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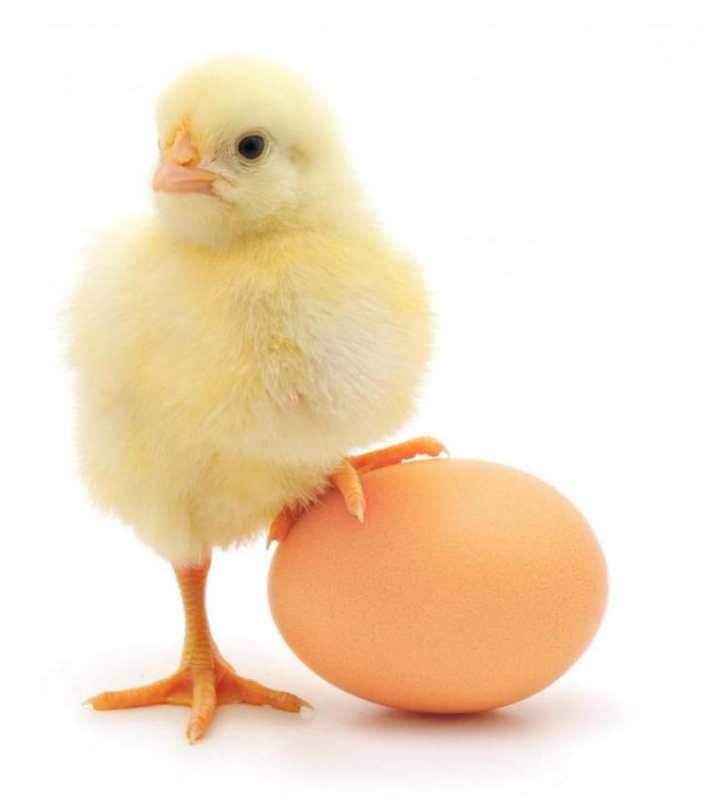

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Gas Chromatographic Prediction of Equilibrium Phase Atrazine after Sorption onto Derived Activated Carbon

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Abstract: Inexpensive remediation method was adopted for Atrazine adsorption by derived Poultry Droppings (PD) and Poultry Wastes (PW) activated carbon. This was proposed to improve the ecological system and add value to the Biomass. GCMS quantitation was employed to investigate the sorption efficiency of the organochlorine herbicide from aqueous phase as it was evidently experimented. Performance of acid catalyzed (PD/A) and Salt treated (PW/Z) sorbents respectively demonstrated about 91.908% and 83.624% atrazine uptake, being highest in their respective series. Both filters however shows a good competitive adsorption though slightly lower than the reference commercial M&B carbon (Comm.) estimated uptake of 23.731 out of 25.00 gdm^{-3} valued as 94.924% removal. The role played by type of activating agent and physicochemical parameters such as density (0.250-0.496) and high porosity (00.952-0.975) were discussed. The major results support the conclusion that Gas Chromatography as a quantitative instrument is critical for isolating and detecting single equilibrium phase analyte from a multicomponent sample especially when coupled with a mass Spectrophotometer detector and with external standards from same matrix.

Key words: GC/MS, atrazine, activated carbon, poultry wastes, poultry droppings

INTRODUCTION

Among the different pollutants of aquatic ecosystem include; herbicides, especially triazines and organophosphorus pesticides. They are considered as priority pollutants since they are harmful to organism even µgL^{-1} levels. These pesticides or herbicides constitute a diverse group of chemical structures exhibiting a wide range of physiochemical properties (Agdi *et al*., 2000). The application of agro-chemicals such herbicides and pesticides is an indication that the mechanism and magnitude of herbicide spreading after application continues to be an active area of research. Paramount interest on which this research focuses is their removal. Triazines are organochlorine pesticides. Just like the organophosphorus pesticides, atrazines were designed to break down fairly quickly owing to their high solubility in water. Thus, their high mobility in the ecosystem cannot be over emphasized (Agdi *et al*., 2000). This research encourages remediation even before their potential level of exposure at a given site becomes unacceptable from the human health or ecological stand point.

Most Agrochemicals are found present in our environment as a result of anthropogenic activities, application to crop land being the prime source. In an intensive farming area where large quantities of herbicides are sprayed, the residues of herbicides and their intermediates in river-water are observed throughout the year. It is expected that the production and sale of pesticide will continue to expand at a rapid rate. Improved agricultural yields, eradication of disease vectors and control of nuisance organisms provide an immense market for these compounds (Schwartz, 1966). Many of the pesticides used are resistant to degradation by chemical and biological agents. It is not surprising, therefore, that small amounts of these chemicals have been isolated from many phases of the environment, including water supplies (Schwartz, 1966). Applicable methods for herbicide removal include a combination of biological, chemical and physical processes. Therefore, adsorption evolved as the most effective, less expensive physical process for herbicide removal. The most commonly used adsorbent has been activated carbon. It is relatively costly hence, suitability of activated carbon from locally available agricultural by-product is sorted (Agdi *et al*., 2000), owing to their economic advantages. Taking into account the specific properties (high cellulosic content, high porosity, low density, weak conductivity etc). Some agro-wastes were selected with the aim of optimizing the effective abatement condition in a cost effective fashion to remove herbicides.

Adsorption is a process in which a soluble chemical (the adsorbate) is removed from a fluid by contact with a solid surface (the adsorbent). It is used in industry for product separation and waste treatment. Adsorption is actually a mechanism in which the forces of interaction between surface atoms and the adsorbate molecules are similar to Van der Waals forces that exist between all adjacent molecules (LaGrega *et al.*, 1994). Due to the increased pollution of water, soil and air, as a result of the increased industrial and agricultural activities, the ability to study and prepare carbon for highly specialized use has increased. There are many modern applications for activated carbon including tertiary treatment for municipal waste water, industrial waste water treatment, involving remediation of hydrocarbon contamination. Activated carbon has several important uses including solution purification such as clean-up of cane, beet and corn-sugar solutions, removing of tastes and odours from domestic and industrial water supplies, vegetable and animal fats and oils, alcoholic beverages and chemicals and pharmaceuticals (Larty *et al.*, 1999) and in waste water treatment (Gimba, 2001; Larty *et al.*, 1999; Hameed *et al.*, 2006;Itodo *et al.*, 2009a,b). It also removes industrial hazards such as carbon tetrachloride, toluene, leadtetraethyl and insecticides vapors (Maggs, 1980). In addition Itodo *et al.* (2009a) reported that activated carbon has been effectively used to remove heavy metal pollutants as well as dye-bearing colors from waste waters.

Surface area and surface functional groups: The surface of an adsorbent is typically composed of various Surface Functional Groups (SFG). Adsorption of organic adsorbate is greatly dependent on the amount and nature of surface oxide groups (Cooney, 1999). Surface functional groups (carbon/oxygen) are created by oxidation occurring during the activation process of an adsorbent. Some of the common basic functional groups created are lactones, quinones and carboxylates (Arun, 2002). Some of the common acidic functional groups created are phenolic, hydroxyl, carbonyl and carboxylic acids (Arun, 2002). The presence of oxygen-containing basic groups such are a key factor in promoting irreversible adsorption (Vidic *et al.*, 1993). Strongly dissociated adsorbates are weakly adsorbed when compared to nondissociated adsorbates (Cooney, 1999). The more non polar an adsorbate, the higher the adsorption capacity. This is attributed to the fact these adsorbate molecules tend to prefer the adsorbent surface rather than being in the solution (Cooney, 1999). It has also been shown that an increase in the molecular weight of the adsorbate will generally enhance adsorption until the size of the adsorbate is larger than the pore size of the adsorbent.

Equilibrium: Equilibrium occurs when the adsorption sites are filled. Equilibrium is a phenomenon when the rate of adsorption and the rate of desorption are equal. This is also the case when the effluent exiting an adsorption column contains pollutants at greater concentrations than is allowed. With a column system the adsorbent is said to be spent (Cooney, 1999). In this present work, chemically Poultry based derived activated carbon was formulated to adsorb atrazine traces from water. The difference between pore structures and sorbent densities was investigated while adsorption efficiency based on GC/MS quantification was done. This work was therefore aimed at evaluating different agro-waste as a substrate for removing atrazine (herbicide) from aqueous solutions or water environment. The research find bases from an initial qualitative study on FTIR spectral characteristics of atrazine sorption described elsewhere by Itodo *et al.* (2009a).

Choice of equipment: Herbicide (containing atrazine) is a multicomponent mixture containing atrazine (Analyte) and other organochlorine moieties, which are very similar to atrazine. Secondly, the GC column has a very high efficiency which was claimed to be in excess of 400,000 theoretical plates. The column is about 100 m long, a very dispersive type of stationary phase retaining the solute approximately in order of increasing boiling point. Helium carrier gas was selected since it can realize high efficiencies with reasonable analysis time (Raymond, 2003).

External standardization: This technique allows the analysis of only one component in the same sample. Peak size is plotted against absolute amount of each component or its concentration in the matrix. Techniques of external standardization entail the preparation of standards at the same levels of concentration as the unknown in the same matrix with the known. These standards are then run chromatographically under ideal conditions as the sample. A direct relationship between the peak size and composition of the target component is established and the unknown is either extrapolated graphically or mathematically (Robert and Eugene, 2004).

GC/MS conditioning/calibration: A gas chromatography equipped with a mass spectrophotometer detector (with a model GCMS QP2010 plus Shimadzu, Japan) was used in this analysis. The column was held at 60°C in injection volume of 1 µL and then programmed to 250°C. it was set at a start m/z of 40 and end m/z of 420. The detector (mass spectrophotometer) was held at 250°C above the maximum column temperature. The sample size was 1 µL, which was split 100^{-1} onto the column and so the total charge on the column was about 1. Helium was used as the carrier gas at a linear velocity of 46.3 cm/sec and pressure of 100.2 kPa. Ionization mode is Electron Ionization (EI) at a voltage of 70eV. In this analysis, amplification and resolution for test herbicide was achieved by adjusting the threshold to 6000. Thus, worse interference and solvent peaks were screened out leaving majorly the deflection of target compound (atrazine) as it was made pronounced on the chromatogram. Baseline disturbance was linked to either hydrocarbon impurities. Impure carrier gas can also cause baseline instability (Robert and Eugene, 2004). It can be corrected by changing the purifier when pressure drops reaches 10-15 pSi (0.7-1.1 bar) routinely monitoring the pressure. Sorption efficiency of an adsorption process is defined based on the fractions of extracted and unextracted solutes (Robert and Eugene, 2004).

MATERIALS AND METHODS

Commercial Atrazine, presumably 2-chloro-4-ethylamino-6-isopropyl amino-1,3,5-trazine with assay of 50% atrazine was procured from a retailer's stand of the Agro-chemical wing of Sokoto central market, Nigeria. Stock standard solution (25 g/L) was prepared and from which ranges of working standard were prepared in chloroform and stored in the dark. This was employed as adsorbate, used in this analysis. Zinc Chloride (98+%) and Ortho Phosphoric acid obtained from prolabo chemicals were used as chemical activants while Chloroform was used as solvent. Hydrochloric acid (0.1 M) and distilled water were used as washing agents.

Sample collection and preparation of activated carbon: The raw materials, Poultry Wastes (PW) and Droppings (PD) were freely collected Labana farms, Aliero in Kebbi state. The raw materials were pretreated as earlier described (Zahangir *et al*., 2008; Itodo *et al*., 2009a,b). By washing several times using tap water and finally with distilled water. The samples dried at 105°C for 24 h in oven to remove excess water content until constant weight. Then, the dried sample was grinded to aperture size of <2.0 mm and stored at room temperature for further use.

The adopted two way scheme activation method involves weighing 3 g each of the initially carbonized, washed and dried char and interacting with 3 cm^3 of each 1 M activants ($ZnCl_2$ and H_3PO_4). This was immediately placed in crucible and heated in a furnace at 800°C and at different dwell times according to the design of experiment for its optimization (Itodo *et al*., 2009a,b; Turoti *et al*., 2007). The activated carbon produced were crushed and sieved using <2 mm aperture size sieve were labeled as PW/A, PW/Z, PD/A and PD/Z denoting samples activated with H_3PO_4 as acid (A) or $ZnCl_2$ as Z. Two variables such as nature of activating agents and activation time were chosen for its optimization for maximum removal of herbicide.

Batch equilibrium experiment: 10 cm^3 of the 25 g/dm^3 Atrazine solution was interacted with 0.1 g of each sorbent and allowed to stand for 12 h. The mixture was filtered and the filtrate was analyzed with a Gas chromatography (coupled with a mass spectrophotometer detector) for atrazine equilibrium phase concentration (Agdi *et al*., 2000). The equilibrium concentration of atrazine (herbicide), q_e and Adsorption efficiency (% Removal) were estimated. The amount of atrazine removal per unit weight of adsorbent is given as q_e (mg/g) from chloroform spiked with 25 g/L of atrazine as equation 1 (Hameed *et al*., 2006):

$$q_e = (C_{in}-C_{out})\ V/M \qquad (1)$$

Where C_{in} and C_{out} are the initial (25 g/dm^3) and equilibrium Atrazine concentration i.e. after interaction (in g/dm^3),V is the volume of aqueous phase Atrazine (dm^3) that was interacted with biosorbent dose, M (in gramme).

Physicochemical parameters: The characterization experiment includes the determination of pH, iodine adsorption number, porosity and density of the PAC. Some of these entailed the preparation and standardization of certain solutions (Aziza *et al*., 2008; Igwe and Abia, 2003). Some of the results were discussed elsewhere (Unpublished).

Determination of porosity: Accurately weighed 0.5 g GAC was dispersed in 20 ml water (Vw) in a graduated tube with the aid of a shaker. This was further centrifuged for 10 min at 4000 r/min (4000 rotation/minute) using Centrifuge 6 (S.M.E. M.I.S T.R.A.L 1000 PEC Medical, USA). The resulting volume was read at V_T and recorded. The equation 2 and 3 below were respectively used to calculate the porosity and density (Aziza *et al*., 2008; Igwe and Abia, 2003):

$$\text{Porosity} = Vw/V_T \text{ or alpha} = Vw/V_T \qquad (2)$$

$$\text{Density (Pa)} = \text{Raw}/1\text{-alpha} \qquad (3)$$

Where; Raw = Ma/Vw; Ma = mass of PAC (g) and Vw = volume of water.

pH: 1 g of PAC was weighed and dissolved in 2 ml of deionized water. A standard confirmatory pH paper was dipped into the solution after it was stirred for 5 sec and allowed to settle (Aziza *et al.*, 2008; Igwe and Abia, 2003). Alternatively, 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 6-7 was reached.

RESULTS AND DISCUSSION

Porosity and density test: Table 1 represent 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; Igwe and Abia, 2003).

Porosity unitless values presented by the sorbents follows the trend PW/Z/15(0.975) > PW/A/15(0.952) = PD/Z/15(0.952) > PD/A/15(0.909) sorbent. These sorbents gave higher porosity than the commercially available sorbent; Comm (0.465). It is evidence that the porosity value (on wet basis) for the sorbent agrees well with that of commercial carbon (0.870). It is also obvious that the commercial PAC has higher surface area than the generated sorbent due to its finer grain size than the <2 mm 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).

Bulk density (Prior to dry weight): The result of bulk density measured on swollen or wet weight basis was also presented (Table 1). 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 (0.165 g/cm^3) was obtained for the commercial activated carbon.

GC-MS quantitation of Atrazine remediation (Equilibrium study): A three point calibration curve was made from 1.0, 5.0 and 10.0 g/L atrazine solution. These standards were run chromatographically under ideal conditions. A direct relationship between the peak height or size and concentration of target is established. The unknown is extrapolated graphically (Robert and Eugene, 2004). Blank samples containing only the adsorbate solution were used to determine if the experimental process considerably reduces the concentration of the pollutant. It was found that significant amounts of the adsorbate were not lost in the procedure.

Procedural blank was obtained by interacting the solvent with same gram of carbon (Eva *et al.*, 2008). Filter paper control experiments were performed to determine if the filter paper used for filtering the solution before instrumental analysis had a significant effect in retaining the adsorbate. It was found that no adsorbate concentration was retained by the filter papers used (Robert and Eugene, 2004).

Determination of sorption efficiency: The equilibrium phase analyte (atrazine) remaining in the test solution was collected and analyzed using a Gas Chromatography (GC) equipped with a Mass Spectrophotometer (MS) as detector and a data processor. The percent dye Removal (RE %) was calculated for each equilibration by the expression as equation (4):

$$RE(\%) = (C_{in}\text{-}C_{out})/C_{in} \text{ x } 100 \qquad (4)$$

Where RE (%) is the percent of dye adsorbed or removed and it a measure of sorption efficiency. The % removal and adsorption capacities were used to optimize the activation condition (Maryam *et al.*, 2008). The tests were done at a constant temperature of 25±2°C.

Figure 3-6 presents the measurements of equilibrium phase concentration of atrazine after interaction with poultry based PW and PD biosorbents. Out of 25 g/L initial atrazine concentration, between 2.032 and 6.064 were left unadsorbed.

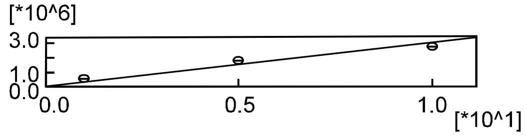
Table 1: Porosity and density estimation for generated biosorbents based on swollen state

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 (alpha) =V_{W1}/V_T	Density (g/cm^3)
Comm.	20	23.00	3.00	10.70	0.870	0.165
PW/A/15	20	21.00	1.00	10.70	0.952	0.496
PW/Z/15	20	20.50	2.00	10.50	0.975	0.475
PD/A/15	20	22.00	2.00	10.30	0.909	0.250
PD/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 min dwell time, PD/A/15-Poultry Droppings, treated with, H_3PO_4 activated for 15 min dwell time

Calibration

ID#:1 Mass:214.00 Name:1,3,5-Triazine-2,4-diamine, 6-chloro-N,N^1-bis(l-methylethyl)- $$ s-Triazine, 2-chloro-4,6-bis(isopropylamino)- $$ G 30028 $$ Ge
f(x) = 299734.261905*x+0.000000
Π1 = 0.987745 Π2 = 0.975639
MeanRF:406146.40 RFSD:147386.27 RFRSD:36.29
CurveType:Least Square Method
ZeroThrough:Through
WeightedRegression:None
External Standard



#	Conc. (g/L)	Mean area
1	1.000	567727.00
2	5.000	1858162.00
3	10.000	2790798.00

Fig. 1: GC/MS external standard calibration curve for 1.0-10.0 g/L concentration range of atrazine

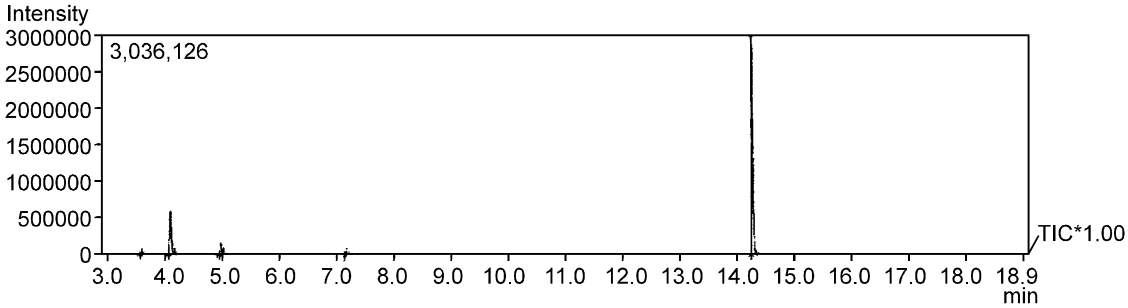
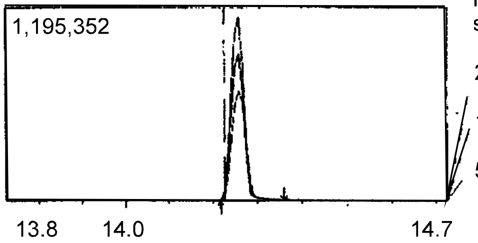


Fig. 2: GC/MS chromatogram of equilibrium concentration atrazine after adsorption onto commercial reference sorbent (Carrier gas-Helium 100.2kpa,Column temperature -60°C, Injection temperature -250°C, Injection volume - 1µL, Flow rate -1.61mL/min, Injection method - split, Linear velocity - 43.6cm/sec)

Quantitation
ID#:1 Mass:214.00
Type:Target
Name:1,3,5-Triazine-2,4-diamine, 6-chloro-N,N'-bis(l-methylethyl)- $$
s-Triazine, 2-chloro-4,6-bis(isopr



214*1.00R.T.:14.256
Area: 1817446
199*1.00SI:93
Conc.:6.06352 g/L
58*1.00

#	m/z	Intensity	Ratio	#	m/z	Intensity	Ratio
1	199.00	996613	124.44	2	58.00	620541	77.48

Quantitative result table

ID#	R.Time	m/z	Area	Height	Conc.	Conc.Un	Recovery	Name
1	14.256	214.00	1817446	909129	6.064	g/L	0.00	Name:1,3,5-Triazine-2,4-diamine, 6-chloro-N,N'-bis

Fig. 3: GC/MS chromatogram, quantitative measurement and spectral information of equilibrium phase atrazine after adsorption onto PW/A sorbent

Comparison of sorption efficiency by commercial and derived sorbents: A control or reference activated carbon (M & B Charcoal), manufactured by M & B Ltd Dadedham was subjected to the same interaction condition as the generated sorbent. A fairly higher percentage removal was evidence. 94.924% was reported to have a total uptake of 23.731 out of the 25 g/L initial sorbate concentration by a 0.1 g sorbent dose per 10 cm^3 sorbate solution (Table 2). The general trend follows the sequence of Comm. (94.924%) >

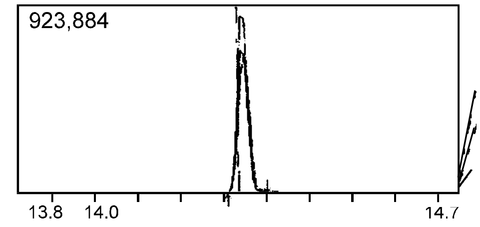
Table 2: GC/MS estimation of sorption efficiency (%RE) of atrazine uptake onto poultry based chemically modified biosorbent

Sorbents	C_0 (g/dm^3)	C_e (g/dm^3)	C_a (g/dm^3)	%RE	Ads.m (10^{-3}mg)	q_e (mg/g 10^{-3})	% q_e
Comm.	25	1.269	23.731	94.924	0.237	2.370	94.92
PW/A/15	25	6.064	18.936	75.744	0.189	1.890	75.74
PW/Z/15	25	4.094	20.906	83.624	0.209	2.090	83.63
PD/A/15	25	2.023	22.977	91.908	0.230	2.300	91.91
PD/Z/15	25	2.986	22.014	88.056	0.220	2.200	88.06

Comm-Commercial activated carbon, PW/Z/15-Poultry Wastes, treated with $ZnCl_2$, activated for 15 min dwell time, PD/A/15-Poultry Droppings, treated with, H_3PO_4 activated for 15 min dwell time

Quantitation

ID#:1 Mass:214.00
Type:Target
Name:1,3,5-Triazine-2,4-diamine, 6-chloro-N,N'-bis(l-methylethyl)- $$
s-Triazine,2-chloro-4,6-bis(isopr



214*1.00R.T.:14.237
Area: 1227230
199*1.00SI:96
Conc.:4.09439 g/L
58*1.00

#	m/z	Intensity	Ratio	#	m/z	Intensity	Ratio
1	199.0	758383	124.90	2	58.00	536754	88.40

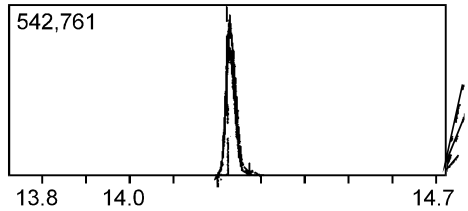
Quantitative result table

ID#	R.Time	m/z	Area	Height	Conc.	Conc.Un	Recovery	Name
1	14.237	214.00	1227230	708815	4.094	g/L	0.00	Name:1,3,5-Triazine-2,4-diamine, 6-chloro-N,N'-bis

Fig. 4: GC/MS chromatogram, quantitative measurement and spectral information of equilibrium phase atrazine after adsorption onto PW/Z sorbent

Quantitation

ID#:1 Mass:214.00
Type:Target
Name:1,3,5-Triazine-2,4-diamine, 6-chloro-N,N'-bis(l-methylethyl)- $$
s-Triazine, 2-chloro-4,6-bis(isopr



214*1.00R.T.:14.232
Area: 606490
199*1.00SI:97
Conc.:2.02343 g/L
58*1.00

#	m/z	Intensity	Ratio	#	m/z	Intensity	Ratio
1	199.00	412863	126.18	2	58.00	394617	120.61

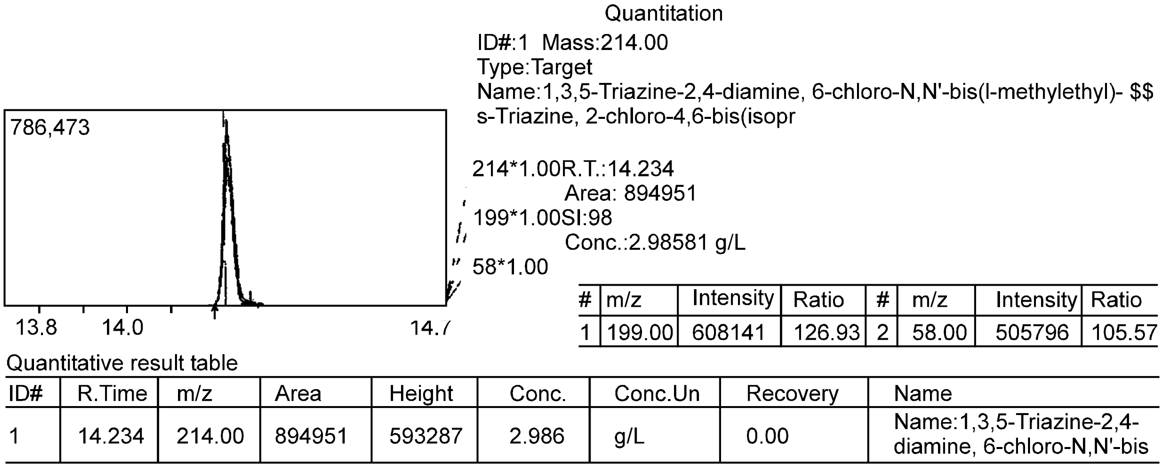
Quantitative result table

ID#	R.Time	m/z	Area	Height	Conc.	Conc.Un	Recovery	Name
1	14.232	214.00	606490	411628	2.023	g/L	0.00	Name:1,3,5-Triazine-2,4-diamine, 6-chloro-N,N'-bis

Fig. 5: GC/MS chromatogram, quantitative measurement and spectral information of equilibrium phase atrazine after adsorption onto PD/A sorbent

PD/A/15(91.908%) > PD/Z/15(88.056%). Adsorption by M α B charcoal and PD/A/15 sorbent falls within the ratio bracket of 1.033:1. It follows that acid catalyzed poultry based adsorbents (i.e. PD/A/15) gave better sorption. Chromatogram on Fig. 7 presents unadsorbed quantity (1.269) by reference activated carbon.

Nature of activating agent: The effect of the nature activants on the general analysis is not pronounced. It could however be observed that the efficacy of a given activating agent as revealed by this analysis could be a function of the nature of biomass since both activating agents favors pore size development to a less distinct level. Figure 8 showed that acid catalyzed Poultry Waste (PW) and Droppings (PD) catalyzed with $ZnCl_2$ and H_3PO_4 respectively gave higher percentage atrazine uptake than their corresponding vices. It can thus be concluded that H_3PO_4 proves a potentially favorable



Quantitation
ID#:1 Mass:214.00
Type:Target
Name:1,3,5-Triazine-2,4-diamine, 6-chloro-N,N'-bis(l-methylethyl)- $$ s-Triazine, 2-chloro-4,6-bis(isopr

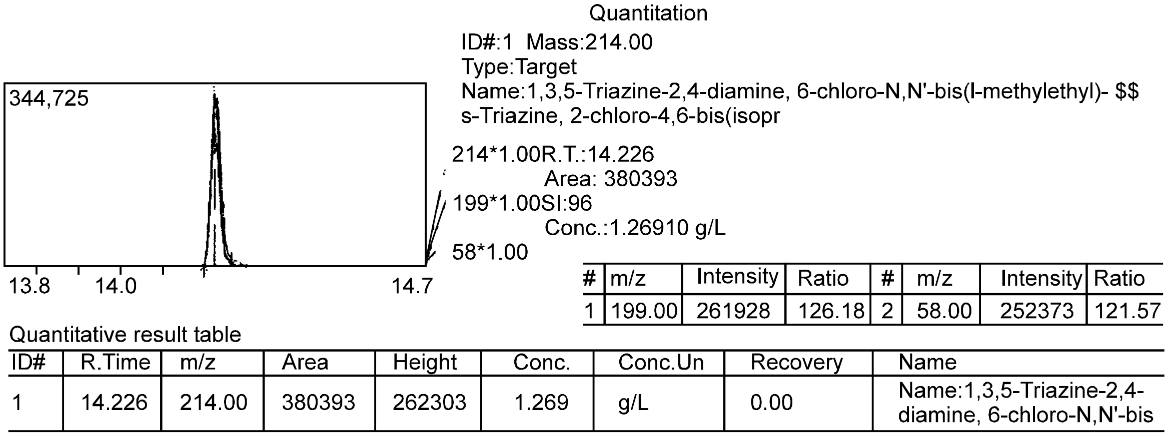
214*1.00R.T.:14.234
Area: 894951
199*1.00SI:98
Conc.:2.98581 g/L
58*1.00

#	m/z	Intensity	Ratio	#	m/z	Intensity	Ratio
1	199.00	608141	126.93	2	58.00	505796	105.57

Quantitative result table

ID#	R.Time	m/z	Area	Height	Conc.	Conc.Un	Recovery	Name
1	14.234	214.00	894951	593287	2.986	g/L	0.00	Name:1,3,5-Triazine-2,4-diamine, 6-chloro-N,N'-bis

Fig. 6: GC/MS chromatogram, quantitative measurement and spectral information of equilibrium phase atrazine after adsorption onto PD/Z sorbent



Quantitation
ID#:1 Mass:214.00
Type:Target
Name:1,3,5-Triazine-2,4-diamine, 6-chloro-N,N'-bis(l-methylethyl)- $$ s-Triazine, 2-chloro-4,6-bis(isopr

214*1.00R.T.:14.226
Area: 380393
199*1.00SI:96
Conc.:1.26910 g/L
58*1.00

#	m/z	Intensity	Ratio	#	m/z	Intensity	Ratio
1	199.00	261928	126.18	2	58.00	252373	121.57

Quantitative result table

ID#	R.Time	m/z	Area	Height	Conc.	Conc.Un	Recovery	Name
1	14.226	214.00	380393	262303	1.269	g/L	0.00	Name:1,3,5-Triazine-2,4-diamine, 6-chloro-N,N'-bis

Fig. 7: GC/MS chromatogram, quantitative measurement and spectral information of equilibrium phase atrazine after adsorption onto commercial reference sorbent

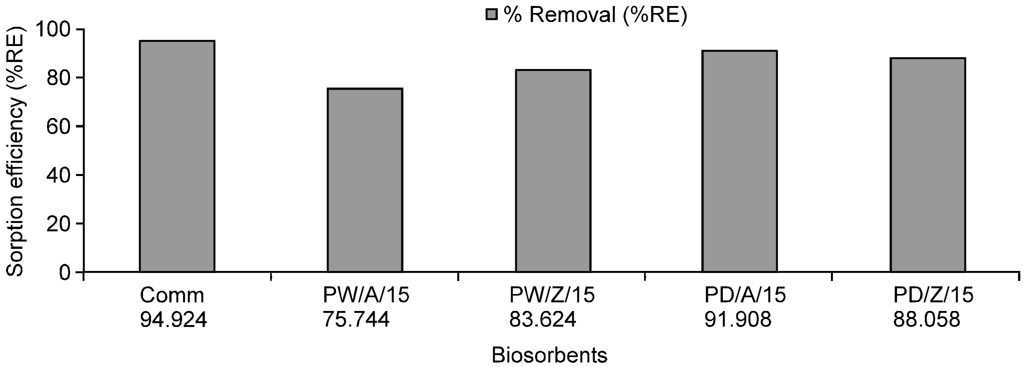


Fig. 8: GC/MS analysis of the level of atrazine removal (%RE) by chemically catalyzed poultry based (PW ans PD) bioadsorbent

Table 3: Mass to charge ratio and peaks data of atrazine uptake onto chemically catalyzed poultry based biosorbents

	Spectral data			Peaks information				
Biosorbents	M/Z	Rt	Scan #	Area	Intensity	Height	Mass	Base
Comm.	214.00	14.226	1,348	380,393	3,036,126	262,303	M-62	199.30
2PW/A/15	214.00	14.258	1,352	1,817,446	8,967,547	909,129	M-95	199.40
2PW/Z/15	214.00	14.237	1,350	1,227,230	7,423,691	708,815	M-90	199.40
2PD/A/15	214.00	14.232	1,349	606,490	4,824,393	411,628	M-77	199.30
2PD/Z/15	214.00	14.234	1,349	894,951	6,347,153	593,287	M-85	199.30

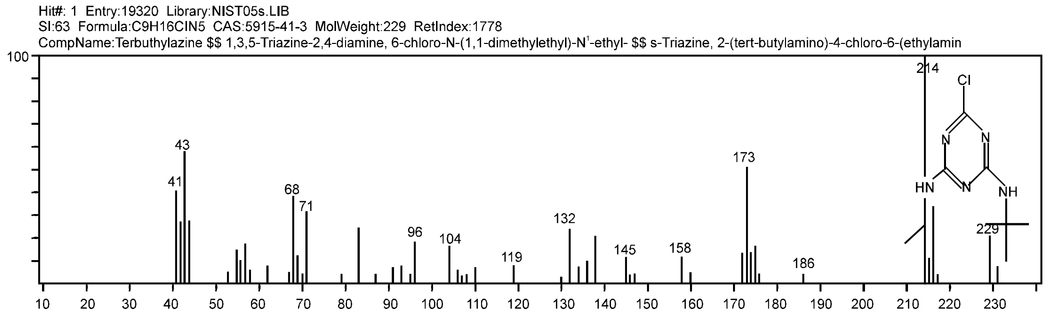


Fig. 9: MS spectral comparison showing triazine compound with a 63% similarity index from the NIST Library (NIST,2005)

activating agent for Poultry dropping sorbents than $ZnCl_2$ which majorly favors adsorption Poultry Waste (PW). It was reported that activating agent such as $ZnCl_2$ dehydrate the cellulose material resulting in the weakening of the precursor structure and creation of pore. According to Malik *et al.* (2006), the space occupied by the activating agent added to pore size formation after intense washing.

Qualitative analysis, spectral and peaks information: Peak is the portion of chromatogram recording the detector response or eluate concentration while peak area is the band area of the peak on the chromatogram. Commercial reference carbon presented value for peak area as 380393 with a corresponding mass peak of M-62 as revealed in Table 3.

The mass peak of the various eluate revealed that the sample GS/A/15 with higher mass peak (M-92) presented a corresponding higher peak intensity (8533008) and peak height (828042) as revealed in Table 3. Such samples presented least percentage recovery i.e. high percentage adsorption. Intensity is a measure of detector response (Robert and Eugene, 2004).

GC analysis of the herbicide sample revealed the presence of numerous components. This investigation focused only on the key analyte (atrazine). The compound is hydrophobic due to the presence of C-H components.

In order to quantitatively analyze the equilibrium concentration, The threshold (amplification of analyte as against impurities) was adjusted to 6000 and the target compound was found to match that of 1,3,5-Triazine-1,4-diamine, 6-chloro - N - N^1 - bis(1-methylethyl)- S-Triazine. The percentage of this component in the herbicide was not reported.

However, the spectral information of similar compounds from the National Institute for Standard Technique (NIST, 2005) MS library as compared to the test sample in this analysis (typical of the spectral type in Fig. 9) were interpreted in the Table 3.

It is expected that the generated sorbents could effectively adsorb the Hit compounds to an extent, approximated as the Similarity Index (SI) of the target analyte.

Among the generated adsorbents presented in Table 3, PD/A/15 eluate has a least peak area of 606490, least peak height of 411628, least mass peak of M-77, lowest value of equilibrium phase atrazine (concentration of 2.023 g/L) presented in Table 2 and implying a higher adsorption efficiency (91.908%) than the other sorbents in the series as earlier revealed in Table 2.

Conclusion: We have demonstrated that chemically derived Poultry based activated carbon has the potential for adsorbing hydrophobic herbicides (Atrazine). it is also likely that the extent of herbicide sorption was influenced by the type of activating agent, which in turn determines the total surface area of the sorption bed that is available for interaction with the atrazine. Pore size development of Poultry biomass upon acid (H_3PO_4) treatment and their use for the adsorption of organochlorine herbicide (atrazine) gave more appreciable results, based on higher sorption efficiencies within the series.

REFERENCES

Agdi, K., A. Bouaid, E. Martin, H. Fernandez, A. Azmani and C. Camara, 2000. Removal of atrazine from environmental water by diatomaceous earth remediation method. J. Environ. Monitor, 2: 420-423.

Arun, S., 2002. Adsorption of organic pollutants onto Natural adsorbent. M.Sc. Thesis. Department of Chemical engineering, Mississippi State University, pp: 32-35.

Aziza, A., A. Odiakosa, G. Nwajei and V. Orodu, 2008. Modification and characterization of activated carbon derived from Bumper sawdust and disk sawdust to remove lead (II) and cadmium (II) effluent water. CSN Conference proceeding. Chemical Society of Nigeria. Deltachem, pp: 235-243.

Cooney David, O., 1999. Adsorption Design for Wastewater Treatment. Lewis. Publishers, CRC Press LLC, Boca Raton, Florida.

Eva, C.L., M.N. Daniela, M. Vincenta and G.R. Antonio, 2008. Interaction of Phenol, aniline and P-nitrophenol on activated carbon surface as detected by TPD. J. Carbon, 46: 870-875.

Gimba, C.E., 2001. Adsorption of methylene blue by activated carbon from coconut shell. Global J. Pure Applied Sci., 4: 765-767.

Hameed, B.H., A.M. Din and A.L. Ahmad, 2006. Adsorption of methylene blue onto Bamboo based activated carbon: Kinetics and equilibrium studies. J. Hazardous Materials, 137: 695-699.

Igwe, J.C. and A.A. Abia, 2003. Maize cob and husk as adsorbent for removal Cd, Pb and Zn ions from waste water. The Physical Sci., 2: 83-94.

Isabella, A.M., 2006. Predicting the Adsorption Capacity of Activated Carbon for Organic Contaminants from Fundamental Adsorbent and Adsorbate Properties. MSc Thesis. North Carolina State University, pp: 45-52 (unpublished).

Itodo, A.U., F.W. Abdulrahman, L.G. Hassan, U.O. Happiness, A. Uba and I.S. Sadiq, 2009a. Enhanced Cr (vi) adsorption from textile effluent by two lignocellulosic acid catalyzed nut shells. Conference paper presented at the 32nd international Chemical Society of Nigera (CSN) conference held on 5th-9th/10/2009 at Bauchi, Nigeria.

Itodo, A.U., F.W. Abdulrahman, L.G. Hassan, A.I. Dogonyaro, I.S. Sadiq and U.O. Happiness, 2009b. Biosorption of Heavy metals and herbicides onto poultry based activated carbon animalis. Conference paper presented at CSN (7th Chemclass 2009) conference held on 11/06/2009 at NARICT, Zaria.

LaGrega, M., P. Buckingham, J. Evans and The Environmental Resources Management Group, 1994. Hazardous Waste Management. McGraw-Hill Inc., New York.

Larty, R., F. Aquah and K. Nkeetia, 1999. Developing National Capability for Manufacture of Activated Carbon from Agricultural Waste. The Ghana Engineer, May, 1999.

Maggs, F., 1980. Activated charcoal (Active carbon). Chemical Defence Establishment, Porton Down, Salisbury, Wiltshire, U.K. Accessed on 10/01/07 from http://www.web.dss.go.th/information/fultex/3.6pdf.

Malik, R., D. Ramteke and S. Wate, 2006. Adsorption of malachite green on groundnut shell waste based activated carbon. Waste Manage., 27: 1129-1138.

Maryam, K., A. Mehdi, T. Shabnam, M. Majdeh and K. Hamed, 2008. Removal of Pb, Cd Zn and Cu from industrial waste water by carbon developed from Walnut, Hazelnut, Almond and Apricot Stones. J. Harzadous Material, 150: 322-327.

NIST, 2005. National Institute for standard techniques: A database MS library in Shidmadju QP2010plus GC/MS. Japan.

Raymond, P.W., 2003. Principle and practice of chromatography. 1st Edn., Chrom. Ed. Book series. pp: 19-26. Retrieved from http://www.library4science.com/enla.html.

Robert, L. and F. Eugene, 2004. Modern practice of chromatography. 4th Edn., Wiley interscience. John Wiley and sons Inc. New Jersey, pp: 425.

Schwartz, H.G., 1966. Studies on Adsorption and Microbial Degradation of the Pesticides isopropyl N-(3-chlorophenyl) carbamate and 2, 4-diisochlorophenoxy acetic acid in aqueous solutions. Ph.D. Thesis, California institute of Technology, Pasadena, California.

Turoti, M., C. Gimba, O. Ocholi and A. Nok, 2007. Effect of different Activation Methods on the Adsorption Characteristics of Activated Carbon from Khaya Senegalensis Fruits and Delonix Regia pods. Chemclass J., 4: 107-112.

Vidic, R.D., M.T. Suidan and R.C. Brenner, 1993. Environ. Sci. Technol., 27: 2079.

Zahangir, A., A. Suleyman and K. Noraini, 2008. Production of activated carbon from oil palm empty fruit Bunch for Zn removal, Bul. Conference Proceedings 12th int.water Tech conf. IWTC12 Egypt, pp: 373-383.