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GCMS Prediction of Organochlorine Herbicide Sorption Rate: A Batch Kinetic Studies

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ABSTRACT

This study was aimed at deriving homemade activated carbon for the rate prediction of liquid phase atrazine uptake. Viable adsorption technique based on sorbate removal by phosphoric acid (H_3PO_4) Poultry Droppings (PD) was proposed to improve the ecological system. Two ways activation schemes generated activated carbons was applied to herbicide uptake and evaluated with three kinetic models. GC/MS quantitation experiment based on external standard method was performed to demonstrate up to 89.216% atrazine removal. The kinetic equilibrium study showed that a 300 min sorbate-sorbent interaction gave 19.293 out of 25 g dm^3 adsorption (being a 77.172% adsorption). This is only 5.140, 1.992, 1.432 and 0.632% higher than the 60, 120, 180 and 240 min interaction with 72.032, 75.180, 75.740 and 76.540% atrazine removal respectively. The pseudo-second order kinetics was observed to be more suitable in predicting the adsorption rate by the sorbate wherein the initial adsorption rate, h was estimated as 0.3646 g/mg/min. A time dependent physisorption phenomenon was evidenced. The major results support the conclusion that the sorted agro-waste has the potential to serve as extractants adsorbents in remediation process.

Key words: Triazines, wastes, poultry droppings, external standardization

INTRODUCTION

Triazines and organophosphorus pesticides are considered as priority pollutants since they are harmful to organism even μg L^{-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 CO_2 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).

The evaluation of different grade of GAC adsorbent for scavenging priority pollutants from waste water was reported by Shaski and Yankie (2002). The biomass is that of bituminous coal and coconuts shell. Results shows that source material used to prepare granulated activated carbon had significant effect on its mechanical strength, pore structure, surface texture and adsorption capacity. Gimba (2001) in his research argued that the feature of activated carbon from coconut shell compete favorably with commercial adsorbent. This conform to the finding of Shaski and Yenkie (2002). Bruce *et al.* (1992) presented an experimental design to optimize the treatment system for household water supplies using activated carbon. In their studies activated carbon was reported to be more effective in removing organic contaminant from water. It was also reported by Bruce *et al.* (1992) that activated carbon filtration does not remove microbes, sodium nitrate, fluoride, hardness, lead and other heavy metals except by specific types of adsorbents. Contrary to this findings, Kadirvelu *et al.* (2000) in their research on removal of heavy metals from industrial waste water, argued that activated carbon from coir pith is capable of removing Cu (II), Cd (II), Ni (II) and Pb (II) from waste water depending on the composition, pH and carbon concentration.

Dyeing industrial waste water was worked upon by Kadirvelu *et al.* (2000). It was reported that activated carbon prepared from coconut tree saw dust, at different agitation time gave an adsorption equilibrium after 60 min. The research state the insignificance of pH on colour removal and presented the importance of high carbon dose in effective removal of colour. Ahmedna *et al.* (2000) reported an experiment on the production of Granular Grade activated carbon, evaluating their physical, chemical and adsorption properties. The result shows that the type of by product and activation method greatly determine properties of activated carbon. In the research AC from pecan shell among other by products were closest to the reference carbon in terms of all the properties investigated. In line of this research, Chilton *et al.* (2002) comprehensively studied the properties of activated carbon from pecan shell and was shown to adsorb variety of metals and organic species in various processing waste water.

Among the conventional techniques for removing dissolved sorbates (heavy metals, dyes, organics etc.) include electrodialysis, phytoextraction (Sprynskyy *et al.*, 2006). Others include ultrafilteration, 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 100 mg L^{-1} (Wong *et al.*, 2000). 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. (Maria and Virginia, 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 (Itodo *et al.*, 2009a). Activated carbon can be prepared either by physical or chemical means, using a variety of starting material such as coconut shells, shell hull palm tree, apricot stones, almond shells etc. with the most popular being wood charcoal or coal (Yoshiyuki and Yutak, 2003).

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. 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 (Yoshiyuki and Yutak, 2003). About 9100 million tons of domestic animal manure was generated in Japan in 2001. The average number of cattle and poultry wastes has increased by 56 and 176% in the world since 1978. These Poultry manure such as wastes and litters, in the absence of suitable disposal methods may pose a threat to the public health and the environment because of potential contamination of air and ground and surface water sources via running off from the manure sites and odor releases (Isabel and Wayne, 2005).

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 the expected adsorption performance, using adsorption isotherms (Dinesh and Pittman, 2007). Knowledge of adsorption kinetics (i.e., the rate of solute uptake, which dictates the residence times of sorbed solute at the solid-liquid interface) is important in carbon adsorption process. Equilibrium is a phenomenon when the rate of adsorption and the rate 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. The amount of Dye at equilibrium, q_e was calculated from the mass balance equation given in Eq. 1 by Hameed *et al.* (2006).

$$q_e = (C_O - C_e)\ v/w \tag{1}$$

where, C_o and C_e are the initial and final Dye concentrations (mg L^{-1}), respectively. The v is the volume of dye solution and w is the mass of the acid catalyzed Poultry waste sorbent (g). While, t is the equilibrium contact time, when q_e = qt, Eq. 1 will be expressed as Eq. 2:

$$q_t = (C_o - C_t)\ v/w \tag{2}$$

where, $q_e = q_t$ and C_t is the concentration at time t. The percent dye removal (RE %) was calculated for each equilibration by the expression presented as Eq. 3:

$$\text{RE}\ (\%) = (C_0 - C_e)/C_o \times 100 \tag{3}$$

where, R (%) is the percent of dye adsorbed or removed. The % removal and adsorption capacities were used to optimize the activation condition (Maryam *et al.*, 2008). The test were done at a constant temperature of 25±2°C (Rozada *et al.*, 2003).

Kinetics of adsorption is one of the important characteristics defining the efficiency of adsorption. According to Dermibas *et al.* (2004), the study of adsorption dynamics describes the solute uptake rate and evidently the rate control the resident time of adsorbate uptake at the solid-solution interface. The adsorption rate constant can be used to compare the performance of activated carbons (Dermibas *et al.*, 2004). Several models have been used by a number of authors to ascertain the kinetics and mechanism of adsorption onto activated carbon surface.

Experimental results were fitted to pseudo-First and pseudo-second order kinetic model. The integrated and linearized pseudo-first order kinetic model expression was given by Lagergren in Ho and Mckay (1999) as Eq. 4:

$$\text{Log}\ (q_e - q_t) = \log q_e - (k_1/2.303)\ t \tag{4}$$

On the other hand, Ho and McKay (1999) presented the second-order kinetic model, integrated and linearized as Eq. 5:

$$t/q = 1/k_2q_e^2 + (1/q_e)\,t \qquad (5)$$

where, k_1 and k_2 stands for the pseudo first and second order rate constants respectively and were determined by regression analysis by fitting on a number of experimental data point, plotting log $(q_e - q_t)$ versus t and t/q against t from Eq. 4 and 5, respectively. q_e was calculated for each model and compared with its experimental value for precision validity test (Okparanma and Ayotamuno, 2008; Itodo *et al.*, 2009b).

Accepted kinetic model for a given adsorption is characterized by three common validity test;

- A good and high correlation coefficient, R^2 indicating the applicability and reliability of a given model
- A close agreement between the calculated and experimental q_e values
- The accepted model must have the least values for the sum of error squares (% SSE), which is determined as Eq. 6

$$\text{SSE}\ (\%) = \sqrt{\ }\ \Sigma\ (q_e\text{.exp.} - q_e\text{cal.})^2/N \qquad (6)$$

where, N is the number of data points (Hameed *et al.*, 2006; Itodo *et al.*, 2009b).

Quantitative analysis in gas chromatography is to convert the size of the peak into some measure of quantity of the particular material of interest. This involves chromatographing known amount of the material to be analyzed and measuring their peak sizes. Then, the composition of the unknown is determined by relating the unknown peaks to the known amounts through peak size. Standards are made from a matrix to be close to the unknown sample as possible not only in the amount of material to be analyzed, but also in the matrix of the sample itself. This standard was prepared, used and discarded within a short period of time owing to evaporation of most of the solvent and stability of standard (Robert and Eugene, 2004).

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).

MATERIALS AND METHODS

Brand name herbicide (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^{-1}) 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. The study was conducted in the Department of Chemistry, Usmanu Danfodiyo University, Sokoto and GCMS analysis was carried out at National Research Knstitute for Chemical Technology (NARICT), Zaria Nigeria during the year 2009.

Sample collection and preparation of activated carbon: Poultry Droppings (PD) (as the raw material for the production of activated carbon) were collected from Labana farms, Aliero in Kebbi state. The raw materials were pretreated as earlier described elsewhere (Zahangir *et al.*, 2008; Itodo *et al.*, 2009a, b). For thermo chemical (heat/chemical) activation, methods by Itodo *et al.* (2009a, b) and Turoti *et al.* (2007) were used after slight modifications. The samples (activated carbon produced) were crushed and sieved using <2 mm aperture size sieve.

Preparation of atrazine standard: Five gram of substrate was diluted to the mark of 100 cm^3 volumetric flask. This concentration of 50 g L^{-1} herbicide is equivalent to 25 g L^{-1} or 25,000 ppm atrazine stock.

Batch equilibrium kinetic studies: Accurately 0.1 g of home based activated carbon was mixed with 10 cm^3 of the 25 g L^{-1} atrazine solution. The residual concentration of atrazine in solution (C_e in g L^{-1}) was measured after different stirring and interaction times (60, 120, 180, 240 and 300 min). The equilibrium phase herbicide was analyzed using a GC/MS. External standard method was used to calibrate the machine beforehand (Min and Yun, 2008; Agdi *et al.*, 2000).

GC/MS conditioning: 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 L, 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^{-1} and pressure of 100.2 kPa. Ionization mode is Electron Ionization (EI) at a voltage of 70 eV. 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 routinely monitoring the pressure. Sorption efficiency of an adsorption process was defined based on the fractions of extracted and unextracted sorbates (Robert and Eugene, 2004).

Calibration curve for GC/MS analysis: A three point calibration curve was made from 1.0, 5.0 and 10.0 g L^{-1} 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).

This research was aimed at evaluating Poultry Droppings as a substrate for removing atrazine (herbicide) from aqueous solutions or water environment. The specific objectives include; Generation of activated carbon thereby adding values to the wastes. Testing the experimental data with 3 different kinetic models viz; (1) First order kinetics, (2) Second order kinetics and (3) apparent first order kinetics. Beside adding value to the waste and arriving at a more ecofriendly environment, contribution by this work was also hoped for its scholarly knowledge in areas like prediction of kinetic models, transport models, sorption energies and their evaluations.

RESULTS AND DISCUSSION

Experimental results were fitted to pseudo-First and pseudo-second order kinetic model. The integrated and linearized pseudo-first order kinetic model expression were given earlier by Lagergren in 1898 as Eq. 4 (Arun, 2002).

Chromatograms presented as Fig. 2 to 6 were typical of charts obtained for the equilibrium phase concentration analyzed using GC/MS.

Figure 1 is a chromatogram from which data typical of the adsorbents were derived. The baseline distortion. The other chromatograms obtained in this study are free from baseline instability, a disturbance, usually caused by either hydrocarbon impurities or impure carrier gas (Robert and Eugene, 2004).

Effects of contact time on sorption efficiency (%RE): The results from Table 1 showed the equilibrium phase concentration at any time C_t. The mass of the unadsorbed sorbates reduces from 0.0693-0.0571 as contact time increases from 60-300 min. This implies that the removal efficiency increases (from 72.032%-77.1325%) with time. Table 1 also shows the effects of sorbate-sorbent contact time on the sorption efficiency. Values presented as F indicates fractional attainment of equilibrium. It shows that as contact time increases adsorption tends to equilibrium which was attained at the 300th min of contact (F = 1).

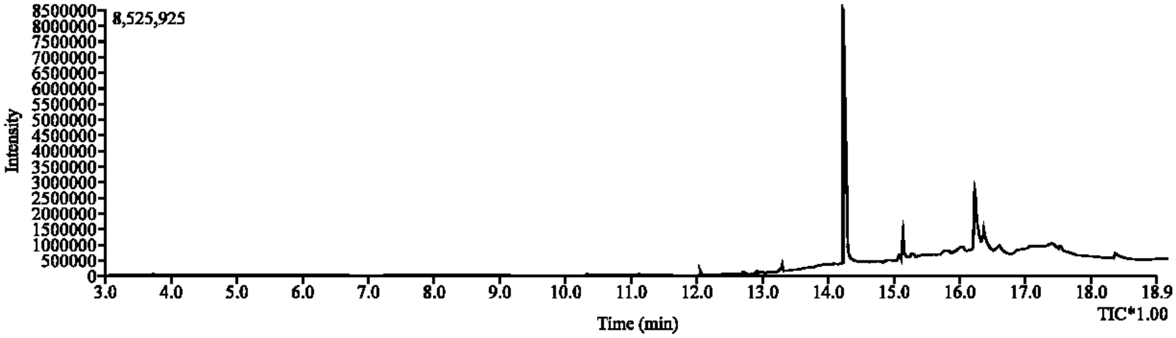
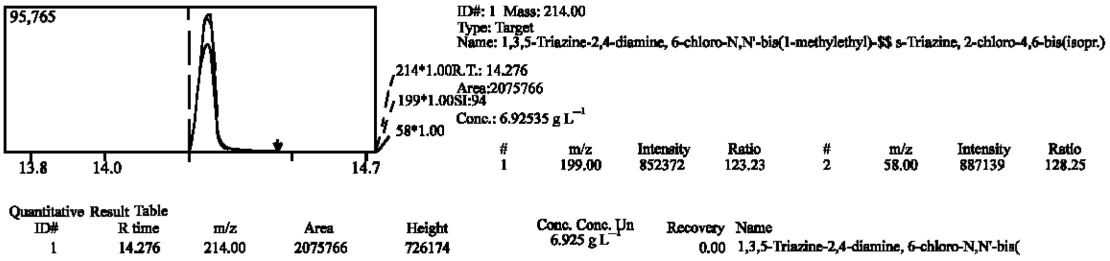


Fig. 1: GC/MS chromatogram of equilibrium concentration atrazine after adsorption onto PD/A/60 min sorbent (Carrier gas-Helium 100.2 kPa, Column temperature -60°C, Injection temperature-250°C, Injection volume-1 µL, Flow rate -1.61 mL min^{-1}, Injection method-split, Linear velocity- 43.6 cm sec^{-1})



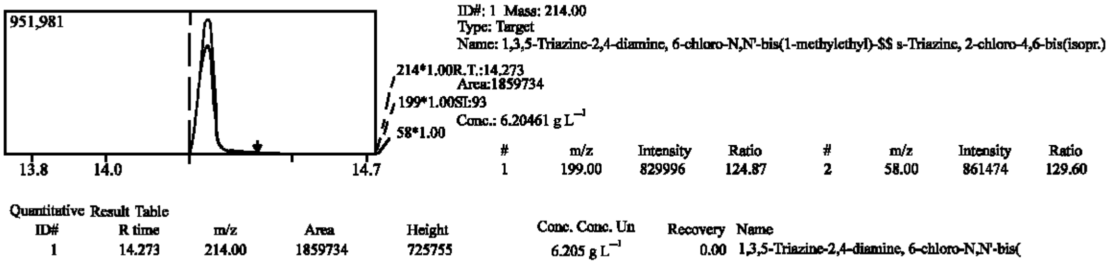
ID#: 1 Mass: 214.00
Type: Target
Name: 1,3,5-Triazine-2,4-diamine, 6-chloro-N,N'-bis(1-methylethyl)-$$ s-Triazine, 2-chloro-4,6-bis(isopr.)
R.T.: 14.276
Area:2075766
SI:94
Conc.: 6.92535 g L^{-1}

#	m/z	Intensity	Ratio	#	m/z	Intensity	Ratio
1	199.00	852372	123.23	2	58.00	887139	128.25

Quantitative Result Table

ID#	R time	m/z	Area	Height	Conc.	Conc. Un	Recovery	Name
1	14.276	214.00	2075766	726174	6.925	g L^{-1}	0.00	1,3,5-Triazine-2,4-diamine, 6-chloro-N,N'-bis(

Fig. 2: GC/MS chromatogram, quantitative measurement and spectral information of equilibrium phase atrazine after adsorption onto PD/A/60 min sorbent



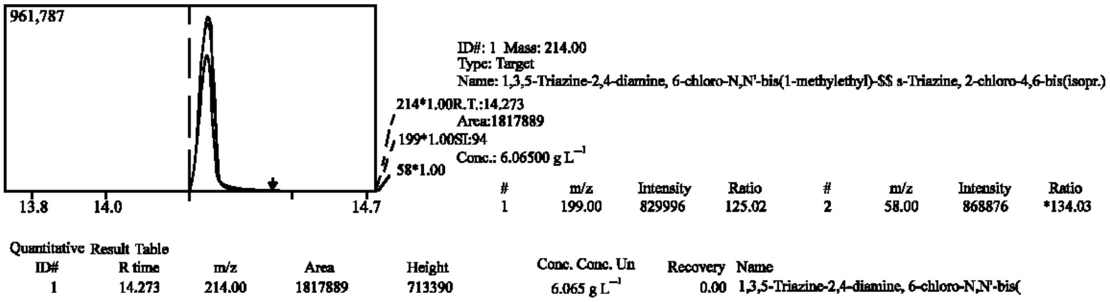
ID#: 1 Mass: 214.00
Type: Target
Name: 1,3,5-Triazine-2,4-diamine, 6-chloro-N,N'-bis(1-methylethyl)-$$ s-Triazine, 2-chloro-4,6-bis(isopr.)
R.T.:14.273
Area:1859734
SI:93
Conc.: 6.20461 g L^{-1}

#	m/z	Intensity	Ratio	#	m/z	Intensity	Ratio
1	199.00	829996	124.87	2	58.00	861474	129.60

Quantitative Result Table

ID#	R time	m/z	Area	Height	Conc.	Conc. Un	Recovery	Name
1	14.273	214.00	1859734	725755	6.205	g L^{-1}	0.00	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 PD/A/120 min sorbent



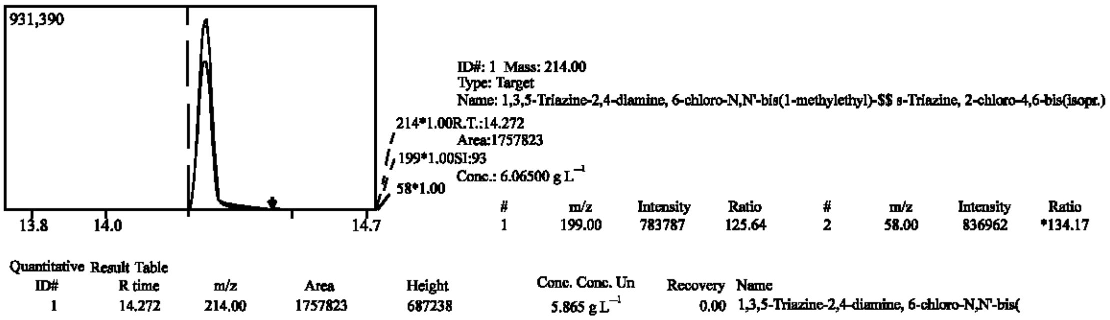
ID#: 1 Mass: 214.00
Type: Target
Name: 1,3,5-Triazine-2,4-diamine, 6-chloro-N,N'-bis(1-methylethyl)-$$ s-Triazine, 2-chloro-4,6-bis(isopr.)
R.T.:14.273
Area:1817889
SI:94
Conc.: 6.06500 g L^{-1}

#	m/z	Intensity	Ratio	#	m/z	Intensity	Ratio
1	199.00	829996	125.02	2	58.00	868876	*134.03

Quantitative Result Table

ID#	R time	m/z	Area	Height	Conc.	Conc. Un	Recovery	Name
1	14.273	214.00	1817889	713390	6.065	g L^{-1}	0.00	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 PD/A/180 min sorbent



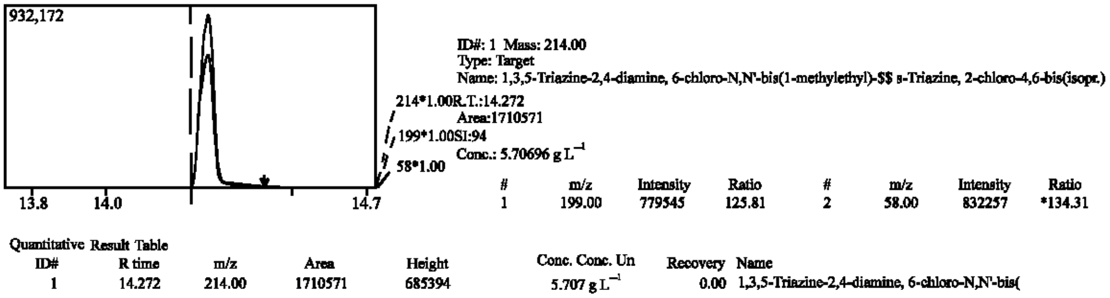
ID#: 1 Mass: 214.00
Type: Target
Name: 1,3,5-Triazine-2,4-diamine, 6-chloro-N,N'-bis(1-methylethyl)-$$ s-Triazine, 2-chloro-4,6-bis(isopr.)
R.T.:14.272
Area:1757823
SI:93
Conc.: 6.06500 g L^{-1}

#	m/z	Intensity	Ratio	#	m/z	Intensity	Ratio
1	199.00	783787	125.64	2	58.00	836962	*134.17

Quantitative Result Table

ID#	R time	m/z	Area	Height	Conc.	Conc. Un	Recovery	Name
1	14.272	214.00	1757823	687238	5.865	g L^{-1}	0.00	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/240 min sorbent



ID#: 1 Mass: 214.00
Type: Target
Name: 1,3,5-Triazine-2,4-diamine, 6-chloro-N,N'-bis(1-methylethyl)-$$ s-Triazine, 2-chloro-4,6-bis(isopr.)
R.T.:14.272
Area:1710571
SI:94
Conc.: 5.70696 g L^{-1}

#	m/z	Intensity	Ratio	#	m/z	Intensity	Ratio
1	199.00	779545	125.81	2	58.00	832257	*134.31

Quantitative Result Table

ID#	R time	m/z	Area	Height	Conc.	Conc. Un	Recovery	Name
1	14.272	214.00	1710571	685394	5.707	g L^{-1}	0.00	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/A/300 min sorbent

Table 1: Adsorption experimental data of atrazine uptake by fixed mass of PD-Sorbents at different contact time, using GC/MS

Biosorbent	Co (g dm^{-3})	Ct (g dm^{-3})	Ca (g dm^{-3})	RE (%)	q_t (mg g^{-1})	Kc = Ca/Ct	F = q_t/q_e
PD/A/60	25	6.925	18.008	72.032	1.801	2.600	0.9385
PD/A/120	25	6.205	10.795	75.180	1.879	3.029	0.9740
PD/A/180	25	6.065	18.935	75.740	1.894	3.122	0.9819
PD/A/240	25	5.865	19.135	76.540	1.914	3.263	0.9922
PD/A/300	25	5.707	19.293	77.172	1.929	3.381	1.000

PD/A/60-Poultry droppings, treated with, H_3PO_4 interacted with atrazine solution for 60 min. PD/A/300-Poultry droppings, treated with, H_3PO_4 interacted with atrazine solution for 300 min

Chromatograms presented as Fig. 2 to 6 were typical of charts obtained for the equilibrium phase concentration analyzed using GC/MS. Analysis was carried out after filtration at the 60, 120, 180, 240 and 300th contact time. As interaction time increases, equilibrium concentration reduces. This implies an increase in adsorbed sorbate concentration with time. Figure 2-6 presented the liquid phase atrazine after attraction onto sorbents, PD/A/60, PD/A/120, PD/A/180, PD/A/240 and PD/A/180, respectively. Their respective equilibrium phase concentrations (6.925>6.205>6.065> 5.865>5.707 g/dm^3) reduces with increase in time. This implies high atrazine uptake with time (minutes). The kinetic theory behind the figures is comparable to that which could be used to explain the sorption process in terms of adsorption being controlled by film-diffusion of particle-diffusion (Omoniyi and Patricia, 2008).

The extent at which contact time affect adsorption is non monotonical in multiplicity. At such, a 300 min sorbate-sorbent interaction gave 19.293 adsorption (being a 77.172% adsorption). This is only 5.140, 1.992, 1.432 and 0.632% higher than the 60, 120, 180 and 240 min interaction with 72.032, 75.180, 75.740 and 76.540% atrazine removal respectively. Summarily, over 72% of atrazine removal was attained within the selected 60-300 min timing.

The values of equilibrium constants, Kc on Table 1 are measures of sorption feasibility ΔG. More positive Kc values indicate a more negative value of ΔG at a given temperature indicate spontaneous nature of adsorption. Result in this study directly agrees with that of Namarsivayan and Kavitha (2007) wherein and that of Dakiky *et al.* (2002) indicating that the thermodynamic equilibrium constant becomes more positive with time.

Effect of contact time on rate studies: Results in this study shows that kinetics is an adsorption dynamics which describes the solute uptake rate and evidently control the resident time of adsorbate and possibilities of desorption as predicted by Dermibas *et al.* (2004).

Result clearly indicates that sorption by PD/A sorbents presents good uptake >70% along the series (60-300 min contact time). However, Table 1 gave results which revealed that the sorption efficiency by PD/A/300 (77.00%) >PD/A/240 (96.540%) while the least was by PD/A/60 (72.032%). Table 2 presents the initial adsorption rate, h was estimated from the second order kinetic model as 0.3646 g/mg/min while the fractional attainment at equilibrium was calculated as F = q_t/q_e (Juliade *et al.*, 2008). F is a measure of the diffusion coefficient D (cm^2 sec^{-1}). In this analysis, the F values tend to unity as the interaction time increases. Equilibration is attained at 300 min with F value of 1 while 60, 120, 180 and 240 contact time gave value of 0.934, 0.974, 0.982 and 0.992, respectively. As reported elsewhere, retention difference can be exclusively attributed to the nature of the stationary phase. In application to this work, Different phase concentrations is connected to different level of GC separation which according to Raymond (2003) is an explanation for demonstrating the effects of phase selectivity.

Table 2: Kinetic experimental data of atrazine uptake onto PD/A-sorbent by fixed mass sorbents at different contact time, using GC/MS

Time (min)	lnt	$t^{1/2}$	Ct	$1/q_t \times 10^{-3}$	$t/q_t \times 10^{-3}$	$\log(q_e - q_t)$	$F = q_t/q_e$	ln (Ca/Ct)
60	4.094	7.746	6.925	0.555	33.315	-0.893	0.934	0.9755
120	4.787	10.954	6.205	0.532	63.864	-1.301	0.974	1.108
180	5.193	13.416	6.065	0.528	95.037	-1.456	0.982	1.138
240	5.481	15.492	5.865	0.522	125.392	-1.824	0.992	1.183
300	5.704	17.321	5.707	0.518	155.521	-	1.000	1.218

Table 3: First order, second order and apparent first order kinetics experimental constants of atrazine uptake onto PD/A-sorbent by fixed mass of Sorbents at different contact time, using GC/MS

Kinetic model	R^2	Constants	Values
First order	0.974	k_1 (min^{-1})	0.00921
		q_e (cal) (mg g^{-1})	0.234
		q_e (exp) (mg g^{-1})	1.929
		%SSE	0.758
Second order	1.00	k_2 (mg g^{-1} min^{-1})	0.0948
		h (g mg^{-1} min^{-1})	0.3646
		q_e (cal) (mg g^{-1})	1.9607
		q_e (exp) (mg g^{-1})	1.929
		%SSE	0.014
Apparent first order	0.876	Ka (min^{-1})	0.001
		C	0.940

Adsorption tends to equilibrium as F-values approaches unity (1.0). F can be used to measure effective diffusibility. This behavioral trend is corroborated by the findings of Ho and McKay (1999) that sorption is influenced by contact time, pH, sorbent concentration, nature of solute and its concentration as re-emphasized by Okparanma and Ayotamuno (2008) and Itodo *et al.* (2009c). In this study, it was evidence that equilibrium time for the chosen concentration (25 g L^{-1}) and sorbent dose (0.1 g) in 10 cm^3 aliquot is 300 min, wherein 19.293 g L^{-1} out of 25 g L^{-1} atrazine was adsorbed.

In Table 3, adsorption constants were presented. In line with the aforementioned validity tests, It was observed that the value of the equilibrium concentration deduced with the pseudo-first-order kinetics is q_e = 1.929 mg g^{-1} while its experimental value is 0.234 mg g^{-1} (low precision). Estimated value of the correlation coefficient (R^2 = 0.974). This is also comparably low while the statistical sum of error is higher (%SSE = 0.758) for the first order kinetics. On the other hand, calculated q_e value for the pseudo-second-order kinetic (q_e = 1.920) is of high precision to the experimental q_e (1.9607) units in mg g^{-1}. A perfect correlation of 1.00 and extremely low statistical sum of error was evaluated and reported (Table 3). This results shows that the pseudo-second order kinetic model is more suitable in predicting atrazine sorption from aqueous medium. Similar result was reported by Hameed *et al.* (2006). Adsorption process in this study was interpreted as fairly high from the rate constants values and such sorbent is said to pocess fairly well developed V_{meso} or mesopore volume. This is in agreement with the result presented by Ana *et al.* (2009).

Generated data were also fed into the apparent first order equation, as described (Ana *et al.*, 2009) in Eq. 7.

$$\ln(C_0/C_e) = K_a t \quad (7)$$

The wide range of apparent first order rate constant (0.001) as compared to that of the pseudo first order kinetics (0.00921) is also an indication that the sorption of atrazine onto PD sorbent does not follow the first order kinetics. Generally, the shape of the graphs and parameters falls within the range of those obtained from the adsorption of methylene blue onto Bamboo based activated carbon by Hameed (2009).

CONCLUSION

The PD activated carbon matrices generated, using the two ways activation scheme with acid (H_3PO_4) and salt ($ZnCl_2$) as activating agents was successfully prepared and reported to provide over 70% atrazine adsorption for a kinetic study of 60-300 min. Contact time. A second order kinetic process was reported. An external standard preparation, followed by GC/MS quantitation proves a good option for analyzing the quantity of single analyte from a multicomponent system such as atrazine from either herbicide or pesticide.

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.

Ahmedna, M., W.E. Marshall and R.M. Rao, 2000. Production of granular activated carbon from select agricultural by-products and evaluation of their physical, chemical and adsorption properties. Bioresour. Technol., 71: 113-123.

Ana, S., P. Joao, M. José, B. Jose, C. Carvalho and O. Ania, 2009. Waste-derived activated carbons for removal of ibuprofen from solution: Role of surface chemistry and pore structure. Bioresour. Technol., 100: 1720-1726.

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

Bruce, S., B. Fred and D. Russell, 1992. Activated carbon filteration process. Agric. Extension Serv. Bull., 1029: 1-4.

Chilton, N., N. Jack, N. Losso, E. Wayne and R. Marshall, 2002. Freundlich adsorption isotherm of agricultural by product based powered activated carbon in geosmin water system. Bioresoru. Technol., 85: 131-135.

Cooney, D.O., 1999. Adsorption Design for Wastewater Treatment. CRC Press, Boca Raton, Florida.

Dakiky, M., M. Khamis, A. Manassra and M. Mer'eb, 2002. Selected adsorption of Cr (Vi) in industrial wastewater using low cost abundantly available adsorbent. Adv. Environ. Res., 6: 533-540.

Dermibas, E., M. Kobya, E. Senturk and T. Ozkan, 2004. Adsorption kinetics for the removal of Cr (vi) from aqueous solutions on the activated carbon prepared from agricultural wastes. J. Water, 30: 533-539.

Dinesh, M. and C.U. Pittman, 2007. Arsenic removal from waste water using adsorbent: A critical review. J. Hazard. Mater., 142: 1-53.

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 Mater., 137: 695-699.

Hameed, B.H. 2009. Evaluation of papaya seed as a non conventional low cost adsorbent for removal of methylene blue. J. Hazard. Mater., 162: 939-944.

Ho, Y.S and G. Mckay, 1999. Pseudo second order model for sorption processes. Process Biochem., 34: 451-465.

Isabel, M. and M. Wayne, 2005. The ultimate trash to treasure: Poultry waste into toxin-grabbing char. Agric. Res., 306: 127-143.

Itodo, A.U., F.W. Abdul-Rahman, L.G. Hassan, A.I. Dogonyaro I.S. Sadiq and U.O. Happiness, 2009a. Biosorption of heavy metals and herbicides onto poultry based activated carbon animalis. Proceedings of the Conference CSN, June 11, NARICT, Zaria.

Itodo, A.U., F.W. Abdulrahman, L.G. Hassan, S.A Maigandi and U.O. Happiness, 2009b. Thermodynamic equilibrium, kinetics and adsorption mechanism of industrial dye removal by chemically modified poultry droppings activated carbon. J. Basic Applied Sci., 17: 38-43.

Itodo, A.U., F.W. Abdulrahman, L.G. Hassan, S.A. Maigandi and H.U. Itodo, 2009c. Gas chromatographic prediction of equilibrium phase atrazine after sorption onto derived activated carbon. Int. J. Poult. Sci., 8: 1174-1182.

Juliade, T., K. Turkan, D. Gulsen and D. Timur, 2008. Dynamic analysis of sorption of MB dye on granular and powdered activated carbon. Chem. Eng. J., 144: 400-406.

Kadirvelu, M., M. Palanival and S. Rajeswari, 2000. Activated carbon from an agricultural by product, for the treatment of dyeing industry waste water. Bioresour. Technol., 74: 263-265.

Maria, P. and M. Virginia, 2009. Guava seed as adsorbent for adsorption of dye. Bioresour. Technol., 100: 2111-2117.

Maryam, K., A. Mehdi, T. Shabnam, M. Majdeh and K. Hameed, 2008. Removal of lead, cadmium, zinc and copper from industrial wastewater by carbon developed from walnut, hazelnut, almond and apricot stones. J. Hazard. Mater., 150: 322-327.

Min, C. and Z. Yun, 2008. Rapid Method for Analysis of Organophosphorus Pesticide in Water: Bulletin Application Note. Agilent Technology, USA., pp: 19-21.

Namarsivayan, C. and D. Kavitha, 2007. Removal of congo red from water by adsorption onto activated carbon prepared from coir pith. Dye Pigments, 54: 47-58.

Okparanma, R.N. and M.J. Ayotamuno, 2008. Predicting chromium (VI) adsorption rate in the treatment of liquid phase oil based drill cuttings. Afr. J. Environ. Sci. Technol., 2: 68-74.

Omoniyi, A. and U. Patricia, 2008. Kinetics of the removal of ovalbumin from wine model solution. Proceeding of 31st international CSN Conference, Chemical Society of Nigeria, sept. 22-26, pp: 75-80.

Raymond, P.W., 2003. Principle and Practice of Chromatography. 1st Edn., Churchill Livingstone, San Francisco, pp: 19-26.

Robert, L. and F. Eugene, 2004. Modern Practice of Chromatography. 4th Edn., John Wiley and Sons Inc., New Jersey, pp: 425.

Rozada, F., F. Calvo, A. Garcia, V. Martin and M. Otaro, 2003. Dye adsorption by sewage sludge based activated carbon in batch and fixed bed system. Bioresour. Technol., 87: 221-230.

Shaski, S.S. and M.K.N. Yankie, 2002. Evaluation of different grade of granular activated carbon adsorbent for scavenging priority pollutant from wastewater. Asian J. Chem., 14: 1009-1026.

Shimabukoro, R.H., 1967. Atrazine metabolism and herbicidal selectivity. Plant Physiol., 42: 1269-1276.

Sprynskyy, M., B. Buszewski, A.P. Terzyk and J. Namiesnik, 2006. Study of the selection mechanism of heavy metal (Pb^{2+}, Cu^{2+}, Ni^{2+} and Cd^{2+})adsorption on clinoptilolite. J. Colloid Interface Sci., 304: 21-28.

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.

Wong, J.P.K., Y.S. Wong and N.F.Y. Tam, 2000. Nickel biosorption by two chlorella species, *C. vulgaris* (a commercial species) and *C. miniata* (a local isolate). Bioresour. Technol., 73: 133-137.

Yoshiyuki, S. and K. Yutak, 2003. Pyrolysis of plant, animal and human waste: Physical and chemical of the pyrolytic product. Bioresour. Technol., 90: 241-247.

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 International Water Technology Conference, (IWTC'08), Egypt, pp: 373-383.