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# Nano Pores Surface Area Evaluation In Palm Kernel Shells And Masonia Wood Derived Activated Carbons.

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**Abstract:** Biomass charcoal was obtained by pyrolysis from Palm kernel shells, Coconut shells and Masonia wood precursors as 33.2%, 30.6% and 24.7% respectively. The conversion of the charcoal to activated carbon was implemented with KOH activation. The active surface area measurement carried out with methylene blue adsorption and Brauner, Emmet and Teller (BET) surface adsorption theory gave values of $80.3 m^2g^{-1}$, $172.14 m^2g^{-1}$ and $140.08 m^2g^{-1}$ respectively. The developed pores were in the mesopores category of pores.

**Keywords:** Charcoal, Pyrolysis, Activated Carbon, Mesopores, Specific Surface Area.

## I.0 INTRODUCTION.

The development of Electric double layer capacitors (EDLC), as energy storage devices forms part of the ongoing worldwide research in alternative energy. In the EDLC energy is stored as charges held by adhesion onto large surface areas of pores in polarisable solid electrode that is immersed in an electrolyte. Examples of materials used for the electrodes are high-surface-area activated carbons, transition metal oxides, and electro-active polymers (Chen et al 2001). Activated Carbon (AC) is a form of carbon that has been processed to make it highly porous. Surface area ranges (m2/g) of 14.5-15.1, 13.5-14.0, 12.3-14.0 and 14.3-14.5 has been reported for Groundnut shells, Sheanut shells, Poultry droppings and poultry waste respectively (Itodo et al 2010). It is derived from the materials through Pyrolysis and Activation. The measurement of their active nanapores surface area and information about the structure of activated carbons can be obtained by the adsorption characteristics of different adsorbates such as methylene blue and iodine (Cleiton et al 2011). In the methylene dye adsorption method, the determination of surface area is evaluated with the Branuer – Emmer and Teller (BET) isotherm theory. In the theory, the rate of adsorption in reciprocal form is given by Equation 1 (Itodo et al 2010 Atkins 1999).

$$1/x = (1/kx_o)1/c + 1/x_o \quad (1)$$

Where $x_o$ is concentration of available adsorption sit, c is concentration of adsorbate (dye) above the absorbent (carbon), and k is adsorption constant.

In its use, x is measured experimentally at different values of c and a plot of 1/x versus 1/c prepared. $x_o$ is obtained from the plot and used to evaluate n in equation 2 with a view to calculating the total available surface area S.

$$S = n N_A a \quad (2)$$

n is the number of molecules of adsorbate taken by the adsorbent. 'a' is the molecular / atomic surface area of the adsorbate. For methylene blue, a = $197.2 Å^2$ and a molecular weight of $373.9 \times 10^{-3}$ kg $mol^{-1}$ (Itodo et al 2010).

A linear relationship between nano pore surface area and the carbon's charge storage ability or capacitance has been observed (Barbieri et al 2005). Also large specific surface area (SSA) of carbon materials used for EDLC's is the most important parameter that leads to a large gravimetric capacitance (Barbieri et al 2005). Surface area ranges of between 446 to $1340 m^2g^{-1}$ has also been reported for Coconut shells (Farma et al 2013).

Prior to the recent upsurge of activities in the development of EDLC's, the common use of activated carbon has been the removal of organic impurities from water. In industries, it has also been used in decolorization, deodorization and contaminant reduction from liquids and gases.

In this work, preparation of AC's from Elaeis guineensis (African oil palm) seed shells (PKS), Coconut shells (CCS) and Masonia hard wood (MW) are investigated. Apart from the Coconut shells no documented report of work on PKS and MW has been seen in literature. The adsorption surface area measurement method employed is methylene blue dye adsorption onto the activated carbon from aqueous solution. The levels of adsorption then measured by BET Isotherm theory. It is hoped that the AC so prepared will be suitable for preparing electrodes for Electric Double Layer Capacitors, Water, Gas and Chemicals purification.

## 2.0 MATERIALS AND METHOD.

**2.1 Materials :-** The precursor materials were Palm Kernel shells, Coconut Shells and Masonia Hard wood, all obtained in Nigeria. Activation agent was Potassium Hydroxide (KOH). Methyl red indicator was used to determine the absence of KOH from the samples after filtration The major equipment utilized were "Carbolite NTF 12/39/400" Tubular Furnace, 450mm/40mm stainless steel pyrolysis chamber constructed at SHESTCO'S mechanical engineering workshop, AVASpec UV/VIS optical fibre Spectrophotometer, Digital "Ainsworh DE – 100" top loading balance, a 250 microns Endecotts sieve and Carl Zeiss MA 10 Scanning Electron Microscope (SEM).

**2.2 Experimental methods**:-

**2.2.1 Carbonization :-** Experimental steps were pyrolysis preparation of the charcoals, chemical activation conversion to activated carbon and specific surface area determination. The preparation process comprised washing of the precursors in water, followed by oven drying at 150$^{o}$C for one hour. The samples was then cooled to room temperature in separate calcium oxide desiccators. This was followed by taking specific weights from the samples and their natural structural densities were evaluated by water displacement method.

The carbonization pyrolysis was implemented in the constructed stainless steel chamber that was inserted into the Furnace. The steel chamber was sealed at one end and the other end vented to air through water, Fig 1.0. The furnace was ramped to 700$^{o}$C and allowed to dwell at that temperature for one hour. After cooling to room temperature, the weights of the carbon yields were recorded.

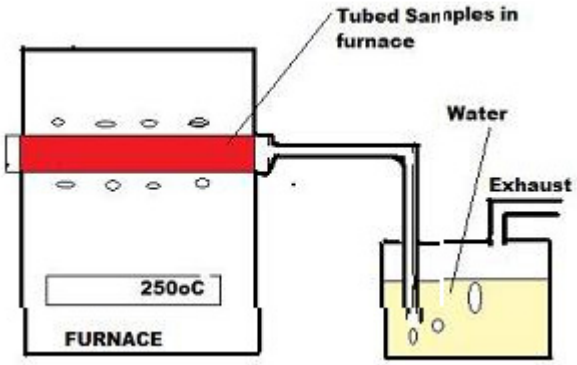


**Fig. 1.0 Carbonization pyrolysis experimental set-up.**

**2.2.2 Activation:-** A mixture ratio of carbon to KOH of 1:3, was heated in the absence of air at 700$^{o}$C for one hour [8]. This was followed by water filtration of the materials to separate the activation agent from the samples. The end point was determined by taking few drops of the filtrate into methyl red indicator, the indicator turns yellow in the presence of KOH. After filtration, the samples were dried at 200$^{o}$C, grinded to powder in a silica mortar and sieved to 250 microns.

**2.3 Specific Surface Area (SSA) determination:-** The first stage involved using the Spectrophotometer to determine the level of Methylene blue dye adsorbance by the carbon as a function of varying carbon quantities. The target was to achieve equilibrium between adsorbance and desorbtion levels of a specific quantity of the carbon. This state was achieved in a period of about eighteen hours for each of the samples with approximately 0.1g of the carbon at a concentration of 15mg/l of the methylene blue in water. This provided the MB concentration and appropriate quantities for the second stage. In the second stage the adsorbance levels of 100mg

of the carbon was measured as a function of various concentrations of the methylene blue in the range of (5.0 - 25) mg/l.

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**3.0 RESULTS AND DISCUSSIONS.**

During the carbonization pyrolysis process, the observed smoke emission which started around 400$^{o}$C and stopped at about 550$^{o}$C was high in the three samples. Table 1.0 presents the carbonization results. The carbon yield trend seems to suggest that charcoal yields from biomass is not necessarily proportional to the hardness of the precursor materials as may be naturally expected.. The coconut shells were thick walled and of high density but their charcoal yield came less than that of the lighter palm kernel shells.

Table 1.0 Charcoal yields and Densities of the different precursors.

| Precursors | Sample wt. (g) | Measured Densities (kgm$^{-3}$) | Derived Charcoal wt. (g) | % Charcoal yield | % Burnt off cellulose /Lignin's. |
|---|---|---|---|---|---|
| PKS | 110 | 1.2048 | 36.5 | 40.1 | 59.9 |
| CCS | 110 | 1.3158 | 33.7 | 37.1 | 62.9 |
| MW | 110 | 0.7692 | 16.2 | 17.8 | 82.2 |

After the AC's adsorption of some of the Methylene blue from the solutions, during spectrophotometric absorbance measurements, the dye was observed to exhibit peak optical absorbance at about 665nm. Sample absorbance vs. wavelength plots of the three samples treated MB solutions and the prepared standard MB solution is presented in Fig. 2 . The peak values for each of the samples were taken at the 665nm.

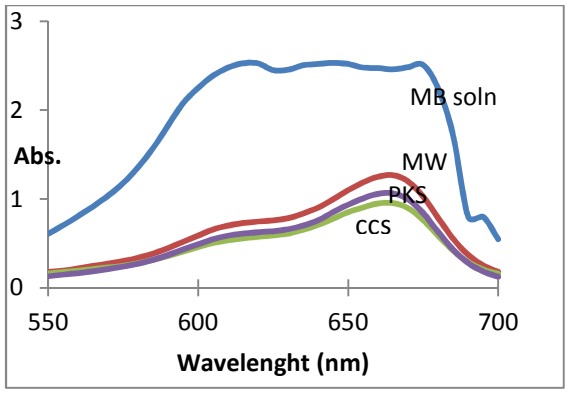



Fig 2 : Spectrophotometric absorbance plots of MB solutions before and after AC adsorbance.

Analytically, taking $C_1$ and $C_2$ to represent concentrations of MB in solution before and after its adsorbance by the AC and $A_1$ and $A_2$ represent their spectrophotometric absorbance respectively, then at equilibrium, $A_2/A_1 = C_2/C_1$ giving $C_2 = (A_2/A_1)*C_1$.

By extension of the same analysis to the masses of the MB in solution, (this is possible since below saturation levels, concentration is directly proportional to mass of dissolved material.). $M_2 = (A_2/A_1)*M_1$

The mass adsorbed into the AC is thus $M = M_1 - M_2$.

A plot of 1/M versus $1/C_2$ as presented in eqn. 1 is linear with intercept at $1/M_0$, where $M_0$ is concentration of available adsorption sites in the adsorbate.

The plot of the MB adsorbance unto the same mass of AC as a function of the MB concentrations is presented in fig. 3.0. linear regression analysis gave the linear equations presented in table 2 for the three plots.

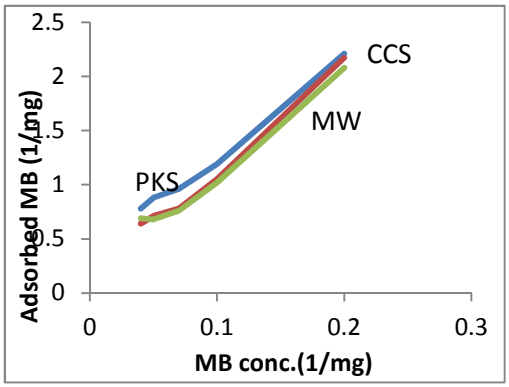


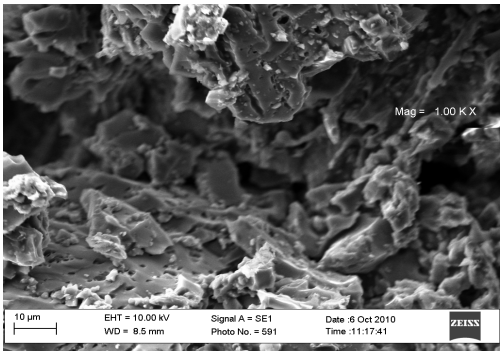

Fig 3.0 : linearised plots of MB adsorbance levels as a function of concentration for the three samples.

Using the intercepts from the linear equations and equations 1.0 and 2.0, the consequent specific surface areas were evaluated. The results are also in Table 2. The coconut shells were observed to have developed the highest surface area.

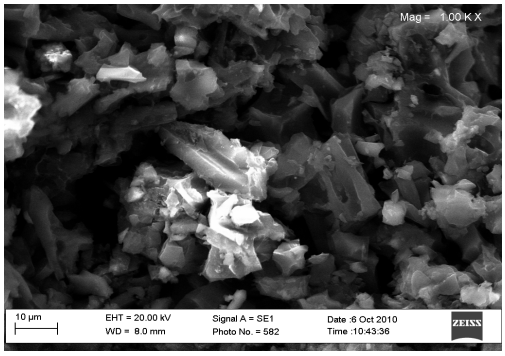
Table 2: Results of obtained specific nano surface areas.

| Activated Carbon sample | Experimental linear regression generated equation | Obtaiaed specific surface area.($m^2/g$) |
|---|---|---|
| PKS | $y = 8.996x + 0.379$ | 80.30 |
| CCS | $y = 9.742x + 0.173$ | 172.14 |
| MW | $y = 9.091x + 0.209$ | 140.08 |

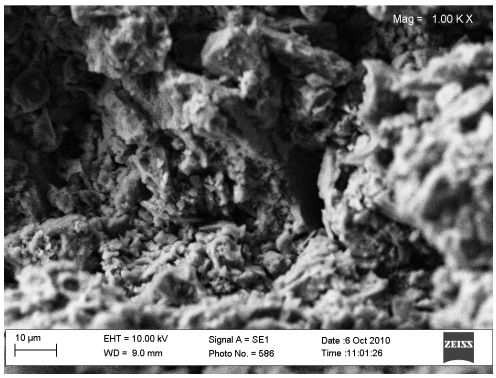
When compared with the other two materials the observed highest yield of charcoal from the Coconut shells was also carried over to its yield of AC with the highest surface area. The obtained value of $172.14 m^2 g^{-1}$ is however below the rangethat has been reported (Farma et al). This low value we attributed to the not very high activation temperature of $700^0$C. The capacity of the utilized furnace limited the temperature to this value. A higher activation temperature will most likely produce more surface areas from the same charcoals. The more defined structure of the coconut shells derived AC is also evident in the SEM plate of figure 4b.




4a : PKS ac.




4b : CCS ac.




4c : MW ac.

Fig: 4 SEM scans of KOH prepared activated carbons from Palm kernel shell, Coconut shells and Masonia wood.

At the x1000 SEM magnification employed, a 2nm micropore diameter will display as 2µm. Also a 50nm mesopore will be 50µm. Using the 10µm marker attached to the figures it is seen that most of the observable developed pores in the CCS AC are in the lower mesopores (4 – 6)nm range. The PKS AC sample seems to have larger mesopores. In all, the microscope resolution did not reveal the micropores.

All the activated carbons demonstrated effective and measurable levels of negative methylene blue ions adsorbance. It was also observed that the adsorbance from solution was made possible partly because the activated carbon got immersed in the solution in contrast to charcoal that floated when poured in water.

The peak optical absorbance of methylene blue dye is given in literature to occur at 609 and 668nm [5]. The peak absorbance of the particular brand employed this project was slightly shifted to 665nm. This shift was attributed to be due to either impurities or equipment calibration errors.

**4.0 CONCLUSION.**

The primary aim of preparing high surface area activated carbons is to make a large surface available for ions to adhere. This present study is geared partly at a comparative study of the yields and the adsorption abilities of the carbons obtained from three precursor materials and partly towards the exploitation of their demonstrated charge attraction and storage ability in the future production of high energy density power storage devices. It has been seen that the AC derived from the Coconut Shells do posses this property.

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**REFERENCES.**

Atkins P.W, (1999). Physical Chemistry 6th Edition. Oxford University Press, Oxford 0X2 6DP.

Barbieri O, Hahn M, Herzog A, Kotz R, (2005). Capacitance limits of high surface area activated carbons for Double Layer Capacitors. Elsevier Publishers, www.sciencedirect.com

Chen J.H, Li W.Z, Wang D.Z, Yang S.X, Wen J.G, Ren Z.F. (2001). Electrochemical characterisation of Carbon Nanotubes as electrode in electrochemical double layer capacitor. PERGAMON Carbon 40(2002)1193 – 1197). Elsevier Science ltd.

Cleiton A. Nunes E. Mario C. Guerreiro. (2011). Estimation of Surface Area and Pore volume of Activated Carbons by Methylene blue and Iodine numbers. Quim, Nova. Vol. XY. No. 00, 1-5, 2011.

Farma R, M. Deraman, Awitdrus, I.A. Talib, R.Omar, J.G. Manjunatha, M.M. Ishak, N.H. Basri, and B.N.M. Dolah. (2013). Physical and electrochemical properties of supercapacitor electrodes derived from carbon nanotube and biomass carbon. Int. J. Electrochem. Sci. 8 (2013) 257 – 273..

Itodo A.U, Abdulrahman F. W, Hassan L. G, Maigandi S.A, Itodo H.U. (2010). Application of Methylene Blue and Iodine Adsorption in the measurement of Specific Surface Area by four acid and salt treated Activated Carbons. New York Science Journal 2010 : 3(5).

Itodo A.U, Itodo H.U, Gafar M.K. (2010) Estimation of Specific Surface Area using Langmuir Isotherm method. J. Appl. Sci. Environ. Manage. Vol.14(4) 141 – 145.

Young-Jang Kim, Byoung-Ju Lee, Hiroaki Suezaki, Teruaki Chino, Yusuke Abe, Takashi Yanagiura, Ki Chul Park, Morinobu Endo. (2006) Preparation and characterization of Bamboo based Activated carbon as Electrode materials for Electric Double Layer Capacitors. Institute of Carbon Science and Technology, Shinshu University, 4-7-1 Wakasato, Nagano, Japan. yik@endomoribu.shinshu-u.ac.jp(y.j.kim)

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