

Comparative Analysis of Methods of Activated Carbon Surface Area Determination

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Abstract: *This work sought to determine the surface area (SA) of prepared activated carbons from palm kernel shells by two methods and to do a comparative analysis of the results obtained. The methylene blue adsorption test (MBT) gave a surface area in the range of 418 to 544 m²/g for the nine prepared activated carbons labelled A1 to C3. The surface area (S_{N2}) obtained by nitrogen gas adsorption< However, ranged from 17 to 217 m²/g. The surface area obtained for the prepared activated carbons by the MBT decreased in the following order: A1 > A2 > C1 > A3 > B1 > B3 > B2 > C2 > C3, while the BET surface area obtained by nitrogen adsorption for the activated carbons was in the order: A1 > A2 > A3 > C1 > B3 > B1 > B2 > C3 > C2. The order shows a comparable trend and it can be deduced that while the MBT measured the mesopore volume of the activated carbon, the nitrogen gas adsorption measured the micropore volume. The MBT was therefore in good agreement with the nitrogen gas adsorption method and can therefore provide a cheaper and affordable method to characterize the surface area of activated carbon.*

Keywords: *Surface Area, nitrogen adsorption, activated carbon, methylene blue*

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1.0 Introduction

The surface area is the major factor in the practical application of activated carbons as adsorbents (Asadullah *et al.*, 2006). Activated carbon is amorphous carbon composed of 85–95% C atoms covalently bonded in a flat hexagonal lattice (Anita, 2023). Activated carbons are often employed for purification purposes, separating toxic molecules, heavy metals, and dyestuffs from industrial waste and for recovery of valuable materials. The use of activated carbon shared advantages due to its low cost, and environmental friendliness (Abubakar *et al.*, 2023). Conventionally, activated carbon is produced through physical and chemical methods, involving activation and carbonization to open up the pores (Anita *et al.*, 2023, Dolas, 2023). Theoretically, the adsorption capacity of activated carbon significantly depends on its pore diameter and is related to its pore volume (Thang *et al.*, 2021). The porosity and surface area of activated carbon are therefore very important parameters that determine the overall performances of activated carbons (Asadullah *et al.*, 2006; Dolas, 2023).

Activated carbon operates through the mechanism of adsorption and the numerous

systems that have been developed for surface area measurement are based on this phenomenon. The determination of the surface area of activated carbon remains a huge challenge. The specific surface areas of different carbonaceous materials have been evaluated most often using, nitrogen, argon, and carbon dioxide adsorption. The adsorption of iodine has also been used for surface area measurement (Jalil, 2012). Iodine is however volatile and difficult to handle. Carbon dioxide adsorption has been employed to determine the surface area of porous materials because it is an inert gas which is easy to obtain and because of its liquid-like behaviour at near room temperature (Sudibandriyo, 2010).

The most widely used technique for surface area determination is that of nitrogen gas adsorption. The amount of gas adsorbed by a solid as a function of pressure is determined either gravimetrically or volumetrically and the surface area calculated from the adsorption isotherm by models such as Langmuir or Bruauer-Emmett-Teller (BET) isotherms. However, it has been reported that the amount of nitrogen adsorbed depended on the temperature and consequently the calculated surface area also depended on the temperature, which is unreasonable (Sudibandriyo, 2010). It is observed that the nitrogen gas is inert and interacts with the activated carbon surfaces weakly, hence the surface must be cooled substantially (up to 77 K) to cause measurable amounts of adsorption enough to cover the entire surface. The pore volume by the Dubinin-Radushkevich (DR) method and the surface area by the Bruauer-Emmett-Teller (BET) method, which is based on the adsorption of N_2 adsorption at $-196^\circ C$. Such low temperatures might affect the structure of the porous materials resulting in inaccurate surface area determination (Sudibandriyo, 2010; Dolas, 2023). The requirement of liquid nitrogen which is not always available added to the bottleneck of accessing the nitrogen adsorption method.

Methylene blue is considered a model adsorbate for adsorption studies due to its wide applications (Mousavi *et al.*, 2021; Abubakar *et al.*, 2023). Methylene blue in an aqueous solution is a cationic dye, $C_{16}H_{18}N_3S^+$, which adsorbs to negatively charge the surface hence the specific surface of adsorbent can be determined by the amount of adsorbed methylene blue (Santamarina *et al.*, 2002). Methylene blue adsorption is done in water suspensions to expose all available surface area. It therefore has the potential of evaluating the surface area of adsorbent by filling all categories of pores developed in the process of activation except for pores smaller than its size. In this study, a comparative analysis of the surface area of activated carbon determined by nitrogen and methylene blue adsorption was carried out.

2.0 Materials and Methods

2.1 Preparation of activated carbon

The activated carbons were prepared as reported in the literature (Abechi *et al.*, 2013). Palm kernel shells were collected from Sabo market in Zaria, Kaduna State, Nigeria. The palm kernel shell was removed, washed, dried and crushed using a locally made grinder. This was sieved to 1.18 mm and carbonized at $400^\circ C$ for 1 hour. A portion of the carbonized material was impregnated with KOH at an impregnation ratio of 1:1(KOH pallet: Char) at $80^\circ C$ with continuous stirring for 2 hours. The impregnated carbon was dried overnight at $120^\circ C$ after the excess solvent was removed using a vacuum pump. The dried sample was activated at temperatures of $800^\circ C$, $900^\circ C$ and $1000^\circ C$ for activation times of 15 minutes, 30 minutes and 45 minutes in a furnace. The activated carbons were gradually cooled to room temperature. It was washed using distilled water and then 0.1 M HCl until the washing water had a pH 7.0. The prepared activated carbons were finally dried at $120^\circ C$ overnight, cooled and stored for further studies.



2.3 Determination of Surface Area of Prepared Activated Carbon by Nitrogen Adsorption Test (NAT)

The Brunauer-Emmett-Teller (BET) Surface area and the pore structure characterizations of the activated carbons were determined by nitrogen adsorption at 77 K using an automatic micropolitics ASAP-2010 volumetric sorption analyzer in Hull City University, United Kingdom. Prior to nitrogen gas adsorption measurements, the carbon was degassed at 300 °C in a vacuum condition for 24 hours. Nitrogen adsorption isotherms were measured over a relative pressure (p/p^0) range from approximately 10^{-5} to 0.995. The BET surface area, mesopore volume and micropore surface area of the activated carbon were determined by the application of the Brunauer-Emmett-Teller (BET) and Dubinin-Asthakov (DA) analysis software respectively, available with the instrument. The BET surface area was determined using the standard BET equation applied in the relative pressure range from 0.06 to 0.3. The pore size distribution was calculated using the method of Guzel and Uzun (2002).

2.3 Determination of Specific Surface Area by Methylene Blue Adsorption Test (MBT)

The method of Abia and Asuquo (2006) was used in the determination of activated carbon surface area by methylene blue adsorption. 25 cm³ of methylene blue solution of initial concentration of 10, 20, 30, 40, 50 and 60 ppm were prepared using deionized distilled water and added to six conical flasks, containing 0.1 g (particle size = 825µm) of sample A1. The flasks were corked and agitated in an electric shaker for 60 minutes. The carbons were separated by filtration using the vacuum pump. The first 5 cm³ were discarded. The concentrations of the filtrates were determined using a UV-Visible spectrophotometer at λ_{max} of 660 nm. The experiment was repeated for the other samples (A2.A3....C3). The monolayer adsorption capacities/points of complete cation

replacement were determined from the Langmuir isotherm plot. The specific surface (SA) is given as (Abia and Asuquo, 2006)

$$SA = \left[\frac{M_{MB} \times A_V \times A_{MB}}{319.87} \right] \times \left[\frac{1}{M_S} \right] \quad (1)$$

In equation 1, M_{MB} = Amount of methylene blue adsorbed at the point of complete cation replacement, M_S = mass of adsorbent, A_V = Avogadro's number, 6.02×10^{23} and A_{MB} = Area covered by one methylene blue (assumed to be 130 \AA^2)

3.0 Results and Discussion

3.1 Surface Area and Pore Characterization of the Prepared Carbons:

The surface area is one very important parameter for the characterization of activated carbon. The specific surface area is defined as the accessible area of solid surface per unit mass of material (Kaewpravit, 1998). The surface areas of the activated carbons were estimated by both the methylene blue adsorption test and the nitrogen gas adsorption technique. The monolayer adsorption capacities which were used for subsequent calculation of the surface area of the carbons were obtained from the linear form of Langmuir's adsorption isotherm plot (Fig. 1 a – 1c).

The methylene blue adsorption test is based on the Langmuir adsorption isotherm. The monolayer adsorption capacities for the samples ranged from 7.41 to 9.62 mg/g. The surface areas were calculated from the Equation 2 (Bansal and Goyal, 2005):

$$SA = N n_m a_m 10^{-18} \text{ m}^2/\text{g} \quad (2)$$

where, N = avogadros constant = 6.023×10^{23} , $N n_m$ = number of moles at the monolayer coverage, a_m = molecular area of the adsorbate (1.200 for methylene blue). The surface area (SA) of the prepared activated carbons obtained by the methylene blue adsorption test (S_{MB}) method ranged from 418 to 544 m²/g (Table 1). Normally, large surface areas signify high adsorption of organic compounds, especially non-polar organic compounds.



Surface area is therefore an important attribute when considering the selection of adsorbents in the separation process (Rao *et al.*, 2003). The surface area obtained for the prepared activated

carbons by the S_{MB} decreased in the following order, A1 > A2 > C1 > A3 > B1 > B3 > B2 > C2 > C3

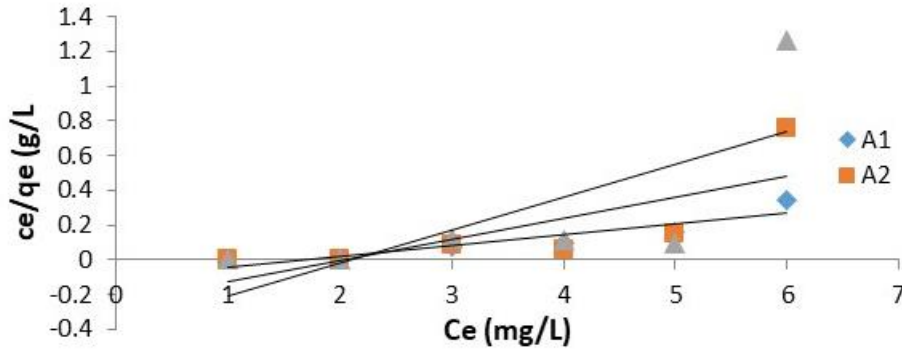


Fig. 1(a): Langmuir isotherm plots for adsorption of methylene blue onto carbons activated at 1000 °C

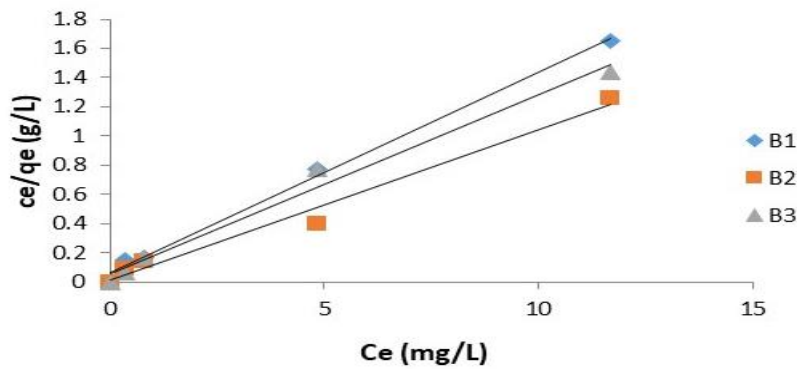


Fig.1(b): Langmuir isotherm plots for the adsorption of methylene blue onto carbon activated at 900 °C

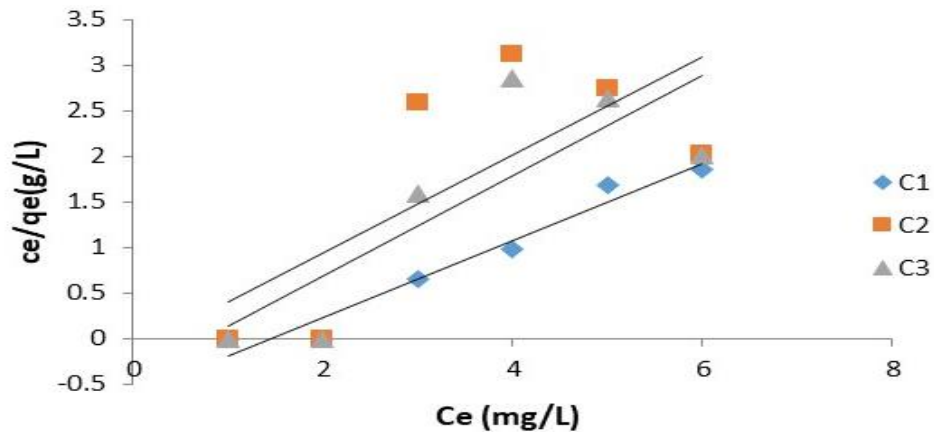


Fig. 1 (c) Langmuir isotherm plots for adsorption of methylene blue on carbon activated at 800 °C.



The surface area obtained by nitrogen gas adsorption (S_{N_2}) however, ranged from 17 to 217 m^2/g (Table 1). The BET surface area is in the order, $A1 > A2 > A3 > C1 > B3 > B1 > B2 > C3 > C2$

The MBT method is in good agreement with the nitrogen gas adsorption method and can be used for comparing the surface area of activated carbons from different sources or

prepared by different methods. The trend showed a comparable pattern and it can be deduced that while the MBT measured the mesopore volume of the activated carbon, the nitrogen gas adsorption measured the micropore volume. This accounts for the slight difference observed in the pattern for the two methods.

Table 1: The surface area and pore size characterization of the prepared activated carbons

Sample code	A1	A2	A3	B1	B2	B3	C1	C2	C3
S_{MB} (gm^{-2})	544	504	475	459	452	455	483	438	418
S_{N_2} (gm^{-2})	217	155	141	72	54	73	127	17	20
V_{μ} (cm^3g^{-1}) $\times 10^{-2}$	11.00	7.80	6.70	3.80	3.00	3.80	6.30	0.92	1.20
V_m (cm^3g^{-1}) $\times 10^{-2}$	1.00	1.20	0.40	1.00	0.70	0.50	0.30	0.58	0.50
V_{μ} (%)	94.04	87.52	95.49	84.89	82.58	86.52	95.31	70.80	74.79
V_m (%)	1.96	12.48	4.51	15.11	17.42	13.48	4.69	29.20	25.21
$V_T \times 10^{-2}$	12.00	9.00	7.10	4.80	3.70	4.30	6.60	1.50	1.60

**MBT surface Area (S_{MB}), N_2 BET surface Area (S_{N_2}), Micropore Volume (V_{μ}), Mesopore Volume (V_m), Microporosity contribution V_{μ} (%), Mesoporosity contribution V_m , Total pore volume (V_T).

Sample codes;

A1 (carbonized at 1000, activated for 45 min), A2 (carbonized at 1000, activated for 30 min) A3 (carbonized at 1000, activated for 15 min), B1 (carbonized at 900, activated for 45 min) B2 (carbonized at 900, activated for 30 min), B3 (carbonized at 900, activated for 15 min) C1 (carbonized at 800, activated for 45 min), C2 (carbonized at 800, activated for 30 min) and C3 (carbonized at 800, activated for 15 min)

Fig. 2 shows the Dubinin-Rushkevich (D-R) plot for the estimation of micropores of the prepared carbons from nitrogen gas adsorption at 77 K. The microporosity and mesoporosity contributions obtained from nitrogen gas adsorption decreased in the same order as the BET surface area (Table 1). The total pore volume ranged from 0.015 to 0.12 cm^3g^{-1} (Table 1) at the highest activation temperature of 1000 °C. Temperature and time of activation which are key factors in the preparation steps were varied to monitor the pore development in the carbon and to optimize the conditions for the preparation of the product (Fig. 3 (a) and (b)). The trend in pore development in the

precursor is such that the tiny micropores formed increased in number as the activation time increased from 15 to 30 minutes.

The very numerous pores formed collapsed to form larger ones of mesopores as the time was increased to 45 minutes. These developments are reflected by the surface area as these increased gradually with time of activation from 418 to 483 m^2/g . It is clear that as the temperature rose to 900°C, the mesopores collapse back to form once again micropores, the number of which increased with time of activation and temperature.



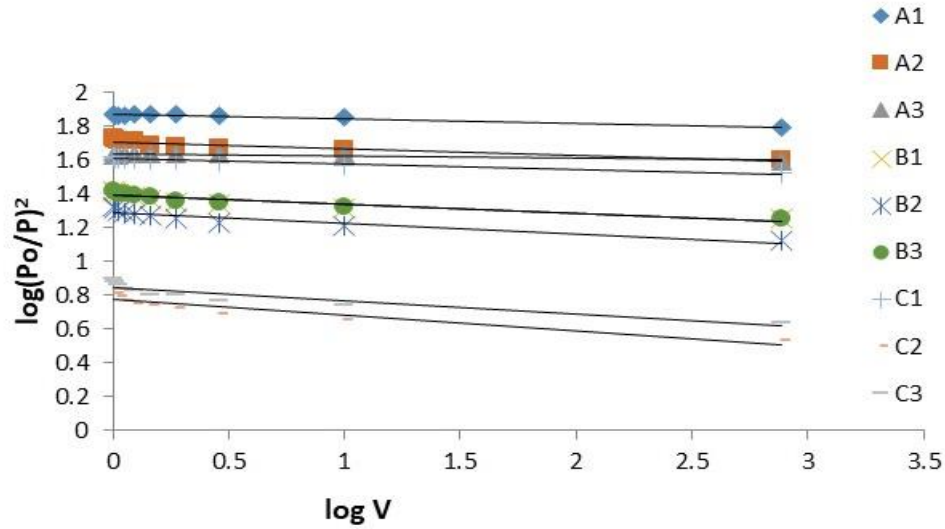


Fig. 2: D-R plots for the determination of micropore volumes of the carbons

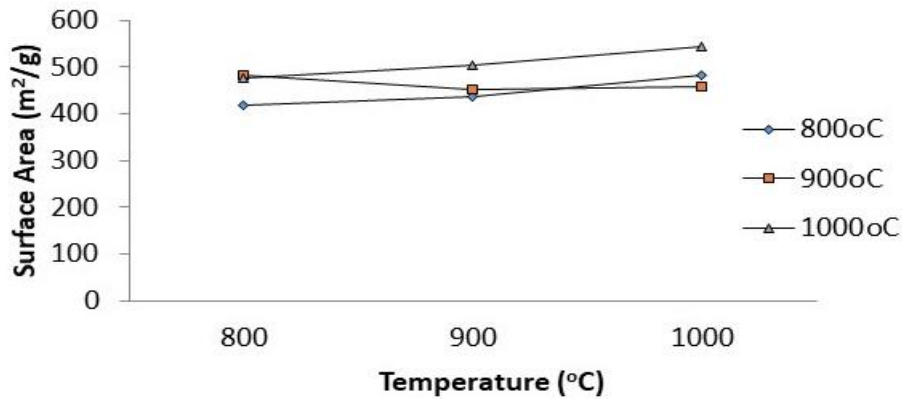


Fig. 3(a): Effect of temperature on MBT surface area of carbons.

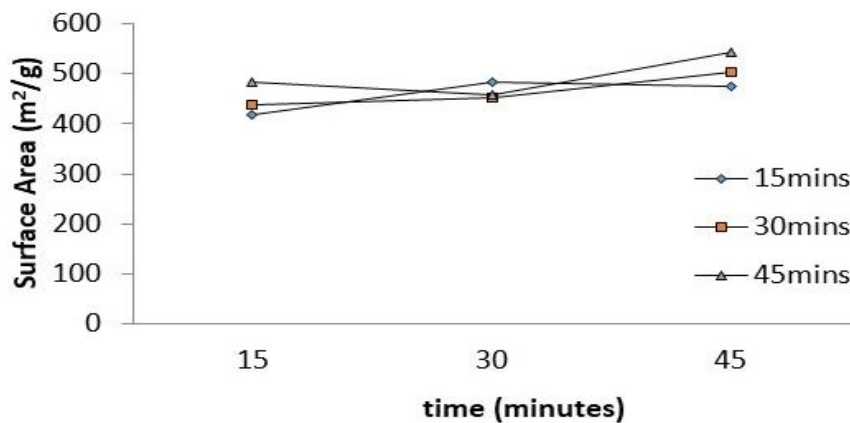


Fig. 3(b): Effect of activation time on MBT surface area of carbons

The internal pore structures of activated carbons may therefore be sub-divided into micropores (radii, $r < 1$ nm), mesopores ($r = 1-$

25 nm) and macropores ($r > 25$ nm). Micropores are especially responsible for the large surface area of activated carbons. The



surface area and pore volume are two important parameters which control the adsorption performance of activated carbons (Asadullah *et al.*, 2006).

Information on pore size distribution and pore structure on activated carbon is largely determined by the nature of the starting raw materials (Ismadji *et al.*, 2006). One other method for estimating the types of pores present in a solid, as employed by Daud and Ali, (2004), is by analyzing the isotherm curve. Adsorption isotherm is a graphical

representation of the relationship between the amount adsorbed and the pressure (concentration) at any constant temperature (Bansal and Goyal, 2005). Most isotherms have been shown to conform to one of the five types of IUPAC classification (Ismadji *et al.*, 2006). Fig. 3 showed that, samples A1, A2, A3, B1, B2, B3 and C1 conform to type 1 isotherm. This indicates that the carbons contain very fine micropores that have pores dimensions $< 20 \text{ \AA}$.

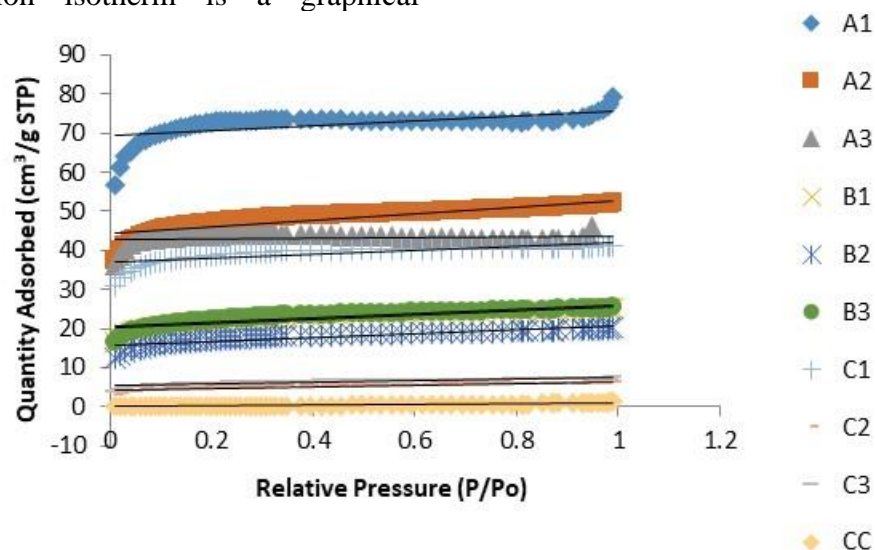


Fig. 3: N₂ - Adsorption isotherm for the samples at 77K

The potential field force from the neighbouring walls of the pores will overlap, causing an increase in the interaction energy between the solid surface and the adsorbate molecules, resulting in an increase in adsorption especially at low concentrations (Bansal and Goyal, 2005).

This may bring about complete pore fillings at low concentrations. However, at high concentrations, adsorption is small and tends to a constant as shown by the plateau that is almost horizontal and parallel to the concentration axis. The plateau is therefore due to the pores being so narrow that they cannot accommodate more than a single molecular

layer. The pore volume controls the size of the molecules that can be adsorbed, while the surface area controls the amount of material which can be adsorbed (Asadullah *et al.*, 2006). The type 1 isotherm is as such common to Chemisorptions. The samples prepared at the higher temperatures of 900 °C and 1000 °C therefore exhibit type 1 isotherm indicating that they are overwhelmingly microporous and there is a near absence of mesopores.

It was also observed that samples C2 and C3 conform to type II isotherm. These samples were prepared at a relatively lower temperature of 800 °C and activated at a relatively low resident time of 30 and 15 minutes respectively. The conformation to type II



isotherm is an indication that samples C2 and C3 are nonporous, where the surface is wholly external. This explains why the BET surface areas are relatively low. The inflection point or kneel of the isotherm as shown in Fig. 3 usually marks the point of completion of monolayer adsorption. Increasing the relative pressure lead to the formation of second and higher layer until the number of adsorbed layer becomes infinite.

The carbonized sample, (CC, the inactivated carbon), exhibits type III isotherm as shown in Fig. 3. The type III also corresponds to nonporous or highly macroporous adsorbent. This, again, accounts for the very low BET surface area of three (3) gm^{-2} . The isotherm is characterized by being convex to the concentration axis. The convexity continued throughout the isotherm. The heat of adsorption is close to the heat of liquefaction, so the net heat of adsorption is very small and close to zero.

4.0 Conclusion

The surface area obtained for the prepared activated carbons by the MBT decreased in the following order, **A1 > A2 > C1 > A3 > B1 > B3 > B2 > C2 > C3**

The BET surface area is in the order, **A1 > A2 > A3 > C1 > B3 > B1 > B2 > C3 > C2**

The order shows a comparable trend and it can be deduced that while the MBT measured the mesopores volume of the activated carbon, the nitrogen gas adsorption measured the micropore volume. This accounts for the change in the positions of A3/ C1, B1/B3 and C2/C. The MBT method was therefore in good agreement with the nitrogen gas adsorption method and can be used for comparing the surface area of activated carbons from different sources or prepared by different methods.

Samples **A1, A2, A3, B1, B2, B3 and C1** conform to type 1 isotherm, indicating that they are overwhelmingly microporous and there is a near absence of mesopores and have pores dimensions $< 20\text{\AA}$. The type I isotherm is characteristic of chemisorptions. However,

samples **C2 and C3** conform to type II isotherm, indicating that they are nonporous or that their pores are in the macropore region.

The methylene blue test can therefore provide a cheaper and affordable method to characterize the surface area of activated carbon.

5.0 References

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Compliance with Ethical Standards Declarations

The authors declare that they have no conflict of interest.

Data availability

All data used in this study will be readily available to the public.

Consent for publication

Not Applicable

Availability of data and materials

The publisher has the right to make the data Public.

Competing interests

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Authors' contributions

Stephen Eyije Abechi conducted the research, with Casimir Emmanuel Gimba and Adamu Uzairu as the supervisory team. Odike Jotham Ocholi provided access to the necessary equipment and edited the manuscript.

