
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, Usman Danfodiyo University, Sokoto, Nigeria
⁴Faculty of Agriculture, Usman Danfodiyo University, Sokoto, Nigeria
⁵Department of Chemistry, Benue State University, Makurdi, Nigeria

Abstract: Three kinetic models were utilized in analyzing the removal of Atrazine from herbicide solution by its adsorption onto acid treated Poultry dropping Activated carbon. The forecasted pseudo-first order (with $K_1=0.00921\text{min}^{-1}$) was proven unfit in predicting the adsorption rate by the Bhattacharya and Venkobacharya rate constant which is approximately the same ($k_a=-0.00921\text{min}^{-1}$) but opposite in sign to the former. The linearity of $(U)T$ shows that atrazine molecule has great accessibility to the adsorbent molecule. Desorption constant by the Elovic model was estimated as 12.987g/mg. Other parameters investigated to increase linearly with contact time include the fractional attainment at equilibrium ($Ca/Co$), equilibrium constants ($K_c$), sorption efficiency ($\%RE$) and Gibbs free energy ($\Delta G$). [Journal of American Science 2010;6(7):8-18]. (ISSN: 1545-1003).

Key words: Poultry dropping, Kinetics, Herbicide, Sorption, Activated carbon, GC/MS

1. Introduction

Herbicide in the soil and water 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. Past studies was built on a strong case that atrazine is hazardous and unsafe to both human and ecosystem. Some of these studies found that the herbicide, atrazine disrupt the production and functionality of human hormones and a higher incidence was reported for cases of cancer in humans and laboratory animals (Zhongren et al., 2006). The sorption of herbicide aqueous phase by activated carbon has been reported (Agdi et al., 2000; Zhongren et al., 2006). Applicable methods for herbicide removal include a combination of biological, chemical and physical processes. 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. The use of active carbon was prescribed by USEPA as the best available technology for the removal of (USEPA, 2002).

In the United States, a predicted 8.6 billion broilers will be produced in 2004, generating approximately 9 million metric tons of manure. Broiler management involves their confinement in concentrated animal facilities which usually results in excessive localized land application of this manure due to over production. This situation may pose a threat to public health and environment.
health and the environment because of potential contamination of air, ground and surface water sources via run-off and odor releases. Other manure uses, beside land application, such as burning for fuel recovery or land filling, produce low-value alternatives (Isabel et al., 2005).

There was report on Pseudo-second-order kinetic for adsorption of methylene blue on papaya seeds activated carbon and on the adsorption of dyes on activated carbon prepared from sawdust (Malik, 2004).

Choice of equipment: The gas chromatographic technique is at best a mediocre tool for qualitative analysis. It is best used with other technique to answer the question of what is present in a sample. Besides the simplicity of the instrument, ease of operation, GC also provides the answer to how much? It is an excellent quantitative analytical tool in quantifying micrograms in a litre or one volume in millions of volumes (Robert and Eugene, 2004). 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). The quantitative principle of GC depends on the fact that the size of the chromatographic peak is proportional to the amount of material (Robert and Eugene, 2004). Peak size is the size of chromatographic peak is proportional to the amount of material contributing to the peak. It is the measure from height and area of the peak while Peak height is proportional to the amount of material contributing to the peak if nothing in the system changes that could cause a change in the width of the peak between sample and standard.

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 equation 1 by Hameed et al., (2006).

\[ q_e = (C_0 - C_e) \frac{V}{W} \]  

where \( C_0 \) 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 \( q_0 = q_t \) equation 1 is expressed as equation 2 below:

\[ q_e = (C_0 - C_t) \frac{V}{W} \]  

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 equation 3

\[ R \ E(\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \]  

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., 2002).

Rate and extent of adsorption: Adsorption is often confused with absorption, where the substance being collected or removed actually penetrates into the other solid (Reynolds and Richards, 1997). Activated carbon uses the physical adsorption process whereby attractive Van der Waals Forces pull the solute out of solution and onto its surface (Reynolds and Richards, 1997). Kinetics of adsorption is one of the important characteristics defining the efficiency of adsorption (Anirudhan and Krishnan, 2003). According to Demirbas 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 (Dianati-Tilaki and Ali, 2003). Several models have been used by a number of authors to ascertain the kinetics and mechanism of adsorption onto activated carbon surface. Among several kinetic models employed for rate studies include Apparent first order (Ana et al., 2009), Pseudo First and second order models (Hameed, 2009), Elovic equation (Badmus et al., 2007; Chen and Clayton, 1980), Pattacharya/Venkobacharya model (Omoniyi and
2. Materials and methods

Brand name herbicide (atrazine® presumably 2-chloro-4-ethylamino-6-isopropylamino-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 (25g/L) was prepared and from which ranges of testing 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 (0.1M) and distilled water were used as washing agents.

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 and b). For thermo chemical (heat/chemical) activation, methods by Itodo et al., 2009a and 2009b; Turoti et al., 2007 were used after slight modifications. The samples (activated carbon produced) were crushed and sieved using <2mm aperture size sieve.

Preparation of Atrazine standard: 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.

Batch equilibrium kinetic studies: Accurately 0.1g of home based activated carbon was mixed with 10cm³ of the 25g/L atrazine solution. The residual concentration of atrazine in solution (C_e in g/L) was measured after different stirring and interaction times (60, 120, 180, 240, and 300mins). 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 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 100³ 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 (Itodo et al., 2009c). 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; Itodo et al., 2009c).

Calibration curve for GC/MS analysis: 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).

3. Results

Experimental results were fitted into Elovic and Bhattacharya/Venkobacharya kinetic model. The integrated and linearized expression were given as equations below.

Effects of contact time on sorption efficiency (% RE): The results from 1 shows the equilibrium phase concentration at any time (Ct). The mass of the unadsorbed sorbates reduces (from 0.0693 – 0.0571) as contact time increases from 60 – 300 minutes. This implies that the removal efficiency increases (from 72.032% - 77.1325%) with time. Table 1 therefore presents the effects of sorbate–sorbent contact time on the sorption efficiency.

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

<table>
<thead>
<tr>
<th>Biosorbent</th>
<th>Co (g/dm³)</th>
<th>Ct (g/dm³)</th>
<th>Ca (g/dm³)</th>
<th>% RE</th>
<th>Ads mass</th>
<th>qt (mg/g)</th>
<th>Kc</th>
<th>ΔG</th>
</tr>
</thead>
<tbody>
<tr>
<td>PD/A/60</td>
<td>25</td>
<td>6.925</td>
<td>18.008</td>
<td>72.032</td>
<td>0.1801</td>
<td>1.801</td>
<td>2.600</td>
<td>2384.428</td>
</tr>
<tr>
<td>PD/A/120</td>
<td>25</td>
<td>6.205</td>
<td>10.795</td>
<td>75.180</td>
<td>0.1879</td>
<td>1.879</td>
<td>3.029</td>
<td>2765.536</td>
</tr>
<tr>
<td>PD/A/180</td>
<td>25</td>
<td>6.065</td>
<td>18.935</td>
<td>75.740</td>
<td>0.1894</td>
<td>1.894</td>
<td>3.122</td>
<td>2844.001</td>
</tr>
<tr>
<td>PD/A/240</td>
<td>25</td>
<td>5.865</td>
<td>19.135</td>
<td>76.540</td>
<td>0.1914</td>
<td>1.914</td>
<td>3.263</td>
<td>2951.233</td>
</tr>
<tr>
<td>PD/A/300</td>
<td>25</td>
<td>5.707</td>
<td>19.293</td>
<td>77.172</td>
<td>0.1929</td>
<td>1.929</td>
<td>3.381</td>
<td>3039.882</td>
</tr>
</tbody>
</table>

PD/A/60 – Poultry droppings, treated with, H₃PO₄ interacted with Atrazine solution for 60 minute. PD/A/300 – Poultry droppings, treated with, H₃PO₄ interacted with Atrazine solution for 300 minute.

Chromatograms presented as Figures 1 to 5 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 minutes contact time. As interaction time increases, equilibrium concentration reduces. This implies an increase in adsorbed sorbate concentration with time.

Figure 1: GC/MS chromatogram, quantitative measurement and spectral information of equilibrium phase atrazine after adsorption onto PD/A/60min sorbent.
Figure 2: GC/MS chromatogram, quantitative measurement and spectral information of equilibrium phase atrazine after adsorption onto PD/A/120min sorbent

Figure 3: GC/MS chromatogram, quantitative measurement and spectral information of equilibrium phase atrazine after adsorption onto PD/A/180min sorbent

Figure 4: GC/MS chromatogram, quantitative measurement and spectral information of equilibrium phase atrazine after adsorption onto PD/A/240min sorbent
4. Discussions

The fraction of Atrazine uptake at a given time was presented (Figure 6). The rise was pronounced from the 60th to 120th minutes. After which the increase steadily adds from 0.752 to 0.772. i.e for every one portion of sorbate, 0.772 part was adsorbed at the 300th minutes. This is the fractional attainment at equilibrium (Ca/Co).

**Effect of contact time on sorption feasibility:** The negative value of ΔG at a given temperature indicates spontaneous nature of adsorption (Namasivayan and Kavitha, 2007). The more negative the value of ΔG, the more spontaneous the nature of adsorption (Itodo et al., 2009b). As the thermodynamic equilibrium constant becomes more positive with time, the negative ΔG value increases (Figure 7). That is, ΔG becomes more negative with interaction time. Hence, the adsorption of dye onto chemically modified poultry droppings becomes more spontaneous with time.

The changes imposed on atrazine uptake by energy changes were investigated. ΔG values estimated in this analysis were all negative. This is an indication of a feasible adsorption. The trend of increase in negative G with time follows the fashion PD/A/60minutes (-2384.400) < PD/A/120mins (-2765.536) < PD/A/180mins (-2841.001) < PD/A/240mins (-2951.233) < PD/A/300mins (-3039.882) units in kJ/mol. This implies that as the contact time increases, G becomes more negative. This result tends to an increase adsorption over time.
The more negative the value of $\Delta G$, the more spontaneous is the adsorption. The thermodynamic equilibrium constant ($K_c$) was studied with interaction time. $K_c$ is a measure the ratio of sorbate (atrazine) in the solid phase (adsorbed) to that in the equilibrium phase (unadsorbed). The magnitude of $K_c$ is determined by the relative affinity of the adsorbent for the adsorbate. For good adsorption, a positive and large $K_c$ value is reported. Table 1 revealed that as contact time increases. The amount of atrazine attracted by the PD-adsorbent increases. This is an indication of good adsorption. The values of $K_c$ at 60, 120, 180, 240 and 300 minutes interaction time are 2.600, 3.029, 3.122, 3.263 and 1.929 respectively. It thus follows that as the $K_c$ value increases, $\Delta G$ value becomes more negative. This is due to the thermodynamic relationship between the two parameters.

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

<table>
<thead>
<tr>
<th>t(min)</th>
<th>lnt</th>
<th>$t^{0.5}$</th>
<th>Ct</th>
<th>$q_t \times 10^3$</th>
<th>$1/q_t \times 10^3$</th>
<th>$t/q_t \times 10^3$</th>
<th>$\ln (C_a/C_t)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>4.094</td>
<td>7.746</td>
<td>6.925</td>
<td>1.801</td>
<td>0.555</td>
<td>33.315</td>
<td>0.9755</td>
</tr>
<tr>
<td>120</td>
<td>4.787</td>
<td>10.954</td>
<td>6.205</td>
<td>1.879</td>
<td>0.532</td>
<td>63.864</td>
<td>1.108</td>
</tr>
<tr>
<td>180</td>
<td>5.193</td>
<td>13.416</td>
<td>6.065</td>
<td>1.894</td>
<td>0.528</td>
<td>95.037</td>
<td>1.138</td>
</tr>
<tr>
<td>240</td>
<td>5.481</td>
<td>15.492</td>
<td>5.865</td>
<td>1.914</td>
<td>0.522</td>
<td>125.392</td>
<td>1.183</td>
</tr>
<tr>
<td>300</td>
<td>5.704</td>
<td>17.321</td>
<td>5.707</td>
<td>1.929</td>
<td>0.518</td>
<td>155.521</td>
<td>1.218</td>
</tr>
</tbody>
</table>

Bhattacharya and Venkobacharya equation is also a pseudo-first order equation given as equation 6 and 7 (Omoniyi and Patricia, 2008; Ho et al., 1995)

$log \left[1 - \left(\frac{U}{T}\right)\right] = (K_{ad}/2.303)t \quad -- \quad (6)$

Where $U(T) = (C_i - C_t)/(C_i - C_e) \quad - \quad (7)$

$C_i$, $C_t$ are initial concentration and concentration at time t respectively, $K_{ad}$ is the rate constant and $C_e$ is the concentration at equilibrium. Figure 8 is a straight line with high correlation coefficient, $R^2$ in the range of 0.968 which indicates acceptability of the model for the sorption process.
Table 3: Bhattacharya and Venkobacharya equation experimental data for atrazine uptake by PD - biosorbent

<table>
<thead>
<tr>
<th>T(min)</th>
<th>C_i</th>
<th>C_t</th>
<th>C_i - C_t</th>
<th>C_i - C_e</th>
<th>U(T)</th>
<th>Log[1-U(T)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>25</td>
<td>6.925</td>
<td>18.008</td>
<td>19.293</td>
<td>0.933</td>
<td>-1.174</td>
</tr>
<tr>
<td>120</td>
<td>25</td>
<td>6.205</td>
<td>18.795</td>
<td>19.293</td>
<td>0.974</td>
<td>-1.585</td>
</tr>
<tr>
<td>180</td>
<td>25</td>
<td>6.065</td>
<td>18.935</td>
<td>19.293</td>
<td>0.981</td>
<td>-1.721</td>
</tr>
<tr>
<td>240</td>
<td>25</td>
<td>5.865</td>
<td>19.135</td>
<td>19.293</td>
<td>0.992</td>
<td>-2.097</td>
</tr>
<tr>
<td>300</td>
<td>25</td>
<td>5.707</td>
<td>19.293</td>
<td>19.293</td>
<td>1.000</td>
<td>----</td>
</tr>
</tbody>
</table>

The Bhattacharya and Venkobacharya plots (Figures 8) also gave a linear plot. It is evidence that B & V value of \( K_{ad} (-0.009212 \text{min}^{-1}) \) is approximately the same with the Lagergren \( K_{ad} \) value (0.00921 min \(^{-1}\)) but of opposite sign. This validity test further reaffirms the unfit of the experimental data by the Lagergren model of pseudo-first order kinetic. The high values of \((U(T)) \) (0.933,0.974,0.981,0.992 and 1.000) from Table 3 shows that atrazine molecules have greater accessibility to the adsorbent surfaces. The kinetic theory behind Figure 8 is that it can be used to explain the sorption process in terms of adsorption being controlled by film-diffusion or particle-diffusion (Ho et al., 1995; Omoniyi and Patricia, 2008). The linearity of the Figures 8 indicate that the adsorption of atrazine is controlled by particle -diffusion. Linearity of the diffusibility plot showed that the Pseudo-first order equation proposed was inadequate in describing the adsorption study. The B&V negative rate constant \((K_a= -0.009212 \text{min}^{-1})\) which is of the same value to a positive value for the Lagergren Pseudo first order rate constant given on Table 4 further suggest a second order kinetics since the statistical sum of error (%SSE) and precision test based on \( q_e \) for the first order kinetics are large and poor respectively. The integrated and linearized pseudo-first order kinetic model expression was given by Lagergren, (1898) in Ho and McKay,(1999) is given as equation 8:

\[
\log (q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t - - -(8)
\]

Table 4: Bhattacharya and Venkobacharya experimental constants of atrazine uptake onto PD/A-sorbent by fixed mass of Sorbents at different contact time, using GC/MS.

<table>
<thead>
<tr>
<th>Kinetic model</th>
<th>Relationship ((y = ))</th>
<th>( R^2 )</th>
<th>Constants</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>B &amp; V model</td>
<td>-0.004x-0.918</td>
<td>0.968</td>
<td>( K_a(\text{min}^{-1}) )</td>
<td>-0.009212</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( C )</td>
<td>-0.919</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( U(T) )</td>
<td>0.933-1.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( k_i(\text{min}^{-1}) )</td>
<td>0.00921</td>
</tr>
<tr>
<td>Pseudo First order model</td>
<td>-0.004x – 0.630</td>
<td>0.974</td>
<td>( q_e(\text{cal})(\text{mgg}^{-1}) )</td>
<td>0.234</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( q_e(\text{exp})(\text{mgg}^{-1}) )</td>
<td>1.929</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>%SSE</td>
<td>0.758</td>
</tr>
</tbody>
</table>

Table 5: Elovic model experimental constants of atrazine uptake onto PD/A-sorbent by fixed mass of PD-Sorbents at different contact time, using GC/MS.

<table>
<thead>
<tr>
<th>Kinetic model</th>
<th>Relationship ((y = ))</th>
<th>( R^2 )</th>
<th>Constants</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elovic equation</td>
<td>0.077x + 1.494</td>
<td>0.946</td>
<td>( \beta(\text{g/mg}) )</td>
<td>12.9870</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( \alpha )</td>
<td>1.9345</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1/ ( \beta )</td>
<td>0.077</td>
</tr>
</tbody>
</table>
Elovic Equation: Elovic equation was developed to describe the kinetics of chemisorption of a sorbent onto solid. The parameter, $\alpha$, represents the rate of chemisorption at zero coverage and the parameter, $\beta$, is related to the extent of surface coverage and the activation energy of chemisorption (Badmus et al., 2007; Chen and Clayton, 1980). $q_t$ (mg/g) is the amount adsorbed at time, $t$. while $\alpha$ and $\beta$ are constant during the experiment. The constant, $\alpha$ can be regarded as the initial rate since $dq/dt$ tends to $\alpha$ as $q_t$ tends to zero (Badmus et al., 2007).

The Elovic equation is generally expressed as equation 9 (Juliade et al., 2008)

$$\frac{dq}{dt} = \alpha \exp(-\beta q_t)$$

$\alpha$ is the initial adsorption rate, $\beta$ is the desorption constant (g/mg), $q_t$ is the amount of sorbate adsorbed at time, $t$.

To further simplify the equation for correlation regression estimation, Dermibas et al., (2004) assumed $\alpha \beta t \gg t$. After applying boundary condition $q_t = 0$ at $t=0$ and $q_t = q_t$ at $t = t$, the equation becomes as expressed in 10;

$$q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln(t)$$

A plot of $q_t$ versus $\ln(t)$ yield a linear plot with a slope of $(1/\beta)$ and intercepts of $(1/\beta) \ln (\alpha \beta)$. Elovic plot obtained in this analysis was presented as Figure 9.
In this analysis, the parameter, representing the desorption constant (β) was estimated as 12.987 g/mg while the value reported for the initial adsorption rate (α) is 1.93453 mg/g/min. Subjecting the kinetic data into this model gave a fitness with a correlation coefficient, $R^2 = 0.946$. This implies that this model, like any other kinetic models could be applicable in describing the solute uptake rate and idea on probable control of resident time of adsorbent and possible prediction of desorption.

In Conclusion, 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. Investigation of the derived PD activated carbon, using the two ways activation scheme with acid (H3PO4) was found to be worthwhile. The fractional attainment at equilibrium (Ca/Co), extent of feasibility ($G$), equilibrium constants ($K_e$) and sorption feasibility (%RE) all presented values that increases linearly with interaction time adsorption for a kinetic study of 60min-300min. Contact time. A second order kinetic process was predicted since validity test relating the Bhattacharya / Venkobacharya and Lagergren Pseudo first order rate constant disagree (as does the %SSE and precision validity test). The adsorption of atrazine is governed by particle diffusion while high level of (U)T shows that atrazine molecules has accessibility to the adsorbent.

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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

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