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 $431.42 m^2 g^{-1}$, $623.60 m^2 g^{-1}$ and $547.00 m^2 g^{-1}$ respectively.
Keywords: Charcoal, Pyrolysis, Activated Carbon, 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. Energy is stored in the EDLC as charges held by adhesion onto large surface areas of pores in polarisable solid electrode that is immersed in an electrolyte. EDLC's have been realized using three principal types of electrode materials namely high-surface-area activated carbons, transition metal oxides, and electro- active polymers (Chen et al 2002). Activated Carbon (AC) is a form of carbon that has been processed to make it highly porous.   About one gram of AC could have a surface area of $500 m^2$ (Grubs 2009). It is derived from charcoal through pyrolysis and activation.   In this respect (Xu et al, 2007) used KOH activation to prepare AC and carbon nanotubes for EDLC. The workers reported that there was a linear dependence of the obtained capacitance on the surface area of the nanotubes. Also a large specific surface area (SSA) of carbon materials used for EDLC's is the most important parameter that leads to a large gravimetric capacitance (Babieri et al, 2005). In addition, a surface area range of between 446 to $1340 m^2 g^{-1}$ has 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 spectrophotomety. It is hoped that the AC so prepared will be suitable for preparing electrodes for Electric Double Layer Capacitors.

2.0 MATERIALS AND METHOD.

2.1 Materials :- The precursor materials were Palm Kernel shells, Coconut Shells and Masonia Hard wood. Activation agent was Potassium Hydroxide (KOH). Methyl red indicator was used to determine the absence of KOH from the samples after filtration.

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^oC for one hour. Each of the samples was then cooled to room temperature in separate calcium oxide desiccators. This was followed by taking specific weights from the samples with the aid of an "Ainsworh DE – 100" top loading balance and their natural structural densities evaluated by water displacement method.

The carbonization pyrolysis was implemented in a constructed stainless steel chamber inserted into a "Carbolite NTF 12/39/400" Tubular 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^oC and allowed to dwell at that temperature for one hour. The observed smoke emission which commenced at about 400^oC and stopped at about 550^oC was high in the three samples. After cooling to room temperature, the weights of the carbon yields were recorded.
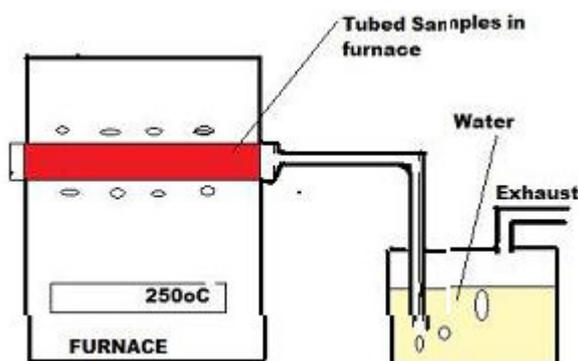
Fig. 1.0 Carbonization pyrolysis experimental set-up.

2.2.2 Activation:-   A mixture ratio of carbon to KOH of 1:3, was heated in the absence of air at 700°C for one hour (Young-Jung et- al 2006). 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°C, grinded to powder in a silica mortar and sieved with 250 microns Endecotts sieve.

2.3 Specific Surface Area (SSA) determination:- The first stage involved using an AVAspec 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 (10 - 25) mg/l.

The determination of the specific surface area was then implemented with the BET isotherm theory. In the theory, the rate of adsorption in reciprocal form is given by Equation 1 (Norwicki and Barbara, 2006), (Atkins 1999).

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

 Where x_o is concentration of available adsorption sites, c is concentration of adsorbate above the absorbent and k is adsorption constant

In use, x was measured experimentally at different values of c and a plot of 1/x versus 1/c prepared.   The total available surface area was evaluated by using equation 2.

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

Where 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, $a = 120A^2$ (Grubs 2009). Symbol A is the Angstrom unit.

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

By the application of the same method to the masses of the MB in solution, $M_2 = (A_2/A_1)*M_1$

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.

3.0 RESULTS AND DISCUSSIONS.
3.1 RESULTS
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.
PK	110	1.2048	36.5	40.1	59.9
CC	110	1.3158	33.7	37.1	62.9
MW	110	0.7692	16.2	17.8	82.2

During spectrometric absorbance measurements, the solutions were observed to exhibit peak optical absorbance at 660nm. 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.
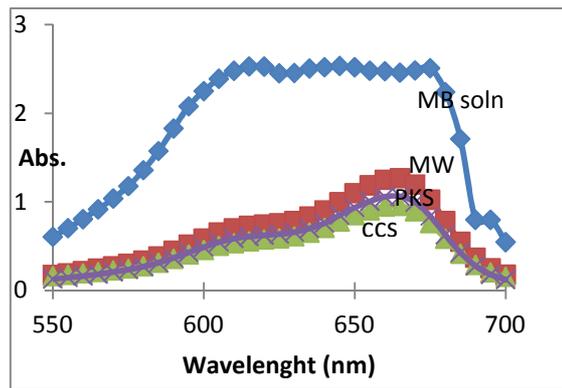
Fig 2 : Spectrophotometric absorbance plots of MB solutions before and after AC adsorbance.

Also the plot of the adsorbance as a function of methylene blue concentrations is presented in fig. 3.0. Using eqn. 1.0, 2.0 and linear regression analysis the consequent specific surface areas were evaluated. The values of 431.42, 623.62 and 547.00 (m^2/g) were obtained respectively for the PKS, CCS and MW derived activated carbons.
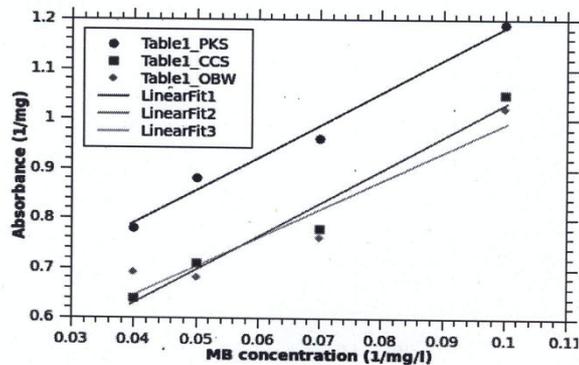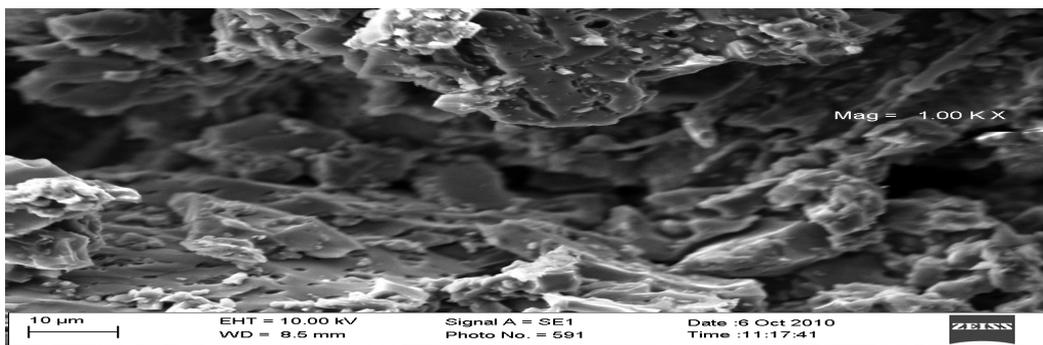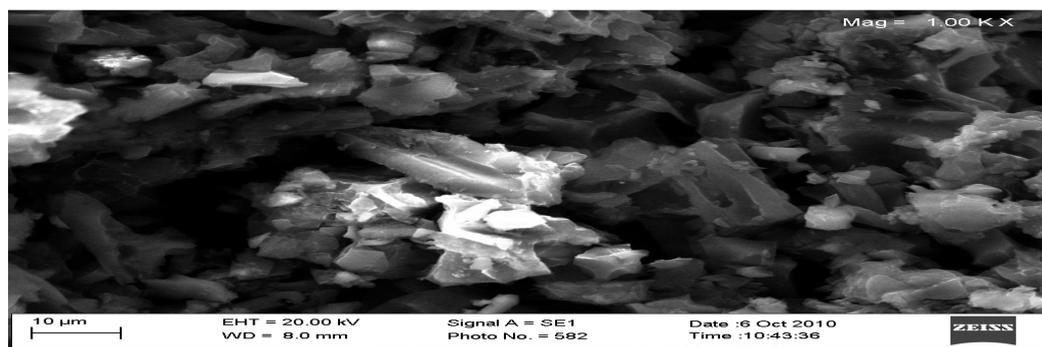
Fig 3.0 : linearised plots of MB absobance as a function of concentration for the three samples.
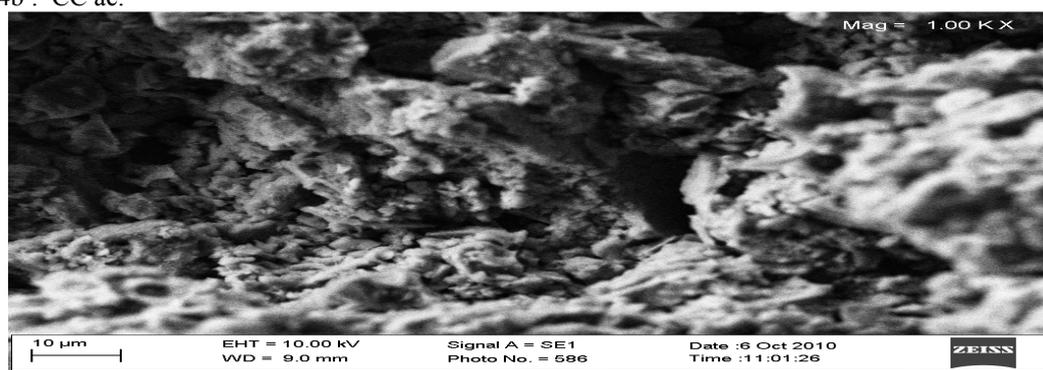
The CARL ZEISS MA10   Scanning electron microscope plots of the three prepared activated carbons is presented in fig. 4.

4a : PK ac.

4b : CC ac.

4c : MW ac.

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

3.2 DISCUSSIONS

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 coconut shells AC's clearly exhibited the highest surface area. Its value of $623.6 m^2 g^{-1}$ falls within the range reported by Mohammad et all. Their more defined structure is also evident in figure 4b.

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 while the pores developed in the MW could not be discerned. 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. This adsorbance from solution was made possible partly because the activated carbon got immersed in the solution in contrast to charcoal that floats.

The peak optical absorbance of methylene blue dye is given in literature to occur at 609 and 668nm (Atkins 1999).   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 studies 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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