Physicochemical parameters of Adsorbents from locally sorted H₃PO₄ and ZnCl₂ modified Agricultural wastes.

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ABSTRACT: In this research, we add to database, using available technology to see the possibility of adding value to four different abundant Agricultural wastes by generating activated carbon. The % yield for the one way and (two steps) schemes ranges from 22.222± 0.01-30.0±0.12% (17.333±0.05-22.667±0.09%) for the Sheanut shell (SS) activated carbon. Estimations of activation yield based on the weight of already pyrolized samples gave up to 40.0±0.07, 59.33±1.1,and 43.333±0.09 % yields for Groundnut shell (GS),Poultry wastes (PW),and Poultry droppings (PD) carbons respectively for the two way scheme. Low conductivity values (< 28.74µS/cm) is an indication that sorbate removal by generated sorbents could be predominantly physisorption other than ion exchange or chemisorption. Other parameters estimated are % burnoff, Porosity, pH, ash and moisture contents. Bulk densities based on dry weight and swollen states were also presented. [New York Science Journal 2010;3(5):17-24]. (ISSN: 1554-0200).

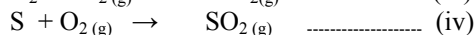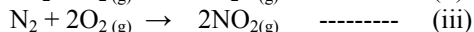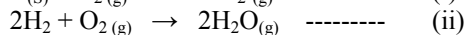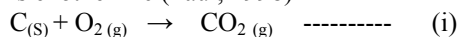**Key words:** Physicochemical, Adsorbents, Activated carbon, Agricultural wastes

INTRODUCTION

Disposal of Agricultural byproduct is currently a major economic and ecological issue, and the conversion of these Agro products to adsorbent, such as activated carbon represents a possible outlet (Itodo *et al*.,2009a). To access adequately the feasibility of activated carbon for normal removal of contaminant, and to design the most effective manner in which it can be used ,it will be necessary to qualitatively and quantitatively predict certain physicochemical variables by characterization .The evaluation of different grade of GAC adsorbent for scavenging priority pollutants from waste water was reported by shaski and Tenkie, (2002). The biomass is that of Bituminious coal and coconuts shell. Results shows that source material used to prepare G.A.C had   significant effect on its mechanical strength, pore structure, surface texture, and adsorption capacity. Gimba *et al*.,2004) in his research argued that the feature of A.C from coconut shell compete favorably with commercial A.C. This conform to the finding of shaski and Yenkie, (2002).Zinc chloride and Orthophosphoric acid were reported by Tsai *et al*.,(2001) to be the most widely used activating agent. It was also pointed that complete removal of these activants from the resulting carbon product presents difficulties leading to environmental contamination with Zn compound and ecological problem of eutrophication with phosphorous compound.
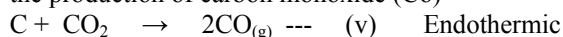
Activation chemistry:
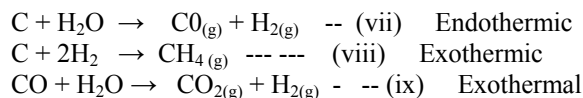Thermal conversion process involves 3 stages (Paul, 1998).

(a)Combustion: this is a complete thermal oxidation of the shear butter shells. At this stage, there is still adequate oxygen in the system to allow breakage of carbon bonds. During reduction of carbonaceous materials, excited oxygen molecule reacts with carbon until the entire available bond is broken. This process is exothermic (Paul, 1998)

$$C_{(S)} + O_{2\,(g)} \rightarrow CO_{2\,(g)} \quad \text{----------} \quad \text{(i)}$$
$$2H_2 + O_{2\,(g)} \rightarrow 2H_2O_{(g)} \quad \text{---------} \quad \text{(ii)}$$
$$N_2 + 2O_{2\,(g)} \rightarrow 2NO_{2(g)} \quad \text{---------} \quad \text{(iii)}$$
$$S + O_{2\,(g)} \rightarrow SO_{2\,(g)} \quad \text{------------------} \quad \text{(iv)}$$

Equation i - iv revealed that the primary emission of combustion are $CO_{2(g)}$, $H_2O_{(g)}$, $NO_{2(g)}$, $SO_{2(g)}$ and $Co_{(g)}$.

(b) Gasification: if the amount of oxygen in the combustion chamber were reduced to below the amount required for combustion, the process is termed gasification. This thermal system leads to a partial burning by forcing carbon molecules to pair with limited (only one) oxygen molecule and thus, increase the production of carbon monoxide (Co)

$$C + CO_2 \rightarrow 2CO_{(g)} \quad \text{---} \quad \text{(v)} \quad \text{Endothermic}$$
$$C + 1/2O_2 \rightarrow CO_{(g)} \quad \text{--} \quad \text{(vi)} \quad \text{Endothermic}$$

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$C + H_2O \rightarrow CO_{(g)} + H_{2(g)}$ -- (vii)   Endothermic
$C + 2H_2 \rightarrow CH_{4\,(g)}$ --- --- (viii)   Exothermic
$CO + H_2O \rightarrow CO_{2(g)} + H_{2(g)}$ - -- (ix)   Exothermal

This system is also exothermic and self sufficient the net process is endothermic for gasification process (Tchobanoglous *et al.*, 1993)

(c) Pyrolyzation (thermal distillation):in this stage, the remaining char from gasification, can be manipulated through a combination of thermal cracking and condensation reaction in the absences of oxygen. This highly endothermic reaction required extensive external energy. distillation of char or pyrolysis yield two usable by–products,(a) combustible gas, mainly saturated hydrocarbon (methane) and (b) activated carbon (Tchobanoglous *et al.,* 1993).
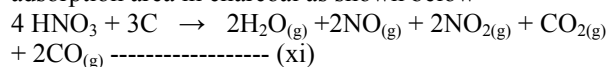   Equation representing complete pyrolysis is given as (x).
$3(C_6H_{10}O_5) \rightarrow 8H_2O_{(g)} + C_6H_8O_{(s)} + 2CO_{(g)} + 2CO_{2(g)}$
        $+ CH_{4(g)} + H_{2(g)} + 7C_{(s)}.$ ---- -- (x)
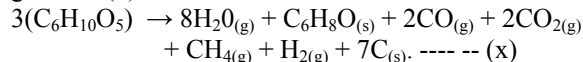
Pyrolising units are designed to achieve temperature ranging from 315° C to 925 ^{o} C. Harvesting of the useful off gases from pyrolysis of municipal solid waste has not been successful because of difficulties obtaining pure final gas, the technical complexity of the system and financial consideration for strict heating control (Itodo *et al.,* 2009b).

(d) Cooling: - carbon is allowed to return to ambient (surrounding) temperature. Experimental results revealed that carbon proceed at high temperature with rapid cooling adsorb basic material more rapidly as does, the slower cooled carbon for removal of acidic substances. As cooling proceed slowly, oxygen came in contact with surface of carbon, forming chemically – attractive oxide groups (Paul, 1998)
The use of activating agent is for pore size development. The area occupied by the activating agent remains as developed pores after the washing process to remove the residual chemical. Such chemical is capable of producing the hot spot adsorption area in charcoal as shown below
$4\,HNO_3 + 3C \rightarrow 2H_2O_{(g)} + 2NO_{(g)} + 2NO_{2(g)} + CO_{2(g)}$
$+ 2CO_{(g)}$ ----------------- (xi)
The water vapor produces the hot spot adsorption area (Itodo *et al.*, 2009b).
        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.

Apparent density: Higher density provide greater volume and normally indicates better quality activated carbon (Elliot *et al*., 1989) since higher density carbon need not be regenerated as frequently since it hold more adsorbate per unit volume. it is a variable in designing adsorption column and important characteristic of carbon.

Ash content: This reduces the overall activities of the activated carbon. i.e it reduces the efficiency of reactivation. The metals (Fe_2O_3) can leach out of activated carbon, resulting in discolouration. Acid/water soluble ash content is more significant than total ash content.

Particle size: the finer the particle size of an activate carbon the better the access to the surface area and the faster the rate of adsorption kinetics.
    This research is in line with the nation's economic objectives of self reliance in motivating local industries to embark on production of activated carbon and in effect, help to conserve foreign exchange used for importing the materials hitherto. The work is also needful due to the diverse application of activated carbon as the most versatile adsorbent (Odebunmi and Okeola,2001).Beside adding value to the waste and arriving at a more ecofriendly environment.

1.   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: The method of sample treatment by Fan *et al*., (2003); Mozammel *et al*., (2002) ; Zahangir *et al*.,(2008);Itodo *et al* .,(2009 a&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.

Carbonization : 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

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dried. This process was repeated until a substantial amount of carbonized samples were obtained (Gimba *et al.,*2004).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 (Rahman *et al* , 2005; Fan *et al*., 2003) the solids were then sun dried, then, dried in the oven at 100^OC for one hour (Odebunmi and Okeola, 2001).Yield on pyrolysis (carbonization) was calculated from the weight, before carbonization (W_{bc}) and after carbonization (W_{ac}). The % yield is thus calculated as stated in 1 below (Yoshiyuki and Yutaka, 2003).

   Yield (%) = (W_{ac}/ W_{bc}) x 100   -- (1)

W_{ac} and W_{bc} = weight of biomass after and weight of sample before carbonization

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 (Gimba *et al.,*2004).The activated carbon generated above were washed, using 10% HCl to removed surface ash, followed by warm water. Rinsing was done with distilled water to removed residual acid (Rahman *et al.,*2005). 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 (Rahman *et al.,*2005). Washing was complete when a pH of 6-8 was ascertained.

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 (Gimba *et al*., 2004). 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 (Rahman *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 (Rahman *et al.,* 2005) and stored in air tight container.

According to Yulu *et al*., 2001; the yield of activated carbon (using the one step process) is defined as the ratio of the weight of the resultant activated carbon to that of the original precursor with both weight on a dry basis.

        % yield = W_i/W_o x 100   -   (2)

Where W_o = original mass of precursor, W_i = mass of AC after activation, washing and drying (Yulu *et al*., 2001).

Burn off : Calculation of burns off is the next step preceding the two step process method of activation. Burn off refers to the weight difference between the original char and the AC divided by the weight of the original char with both weights on dry basis.

% burn off = (W_o-W_i)/W_o x 100   - -   (3)

W_o= weight of char after pyrolysis, washing and drying. W_i = weight of carbon after activation, washing and drying,% burns off = mass after activation/original mass of char   x 100

Moisture content: 2g each of the fresh biosolids were weighed in clean dried and preweighed petridishes. This samples were thinly spread in the dishes. They were dried in air- circulated oven at 105^Oc overnight (for 24 hours). The dried samples were cooled in a desiccator for 30 minutes. To ascertain constant weight, the process was repeated in one hour interval. The percentage moisture content (% loss in weight) was calculated.

Moisture (%) = (W_i – W_f)/ W_i x 100   - - (4)

                = (loss in weight on drying (g)/ initial sample weight (g))   x 100

where; W_i ,W_f are weight of sample before drying and after drying respectively. Each analysis was carried out in triplicate and the average, recorded as mean± standard deviation.

Ash content: Copper crucible were first heated in a crucible at 500^OC for 2 minutes, cooled   in a desiccator and weighed. Two grammes (2g) of the samples were placed in the muffle   furnace   and temperature was allowed to rise to 500^OC for three hours. They were removed and allowed to cool, first at room   temperature, then in a dessicator before weighing. The percentage ash content was calculated using the equation 5 below (AOAC, 1999). Ash (%) is given as ratio of Weight of ash (g) and Weight of dry sample (g)   multiplied by 100

Ash (%) =(W_2 – W_o)/ W_1 – W_o x 100 - - (5)

where; W_o, W_1 and W_2 are weight of empty crucible, crucible + fresh sample and weight of crucible + Ashed sample respectively with units in gramme. % volatile matter or organic matter is by difference i.e

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pH measurement :3g of the sample (when raw and when activated) was mashed and soaked in 10cm^3 distilled water, boiled for 5 minutes and allowed to cool (Yoshiyuki and Yukata, 2003) 1% solution (w/v i.e. 1g/100cm^3 or 0.1g/10cm^3) of the samples were made using Distilled water. pH of the supernatant was obtained after I hour . A pH electrode was dipped into the solution and the value was read from the meter. Samples with undesirable pH were washed continuously until a pH between 6-8 was reached (Ahmedna *et al.,* 2000).

 Bulk density: Density was measured on activated sample of < 2mm. It is estimated by placing the product into a graduated cylinder and compacted by tapping on the bench top until an expected volume, v (cm^3) was occupied by mass, m(g)). The cylinder was tapped on the bench top until the volume of the sample stop decreasing. The mass and volume were recorded and density calculated as equation 6. (Yoshiyuki and Yukata, 2003;Aziza *et al*.,2008)

ρ =   Mass/Vol. occupied   - - (6)

2.   RESULTS
Physicochemical parameters of adsorbents: Table 1– Table 4 shows the percentage yield and percentage

burnoff of the generated activated carbons. Zabaniou and Ioannidou,(1996) defined burn off as the weight difference between the raw sample (W$_o$) and activated sample,(W$_1$) divided by the weight of the raw sample. The Tables presented higher values for the samples activated at longer dwell time with corresponding lower yield. The % burn off for the two stage method was based on the weight of char (Wo),hence, low values were reported. The expected low yield with a corresponding high burn off is more feasible for the one stage process.It was therefore evident that at longer dwell time ,more volatiles are released from the char thereby resulting to higher burnoff with reduced yield (Ahmedna *et al*.,2000).

Throughout the literature reviewed for this project, many scientists praised the capacity for carbon to adsorb ionic species from concentration. It was believed that monitoring conductivity levels of the water before filtration would indicate whether there was a reduction in ion concentrations, provided substantial ions were present in the raw water.(Paul ,1998).Average conductivity levels throughout the experiment are such that it is improbable that there were an unusually high level of ions in solution. Besides the conductivity measurements whose estimation ranges between 12.90-34-05 µS/cm.

Table 1: Characterization of sorbents produced by acid and salt modified 5 and 15 minutes activated shear nut shell carbon.

sorbents	%yield		%burn off		Bulk ρ (g/cm^3)		pH		Conductivity (µS/cm)	
	(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)
SS/A/5	30.0 ±0.12	(21.333) ±0.15	70.0	(78.667)	0.170	(0.30)	6.24 ±0.005	(6.82) ±0.005	16.20	(16.00)
SS/Z/5	28.88 ±0.52	(22.667) ±0.09	71.112	(77.333)	0.256	(0.341)	6.32 ±0.001	(6.42) ±0.004	22.00	(18.98)
SS/A/15	27.778 ±0.12	(15.333) ±0.06	72.222	(84.667)	0.152	(0.298)	6.24 ±0.005	(6.64) ± 0.004	21.30	(14.33)
SS/Z/15	22.222 ±0.01	(17.333) ±0.05	77.778	(82.667)	0.274	(0.383)	6.39 ±0.003	(7.26) ±0.005	18.70	(16.59)

(i) -1 step process, (ii) - 2 step process,   SS/A/5-shea nut shell, SS, activated with acid, A or H$_3$PO$_4$,activated for 5 minutes SS/Z/15-shea nut shell, SS, activated with salt, Z or ZnCl$_2$,activated for 15 minutes

Table 2: Characterization of sorbents produced by acid and salt modified 5 and 15 minutes activated Groundnut shells carbon.

sorbents	%yield		%burn off		Bulk ρ (g/cm^3)		pH		Conductivity (µS/cm)	
	(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)
GS/A/5	37.778 ±0.05	(48.00) ±0.07	62.222	(52.0)	0.208	(0.202)	5.903 ±0.001	(6.00) ±0.000	18.96	(16.44)
GS/Z/5	28.889 ±1.01	(34.000) ±0.9	71.111	(64.000)	0.301	(0.209)	6.77 ±0.001	(6.34) ±0.008	18.04	(18.00)
GS/A/15	28.889 ±0.12	(42.607) ±0.40	71.111	(57.333)	0.206	(0.205)	6.43 ±0.005	(6.26) ± 0.005	20.32	(18.64)
GS/Z/15	17.779 ±1.2	(26.667) ±0.7	82.221	(73.333)	0.300	(0.214)	6.89 ±0.005	(6.11) ±0.005	19.56	(19.76)

(i) -1 step process, (ii) - 2 step process,   GS/A/5- groundnut shell, GS, activated with acid, A or H$_3$PO$_4$,activated for 5 minutes GS/Z/15-groundnut shell, GS, activated with salt, Z or ZnCl$_2$,activated for 15 minutes

Table 3: Characterization of sorbents produced by acid and salt modified 5 and 15 minutes activated Poultry wastes carbon.

sorbents	%yield		%burn off		Bulk ρ (g/cm^3)		pH		Conductivity (µS/cm)	
	(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)
PW/A/5	40.0 ±0.4	(22.667) ±0.6	60.0	(77.333)	0.204	(0.204)	6.24 ±0.00	(6.62) ±0.001	21.40	(20.96)
PW/Z/5	36.667 ±0.50	(59.333) ±1.1	63.333	(40.667)	0.201	(0.206)	6.27 ±0.005	(6.332) ±0.00	26.53	(20.31)
PW/A/15	37.778 ±0.09	(17.333) ±1.1	62.222	(82.667)	0.259	(0.211)	6.80 ±0.005	(6.42) ± 0.001	20.56	(21.40)
PW/Z/15	26.667 ±0.22	(48.000) ±0.061	73.333	(52.000)	0.201	(0.213)	6.34 ±0.005	(5.90) ±0.001	20.11	(28.74)

(i) -1 step process, (ii) - 2 step process, PW/A/5- poultry waste, PW, activated with acid, A or H$_3$PO$_4$,activated for 5 minutes PW/Z/15-poultry waste, PW, activated with salt, Z or ZnCl$_2$, activated for 15 minutes

Table 4: Characterization of sorbents produced by acid and salt modified 5 and 15 minutes activated Poultry droppings carbon.

Sorbents	%yield		%burn off		Bulk ρ (g/cm^3)		pH		Conductivity (µS/cm)	
	(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)
PD/A/5	50.0 ±0.52	(43.333) ±0.09	50.0	(76.667)	0.501	(0.540)	5.31 ±0.001	(5.90) ±0.001	32.00	(14.60)
PD/Z/5	31.11 ±0.05	(39.333) ±0.09	68.888	(60.667)	0.588	(0.591)	5.49 ±0.000	(6.01) ±0.005	34.05	(13.90)
PD/A/15	45.560 ±0.08	(28.667) ±0.13	54.440	(71.3337)	0.600	(0.600)	5.60 ±0.001	(6.10) ± 0.005	34.00	(14.66)
PD/Z/15	21.111 ±0.01	(34.000) ±0.02	78.889	(66.000)	0.603	(0.698)	5.54 ±0.005	(6.22) ±0.003	34.23	(14.34)

(i) -1 step process, (ii) - 2 step process, PD/A/5- poultry droppings, PD, activated with acid, A or H$_3$PO$_4$,activated for 5 minutes PD/Z/15-poultry droppings, PD,activated with salt, Z or ZnCl$_2$,activated for 15 minutes

Table 5 : Porosity and density estimation for generated Biosorbents based on swollen state.

Biosorbents	V_{W1}(cm^3)	V_T(cm^3)	V_F(cm^3)= V_T- V_{W1}	V_{W2}(cm^3) $=V_T$-m	Porosity($α_s$)= V_{W1}/V_T	Density (g/Cm^3)
Comm.	20	23.00	3.00	10.70	0.870	0.165
2GS/A/15	20	23.00	3.00	10.80	0.870	0.165
2GS/Z/15	20	21.10	1.50	10.70	0.930	0.137
2SS/A/15	20	21.00	1.00	10.70	0.952	0.496
2SS/Z/15	20	24.00	4.00	10.60	0.833	0.125
2PW/A/15	20	21.00	1.00	10.70	0.952	0.496
2PW/Z/15	20	20.50	2.00	10.50	0.975	0.475
2PD/A/15	20	22.00	2.00	10.30	0.909	0.250
2PD/Z/15	20	21.00	1.00	10.60	0.952	0.496

Comm- Commercial activated carbon, PW/Z/15 – poultry wastes, treated with ZnCl$_2$, activated for 15 minute dwell time, PD/A/15 – poultry droppings, treated with, H$_3$PO$_4$activated for 15 minute dwell time.

4. DISCUSSION
Effect of temperature on activation time, yield and bulk density.

The optimum temperature for activation was earlier experimentally determined to be 800°c above which high level of residual ash sets in. Result in tables 1a-d shows that activation burn off is high with a resultant low % yield at a longer activation dwell time. The % yield is least for the 2-step scheme as a result of a double thermal decomposition with more ash deposition or volatilization, resulting from an initial pyrolysis followed by activation. The entire results fall within the range for published data (Odebunmi and Okeola, 2001). Comparison between tables 1a and 2a revealed that the bulk density of the Shea nut carbon reduced considerably after activation. Raw grinded and activated samples gave values of the range, 0.563 and 0.152-0.274 g/cm^3 respectively. Similar trend was observed for the PW series. Contrary to this, a similar or slight increament was observed for both raw and activated PD and GS series. It follows that temperature could affect both mass and volume to the same extent for the later case.

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Effect of temperature and activating agents on % yield.

No considerable impact of activating agent on yield is observed. This could be linked to the fact that none of the activants reasonably supports combustion during activation or due to the completeness of washing away the residual chemicals after activation. This facts were however, seldom argued in literatures.

Porosity and density test: Activated carbon is a microcrystalline, nongraphitic form of carbon that has been processed to develop internal porosity. It is the porosity that yield the surface areas on which adsorbates attaches. Activated carbon has the highest volume of adsorptive porosity than any known material (Aziza *et al*., 2008).

Table 5 represents the porosity and density of sorbent based on swollen state. These approximations revealed that porosity measurement of sample in solution is substantially different from those measured in dry state (Aziza *et al*., 2008).

Values presented by the sorbents follows the trend SS/A/15(0.560) > PW/A/15(0.510) > PW/Z/15(0.505) > GS/Z/15(0.498) > PW/Z/15(0.477) > GS/A/15(0.469) > PD/A/15(0.468) in cm^3/0.5g sorbent. These sorbents gave higher porosity than the commercially available sorbent; com (0.465) whose porosity is only slightly higher than the Shea nut shell sorbent, SS/Z/15(0.442). It is evidence that the porosity value (on wet basis) for the sorbent agrees well with that of commercial carbon and they all falls within the range of 0.465-0.560. It is also obvious that the commercial PAC has higher surface area than the generated sorbent due to its finer grain size than the <2mm aperture size of the generated sorbents. This could also be linked to why the latter has higher porosity. There is an assumption that all pores are accessible to all contaminants. However, for larger molecules, steric hindrance leads to decrease in the maximum adsorption capacity (Isabella, 2006). On the basis of the wet carbon, it was observed that sorbent GS/A/15 and SS/Z/15 gave pore volume values of 0.870 and 0.833 respectively. These values are in good agreement to that obtained for the commercial activated carbon, 0.870. This is an indication that plant based sorbents gave porosity of good similarity. The pore volume value of the reference carbon (0.870) is low compared to those of the generated carbon (0.833-0.952). It could be argued that finer sorbents has more surface area but could be less porous than the coarse ones. In this research, the nature starting material or biowaste plays more role in pore size development than does the other

parameters. However, the type of activating agent plays significant role. Besides the Shea nut shell carbon, all other sorbent gave higher pore size with $ZnCl_2$ catalysis. The values include; 0.930, 0.975, 0.952 for GS/Z/15, PW/Z/15 and PD/Z/15. These values are higher than those of their corresponding acid modified sorbents; 0.870, 0.952 and 0.909 for GS/A/15, PW/A/15 and PD/A/15 respectively. The porosity range for all the adsorbents tends to similarity with the same activation temperature and dwell time. These parameters are also critical for pore size development. The porosity values obtained in this research is close to those of activated sawdust (0.939-0.990) by Aziza *et al*.,(2008).

Bulk density (Prior to Adsorption): Generally, Bulk density on dry basis was usually estimated by placing a known weight of PAC in a graduated cylinder and tapping until the PAC occupies a minimum volume and thus calculated as; Density = m / v. The result of bulk density measured on swollen or wet weight basis was also presented (Table 5). Calculation was based on porosity. It is evidence that there is a linear relationship between porosity and bulk density prior to adsorption. More porous carbon was reportedly more denser. This could be linked to the extra mass gained from the occupation of more sorbate (water) into the pore sizes. It should be noted that the density measurement on dry weight bases is substantially different from when it is in swollen state. Low value ($0.165g/cm^3$) was obtained for the commercial activated carbon. Similar to this are those of GS/A/15 (0.165), GS/A/15(0.137) and SS/Z/15(0.125).The relationship between porosity (on wet basis) and density (also on swollen basis) is given in the equation already stated above and as recapped below (Aziza *et al*., 2008).

Density = (Ma/Vw) α / $(1-\alpha)$;Where α = porosity = Vw/V_T;Ma = mass of sorbent (g), Vw = initial volume of water (cm^3) ;V_T = final volume of water + dispersed sorbent (cm^3).This density measurement on wet basis is different from those involving dry sorbents, (Aziza *et al*., 2008).

Conclusion: Highlights of results in this research showed that;

- Precursors of high % burnoff gave corresponding low yield.
- Low conductivity values (< 28.74µS/cm) is an indication that sorbate removal by generated sorbents could be predominantly physisorption other than ion exchange or chemisorption.

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- The high ash contents estimated for PW sorbent is a probable reason for their high pore size development.
- Yield was least for the two steps method due to the double thermal decomposition but are high when estimation is based on initial char weight
- Porosity measurement of samples in solution are substantially different from those measured in dry state.
- Finally, the sorted precursors could be prescribed as potential substrates for sorbent generation and utilization

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