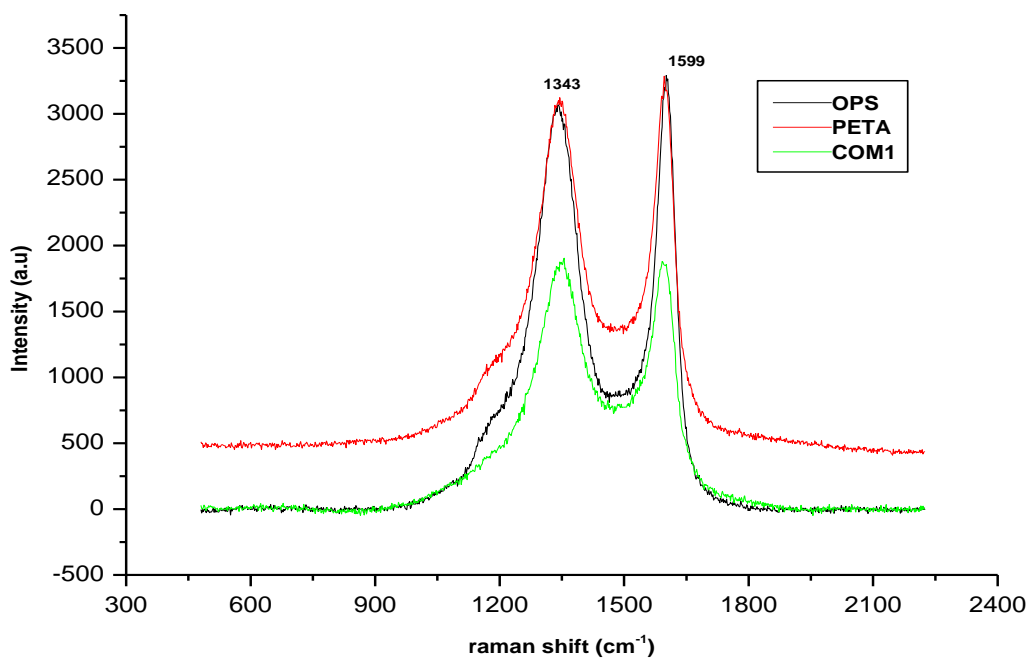


Figure 6. Raman spectra of post-consumer plastics, oil palm shell and composite AC showing the D and the G-band in their structure.

Raman spectra of ACs samples (figure 6) show a line at 1350 cm⁻¹ in addition to the line near 1600 cm⁻¹. It has been shown that the peak at 1600 cm⁻¹ named G-band (G=graphite) corresponds to an E_{2g} mode of hexagonal graphite and is related to the vibration of sp² hybridized carbon networks in a graphite layer. The D-band (D=disorder) at about 1343 cm⁻¹ is due to the breathing modes of six-atom rings and requires a defect for its activation. The presence of defects improves the performance of carbon materials because of the high anisotropy of the mechanical strength or the electrical conductivity between the in-plane and out-of-plane direction [15-19].

IV. Conclusion

Four activated carbons were prepared by physical activation (carbonization at 600°C using N₂ atmosphere, then activation at 850°C with steam) and subjected for characterization. The results revealed that the samples showed good adsorption capacities for iodine and methylene blue and as such will have good adsorption towards organic and inorganic compounds in aqueous solution. It was observed that the adsorption capacity was higher for composite activated carbons COM1 and COM2 compared to others obtained from pure plastics and lignocellulosic materials.

The prepared activated carbons exhibit large surfaces between 800 and 1500 m²/g with higher development of micropores since mesopores stand as the gateways for micropores. The average pore diameters were between 1.9 nm and 2.4 nm. The narrowness of the pores renders them suitable for the fixation of metals and thus, could be used as catalysts support.

As a matter of fact, the activated carbons were obtained at lower energies with the objective to produce low-cost adsorbents. As a consequence, they are economically viable and have the potential to compete with existing commercial products. Primarily, the results presented in this work mainly show that the obtained activated carbon (composite) was better in yield compared to that obtained exclusively from synthetic polymer.

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