

GC/MS Batch Equilibrium study and Adsorption Isotherms of Atrazine Sorption by Activated H₃PO₄ - Treated Biomass.

Itodo Adams Udoji¹, Funke Wosilat Abdulrahman², Lawal Gusau Hassan³, S.A. Maigandi⁴, Happiness Ugbede Itodo⁵

¹Department of Applied Chemistry, Kebbi State University of Science and Technology, Aliero, Nigeria

²Department of Chemistry, University of Abuja, Nigeria

³Department of Pure and Applied Chemistry, Usmanu Danfodiyo University, Sokoto, Nigeria

⁴Faculty of Agriculture, Usmanu Danfodiyo University, Sokoto, Nigeria

⁵Department of Chemistry, Benue State University, Makurdi, Nigeria

itodoson2002@yahoo.com

Abstract: Acid modified abundant lignocellulose Agricultural wastes, Sheanut shells (SS/A) was used to develop activated carbon and applied to removal of Agrochemical (Atrazine) from a multicomponent herbicide solution. A GCMS which can separate, detect and measure the target (sorbate) was applied to estimate equilibrium phase atrazine. Generated data were tested with 3 isotherm models. Extent of fitness follows the order Freundlich ($R^2=0.994$) > Langmuir ($R^2=0.977$) > BET ($R^2=0.894$) implying that surface coverage is more of heterogeneous. Freundlich adsorption capacity was valued at $0.045 \cdot 10^{-3} K_F$ (units in $\text{mgg}^{-1} (\text{1mg}^{-n(n)})$). Study of the effect of initial sorbate concentration (%RE) revealed that adsorption efficiency increases linearly with time in a range of 46.08% (for SS/A/5gdm³) to 66.324 (for SS/A/25gdm³). Generally, the GCMS quantitation via external standard methods shows that sorted waste could be a potential source of active filter for atrazine sorption. [Journal of American Science 2010;6(7):19-29]. (ISSN: 1545-1003).

Keywords: Sheanut shells; Atrazine; Activated carbon; GCMS.

1. Introduction

Water pollution by Organochlorine and Organophosphorus pesticide and herbicides are worldwide ecoproblem, particularly in the Agricultural regions. Among the different pollutants of aquatic ecosystem include; Herbicides, especially triazines. 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). Atrazine (2-chloro-4-, amino-6-isopropylamino-s-triazine) and related substituted chlorotriazine compound, 2-chloro-4,6-bis(ethylamino)-s-triazine) finds extensive use as herbicides (Shimabukoro, 1967). They are widely used for the control of broadleaf and grassy weeds. Contrary to expectations, these compounds reduce the rate of CO₂ fixation in plants and act as inhibitors of hill reaction during photosynthesis. Unfortunately too, it is also widely detected in water supplies (Itodo *et al.*,

2009a). Herbicide in the soil and water sometime contains ingredients that are poisonous to human and other organism. Atrazine for example is the most widely used agricultural herbicide. The application of Agro-chemicals such as 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. Industries cannot afford the conventional waste water treatment chemicals like Alum, Ferric chloride, polymer flocculants and coal based activated carbon because they are cost intensive (Namasivayan and kavitha, 2009).

Disposal of Agricultural by-product 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 (Malik *et al.*, 2006). This measure, to some extent, agrees with the concept of zero emission" as

proposed to be an idea of reducing environmental impact produced by discarded waste products and increase the effective and repeated utilization of resources. 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). The Shea Tree is a sacred tree from the Sahel region in Africa. The shells are known to be poor source of energy while its biodegradation takes time. its menaces cuts across eye sores, space occupancy to injurious nature due to its strength and sharpness (Itodo *et al.*, 2009a).

Among the conventional techniques for removing dissolved sorbates (heavy metals, dyes, organics etc.) include electrodialysis, phytoextraction (Myroslav *et al.*, 2006). Others include ultrafiltration, reverse osmosis, chemical precipitation, ion exchange, carbon adsorption, evaporation and membrane adsorption. Most of this methods are expensive and ineffective when applied to low strength wastes with heavy metal concentration less than 100mgL^{-1} . Non conventional methods, studied for sorbate uptake include the use of wood, fullers earth, fired clay, fly ash, biogas waste slurry, waste orange peels, chitin, silica etc (Namasivayan and kavitha, 2009). Adsorption is the adhesion of a chemical substance (adsorbate) onto the surface of a solid (adsorbent). The most widely used adsorbent is activated carbon (Reuben and Miebaka, 2008).

Activated carbons are high porosity, high surface area material manufactured by carbonization and activation of carbonaceous materials, which find extensive use in the adsorption of pollutants from gaseous and liquid streams (Itodo *et al.*, 2009a). Commercial sources activated carbon appear to be made from a variety of activating agents, and binders (USDA, 2002). According to Gimba *et al.*, (2004), a wide range of activating agents can be used. These include Acid, Inorganic Salts, Organic Salts, Bases, Steam, CO_2 , Cyanides, Dolomite. Others include Boric acid, Calcium hydroxide, Calcium phosphate, Nitric acid Ortho phosphoric acid, Potassium carbonate, Potassium sulfide, Potassium thiocyanate, Sodium hydroxide, Sodium phosphate, Sulphur, Sulphur dioxide, Sulfuric acid and Zinc chloride (Gimba *et al.*, 2004).

Adsorption isotherm: Isotherm are empirical relationship used to predict how much solute can be adsorbed by activated carbon (Steve and Erika, 1998). Chilton *et al.*, (2002) defined Adsorption isotherm as a graphical representation showing the relationship between the amount adsorbed by a Unit

weight of adsorbent (eg activated carbon) and the amount of adsorbate remaining in a test medium at equilibrium. It maps the distribution of adsorbable solute between the liquid and solid phases at various equilibrium concentration (Chilton *et al.*, 2002). The adsorption isotherm is based on data that are specific for each system and the isotherm must be determined for every application. An adsorption isotherm beside providing a panorama of the course taken by the system under study in a concise form indicate how efficiently a carbon will allow an estimate of the economic feasibility of the carbons' commercial application for the specific solute (Chilton *et al.*, 2002). The three well known isotherms are (a) Freundlich (b) Langmuir and (c) BET adsorption isotherm (Steve and Erika, 1998).

Equilibrium is a phenomenon when the extent of adsorption and of desorption are equal (Cooney, 1999). 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." The relationship between the amount of adsorbate adsorbed onto the adsorbent surface and the equilibrium concentration of the adsorbate in solvent at equilibrium at a constant temperature may be estimated by various adsorption isotherm models.

Choice of Equipment: The sample herbicide (containing atrazine) is a multicomponent mixture containing atrazine (test sample) 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 100m 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).

2. Material and Methods

Sample collection: Presumably 2-chloro-4-ethylamino-6-isopropyl amino-1,3,5-triazine with specification of 50% atrazine was procured from a retailer's stand of the agro-chemical wing of Sokoto central market, Nigeria. Zinc Chloride (98+ %) and Ortho Phosphoric acid obtained from prolabo chemicals were used as chemical activants while Chloroform was used as received. Hydrochloric acid (10%) and distilled water were used as washing agents. Shea nut shells (SS) were obtained from waste hip sites at Rikoto- Zuru, in Kebbi state, Nigeria.

Sample treatment and preparations: The method of sample treatment by Fan *et al.*, (2003); Itodo *et al.*, (2009a&b) were adopted. The samples were washed with plenty of water to remove surface impurities and sundried, then, dried in an oven at 105°C 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. 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°C 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). 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°C for one hour. Accurately weighed 2g each of already carbonized samples were separately mixed with 2cm³ of each 1M activating agent (H₃PO₄ and ZnCl₂). The samples were introduced into a furnace, heated at 800°C 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 (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°C overnight and milled or grounded, followed by filtration to different mesh size and stored in air tight container.

Atrazine standard solution for equilibrium studies: For the sorption/equilibrium studies, several concentrations viz; 10, 20, 30, 40 and 50g/L Herbicide equivalent of 5, 10, 15, 20 and 25g/L Atrazine was prepared by respectively dissolving 0.25, 0.5, 0.75, 1.0 and 1.25g of herbicide into a conical flask, poured gently into a 25cm³ volumetric flask, homogenized and made to the mark with chloroform (i.e. 5,000ppm – 25,000ppm atrazine). A three point calibration curve based on external standard method was prepared with the GC/MS run.

External standardization (Calibration) for GC/MS: Techniques of external standardization entails 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 was extrapolated graphically. 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 (Robert and Eugene, 2004). A three point calibration curve was made from 1.0, 5.0 and 10.0g/L atrazine solution. These standards were run chromatographically under ideal conditions. A direct relationship between the peak height or size and concentration of target was established. The unknown was extrapolated graphically (Robert and Eugene, 2004). The column was held at 60°C in injection volume of 1μL 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 1μL, 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 46.3cm/sec and pressure of 100.2kPa. 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. (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).

Batch equilibrium experiment: 5g of substrate was diluted to the mark of 100cm³ volumetric flask. This concentration of 50g/L herbicide is equivalent to 25g/L or 25,000ppm atrazine stock. 10cm³ of the atrazine solution was interacted with 0.1g of each sorbent and allowed to stand for 12hours. The mixture was filtered and the filtrate was analyzed with a gas chromatography (coupled with a mass spectrophotometer detector) for atrazine equilibrium phase concentration (Min and Yun, 2008; Agdi *et al.*, 2000).

The amount of atrazine at equilibrium, q_e was calculated from the mass balance equation given in equation 1 by Hameed *et al.*,(2006).

$$q_e = (C_o - C_e) V/W \dots\dots\dots(1)$$

where C_o and C_e are the initial and final Dye concentrations (mg/L) respectively. V is the volume of dye solution and M is the mass of the acid catalyzed Poultry waste sorbent (g). while t is the equilibrium contact time, when $q_e = q_t$, equation 1 will be expressed as equation 2 below:

$$q_t = (C_o - C_t)v/w \dots\dots\dots(2)$$

where $q_e = q_t$ and C_t is the concentration at time, t . The percent dye removal (RE %) was calculated for

3.Results

The chromatogram shown as Figure 1 stands for unadsorbed sorbate out of the $5g/dm^3$ atrazine which was interacted with SS/A sorbent. The chromatogram was characterized by a baseline disturbance. This is caused by either hydrocarbon impurities or by impure carrier gas (Robert and Eugene, 2004). The former could be linked to the fact that the sorbate concentration ($5g/dm^3$) is too low for the 0.1g carbon dose. Unoccupied pore size could as well, lead to desorption of the sorbate with a resultant poor percentage removal (46.08%).

each equilibration by the expression presented as equation 3

$$RE(\%) = (C_o - C_e)/C_o \times 100, \dots\dots (3)$$

Where RE (%) is the percent of dye adsorbed or removed. The % removal and adsorption capacities were used to optimize the activation condition. The test were done at a constant temperature of $27 \pm 2^{\circ}C$.(Rozada *et al.*,2002). The equilibrium concentration of atrazine (herbicide), q_e and Adsorption efficiency (% Removal) were estimated. The extent of atrazine removal (by difference) from chloroform spiked with 25g/L of atrazine was expressed as equation 3 (Hameed *et al.*,2006)

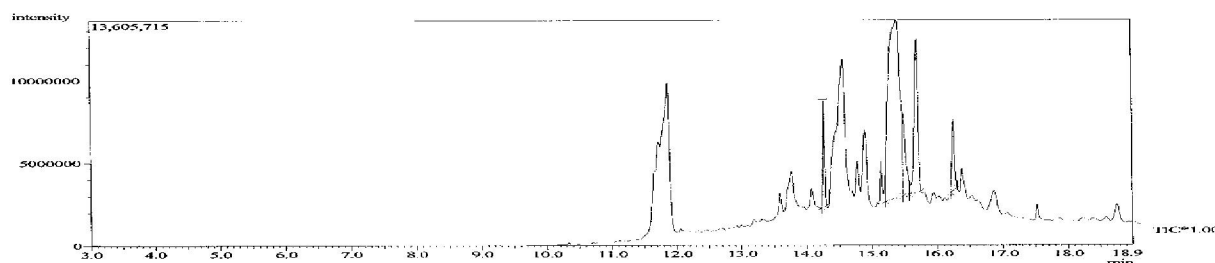


Figure 1: GC/MS chromatogram of equilibrium concentration atrazine after adsorption onto $SS/A/5g/L^{-1}$ sorbent (Carrier gas-Helium 100.2kpa, Column temperature $-60^{\circ}c$, Injection temperature $-250^{\circ}c$, Injection volume $-1\mu L$, Flow rate $-1.61mL/min$, Injection method- split, Linear velocity- 43.6cm/sec.)

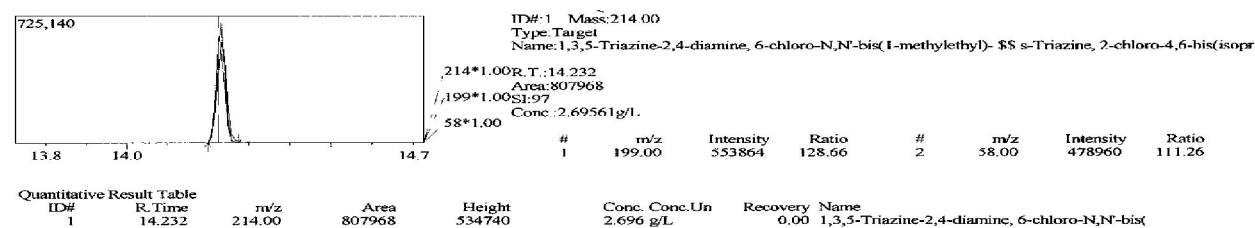


Figure 2: GC/MS chromatogram, quantitative measurement and spectral information of equilibrium phase atrazine after adsorption onto $SS/A/5g/L^{-1}$ sorbent

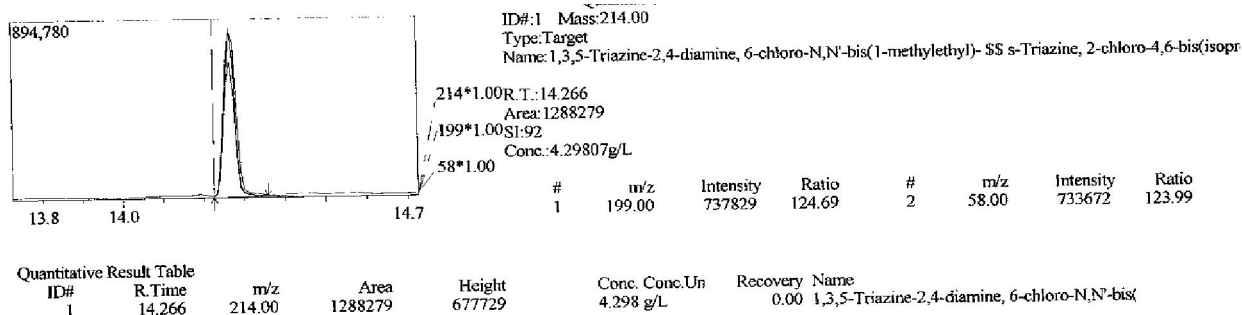


Figure 3: GC/MS chromatogram, quantitative measurement and spectral information of equilibrium phase atrazine after adsorption onto SS/A/10g/L⁻¹ sorbent

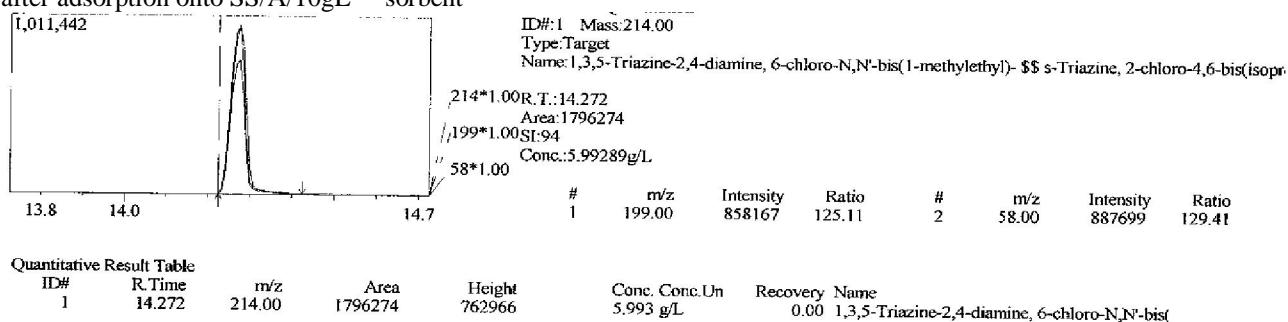


Figure 4: GC/MS chromatogram, quantitative measurement and spectral information of equilibrium phase atrazine after adsorption onto SS/A/15g/L⁻¹ sorbent

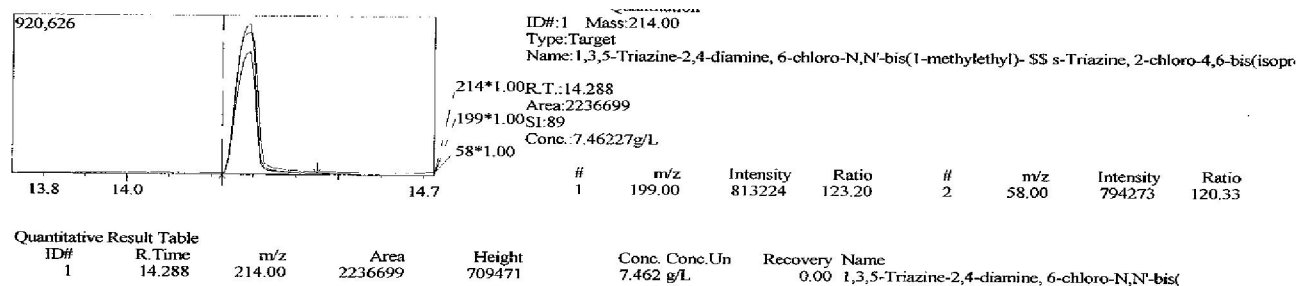


Figure 5: GC/MS chromatogram, quantitative measurement and spectral information of equilibrium phase atrazine after adsorption onto SS/A/20g/L⁻¹ sorbent

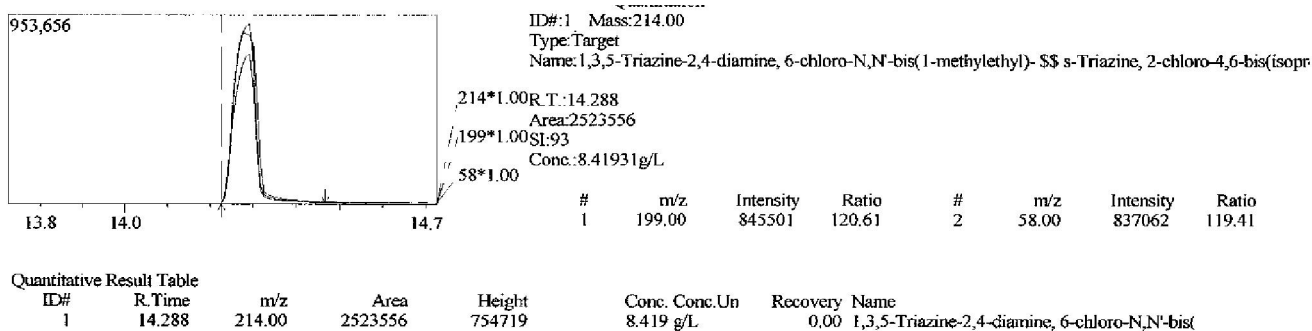


Figure 6: GC/MS chromatogram, quantitative measurement and spectral information of equilibrium phase atrazine after adsorption onto SS/A/25gL⁻¹ sorbent

Equilibrium experimental data from figures 2to 6 were treated as Table 1

Table 1: Adsorption experimental data of atrazine uptake by fixed mass of SS-Sorbents at different initial sorbate concentration, using GC/MS

Sorbent	Co (g/dm ³)	Ce (g/dm ³)	Ca (g/dm ³)	% RE	Ads.m (mg.10 ⁻³)	q _e (mg/g x 10 ⁻³)	Kc	G (kJ/mol)
SS/A/5	5	2.696	2.304	46.08	0.0230	0.230	0.854	+393.941
SS/A/10	10	4.298	5.702	57.02	0.0570	0.570	1.327	-705.381
SS/A/15	15	5.993	9.007	60.047	0.0901	0.901	1.503	-1016.670
SS/A/20	20	7.462	12.558	62.69	0.1254	1.254	1.680	-1294.989
SS/A/25	25	8.419	16.581	66.324	0.1658	1.658	1.969	-1691.330

SS/A/5 -Sheanut shells, treated with H₃PO₄,interacted with Atrazine for 15 minute contact time, SS/A/5 -Sheanut shells, treated with H₃PO₄,interacted with Atrazine for 15 minute contact time,

4. Discussions

Effect of initial atrazine concentration on removal efficiency:

Table 1 presents the role played by initial sorbate concentration and its effect on sorption efficiency. The highest percentage atrazine removal was observed with the interaction of 0.1g atrazine with 10Cm³ of a 25g/L atrazine solution. Hence, out of 25g/L, 20g/L, 15g/L, 10g/L and 5g/L initial atrazines concentration, a total of 16.581, 12.538, 9.007, 5.702 and 2.696g/L atrazine was attracted onto the sheanut shell (SS) bioadsorbent. These accounts for a 66.324, 62.69, 60.007, 57.020 and 46.080% removal efficiency respectively. Findings in this research showed that for the selected time (1hour interaction) and within the 0.1g sorbent dose on 10Cm³ sorbate solution, (i) Adsorption efficiency increases with initial sorbate concentration.

(ii) Adsorption within the low sorbate concentration (5 – 10g/dm³) range could possibly be followed by

Table 2: batch adsorption isothermal experiment data of herbicide (atrazine) uptake by SS at different initial concentration, using GC/MS quantitation

biosorbent	Ce	log Ce	ln Ce	1/Ce	log(1+ 1/Ce)	q _e x 10 ⁻³	1/q _e	Log q _e
SS/A/5	2.696	0.431	0.993	0.371	0.137	0.230	4347.836	-3.638
SS/A/10	4.298	0.633	1.458	0.233	0.091	0.570	1754.386	-3.244
SS/A/15	5.993	0.778	1.791	0.167	0.067	0.901	1109.878	-3.045
SS/A/20	7.462	0.873	2.010	0.134	0.055	1.254	794.448	-2.902
SS/A/25	8.419	0.925	2.130	0.119	0.052	1.658	603.136	-2.780

SS/A/5 -Sheanut shells, treated with H₃PO₄,interacted with Atrazine for 15 minute contact time, SS/A/5 -Sheanut shells, treated with H₃PO₄,interacted with Atrazine for 15 minute contact time,

The Freundlich isotherm: The Freundlich isotherm model was chosen to estimate the adsorption intensity of the sorbent towards the adsorbent. It is an empirical equation employed to describe the isotherm data and presented on Table 2.

desorption. Hence, a less than 50% adsorption was investigated.

(iii) Adsorption of fairly high concentrated atrazine (15 – 25g/L) could be governed by a multilayer adsorption with resultant intraparticle attraction. In light of this, sorption efficiency or percentage sorbate uptake is greater than 60%.

Sorption isotherm modeling

The GC/MS quantitative results were fitted into 3 different isotherm models. These isotherms were used to investigate mode of surface coverage (Langmuir, Freundlich and BET models), while sorption capacity and intensities were investigated with Langmuir and Freundlich models only.

The Freundlich model is by far the most utilized isotherm model in wastewater treatment. It has been reported that data for the adsorption involving adsorbates within a liquid phase is best fitted using the Freundlich model (Cooney, 1999). The Two-Parameter Freundlich model relates the sorbed phase

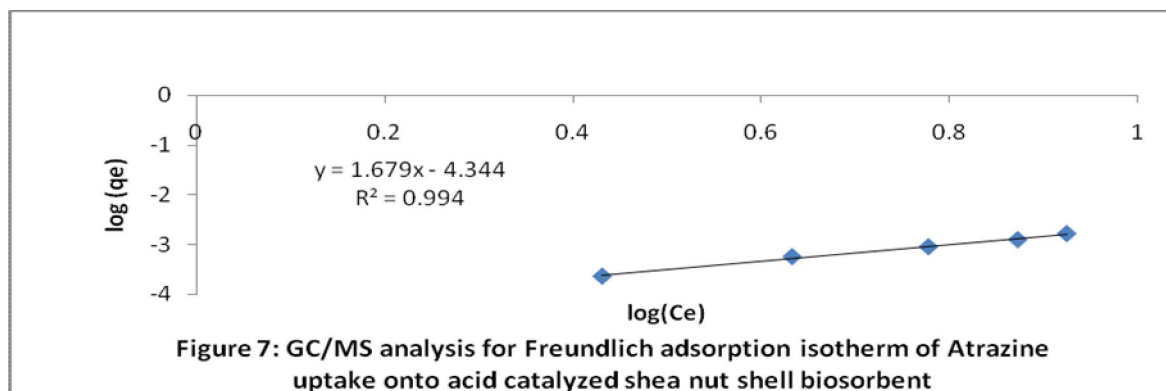
concentration to an equilibrium concentration of the adsorbate. The equation, which has a wide use in effluent or water treatment application, is given in logarithm form as equation (4) Hameed *et al.*, (2006)

$$\log q_e = \log k_f + 1/n \log C_e \quad (4)$$

The Freundlich model implies that the energy distribution for the adsorption sites is exponential in nature (Cooney, 1999). The rates of adsorption and desorption vary with the adsorption energy of the sites and there is a possibility for more than one monomolecular layer of adsorptive coverage. The Freundlich model also does not require that the surface coverage must approach a constant value corresponding to one complete monolayer, as C_e gets larger. At high concentrations, the equation would fail to fit experimental (Cooney, 1999).

The values of K_f , the binding constant and n , the exponent, are shown the values of K_f and n determine

the steepness and curvature of the isotherm (Igwe and Abia, 2007). The Freundlich equation frequently gives an adequate description of adsorption data over a restricted range of concentration, even though it is not based on the theoretical background. Apart from homogeneous surface, the Freundlich equation is also suitable for a highly heterogeneous surface and an adsorption isotherm lacking a plateau, indicating a multi-layer adsorption (Igwe and Abia, 2007). The values of $1/n$, less than unity is an indication that significant adsorption takes place at low concentration but the increase in the amount adsorbed with concentration becomes less significant at higher concentrations and vice versa (Igwe and Abia, 2007). The higher the K_f value, the greater the adsorption intensity (Igwe and Abia, 2007). Figure 7 is the Freundlich isotherm plot for atrazine removal by SS sorbents.



Langmuir isotherm: The affinity between the biomass and the different sorbates was quantified by fitting the obtained sorption values to the Langmuir isotherm model

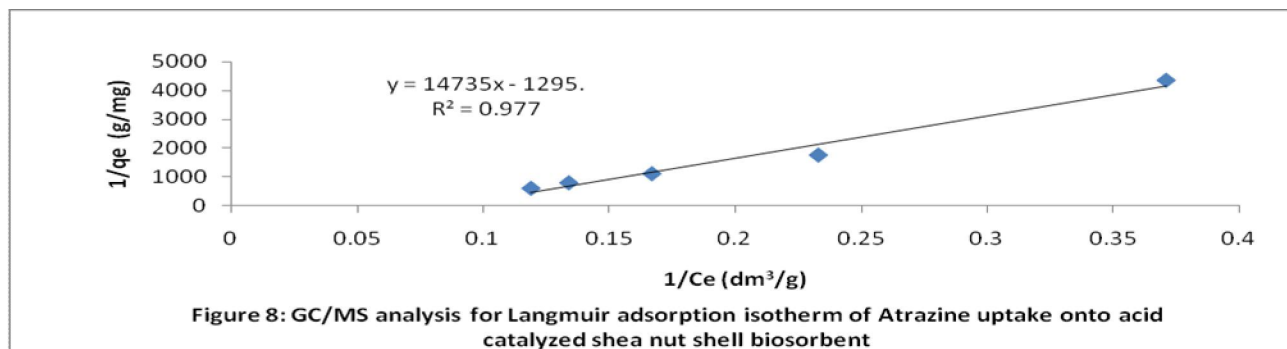
$$q = bC_e q_{\max} / (1 + bC_e) \quad (5)$$

Where q_{\max} is the maximum sorption uptake and b the, Langmuir constant, which establishes the

relationship between sorption and desorption rate. According to the Langmuir equation; adsorption is modeled as equation (6) below (Hameed, 2009).

$$1/q_e = 1/k_a q_m \cdot 1/C_e + 1/q_m \quad (6)$$

A plot of $1/q_e$ against $1/C_e$ gave the slope, $1/K_a q_m$ and intercept, $1/q_m$.



The model assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies with no transmigration of

adsorbate in the plane surface (Hameed *et al.*, 2006). A confirmation of the fitness of experiment data into Langmuir isotherm model indicates the homogenous

nature of the adsorbent surface. The result will also demonstrate the formation of monolayer coverage of dye molecule at the outer layer of the adsorbent (Hammed *et al.*, 2006). The essential characteristic of the Langmuir isotherm can be expressed in term of a dimensionless equilibrium parameter (R_L) defined as equation (7) by Hameed *et al.*, (2006) It is a dimensionless equilibrium parameter .

$$R_L = \frac{1}{1 + K_a C_o} \quad - \quad - (7)$$

Where R_L is the magnitude that determine the feasibility of the adsorption process . K_a = Langmuir constant related to energy of adsorption. while C_o is the highest initial dye concentration in the series of concentrations. The value of $R_L = 1$ shows linear Langmuir adsorption, $R_L > 1$ and < 1 are unfavourable and favourable adsorption respectively while adsorption is irreversible when $R_L = 0$

It is well known that the Langmuir equation is intended for a homogeneous surface. A good fit of

Table 3: Freundlich, Langmuir and BET isotherms experimental constants of herbicide (atrazine) uptake by SS at different initial concentration, using GC/MS

Isotherms	Relationship (y =)	R^2	Parameters	Values.
Freundlich	$1.679x4.344$	0.994	$1/n$ k_f	1.679 0.596 0.045×10^{-3}
Langmuir	$14735x-1295$	0.977	$q_m(\text{mg/g})$ $K_a(\text{Lmg}^{-1})$ R_L	-0.772×10^{-3} 0.0879 0.3127
BET	$4032x-1393$	0.894	BQ^0 B Q^0	-0.718×10^{-3} -1.895 0.379×10^{-3}

Beside the fact that adsorption isotherm described how the solute interact with the adsorbent, it is also used to optimize the use of adsorbent and to explain the adsorption capacity, intensity, and certain energy parameter. Freundlich k_f (0.0453×10^{-3}) and Langmuir q_m (0.772×10^{-3}) are measures of the adsorption capacity and maximum adsorption capacity respectively. It follow that q_m value is greater than K_F . This is in good agreement with earlier work conducted by this team (Itodo *et al.*, 2009b). K_F (units in mgg^{-1} ($1\text{mg}^{-n(n)}$) is defined as the distribution coefficient and represents the quantity of dye, adsorbed onto the activated carbon for a unit equilibrium concentration. It should not be unknown that $1/n$ ranging between 0 and 1 is a measure of adsorption Intensity. Hence, $1/n < 1$ and > 1 are indication of normal and cooperative adsorption

this equation reflects monolayer adsorption (Igwe and Abia, 2007). Results obtained in the analysis were presented in Table3.

From Table 3, it is evidence that Langmuir isotherm predict favorable absorption as depicted from Langmuir R_L and Freundlich $1/n > 1$, implying a cooperate adsorption. $1/n$ is an indication of a measure of surface heterogeneity (Dinish *et al.*, 2007). adsorption become more heterogeneous as $1/n$ tends to zero). Another parameter for selecting the best of isotherms is the correlation coefficient values, R^2 . Table 3 revealed that the Langmuir R^2 value (0.977) is higher than that obtained for Freundlich isotherm (0.994) .it thus implies that the adsorption process is well patterned by the Langmuir Isotherm: this, we can conclude with high proximity that adsorption is monolayer and on to a surface containing finite number of adsorption sites or uniform strategy of adsorption .This model also predicts that there is no transmigration of adsorbate in the plain of the surface (Hammed *et al.*, 2006).

respectively. It thus implies that the adsorption of atrazine onto sheanut shell biosorbent is a cooperative type of adsorption which could be linked to the nature of adsorbate (a multicomponent sample), atrazine in herbicide moiety (Hameed *et al.*, 2006). The Langmuir, constant related to energy of adsorption, K_a is 0.0879 Lmg^{-1}

Brunauer-Emmett-Teller (BET) Theory:

This theory was proposed in 1938 by Brunauer – Emmett – Teller. It relates to the formation of multilayer on adsorbent surface. According to the theory, the rate of adsorption onto the bare surface equals the rate of evaporation from the first layer of adsorbate. The inherent assumptions in the BET theory which are important to note are; (i) No interaction between neighboring adsorbed molecules

and (ii) The heat evolved during the filling of second and subsequent layers of molecules equals the heat of liquefaction. Neither of these assumptions is strictly valid, but despite this, the BET equation has been widely applied as a semi-empirical tool for the investigation of the characteristics of porous adsorbent. The BET isotherm has an empirical equation which reduces to the Langmuir model when the limit of adsorption is monolayer. Weber,(1972) presented the BET equation as 8 :

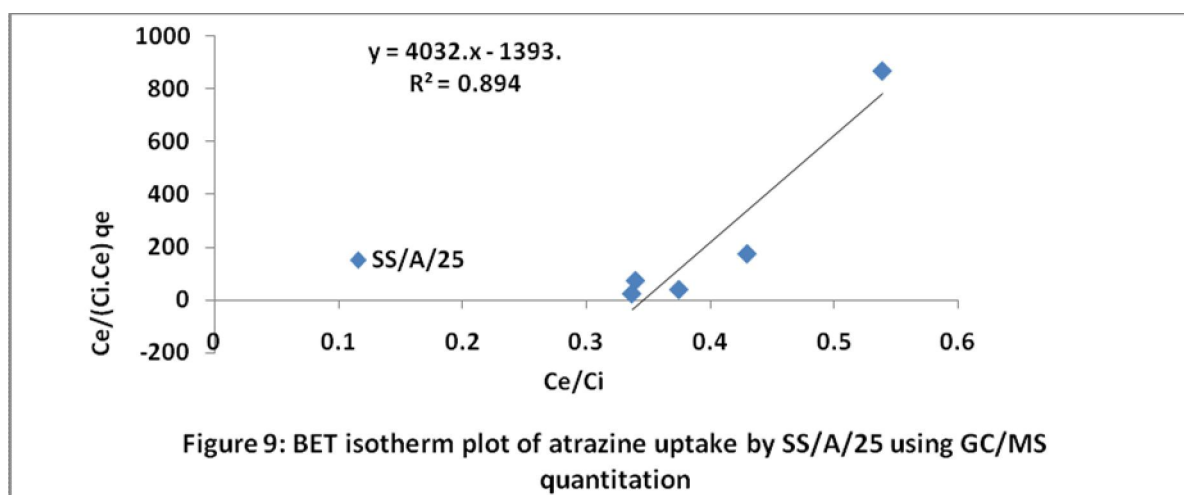
$$q_e = (BC_e Q^0) / (C_i - C_e) [1 + (B-1)(C_e/C_i)] \text{ ----- (8)}$$

C_i = saturation concentration of the solute, C_e = measured concentration in solution at equilibrium, Q^0

= number of moles of solute adsorbed per unit weight of adsorbent in forming a complete monolayer on the surface, q_e = number of moles of solute adsorbed per unit weight at concentration C_e , B = a constant expressive of the energy of interaction with the surface. To facilitate the application to experimental data, the equation could be transformed to the linear form as equation 9.

$$C_e / (C_i \cdot C_e) q_e = 1/BQ^0 + [(B-1)/BQ^0][C_e/C_i] \text{ -----(9)}$$

A plot of $C_e / (C_i \cdot C_e) q_e$ versus C_e/C_i gives a straight line with Slope = $(B-1)/BQ^0$ and Intercept = $1/BQ^0$ (Figure 9). This is for data which fits into the BET model (Weber, 1972).



From the analysis, the number of moles of solute adsorbed per unit weight of adsorbent in forming a complete monolayer on the surface was reported as $Q^0 = 0.379 \times 10^{-3}$

In Conclusion, a critical view of the present investigation shows that acid modified poultry waste based biosorbent is an effective absorbent for removal of Atrazine removal (with% RE range of over 66.324%)

Adsorption was studied using aqueous herbicide (atrazine) as adsorbate through fixed mass of adsorbent in batch. Sheanut shell activated carbon matrix gave a sorption efficiency (% removal) values which increases linearly with increase initial sorbate concentration from 46.08-66.324% for a 5-25g/dm³ initial sorbate concentration. Adsorption efficiency of a given sorbate concentration is non linear as concentration increases. A GC/MS quantitation, using an external standard method gave values which were fitted into five different isotherm models. Langmuir isotherm gave best fit (High $R^2 = 0.977$), favorable against the Freundlich model

which presented linear R^2 value ($R^2 = 0.994$) and a constant $1/n$ representing surface heterogeneity, $1/n = 1.679$ which implies a cooperative (not normal) adsorption ($1/n > 1$). It thus implies that adsorption of atrazine onto acid catalyzed sheanut shell is best explained as one on a uniform strategies of adsorption (Monolayer) and predicts that there is no transmigration of adsorbate in the plane of the surface.

Acknowledgements:

Authors are grateful to the Department of Pure and Applied Chemistry of both Usmanu, Danfodiyo University, Sokoto and Kebbi state University of Science and Technology, Aliero, Nigeria for supervisory guidance and to NARICT, Zaria for GCMS Analysis.

Corresponding Author:

Dr. Itodo Udoji Adams

Department of Applied Chemistry,

Kebbi state University of Science and Technology,

P.M.B 1144, Aliero, Kebbi state

Nigeria

E-mail: itodoson2002@yahoo.com

TEL: +2348073812726, +2348039503463

References

1. Agdi K, Bouaid A, Martin E, Fernandez H, Azmani A, Camara C. Removal of atrazine from environmental water by diatomaceous earth remediation method. *Journal of Environmental monitor* 2000; **2**: 420-423.
2. Ahmedna M, Marshal W, Rao M. Production of Granular activated carbon from selected Agric by products. *Bioresource and Technology* 2000; **71**(2): 113 – 123.
3. Bansode R, Losso J, Marshall E, Rao M, Portier J. Adsorption of volatile organic compd by pecen and almond shell based activated carbon. *Bioresource Technology* 2003; **90**. (2):175-184.
4. Chilton, N; Jack, N; Losso, N; Wayne, E. and Marshall, R. Freundlich adsorption isotherm of Agricultural by product based powered Activated carbon in Geosmin water system. *Bioresource Technology* 2002; **85** (2): 131-135
5. Cooney, David O. Adsorption Design for Wastewater Treatment. First Edn. Lewis. Publishers, CRC Press LLC, Boca Raton, Florida, 1999.
6. Dinesh M, Charles U, Pittman T. Arsenic removal from waste water using adsorbent; A critical review. *Elsevier* 2007; **B.V** :16-42
7. Eva, C.L; Daniela, M.N; Vincenta, M. and Antonio, G.R. Interaction of Phenol, aniline and P-nitrophenol on activated carbon surface as detected by TPD. *J. carbon* 2008; **46**(6): 870-875.
8. Fan, M; Marshall, W; Dugaard, D. and Brown, C. Steam activation of chars produced from oat hulls *Bioresource technology* 2003; **93** (1):103-107.
9. Gimba C, Ocholi O, Nok A. Preparation of A.C from Agricultural wastes II. Cyanide binding with activated carbon matrix from groundnut shell. *Nigerian journal of scientific research* 2004; **4** (2): 106-110.
10. Hameed BH. Evaluation of papaya seed as a non conventional low cost adsorbent for removal of MB. *Hazardous materials* 2009 ; **162**:939-944.
11. Hameed BH, Din AM, Ahmad AL. Adsorption of methylene blue onto Bamboo based activated carbon: kinetics and equilibrium studies. *Hazardous materials*. 2006; **137**(3):695- 699
12. Igwe JC, Abia AA. Maize cob and husk as adsorbent for removal Cd, Pb and Zn ions from waste water. *The physical science* 2003; **2**: 83-94.
13. Itodo AU, Abdulrahman FW, Hassan LG, Maigandi SA, Abubakar MN. Activation Chemistry and kinetic studies of shea nut shells biosorbent for textile waste water treatment. *Journal of research in Science, Education, Information And Communication Technology* 2009a; **1**(1):168-177.
14. Itodo AU, Abdulrahman FW, Hassan LG, Happiness UO; Uba A, Sadiq IS. Enhanced Cr (vi) adsorption from textile effluent by two lignocellulosic acid catalyzed nut shells. paper presented at the 32nd international Chemical Society of Nigera (CSN) conference held on 5th-9th /10/2009 at Bauchi, Nigeria
15. Malik, R; Ramteke, D. and Wate, S. Adsorption of Malachite green on groundnut shell waste based activated carbon. *Waste management*. 2006; **27** (9): 1129-1138.
16. Min C, Yun Z. Rapid method for analysis of organophosphorus pesticide in water: Bulletin application note. *Agilent Technology, USA* 2008; 19-21.
17. Myroslav S, Boguslaw B, Arthur T, Jacek N. Study of the selection mechanism of heavy metals adsorption on clinoptilolite. *J. Colloid and interface Science*. 2006; **304** (1): 21-28.
18. Namarsivayan C, Kavitha D. Removal of congo red from water by adsorption onto activated carbon prepared from Coir pith. *Dye and pigments*. 2007; **54**:47-58.
19. Omomnhenle, S; Ofomaja, A. and Okiemen, F.E. Sorption of methylene blue by unmodified and

modified citric acid saw dust. Chemical society of Nigeria 2006; **30** (1 & 2): 161- 164.

20.Raymond, P.W. Principle and practice of chromatography. First edition. Chrom. Edn. Bookseries, 2003;19 – 26. Retrieved from <http://www.library4science.com/enla.html>.

21.Reuben N.O, Miebaka J.A. Chromium (VI) adsorption rate in the treatment of liquid phase oil based drill cuttings. Africa journal of Environmental Sci and Tech. 2008;**2** (4): 68 - 74.

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

23.Rozada F, Calvo F, Garcia A., Martin V, Otaro M. Dye adsorption by sewage sludge based activated carbon in batch and fixed bed system. Bioresource technology 2003; **87** (3): 221 – 230.

24.Shimabukoro R.H. Atrazine metabolism and herbicidal selectivity. plant physiol. 1967;**42**:1269-1276.

25.Steve K, Erika T, Reynold, T., Paul M. Activated carbon :A unit operations and processes of activated carbon. Environmental engineering 2nd edn. PWS Publishing Co. 1998; 25, 350, 749.

26.USDA,.Activated Carbon processing. Review by National organic standard board panel 2002; 1-23

27.Weber WJ. physiochemical processes for water quality control. Wiley inter.science, London. 1972; 199 – 245.

28.Yoshiyuki S, Yutaka K. Pyrolysis of plant, animal and human waste: Physical and chemical characterization of the pyrolytic product. Bioresource Technology 2003;**90** (3): 241-247.

2/1/ 2010