Application of Methylene Blue and Iodine Adsorption in the Measurement of Specific Surface Area by four Acid and Salt Treated Activated Carbons.

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ABSTRACT: In order to further characterize the adsorptive nature of locally sorted activated carbon in technologically deficient Laboratories, this team utilizes the application of Methylene blue and Iodine number adsorption to estimate surface area and activated carbon performance. Mesopores structural parameters (S_{MB}) in $10^{-3}km^2kg^{-1}$ was estimated to range between 14.545-15.100,13.548-14.011,12.313-13.970 and 14.275-14.551 for the Groundnut shells(GS),Sheanut shells (SS),Poultry droppings (PD) and Poultry waste (PW) sorbents respectively. Their corresponding degree of activation and micropores level was presented as IAN (in mlM iodine per gramme of activated carbon) following the range of 2.156-2.171,2.174-2.191,2.163-2.193 and 2.157-2.168.The data were only slightly lower than those of commercial reference carbon (S_{MB} =15.627$10^{-3}km^2kg^{-1}$ and IAN= 2.230 mlM/g) and of wide difference to those of their respective pyrolized materials. Methylene blue sorption efficiency (%RE) was also estimated. [New York Science Journal 2010;3(5):25-33]. (ISSN: 1554-0200).

Key words : Methylene Blue, Iodine number, Surface area, Activated carbon

1.   INTRODUCTION

The concept of "zero emission" was proposed to be an idea of reducing environmental impact produced by discarded waste products and increase the effective and repeated   utilization of resources (Yoshiyuki and Yukata, 2003).Various carbonaceous material, such as coal, lignite, coconut shell, wood and peat are used in the production of commercial activated carbon (Bansode *et al.,* 2003). However, the abundancy and availability of Agricultural by products make them good sources of raw materials for activated carbon. Thermo – chemical processes such as pyrolysis have been widely applied to biomass. Pyrolysis is one form of energy recovery process with high potential of generating char, oil or gas products. Because of the thermal treatment, the biomass loses moisture and volatile matter content, thereby, possessing a different quality and properties that makes the char different from the precursors. The remarkable difference are mainly porosity, surface area, pore structure (micropore, mesopores and macropores/ and physiocohemical properties such as composition,   ash,   and   elemental   analysis (Zabaniotou and ioannidou, 2006). These changes in

properties usually lead to high reactivity, an hence, an alternative usage of char as an adsorbent material become possible.Thus, the char becomes an attractive by product, thus, attracting the interest of many researchers. Tsai *et al* worked on the preparation of AC from corn cob. According to this research, the parameters, which largely influence the products of pyrolysis are temperature, particle size heating rate and residual time. Others are the nature of biomass, nature of chemical used etc. Any cheap material with high carbon content and low inorganic can be used as raw material for the production of AC (Tsai *et al.,*2001).The evaluation of different grade of GAC adsorbent for scavenging priority pollutants from waste water was reported by shaski and Tenkie, (2002).

Yulu *et al.,* (2001) stated that phosphoric acid is preferred because of the problem of corrosion, inefficient recovery and environmental disadvantage of $ZnCl_2$. In their research on phosphoric acid activation of grain sorghum, 35% phosphoric acid was employed at 600 and 500°C for the one and two stage processes respectively(Yulu *et al.,*2001).

Properties   and   characteristics   of Agricultural   residues   were   studied   by   various

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authors(Tsai *et al.*,1997; Savara *et al.*,2001, Ahmedna *et al.*,2000 etc). In their reviews Zabaniotou and Ioannidou, (2006), presented yield, surface area, pore size and volume, Burn off, iodine number, molasses number methylene blue adsorption, apparent density, Hardness (abrasion) number, Ash content, particle size, adsorption etc as properties whose studies are essential.

Characterization of Activated Carbon:
The performance of A.C is characterized by the following parameters or properties, Iodine Number, Molasses, Tannin, Methylene blue, Apparent density, Hardness/ Abrasion number, Ash contents, Carbon tetrachloride activities, and particle size distribution.

(A)Iodine adsorption number: This is the most fundamental parameter used to characterize activated carbon performance. It is a measure of activity level (Higher degree indicates higher activation), often reported in mg/g (with typical range of 500 – 1200 mg/g). It is a measure of the microspore content of the activated carbon (values > 0 to 20 A^O, or up to 2nm) by adsorption of iodine from solution. It is equivalent to surface area of activated carbon between $900 m^2/g$ and $1100/m^o/g$ and. (Elliot *et al.,* 1989). It tells of carbon that preferentially adsorb small molecules.

(B)Methylene blue Adsorption: Some carbon have mesopores structure which adsorb medium size molecules such as dye Methylene blue. Methylene blue adsorption is reported in g/100g (range of 11-28g/100g) (Elliot *et al.*, 1989). Methylene blue was chosen in this study because of its known strong adsorption onto solids and its recognized usefulness in characterizing adsorptive material Methylene blue has a molecular weight of 373.9×10^{-3} kg mol^{-1}

Principles: The Langmuir equation was used to calculate the specific surface area of the sorbents. The general form of Langmuir isotherm is as Eqn. 1:
$$Y=KC/(1+KC) \quad - \quad - \quad (1)$$
where *Y* is the fraction of sorbent surface covered by adsorbed methylene blue molecules, *K* is a constant, and *C* is the equilibrium methylene blue solution concentration. In this research, $Y = N/N_m$, where *N* represents the number of moles of methylene blue adsorbed per gram sorbent at equilibrium concentration, *C*, and *N*m is the number of moles of methylene blue per gram of sorbent required to form a monolayer. After making the substitution and rearranging Eqn. 2, we obtain :
$$C/N=C/N_M + 1/KN_M \quad - \quad - \quad (2)$$

For all adsorption isotherms of methylene blue. A plot of *C*/*N* vs. *C* gives a straight line with slope equal to 1/*N*m, and intercept equal to 1/*KN*m. Therefore, the Langmuir isotherm is an adequate description of the adsorption of the methylene blue onto sorbents. The specific surface area was calculated by equation 3 (Chongrak *et al.*,1989):
$$S_{MB}=(N_g \times a_{MB} \times N \times 10^{-20})/M \quad - - \quad (3)$$
where S_{MB} is the specific surface area in $10^{-3} km^2$ kg^{-1}; *N*g is the amount of methylene blue adsorbed at the monolayer of sorbents in kg kg^{-1} .(In this research we defined experimental q_e as Nm,which is the amount methylene blue adsorbed at the monolayer of sorbents in mg/g or 10^{-3} kg/kg), a_{MB} is the occupied surface area of one molecule of methylene blue $=197.2$ $Å^2$ (Graham,1955) ; *N* is Avogadro's number, 6.02×1023 mol^{-1}; and *M* is the molecular weight of methylene blue,$373.9 \times 10^{-3} Kg$ $mol^{-1.}$

2. MATERIALS AND METHODS
The substrates were Groundnut shells (GS), Shea nut shells (SS), Poultry wastes (PW), and Poultry droppings (PD). They were collected from local oil mill at Sokoto, Rikoto- Zuru, while PW and PD were obtained from Labana farms, Aliero in Kebbi state respectivelly.

Sample treatment. Precursors: The method of sample treatment by Fan *et al.*, (2003);Itodo *et al* .,(2009a &b) were adopted. The samples were separately washed with plenty of water to removes surface impurities and sundried . each samples was dried in an oven at 105^OC overnight (Omonhenle *et al.,*2006). The samples were separately pounded/ grounded followed by sieving with a <2mm aperture sieve. The less than 2mm samples were stored in airtight containers.

Pyrolysis: About 3g of each pretreated biosolid (< 2mm mesh size) were introduced into six (6) different clean and pre weighed crucibles. They were introduced into a furnace at 500^Oc (PW and PD),600^oc (GC and SS) for 5 minutes after which they were poured from the crucible into a bath of ice block. The excess water was drained and the samples were sun dried. This process was repeated until a substantial amount of carbonized samples were obtained (Gimba *et al.,*2004;Turoti *et al.*,2007).The carbonized sample was washed, using 10% HCl to remove surface ash, followed by hot water wash and rinsing with distilled water to remove residual acid (Fan *et al.*, 2003) the solids were then sun dried, then, dried in the oven at 100^OC for one hour (Itodo *et al.,*2009a & b).

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Activation (one step process)
Approximately 3g of each pretreated (raw sample), of < 2mm mesh size) were mixed separately with $3cm^3$ of each 1M activating agent (H_3PO_4, $ZnCl_2$) .The sample mixtures were subjected to the furnace at 800^OC for 5 minutes. The samples were removed, poured into ice water bath, excess water was drained and allowed to stand at room temperature. The procedure was repeated for different residual time (5min, 10min) for the different activating agents (Turoti *et al.,*2007).The activated carbon generated above were washed, using 10% HCl (Fan *et al,* 2003) to removed surface ash, followed by warm water. Rinsing was done with distilled water to removed residual acid (Fan *et al*., 2003).The sample was then dried in an oven at 110^OC overnight and ball milled into sizes that passes through both <0.5 and< 2mm sieve (Fan *et al*., 2003). Washing was complete when a pH of 6-8 was ascertained (Ahmedna *et al.,* 2000).

Activation (two step process)
Accurately weighed 2g each of already carbonized samples were separately mixed with $2cm^3$ of each 1M activating agent (H_3PO_4 and $ZnCl_2$). The samples were introduced into a furnace, heated at 800^Oc For 5 minutes. The activated samples were cooled with ice cold water. Excess water was drained and samples were allowed to dry at room temperature (Turoti *et al*.,2007). The above procedure was repeated for different residual time (5min and 15 min).Washing of the above sample was done with 10% HCl to remove surface ash, followed by hot water and rinsing with distilled water to remove residual acid (Fan *et al*, 2005). Washing was completed when pH of the supernatant of 6-8 was ascertained (Ahmedna *et al.,* 2000). The sample were dried in an oven at 110^OC overnight and milled or grounded, followed by filtration to different mesh size and stored in air tight container.

Methylene blue stock(1000mgl[-1]) and standard solution
Procedure: Methylene blue was dried at 110°c for 2 hours before use. All of the Methylene blue solution was prepared with distilled water. The basic dye (Methylene blue) was used without further purification.

(i) A stock solution of 1000mgl[-1] was prepared by dissolving 1.127g Methylene blue in 1000ml distilled water (Omomnhenle *et al.*, 2006). This gives the Methylene stock. The experimental solution was prepared by diluting the stock solution with distilled water (to between 10 and 50mgl [-1]. The concentration

of MB was determined at 630nm by the UV – visible spectrophotometer (Chongrak *et al.,*1998).

(ii)A calibration curve of optical densities against methylene blue concentrations was obtained by using standard methylene blue solutions of known concentrations at pH values between 7 and 8. This was done to verify the wavelength for a 50mg/L concentration. An adsorption study was carried out to find the equilibrium time. This time was determined by a series of absorbance

Preparation of 0.1M sodium thiosulphate solution.
Procedures: About $500cm^3$ of distilled water was boiled for 15mins and allowed to cool followed by the dissolution of 25g Sodium thiosulphate $(NaS_2O_2.5H_2O)$ in it. The resulting solution was further made up to the mark in a 1L volumetric flask with distilled water. The solution was used immediately and so this precluded its usual preservation treatment by adding 0.1g Sodium carbonate (Na_2CO_3), 3 drops of Chloroform and storage in a dark place (Aziza *et al*., 2008, Igwe and Abia, 2003).

Preparation of 0.02M Potassium iodate.
Procedures: 4.28g Potassium iodate was accurately weighed and dissolved in a minimum of distilled water in a 250ml beaker. The solution was finally made to the 1litre-graduated mark to give a 0.02M solution (Aziza *et al*., 2008, Igwe and Abia, 2003).

Standardization of sodium thiosulphate solution.
Procedures: A 25ml aliquot of the prepared standard was pipetted into a 25ml Erlenmeyer flask. 1g of KI was added and the mixture was swirled for dissolution. $3cm^3$ of 1M H_2SO_4 was added and the liberated Iodine was immediately titrated with the Thiosulphate solution, with a constant shaking until the solution becomes pale yellow. The solution was then diluted to $100cm^3$ followed by the addition of 2ml freshly prepared starch indicator solution. Titration of the resulting blue black solution was resumed with constant swirling to the disappearance of the blue black coloration. The entire procedure was repeated 3 more times for each set of sample. The concentration of the thiosulphate was determined from the average titre value and the concentration of iodate the stoichiometry of the reaction equation (Aziza *et al*., 2008, Igwe and Abia, 2003).

Preparation of 0.02M iodine solution
Procedure: 20g iodate free KI was dissolved in 40ml distilled water in a glass stoppered $1000cm^3$

volumetric flask 12.7g of Iodine was weighed and transferred by means of small dry funnel into the concentrated KI solution. The flask was stoppered and shaken while still in cold until all the Iodine dissolved. The solution was allowed to attain room temperature and made to the mark with distilled water (Aziza *et al*., 2008).

Preparation of 1% starch indicator
Procedure: A paste was made of 1g Starch with little water and poured with constant stirring into 100ml of boiling water and allowed to boil for 1 minute. The solution was allowed to cool and stored. (Aziza *et al*., 2008; Igwe and Abia, 2003).

Standardization of iodine solution
Procedure: 25cm^3 portion of iodine was transferred by means of measuring cylinder to a 250cm^3 Erlenmeyer flask. The contents of the flask were diluted to 100ml and titrated with standardized thiosulphate solution from a burette until the solution turn pale yellow. 2ml of freshly prepared starch indicator were added and the titration with thiosulphate resumed slowly until the solution was became colorless. The procedure was carried out two more times with concentrated Iodine solution and concentration of the Iodine solution was determined from the average titre value of the standard thiosulphate and the stoichiometry of the reaction equation (Aziza *et al*., 2008).

Determination of iodine adsorption number of sorbent
0.5g AC from each precursor was weighed into a beaker and 25ml of standard Iodine solution (0.0229M) confirmed concentration after

standardization was added. The mixture was swirled vigorously for 10mins and filtered by means of a funnel impregnated with clean filter paper. 20ml of the clear filterate was titrated with the standard (0.1115M) thiosulphate confirmed concentration after standardization to a persistence of a pale yellow color. 5ml of freshly prepared Starch indicator solution was added and titration resumes slowly until a colorless solution appeared, the procedure was repeated for two more times.The titration was also repeated with 20cm^3 portions of the standard iodine solution (not treated with AC from the precursor) to serve as blank titration. The iodine adsorption number (IAN) was calculated from the relationship as equation 4;

$$IAN = Ms (Vb - Vs) / 2Ma - - - (4)$$

Where: Ms = molarity of thiosulphate solution (mol/dm^3).

Vs = volume of thiosulphate (cm^3) used for titration of the PAC aliquot.

Vb = volume of thiosulphate (cm^3) used for blank titration.

Ma = mass of AC (g).

measurements extending from 2 to 12 hours at 27±2°C on reference carbon It was noted that the curve seems to reach complete equilibrium (least absorbance or highest adsorption value) in about 8 hours, then, fluctuations in plateau sets in before the 10th hour of adsorption. Therefore, we suppose that the adsorption of methylene blue onto the adsorbent has reached its maximum capacity. Consequently, this time was chosen as interaction time for adsorption of all samples.We assume that there is a complete adsorption of methylene blue as a monolayer onto the surface of sorbent at the chosen time and concentration

3. Results

Table 1: Measurement of the Adsorption efficiency (%RE) and specific surface areas of pyrolized adsorbents by Methylene blue adsorption (S$_{MB}$) Co=50g/dm^3,adsb=1.992,F=25.1004

Sorbent	Absorbnce	C_e(g/dm^3)	C_o-C_e(g/dm^3)	q_e(mg/g)	S$_{MB}$(10^{-3}km^{2}kg^{-1})	%RE
GS	0.824	20.68273	29.31727	2.931727	9.308233	58.63454
SS	1.193	29.94478	20.05522	2.005522	6.367533	40.11045
PD	0.878	22.03815	27.96185	2.796185	8.877887	55.9237
PW	1.091	27.38454	22.61546	2.261546	7.18041	45.23093

SS-Sheanut shells ,GS- Groundnut shells ,PW- Poultry wastes, PD-Poultry droppings.

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Table 2: Measurement of the Adsorption efficiency (%RE) and specific surface areas of one steps generated adsorbents by Methylene blue adsorption (S_{MB})

Sorbent	Absorbnce	$C_e(g/dm^3)$	$C_o-C_e(g/dm^3)$	$q_e(mg/g)$	$S_{MB}(10^{-3}km^2kg^{-1})$	%RE
GS/A/5	0.367	9.211847	40.78815	4.078815	12.95024	81.57631
GS/A/15	0.354	8.885542	41.11446	4.111446	13.05384	82.22892
GS/Z/5	0.386	9.688754	40.31125	4.031125	12.79882	80.62249
GS/Z/15	0.302	7.580321	42.41968	4.241968	13.46825	84.83936
SS/A/5	0.428	10.74297	39.25703	3.925703	12.46411	78.51406
SS/A/15	0.371	9.312248	40.68775	4.068775	12.91836	81.3755
SS/Z/5	0.469	11.77209	38.22791	3.822791	12.13736	76.45582
SS/Z/15	0.434	10.89357	39.10643	3.910643	12.41629	78.21285
PD/A/5	0.488	12.249	37.751	3.7751	11.98594	75.50201
PD/A/15	0.482	12.09839	37.90161	3.790161	12.03376	75.80321
PD/Z/5	0.496	12.4498	37.5502	3.75502	11.92219	75.1004
PD/Z/15	0.444	11.14458	38.85542	3.885542	12.3366	77.71084
PW/A/5	0.339	8.509036	41.49096	4.149096	13.17338	82.98193
PW/A/15	0.402	10.09036	39.90964	3.990964	12.67131	79.81928
PW/Z/5	0.469	11.77209	38.22791	3.822791	12.13736	76.45582
PW/Z/15	0.483	12.12349	37.87651	3.787651	12.02579	75.75301
Comm	0.031	0.778112	49.22189	4.922189	15.62795	98.44378

Comm- Commercial activated carbon , GS/A/15– Groundnut shells, treated with H_3PO_4(Acid), activated for 15 minutes. SS/A/15 -Sheanut shells, treated with H_3PO_4 activated for 15 minute . PD/A/15 – poultry droppings, treated with, H_3PO_4 activated for 15 minute, PW/A/15 – poultry wastes, treated with, H_3PO_4 (Acid) activated for 15 minutes, GS/Z/15– Groundnut shells, treated with $ZnCl_2$, activated for 15 minutes, SS/ Z/15 -Sheanut shells, treated with $ZnCl_2$ activated for 15 minute dwell time, PD/ Z/15 – poultry droppings, treated with, $ZnCl_2$,activated for 15 minute, PW/ Z/15 – poultry wastes, treated with, ZnCl2,activated for 15 minutes, GS/A/5– Groundnut shells, treated with H_3PO_4(Acid), activated for 5 minutes. SS/A/5 -Sheanut shells, treated with H_3PO_4 activated for 5 minute; Co=50g/dm^3,adsb=1.992,F=25.1004

Table 3 : Measurement of the Adsorption efficiency (%RE) and specific surface areas of two steps generated adsorbents by Methylene blue adsorption (S_{MB})

Sorbent	Absorbnce	$C_e(g/dm^3)$	$C_o-C_e(g/dm^3)$	$q_e(mg/g)$	$S_{MB}(10^{-3}km^2kg^{-1})$	%RE
GS/A/5	0.167	4.191767	45.80823	4.581	14.54468	91.61647
GS/A/15	0.18	4.518072	45.48193	4.581	14.54468	90.96386
GS/Z/5	0.146	3.664658	46.33534	4.632	14.7066	92.67068
GS/Z/15	0.097	2.434739	47.56526	4.756	15.1003	95.13052
SS/A/5	0.228	5.722891	44.27711	4.428	14.0589	88.55422
SS/A/15	0.292	7.329317	42.67068	4.267	13.54773	85.34137
SS/Z/5	0.268	6.726907	43.27309	4.327	13.73823	86.54619
SS/Z/15	0.234	5.873494	44.12651	4.413	14.01128	88.25301

PD/A/5	0.447	11.21988	38.78012	3.878	12.31265	77.56024
PD/A/15	0.287	7.203815	42.79619	4.279	13.58583	85.59237
PD/Z/5	0.291	7.304216	42.69578	4.27	13.55725	85.39157
PD/Z/15	0.239	5.998996	44.001	4.4	13.97	88.00201
PW/A/5	0.195	4.894578	45.10542	4.511	14.32243	90.21084
PW/A/15	0.201	5.04518	44.95482	4.496	14.2748	89.90964
PW/Z/5	0.169	4.241968	45.75803	4.576	14.5288	91.51606
PW/Z/15	0.166	4.166666	45.83333	4.583	14.55103	91.66667
Comm	0.031	0.778112	49.22189	4.922	15.62735	98.44378

Comm- Commercial activated carbon , GS/A/15– Groundnut shells, treated with H_3PO_4(Acid), activated for 15 minutes. SS/A/15 -Sheanut shells, treated with H_3PO_4 activated for 15 minute . PD/A/15 – poultry droppings, treated with, H_3PO_4 activated for 15 minute, PW/A/15 – poultry wastes, treated with, H_3PO_4 (Acid) activated for 15 minutes, GS/Z/15– Groundnut shells, treated with $ZnCl_2$, activated for 15 minutes, SS/ Z/15 -Sheanut shells, treated with $ZnCl_2$ activated for 15 minute dwell time, PD/ Z/15 – poultry droppings, treated with, $ZnCl_2$,activated for 15 minute, PW/ Z/15 – poultry wastes, treated with, ZnCl2,activated for 15 minutes, GS/A/5– Groundnut shells, treated with H_3PO_4(Acid), activated for 5 minutes. SS/A/5 -Sheanut shells, treated with H_3PO_4 activated for 5 minute; Co=50g/dm^3,adsb=1.992,F=25.1004

4. Discussion

Table 1 showed that pyrolized samples without activating agents had developed pore size and could remove over 40.1104% MB from water medium. The surface area (10^{-3}km^{2}kg^{-1}) of the char ranges between 9.308 (GS) >8.877(PD)>7.184(PW)>6.368(SS). The activities of groundnut shells and poultry droppings as better molecular sieves could be linked to the nature of the biomasses and response of its pore size to heat.

Longer activation dwell time $ZnCl_2$ treated GS gave a % adsorption (%RE) of 84. 839%,being the highest in both the $ZnCl_2$ and one-way activated sorbent series. An improvement for the activated SS series (%RE=76.456-78.514%) when compared to the performance of the pyrolized char(40.1145%) could be due to the favourable activation .This also cuts across the entire series. The specific surface are (10^{-3}km^{2}kg^{-1}), which has direct proportionality with

the sorption efficiency (% RE) was estimated for sorbents to include the following value ranges: GS;12.799 – 13.054 (14.545-15.100),SS ;12.137-12.404 (13.548-14.059),PD;11.922-12.337 (12.313-13.970) and PW;12.026-13.173 (14.2748-14.551) 10^{-3}km^{2}kg^{-1} for the one way and (two steps) scheme generated biosorbents respectively. Sorbents activated using the two steps method provides higher surface area. In these series, the effects of longer dwell time is not effective for the SS sorbents in which values for SS/A/5 (14.059)>SS/A/15(13.548) as does the PW/A sorbents on Table 3. Results were compared to values obtained for commercially reference AC which gave S_{MB} of 15.267 and % RE of 98.444%. The role played by type of activating agents widely relies on the nature of samples since unlike GS sorbent, H_3PO_4 treatment favours SS and PD/A/15 sorbents.

Table 4: Estimation of Surface area using Iodine Adsorption Number (IAN) for pyrolized (carbonized) carbon.

Sorbent	$V_b(cm^3)$	$Vs(cm^3)$	IAN (mlM/g)	$V_b(cm^3)$	IAN(mlM/g)
GS	1.75	0.8	0.105925	20	2.1408
SS	1.75	1.2	0.061325	20	2.0962
PD	1.75	1.6	0.016725	20	2.0516
PW	1.75	1.5	0.027875	20	2.06275

SS-Sheanut shells ,GS- Groundnut shells ,PW- Poultry wastes, PD-Poultry droppings.

Table 5: Estimation of Surface area using Iodine Adsorption Number (IAN) for generated one step (1) and two steps (2) activated carbon.

Sorbent	V_b (cm³)	Vs (1) (cm³)	VS (2) (cm³)	IAN (1) (mlM/g)	IAN (2) (mlM/g)	V_b (cm³)	IAN (1) (mlM/g)	IAN(2) (mlM/g)
GS/A/5	1.75	0.7	0.66	0.117075	0.12535	20	2.15195	2.15641
GS/A/15	1.75	0.5	0.55	0.139375	0.138	20	2.17425	2.168675
GS/Z/5	1.75	0.75	0.63	0.1115	0.1288	20	2.146375	2.159755
GS/Z/15	1.75	0.6	0.52	0.128225	0.14145	20	2.1631	2.17202
SS/A/5	1.75	0.54	0.46	0.134915	0.14835	20	2.16979	2.17871
SS/A/15	1.75	0.4	0.4	0.150525	0.15525	20	2.1854	2.1854
SS/Z/5	1.75	0.55	0.5	0.1338	0.14375	20	2.168675	2.17425
SS/Z/15	1.75	0.5	0.35	0.139375	0.161	20	2.17425	2.190975
PD/A/5	1.75	0.6	0.6	0.128225	0.13225	20	2.1631	2.1631
PD/A/15	1.75	0.55	0.5	0.1338	0.14375	20	2.168675	2.17425
PD/Z/5	1.75	0.5	0.5	0.139375	0.14375	20	2.17425	2.17425
PD/Z/15	1.75	0.4	0.33	0.150525	0.1633	20	2.1854	2.193205
PW/A/5	1.75	0.8	0.65	0.105925	0.1265	20	2.1408	2.157525
PW/A/15	1.75	0.7	0.6	0.117075	0.13225	20	2.15195	2.1631
PW/Z/5	1.75	0.6	0.56	0.128225	0.13685	20	2.1631	2.16756
PW/Z/15	1.75	0.75	0.6	0.1115	0.13225	20	2.146375	2.1631
Comm	1.75	0.3		0.161675		20	2.19655	2.23

Comm- Commercial activated carbon , GS/A/15– Groundnut shells, treated with H_3PO_4(Acid), activated for 15 minutes. SS/A/15 -Sheanut shells, treated with H_3PO_4 activated for 15 minute . PD/A/15 – poultry droppings, treated with, H_3PO_4 activated for 15 minute, PW/A/15 – poultry wastes, treated with, H_3PO_4 (Acid) activated for 15 minutes, GS/Z/15– Groundnut shells, treated with $ZnCl_2$, activated for 15 minutes, SS/ Z/15 -Sheanut shells, treated with $ZnCl_2$ activated for 15 minute dwell time, PD/ Z/15 – poultry droppings, treated with, $ZnCl_2$,activated for 15 minute, PW/ Z/15 – poultry wastes, treated with, $ZnCl_2$,activated for 15 minutes, GS/A/5– Groundnut shells, treated with H_3PO_4(Acid), activated for 5 minutes. SS/A/5 -Sheanut shells, treated with H_3PO_4 activated for 5 minute.

The iodine adsorption number (IAN) in Tables 4 and 5 measures the adsorption of iodine from an aqueous solution. It is a measure of micropores and it is used as an indication of the total surface area. Sorbents with high iodine number performs better in removing small sized contaminants. It is the most fundamental parameter used to characterize the performance of activated carbon. High value indicate high degree of activation (Aziza *et al*.,2008;Elliot *et al.*,1989). From

the result displayed on Table 5, activated carbon generated using the two way activation scheme gave fairly high IAN values of 0.1215-0.1371, 0.1394-0.1561,0.1282-0.1583 and 0.1282-0.1326 than the values (0.1115-0.1394,0.1338-0.1505,0.1282-0.1505 and 0.1059-0.1282) estimated in mlM iodine per gram of adsorbent for their corresponding one step activated GS,SS,PD and PW sorbents respectively. It thus implies that the former presented high degree of

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activation and high affinity for small sized contaminants and could also be more susceptible to steric hindrances when sorbates of medium and large sized molecules are involved. The IAN(2) for sorbents, PD (0.128-0.1583) > SS (0.1394-0.1561) > GS (0.1215-0.1371) > PW (0.1282-0.1326) units in mlM/g. A comparison of this results with those of carbonized samples is an indication that activation of carbonized samples further increases the surface area. The high values obtained for PW (0.027875) and SS (0.061325) could be linked to their low ash contents. These values were lower the ranges reported for activated samples ; PW(0.1282-0.1326) and SS (0.1394-0.1561).

Conclusion: In this research, it was deduced that;
Uninteracted "pyrolysed only" samples could serve as molecular sieve for both methylene blue (%RE <58.64) and iodine (IAN< 0.0613mlM/g).
Highest Methylene blue adsorption was estimated for the reference carbon (98.444%) corresponding to a specific surface area (S_{MB}) of 15.628 x 10^{-3}km^{2}kg^{-1}
The high specific surface (S_{MB}) area for GS and PW are indication that they could remove medium sized particles than the SS and GS sorbents
SMB values obtained for the two way scheme generated activated carbon proves to be slightly higher due to the double thermal distillation and subsequent pore size development.
SS and PD sorbents (with high iodine adsorption numbers) could serve better in removing small sized contaminants and reflects high degree of activation and micro porosity.
Comparison of the activated and carbonized samples revealed that activation after carbonization further increases the total surface area. Generally, this research showed that the smaller the volume of iodine adsorbed, the higher the iodine number with a corresponding high surface area, high degree of activation, and expected sorption effectiveness in removal of small sized sorbates.

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