COMPARISON OF BET AND WATER ADSORPTION TECHNIQUES

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ABSTRACT

The effect of activated carbon surface area on the amount of fluid adsorbed is significant. Thus, the surface area of an adsorbent is an important factor. The use of the costly BET measurement method is the standard. However, water adsorption method was proposed as an alternate method. Nevertheless, results presented were for activated carbon prepared and surface areas reported were based on BET literature values. In this study, chemically activated carbons were produced from corn cobs by impregnation using 25 wt% $CaCl_2$ as activating agent. Surface area of the activated carbons was then determined using both BET technique and water adsorption techniques by determining the volume at monolayer coverage. Comparison between the results of surface areas obtained from the two techniques was performed. From the present experimental investigations, water adsorption technique showed a wide range of deviation with increase in surface area of adsorbent. It was established from the analyses that water adsorption technique approximate the BET technique reasonably well for surface areas below $200 \ m^2 \ g^{-1}$, above this value results from water adsorption technique are not reliable.

Keywords: BET, Water Adsorption, Activated Carbon, Surface Area Measurement

1. INTRODUCTION

The use and efficiency of activated carbon as an adsorbent is well established. Activated carbon enjoys a wide range of considerable application and has brought about diversification of its usage (Zuorro and Lavecchia, 2010) separation processes, electron base material for manufacture of high-performance double layer super capacitors and storage for large quantities of CH_4 and H_2 at the same pressure (Kim *et al.*, 2001), wastewater and drinking water treatment and as electrode base material for super capacitors. Among the factors making the activated carbon application attractive are (i) availability, (ii) environmentally friendly material, safe and very low cost of the starting materials coupled with its high surface area. This relationship between surface area and the extent of adsorption has led to the development of highly porous material with areas as high as $3,000 \ m^2 \ g^{-1}$ (Tseng, 2007; Kim *et al.*, 2001; Lillo-Rodenas *et al.*, 2001).

Abundant literature exists on the methods of activated carbon production namely chemical and physical activation but the chemical method have been established to be more effective than physical activation in terms of obtaining higher surface areas (Teng *et al.*, 2000; Lillo-Ródenas *et al.*, 2003).

There are various methods of determining surface areas of an adsorbent which include water adsorption (Adefila *et al.*, 2003), inverse of iodine value (Okafor and Aneke, 2005) and BET machine. The most reliable and recognized internationally results are those obtained from BET machines. However, as mentioned in literature, traditional methods are somewhat time-consuming and require costly equipment (Abayazeed and El-Hinnawi, 2011). In our case, there are three major identified drawbacks to using the BET technique in developing countries namely purchasing cost (because average cost the BET machine stands at about $100,000.00), energy/power (because the machine needs constant power supply for its operation; average

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time of degassing a sample is 16 h while the analysis time ranges from 20-50 h) and operating cost (because the procedure consumes a lot of liquid nitrogen at temperature of-198.5°C). This brought about the development of water adsorption technique by the researchers Adefila *et al.* (2003), the technique utilizes water vapor as the adsorbate from saturated solution of salts at ambient conditions. Thus BET and water adsorption techniques are the only techniques that involves isothermal physical adsorption of a fluid on solid surface at low temperatures in the pressure range where a monomolecular layer of fluid is adsorbed on the adsorbent surface.

This study was aimed at preparing activated carbon adsorbents from corn cobs, determining the surface areas of same samples using both BET and water adsorption techniques and comparing the results obtained to ascertain the validity of results from water adsorption technique.

2. MATERIALS AND METHODS

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2.1. Sample Preparation

The precursor was obtained from Shika farms of A.B.U. Zaria; it was grounded in a roll crusher and sieved to the desired particle size of 350 µm. Analytical grade (BDH) $CaCl_2$ was used as the chemical activation agent. Deionized water was used for preparing saturated solutions of $CaSO_4,$ LiCl, $CaCl_2$ and NaCl.

2.2. Production of Activated Carbon

Activation of the samples was carried in muffle furnace which does not allow air thus limiting excess air necessary for combustion. Activation temperature of 550°C and activation time of 2h was used for activating the precursor.

Samples were weighed into a crucible and charged into the furnace and switched on, at temperature of about 550°C the system was allowed to remain for the period of the activation time and the furnace is switched off at the end of the desired time.

High purity nitrogen gas was introduced at a rate of 150 mL min^{-1} (enough pressure to maintain an inert environment without flushing the sample). The activated corn cobs were then removed from the furnace at the end of each activation time using metal forceps allowed to cool in a dessicator to room temperature and weighed.

The resulting final product were all rinsed with distilled water (Gua and Lua, 2003) and dried in an oven (Gallenkamp, OV-420) at 100°C overnight and kept in an air tight nylon envelope (Odebunmi and Okeola, 2001).

2.3. Characterization of Activated Carbon

2.3.1. Determination of Apparent Density

Sample was placed in a previously weighed glass tube and the new weight recorded. It was tapped until there was no change in volume and the tube and its content reweighed. The weight difference is calculated and Equation 1 (Ahmedna *et al.*, 1997; Akinyemi and Taiwo, 2004) was used to calculate the bulk density:

$$\% \text{ Apparent density} = \frac{\text{weight of sample}}{\text{volume of sample}} \times 100\% \qquad (1)$$

2.4. Determination of Solid Density

An Ultrapycnometer (UPY 1000) was used to determine the solid density. Samples were weighed on a weighing balance, placed in the sample holder of the machine and the relevant options selected.

2.5. Porosity

This was calculated from the values of true and bulk densities (Ahmedna *et al.*, 1997) obtained above for each sample using Equation 2:

$$\% \text{ Porosity} = \frac{\text{Apparent density - SolidDensity}}{\text{Apparent density}} \times 100\% \qquad (2)$$

2.6. Surface Area Determination

2.6.1. Water Adsorption Technique

Saturated solution of the four salts $CaSO_4$, LiCl, $CaCl_2$ and NaCl was prepared by dissolving the salts in a 100 mL beaker using deionised water.

Sixteen (16) plastic containers with air tight covers were obtained and four (4) sample were weighed from the activated carbon and placed in four (4) of the plastic containers. Each of the saturated was weighed into four (4) petri dishes, placed into the covered plastic containers and the containers covered. All the containers were left for 24h to reach equilibrium after which the difference in weight was determined (Adefila *et al.*, 2003).

2.7. BET Technique

Sample cell with 9mm bulb diameter was weighed empty, sample C224 put into the cell and placed in the heating mantle. Clamp was set in place, cell inserted into the fitting and tightened on outgassing station 1 on the front panel of the BET machine (AUTOSORB-

1, Quantrachome). A degassing temperature of 300°C was selected and the heating mantle switched on. Mantle power and thermocouple connectors were then plugged into the jacks, mantle was placed over the sample cell, a clamp was slided over the mantle and the heater enable switch was turned on.

The outgassed sample was immediately transferred to the p/po analyses station dewar which has a thermistor level sensor that detect and control (raise or lower) the level of the dewar during analyses when the stem cell is not fully dipped in the liquid adsorbate.

3. RESULTS

The amount of water adsorbed on the surface of the activated carbon after equilibrium from the saturated solutions of the salts is presented in **Table 1** and **Table 2** relative humidity and volume of water adsorbed values for all samples. The outputs from the BET surface area analyser (AUTOSORB-1) are presented alongside the computed surface area from water adsorption in **Table 3**. Porosities and densities calculated are also shown in the table.

Table 1. Amount of water adsorbed by samples with each salt

S/No	Sample	$CaSO_4$	LiCl	$CaCl_2$	NaCl
1	C224	0.2246	0.1983	0.2292	0.1881
2	C212	0.2246	0.1421	0.0771	0.1347
3	C203	0.0534	0.0725	0.0193	0.0367
4	C206	0.1147	0.0195	0.0463	0.0559

ACC203: Activated corn cobs for 2 and 03h impregnation time; ACC206: Activated corn cobs for 2 and 06 h impregnation time; ACC212: Activated corn cobs for 2 and 12h impregnation time; ACC224: Activated corn cobs for 2h and 24h impregnation time;

Table 2. Relative humidity and volume of water adsorbed values for all samples

Sample	Salt	Salt	V (g/g)	(P/P_o) (1/V)
C224	$CaSO_4$	0.0100	0.2246	00.0445
	LiCl	0.1130	0.1983	00.5698
	$CaCl_2$	0.3230	0.2292	01.4092
	$NaCl_2$	0.7530	0.1881	04.0032
C212	$CaSO_4$	0.0100	0.1094	00.0914
	LiCl	0.1130	0.1421	00.7952
	$CaCl_2$	0.3230	0.0771	04.1894
	$NaCl_2$	0.7530	0.1347	05.5902
C206	$CaSO_4$	0.0100	0.1147	00.0872
	LiCl	0.1130	0.0195	05.7945
	$CaCl_2$	0.3230	0.0463	06.9762
	$NaCl_2$	0.7530	0.0559	13.4705
C203	$CaSO_4$	0.0100	0.0144	00.6944
	LiCl	0.1130	0.7410	00.1525
	$CaCl_2$	0.3230	0.0915	03.5301
	$NaCl_2$	0.7530	0.0391	19.2583

RH: Relative Humidity V_m: Volume of water adsorbed

Table 3. Surface area, densities and porosities data of the activated carbon

S/No	Sample	BET	Water adsorption
		$(m^2\ g^{-1})$	$(m^2\ g^{-1})$
1	C224	385.16	764.24
2	C212	294.10	579.68
3	C206	147.53	198.95
4	C203	211.33	245.33

4. DISCUSSION

Salts with low relative humidities were selected because they give better results than salts with high relative humidities (Adefila *et al.*, 2003). The adsorption isotherms were plotted in order to obtain the volume at monolayer coverage (V_m). The slope of the figures gives $1/V_m$ which was then used to obtain the surface area by employing Equation 3 (Adefila *et al.*, 2003):

$$S_g = 3897.63V_m\ (m^2/g) \tag{3}$$

From **Table 3**, it is seen that impregnation time directly affect the surface areas and porosities of the adsorbent as evident in the linear increase of those two parameters with increase in impregnation time. Also water adsorption surface areas are observed to be higher than BET.

The wide difference of surface areas observed in the two techniques for the adsorbents could be attributed to the fact that to achieve monolayer coverage the adsorbate used in BET technique was nitrogen gas which has a molecular size of 16Å while water adsorption uses water molecule which has a molecular size of 2.8Å as such all the micropore volume in the adsorbent would not be accessible in the water adsorption technique as micropore has pore width of 20Å.

5. CONCLUSION

From the result of the analysis it has been found that comparing the BET surface areas values with water adsorption values for the activated carbon samples shows that water adsorption technique closely approximates water adsorption technique for surface area determination for sample with surface around areas exceeding 200 $m^2\ g^{-1}$.

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