

Preparation And Surface Characteristics Of Activated Carbon From *Brachystegia eurycoma* And *Prosopis africana* Seed Hulls

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Abstract: Activated carbons were prepared from *brachystegia eurycoma* and *prosopis africana* seed hulls (BESH and PASH) by chemical and physical activation and their surface characteristics determined. Weight lost characteristics of the precursors was influenced by temperature, time in furnace and impregnation ratio of phosphoric acid to precursor. Carbonization at 400°C, impregnation ratio 1.5 for 60min yielded 66 and 70% activated carbon from BESH and PASH respectively. Activated carbon yield by physical carbonization at temperatures 500°C was 25% and of poor quality. The surface area of activated carbons from BESH and PASH were 900 and 869m²/g respectively. High surface area of activated carbon from BESH was evident in its low average heat flow of 0.0084Jmin⁻¹, MB number (204mg/g), and iodine sorption capacity(76%) which is comparable to those obtained for commercial activated carbon (1006m²/g; 0,0078Jmin⁻¹; 234mg/g and 84%). Results indicated AC from BESH to contain more micropores, mesopores and macropores than PASH carbon. However, the AC obtained by phosphoric acid carbonization from BESH and PASH are of commercial grade and have the potential for application in liquid and gaseous phase adsorption.

Key word: Activated carbon; Surface area; *Brachystegia eurycoma*; *Prosopis africana*.

Introduction

Porous carbon is one of the most popular adsorbents used in numerous industries for the removal and recovery of organic and inorganic compounds from gaseous and liquid streams. It has high adsorption capability due to its high internal surface area and porosity formed during carbonization process. The presence of activating agents and carbonization conditions influenced the development of pore structures¹. However, the usage of porous carbon, also known as activated carbon (AC) is limited by its high cost which is a consequence of high cost of production. Moreover, coal which is the major raw material for the production of AC in the industry is becoming depleted, difficult and risk to mine. There is the need to source for readily available and cheap sources of AC precursors.

Agricultural wastes are potential precursors because of their abundant supply and low cost. Moreover, transforming agricultural wastes into valuable end products may help to reduce environmental pollution problems associated with solid wastes disposal. Many attempts have been made to produce activated carbon with agricultural wastes such as fluted pumpkin stem waste², cassava peel³, macadamia nut-shell⁴, apricot stones⁵, coconut shells⁶, sugarcane bagasse⁷, *Ceiba pentandra* hulls⁸, corn cob⁹ and sago waste¹⁰.

To the best of our knowledge, there is no literature on the preparation of AC from *brachystegia eurycoma* and *prosopis africana* seed hulls. The seeds of these plants are used as food in Nigeria. Seeds of *brachystegia eurycoma* found in abundance in south East Nigeria are processed and used as soup thickener while *prosopis africana* seeds are used as seasoning in the central states of the country. After processing, the seed hulls are usually disposed as solid wastes. Hence, *brachystegia eurycoma* and *prosopis africana* seed hulls are potential precursor for the preparation of porous carbon. AC is usually prepared by physical or chemical activation method. In physical activation, the precursor is first carbonized in an inert atmosphere and then activated in a stream of carbon dioxide or steam; whereas for chemical activation, the precursor is impregnated with inorganic acids or salts, before carbonization in an inert environment.

The main objective of this study is to contribute to the search for less expensive AC adsorbents. Therefore, AC was prepared from both precursors, applying both physical and chemical carbonization method to determine the protocol that will yield highly porous AC adsorbent.

Materials And Methods

Sample collection and pretreatment

Samples of *brachystegia eurycoma* seed hulls (BESH) were collected from processing points in Sabon Gari Local Government area of Zaria, Kaduna state, while *prosopis africana* seed hulls (PASH) from farms in Agila, Ado Local Government area of Benue State, Nigeria in November and December 2010. Samples were packaged in clean polythene bags and transported to the laboratory. They were dried at ambient conditions in the laboratory for six (6) months. When the samples were adjudged to be dry they were grounded to powder in an agate mortar and sieved into different particle size of 710 μ m. We had earlier reported that 710 μ m of particle size is the most suitable for the preparation of porous carbon from BESH and PASH¹¹.

Preparation of Activated carbon

For chemical carbonization 1.0g each of the precursors were impregnated with 3cm³ H₃PO₄ (S.G 1.7gcm⁻³; 85% purity) corresponding to 2g of the acid. The mixtures were carbonized at 100, 200,300,400 and 500°C for residence time in furnace of 10, 20, 30, 40,50and 60 minutes. Physical carbonization was performed at 600, 700, 800, and 900°C. The carbon residues obtained were washed with dilute HCl and de-ionized water. They were dried at 110°C for 24hours in a Gallenkemp hotbox oven. 2g each of BESH and PASH samples was impregnated with 0.7, 1.4, 2.1, 2.8, 3.5and 4.2cm³ of the acid equivalent to 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 impregnation ratio respectively and were carbonized at 350°C for 1hour.

Scanning Electron Microscopy (SEM) Observation

The texture and pore structure of the porous carbon was observed under a EVO/MAIO Carl zeiss scanning electron microscope.

Fourier Transfer Infrared Spectroscopy (FTIRS) Analysis

Surface organic functional group analysis of the carbon precursors were performed before and after activation by mixing the samples with potassium bromide (KBr) in the ratio 1:10. These were then subjected to spectral analysis by Fourier Transform Infrared spectroscopy (FTIR 8400S from Shimadzu). The spectra were recorded from a wavenumber of 500-4500cm⁻¹.

Determination of Surface Area

The surface area of activated carbon was determined using the ethylene glycol method described by¹². 1g each of activated carbon samples were weighed and transferred into different beakers. 3.0cm³ of ethylene glycol was measured and gently added to each of the beaker with sample. The mixtures were carefully swirled until uniform slurry was formed. The slurry was placed in vacuum desiccators having anhydrous calcium chloride and ethylene glycol as desiccant. The mixtures were weighed at intervals of 12 hours until the difference between two successive weights was less than 0.001g, the weight obtained at this stage was taken as the final slurry weight. The final slurry weight of samples was obtained after 60 hours, which was used for the calculations. The specific surface area (SSA) was calculated using equation (1)

$$SSA = W_{fs} - W_s / 0.000286 = W_a / 0.000286 \quad (1)$$

Where; SSA is the specific surface area, W_{fs} is weight of final slurry, W_s is the weight of

Sample, W_a is the weight of ethylene glycol retained by the sample in grams. 0.000286 is a constant representing the weight of ethylene glycol required to form a mono molecular layer on a square meter surface per gram of adsorbent (m^2/g).

Determination of Iodine Sorption Capacity

1.0g each of the activated carbon samples were weighed into a 250 mL flask and 10 mL of 5% HCl was added. The flask was swirled until the carbon became wet. 100 mL of iodine solution (2.7 g of Iodine and 4.1 g of potassium iodide in 1 L of de-ionized water) was added and the mixture was shaken for 5 minutes. All the samples were filtered using Whatman No.1 filter paper. 50ml of filtrate was titrated with 0.1 M sodium thiosulphate until the solution become pale yellow. Then 1ml 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 activated carbon and titrated similarly. The percent iodine sorption by each activated carbon sample was calculated by applying the following formula:

$$\text{Iodine sorption (\%)} = \frac{V_{sb} - V_{ss}}{V_{sb}} \times 100$$

Where;

V_{sb} is ml of sodium thiosulphate used for blank and V_{ss} ml thiosulphate used for sample.

Methylene blue (MB) Number

The procedure described by ASTM D2330¹³ was applied for MB number determination. MB (0.15g) was weighed and dissolved in 100 ml de-ionized water. The activated carbon samples (0.1g) each were weighed and transferred into 50ml stoppered flask. 10ml MB solution was added from a burette and the mixture shaken for 5 minutes. Once the 10ml solution was decolorized, MB solution was added 1ml at a time until there was no further decolorization. The end point was considered to be reached when the blue color persisted for 5 minutes. The amount of MB adsorbed was calculated as follows:

$$\text{MB number (mg/g)} = \frac{(15 \times V)}{(10 \times m)}$$

Where,

V= Volume of the methylene blue solution consumed (ml)

m= Mass of activated carbon sample used for the test (g)

Differential Scanning Calorimetric (DSC) Measurement

Most adsorbent exhibits poor heat transfer properties, mainly due to high porosity of the material. The heat flow pattern of the porous carbon obtained from BESH and PASH BDH Chemicals Ltd, Poole England) which served as baseline. Differential Scanning Calorimeter (DSC-60 from Shimadzu) coupled with TA-60 Workstation was used for the measurements. Temperature program applied was temperature rate (5.0C/min), hold temperature (50°C) and hold time (4min).

Results And Discussion

The effect of temperature and residence time in furnace on weight of carbon residue for chemical carbonization of BESH and PASH are presented in Fig 1 and Fig 2 respectively. The results showed a significant influence of temperature and time of carbonization on carbon yield. A significant reduction in bulk matrix of BESH precursor was observed from 10 to 40min residence time in furnace and carbonization temperature of 300-500°C. Also, for PASH reduction in precursor matrix was significant between 10-40min and carbonization

temperature range of 400-500°C. However, the chemical carbonization conditions that gave sizable quantity of carbon yield for both precursors were, carbonization temperature of 400°C for 60min. From Table 1, washing of carbon residues obtained from these treatment conditions with acid and de-ionised water gave 66% and 70% porous carbon yield for BESH and PASH respectively.

Results for physical carbonization of BESH and PASH are presented Fig 3 and Fig 4 respectively. The effect of temperature and residence time on weight of carbon residue obtained is more conspicuous for this method of carbonization than the chemical method. As shown in Table 2, carbonization of the precursors for 1hour between 600- 700°C produced 21-25% yield of porous carbon for BESH and 20-24% for PASH. Carbon yield was observed to be extremely poor for temperatures above 700°C with, yield lower than 20%. To obtain highly porous carbons from these precursors by physical carbonization, the optimum temperature and residence time for carbonization was 700°C and 60min. Comparatively, the chemical method of carbonization using H₃PO₄ as activating agent proved to be a better method of obtaining porous carbons from BESH and PASH than the physical method, due to the high carbon yield at lower temperature without compromising the porosity of carbon obtained.

The effect of acid impregnation ratio on porous carbon yield for 0.5g each of BESH and PASH at 350°C for 60 min residence time in furnace is presented in Fig 5. The results indicated that amount of H₃PO₄ added to the carbon precursors had strong influence on the carbon yield. For acid impregnation ratio of 0.5-3.0 carbon yield was below 50% for both precursors. A steady decline in carbon yield was observed for BESH as acid impregnation ratio was increased, but became almost constant at 3.0. The effect of acid impregnation ratio on carbon yield for PASH was constant between 0.5-1.5, but decreased sharply at 3.0 with a poor carbon yield of 23%. Acid impregnation ratio which was sufficient to produce highly porous carbon with good yield for both precursors was observed to be 1.5. The pattern observed for the effect of the acid on the carbon precursors investigated could be largely due to their nature.

From the SEM micrographs of raw BESH and PASH in Fig 6 and 7 respectively, it was found that the precursors had smooth surfaces, which the presence of minerals distributed in the organic matrices and as a result the surface coverage. An analysis of the micrographs presented in Fig 8-11, showed that the carbonization and activation processes had strong influence on the external structure of the precursors after chemical and physical carbonization and activation. The porous carbons from the precursors had rough and eroded surface with holes and cave-like openings. The surface morphology was similar for all the carbons prepared, but the pores were more pronounced for the precursors subjected to treatment with phosphoric acid fig 8 and 9. The acid may have played a critical role in control the pore development process. The SEM results has revealed that the carbon adsorbents prepared from the precursors at lower temperature with phosphoric acid as activating agent had more pores, which implies more surface area available for absorption.

Differences in surface functionality of both raw and activated BESH and PASH were noted. From Fig 15, before activation BESH showed absorption at 3417.01, 2919.36, 1633.76, and 1044.49cm⁻¹ attributed to O-H stretch of phenols and alcohols, C-H stretch of methylene, C=O stretch and N-H bend in amides and C-O stretch of esters and ethers respectively. Presented in Fig 16 are the spectra of raw and carbonized PASH. Signals were also observed for raw PASH at 3437.26, 2927.05, 1626.05, 1443.77 and 1050.28cm⁻¹. These signals indicate same functional groups as in BESH except for the signal at 1443.77cm⁻¹ assigned to N-H bend in secondary amines. The spectra for porous carbons obtained by chemical and physical carbonization showed that the functional groups present in the precursors were completely removed by the conditions of carbonization. This suggests that the mechanism of adsorbate uptake by these porous carbons is expected to be physic-sorption or the existence of Van der Waal forces between the adsorbents and their adsorbates.

Results for the surface area of the CAC and AC from BESH and PASH are presented in Fig 12. Most widely used commercial activated carbons have specific surface areas of the order of 800-1500 m²/g¹⁴. The value obtained for the surface area of CAC was 1006m²/g. Surface area of acid activated carbon from BESH and PASH were 900 and 869m²/g respectively. Physical carbonization of the precursors produced carbon adsorbents with surface area of 709m²/g (BESH) and 703m²/g (PASH). The CAC and the chemically carbonized precursor produced carbon with surface area within the commercial range. However, the surface area of the carbons from BESH is greater than carbons from PASH using both methods of preparation. The nature of the precursors may be the reason for the difference.

Results for heat transfer properties of CAC and the AC from BESH and PASH are presented in Table 3. Most adsorbents exhibit poor heat transfer property mainly due to the porosity of the material. The discontinuity

of adsorbents material leads to poor heat flow pattern¹⁵. The lowest average heat transfer value of 0.0078Jmin^{-1} was obtained for CAC due to its high porosity. The order of porosity of the AC obtained from BESH and PASH by chemical carbonization method was BESH > PASH with average heat transfer values of 0.0084 and 0.009Jmin^{-1} respectively. The results also indicate that the carbons prepared by phosphoric acid carbonization method have porosity almost like CAC. AC prepared by Physical activation from BESH and PASH at high temperature was observed to both have high average heat transfer value of 0.0102Jmin^{-1} . The low porosity of the carbons obtained by physical activation method may be responsible for the high value of average heat transfer.

The results for MB number and iodine sorption capacity of CAC the activated carbon from BESH and PASH are presented in figures 13 and 14. MB number and iodine sorption capacity have relationship with the pore structure of adsorbents¹⁶. MB number indicate the capacity of an adsorbent to adsorb large molecular size species into its macro pores, while the iodine sorption capacity is related to the degree of micro and mesopores present in the adsorbent. The results obtained for both parameters showed that the AC prepared from the precursors by chemical carbonization has more micropores, mesopores and macropores than those prepared by physical carbonization. CAC which served as baseline had MB number of 234mg/g and iodine sorption capacity of 84% . The AC obtained from BESH by acid pyrolysis is comparable to CAC because its MB number was 204mg/g and iodine sorption capacity 76% . Values for PASH carbon prepared by chemical carbonization were 195mg/g and 71% MB number and iodine sorption capacity respectively.

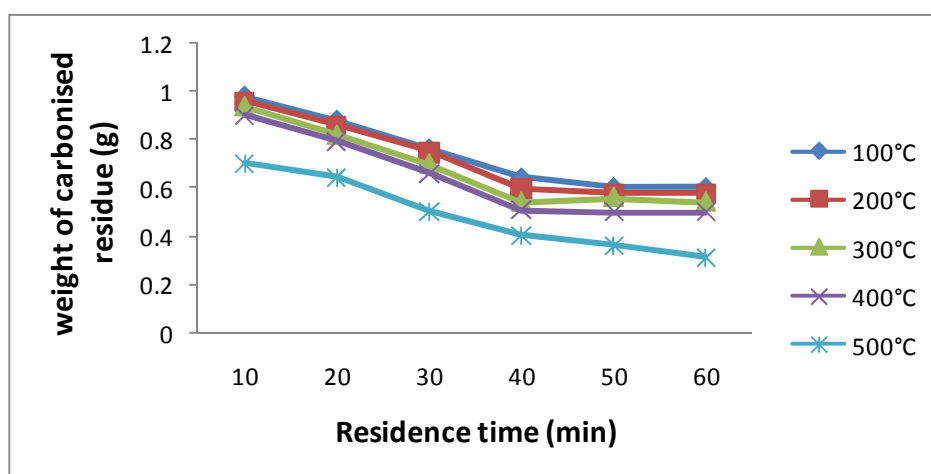


Fig 1: Variation in weight of carbonized BESH with residence time at different temperature with equal amount of H_3PO_4 acid impregnation.

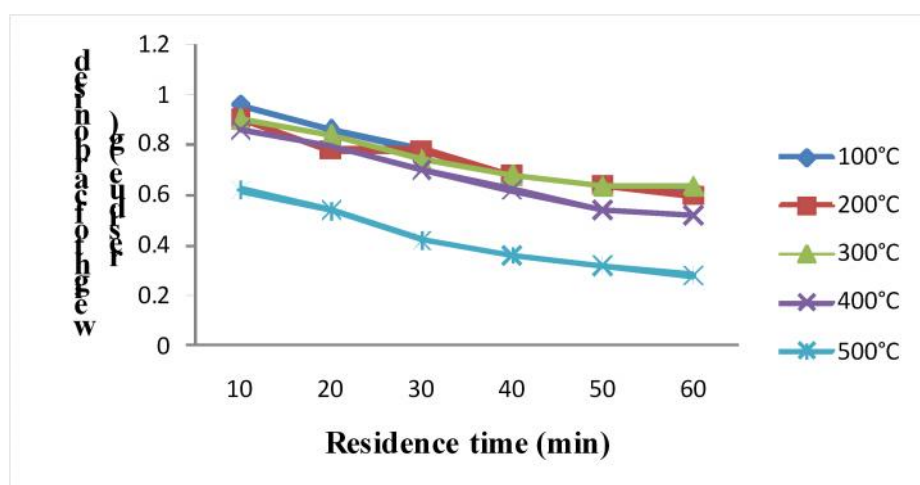


Fig 2: Variation in weight of carbonized PASH with residence time at different with equal amount of H_3PO_4 acid impregnation. .

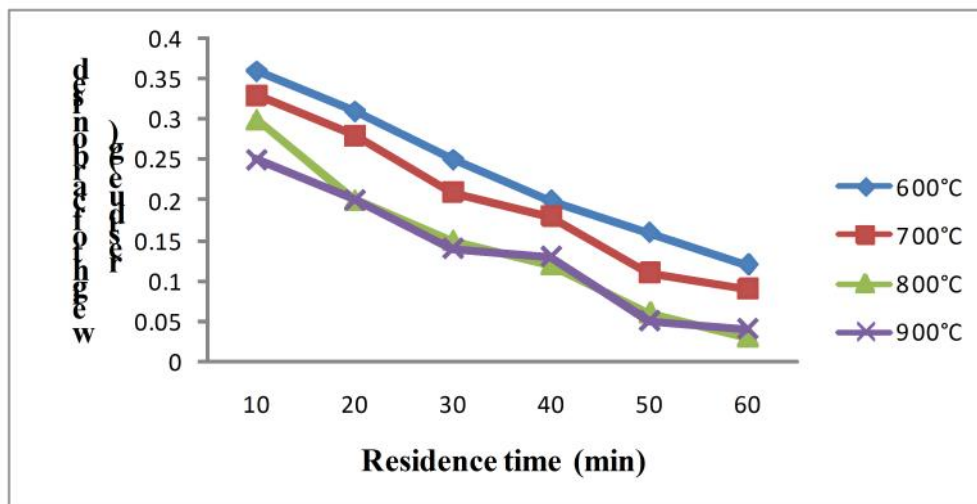


Fig 3: Variation in weight of carbonized BESH with residence time at different temperature of physical carbonization.

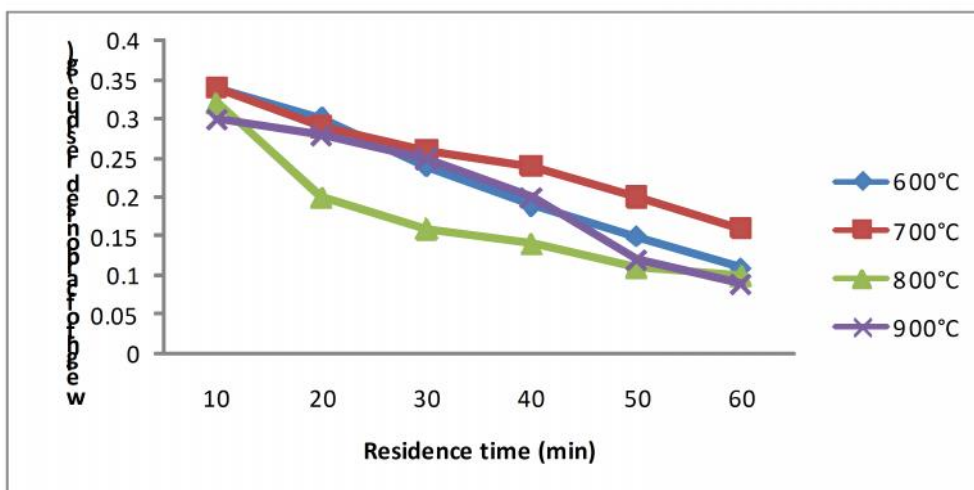


Fig 4: Variation in weight of carbonized PASH with residence time at different temperature of physical carbonization.

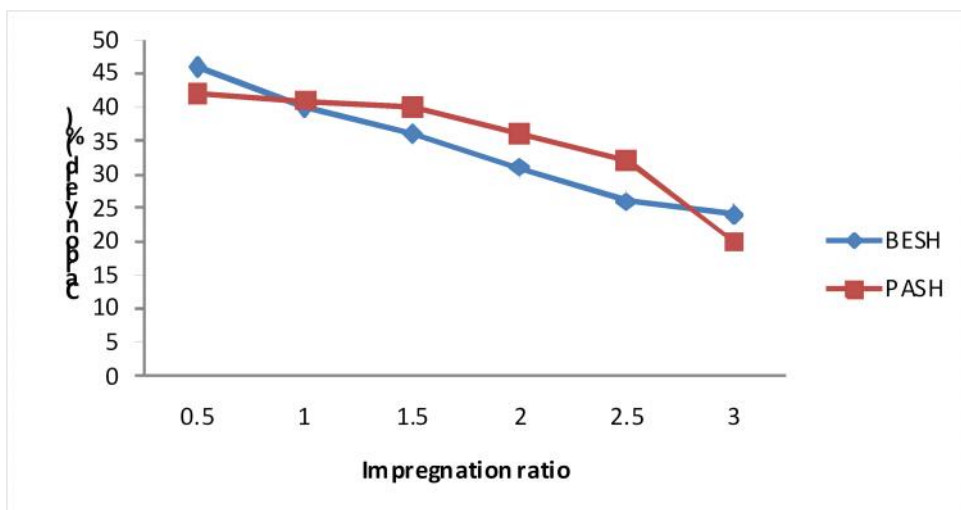


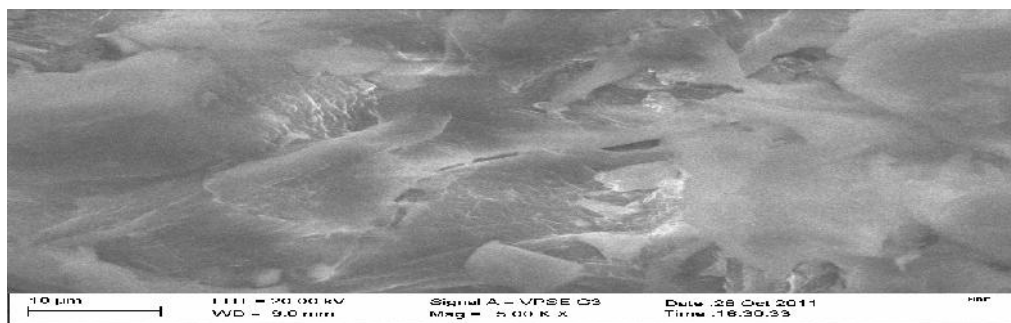
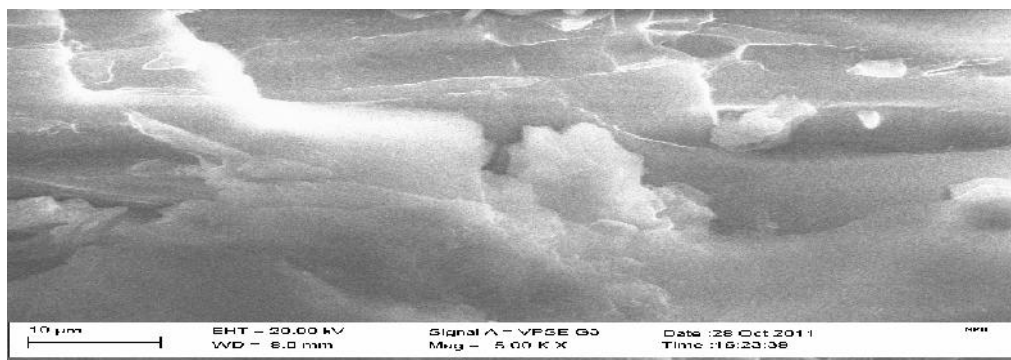
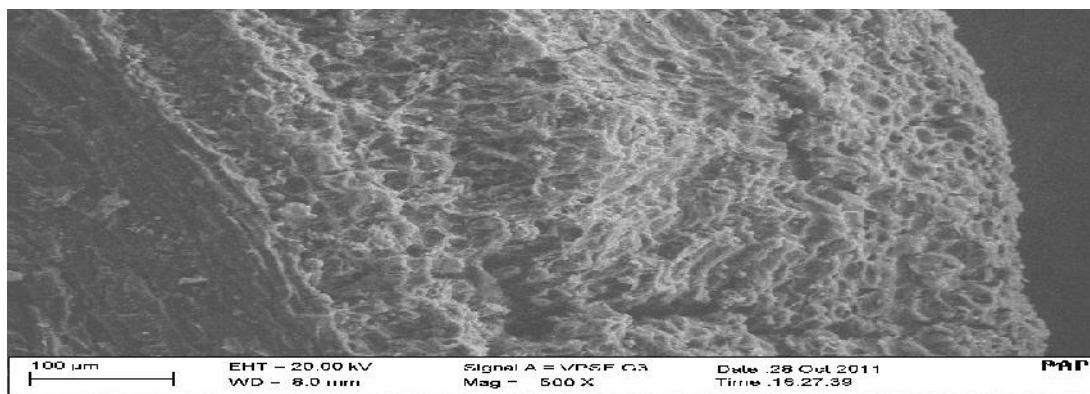
Fig 5: Effect of impregnation ratio on AC yield from 0.5g each of BESH and PASH at 350°C for 60 min residence time in furnace.

Table 1: AC yield at different carbonization temperatures for residence time of 60min with H₃PO₄ acid impregnation.

Precursor	Activated carbon yield (%)				
	100 ⁰ C	200 ⁰ C	300 ⁰ C	400 ⁰ C	500 ⁰ C
PASH	78	78	74	70	42
BESH	76	75	70	66	50

Table 2: AC yield at different carbonization temperatures for residence time of 60min.

Precursor	Activated carbon yield (%)			
	600 ⁰ C	700 ⁰ C	800 ⁰ C	900 ⁰ C
BESH	25	21	15	10
PASH	24	20	19	14

**Fig 6: SEM Micrograph of BESH before carbonization****Fig 7: SEM Micrograph of PASH before carbonization****Fig 8: SEM micrograph of AC from PASH after Carbonization at 400°C for 1 hour with H₃PO₄ impregnation.**

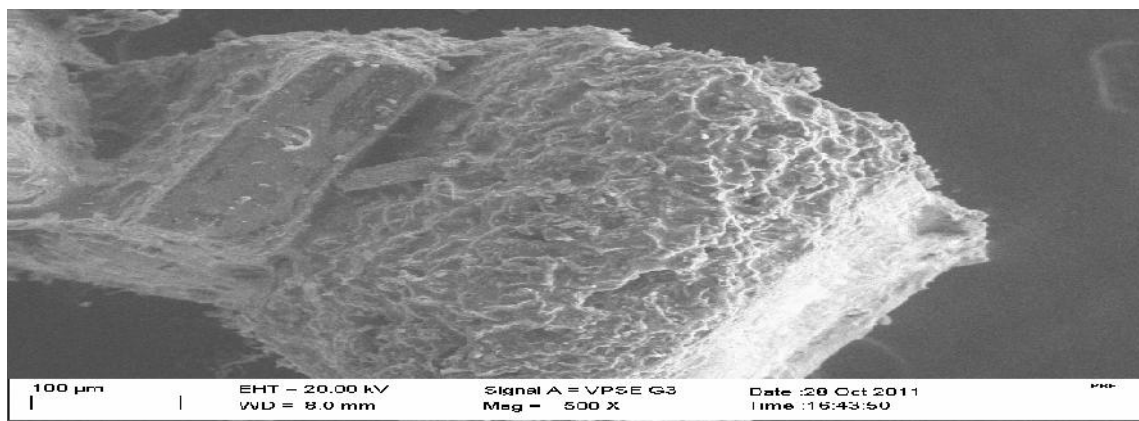


Fig 9: SEM micrograph of AC from BESH after carbonization at 400°C for 1hour with H₃PO₄ impregnation.

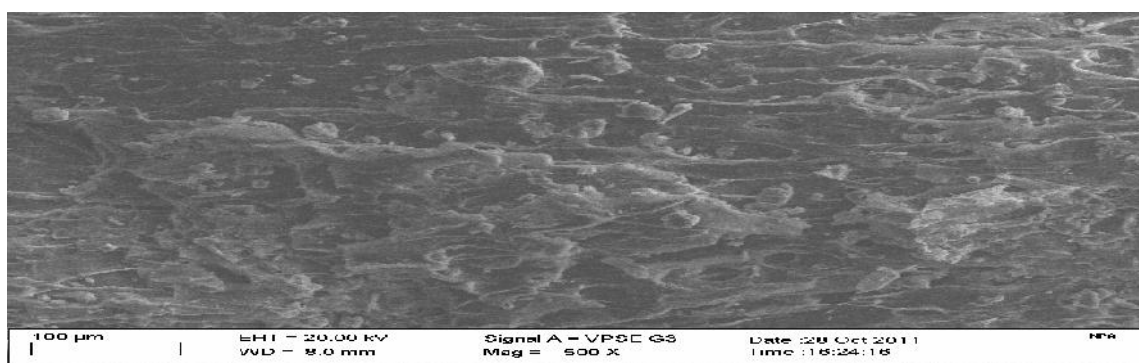


Fig 10: SEM micrograph of AC from PASH carbonized at 700°C for 1hour

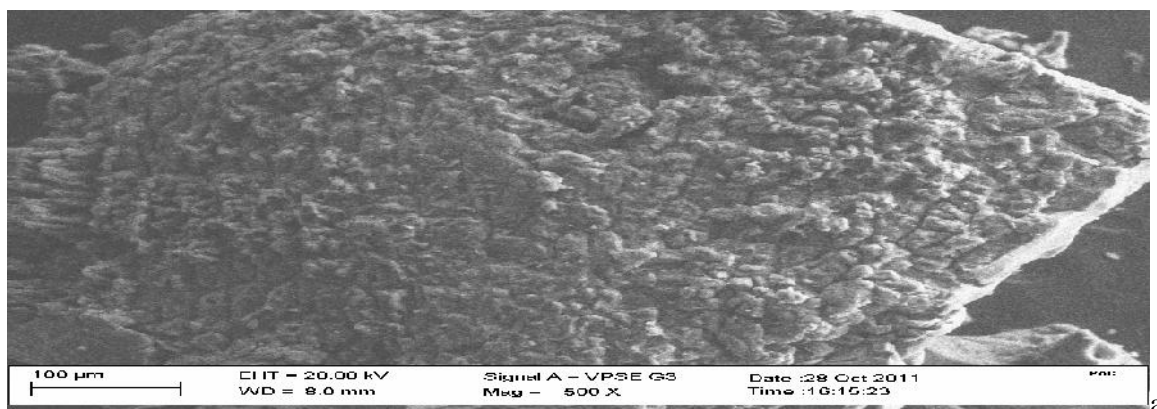


Fig 11: SEM micrograph of AC from BESH carbonized at 700°C for 1hour.

Table 3: Heat transfer pattern of CAC and AC from BESH and PASH

Sample	Time (min)	Heat flow (mW)	DSC	Average Heat flow Jmin ⁻¹
CAC	1	-1.48		0.0078
	2	-1.35		
	3	-1.21		
	4	-1.08		
<u>BESH</u> Chemical Activation	1	-0.93		0.0084
	2	-0.79		
	3	-0.66		
	4	-0.50		

Physical Activation	1	-0.89	0.0102
	2	-0.69	
	3	-0.52	
	4	-0.39	
<u>PASH</u> Chemical Activation	1	-0.91	0.009
	2	-0.76	
	3	-0.60	
	4	-0.45	
Physical Activation	1	-0.84	0.0102
	2	-0.67	
	3	-0.49	
	4	-0.32	

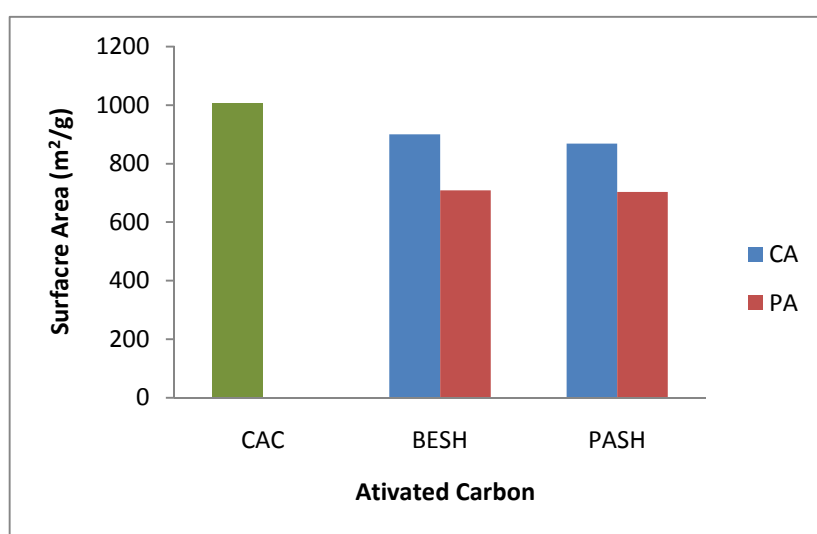


Fig12: Surface area variation of AC from BESH and PASH with CAC

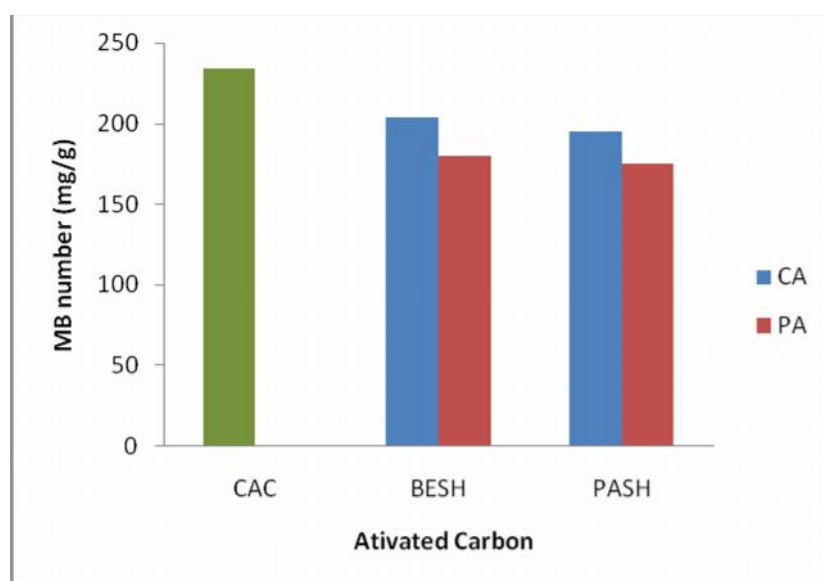


Fig13: MB number of the prepared AC and CAC

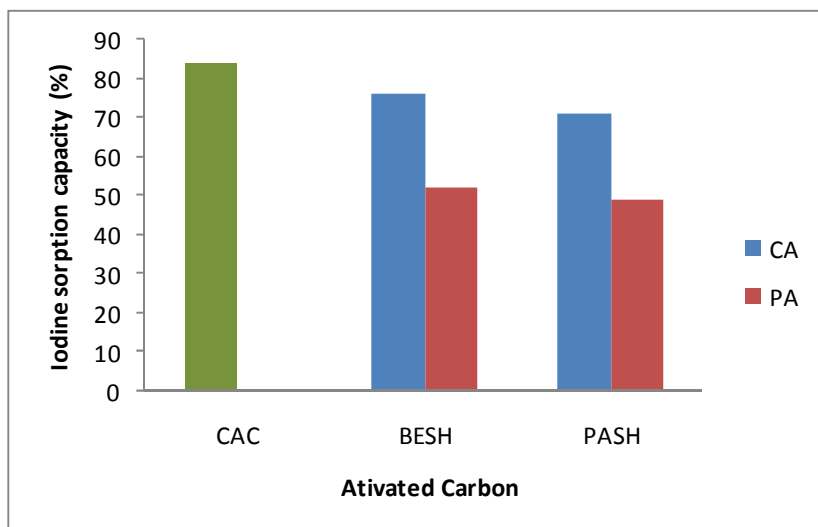


Fig 14: Iodine sorption capacity of prepared AC and CAC

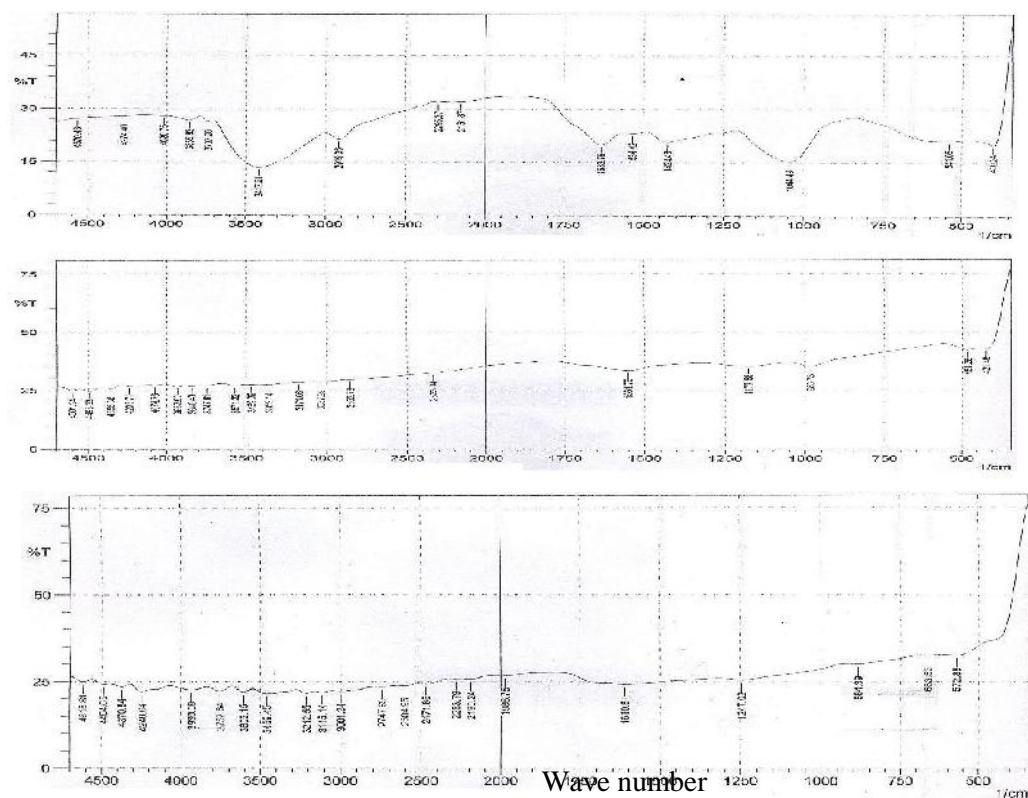


Fig 15: FTIR spectra of BESH before and after chemical and physical carbonization

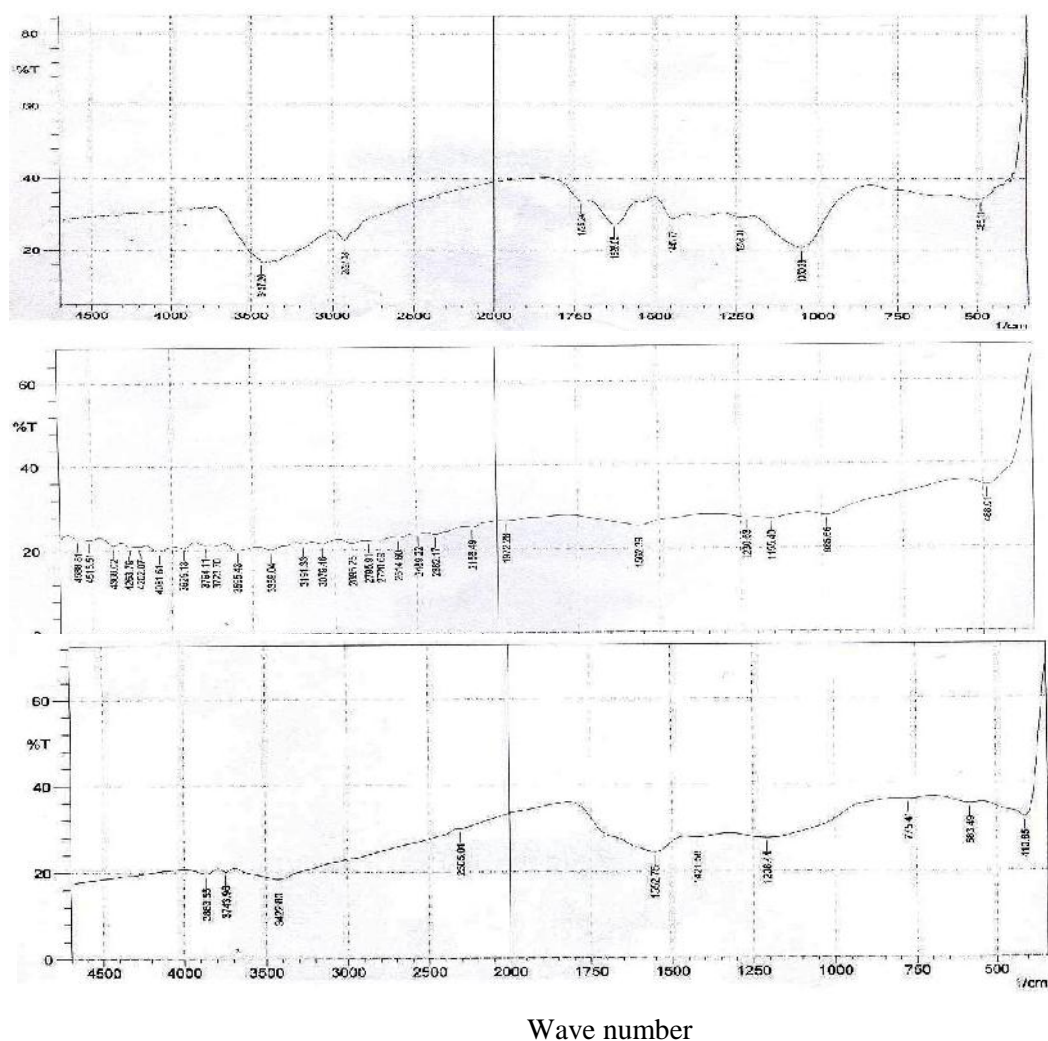


Fig 16: FTIR spectra of PASH before and after chemical and physical carbonization

Conclusion

Activated carbons were prepared from the pyrolysis of *brachystegia eurycoma* and *prosopis africana* seed hulls at 400°C by chemical activation with H_3PO_4 and precursors impregnation ratio of 1.5. The yields of the activated carbons produced by chemical activation were found to be higher and more porous than activated carbon prepared by physical activation. The properties of the activated carbons produced in this work such as surface area, heat flow, iodine sorption capacity and methylene blue number reveals that they have pore structures comparable to those of commercial activated carbon adsorbents. Consequently, the activated carbons produced from these wastes biomass can be used as adsorbents for various environmental applications including the removal color and heavy metals from industrial effluents, and treatment of drinking water.

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