



Isotherm and Kinetic Studies of Chlorpyrifos Adsorption onto Agricultural By-Products

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Abstract The increased use of pesticides in agriculture have resulted in the increased concentration of pesticides and pesticide products in the environment. As a result, many methods have been sought for the de-contamination of these pesticides. The isotherm and kinetic studies of Chlorpyrifos adsorption onto activated and unactivated boiler fly ash and maize cob was studied. The amount of Chlorpyrifos adsorbed increased as contact time and initial pesticide concentration was increased. The pesticide adsorbed increased with increase in contact time but decreased with increase in initial pesticide concentration. Activation of the adsorbents improved the sorption capacity of the adsorbent with activated boiler fly ash giving the higher sorption capacity of 82.50% at initial pesticide concentration of 10 mg/L. The sorption kinetic data was modeled by Pseudo-first order, pseudo-second order, Ritchie's second order, penetrant transport, Elovich equation and McKay and Poots models. The Ritchie's second order model gave a better fit and the sorption process was found to be film diffusion controlled. The equilibrium data was modeled by six isotherm equations and the fitness of these isotherms based on the average R^2 values was found to follow the trend: Freundlich (0.9402) > Temkin (0.9059) > Flurry-Huggins (0.8547) > Langmuir (0.7409) > Dubinin-Radushkewich (0.7150) > Harkins-Jura (0.7093). From the values of the apparent energy of adsorption, which ranged from 223.61-1118.03 KJ/mol, the sorption process was found to follow chemisorption mechanism probably through hydrophobic pesticide-pesticide interactions. Therefore, activated and unactivated boiler fly ash and maize cob can effectively be used as an adsorbent for pesticide decontamination from the environment.

Keywords adsorption, environment, pesticides, Chlorpyrifos, Isotherm, Kinetics

Introduction

Environmental safety has been the focus in recent times and one of the major factors contributing to enormous unsafe environment is pesticides pollution. Pesticides have made a great impact on human health, production and preservation of foods and other cash crops by controlling disease vectors and by keeping in check many species of unwanted insects and plants [1]. The use of pesticides in agriculture and other sectors has increased and their detrimental effects cannot be overlooked. However, the rate of increase in the use of pesticides in developing countries is considerably higher than that of the developed countries.

Although there are benefits to the use of pesticides, there are also drawbacks, such as bioaccumulation, potential toxicity in humans and other animals [2]. Chlorpyrifos is a broad spectrum insecticide manufactured by reacting 3,5,6-trichloro-2-pyridinol with diethyl-thiophosphoryl Chloride [3, 4]. Chlorpyrifos is widely used active ingredient for the protection of important agricultural crops such as corn, citrus, peanuts etc and also effective in controlling a variety of insects including worms, corn root worms, cockroaches, flea beetles, flies, termites, fire ants and lice [5]. It is a crystalline organophosphate insecticide that inhibits acetyl-cholinesterase. An acetyl-cholinesterase inhibitor or anti-cholinesterase (AChEI) is a chemical that inhibits the cholinesterase enzyme from breaking down acetylcholine, thereby resulting in the accumulation of the neurotransmitter at nerve endings. This results in

excessive transmission of nerve impulse which causes mortality in the target [6]. Chlorpyrifos exposure causes tremendous health effects such as birth defects [2], persistent deficits in cognitive function and developmental neurotoxicity [7]. Many other pesticides and pesticide products have been reported to cause tremendous health effects [8]. Therefore, their removal from the environment is very important.

Many methods have been used for the removal of pesticides from the environment such as extraction using metal nanoparticles [6, 9] and solar photo-Fenton induced degradation [10]. Adsorption has been reported as one of the unit operations used in waste de-contamination. Adsorption is one of the most important factors that affects the fate of pesticides in soil and determines their distribution in the soil/water environment [11, 12]. The leaching potential of chlorpyrifos have also been investigated [13]. A major conventional means of adsorption is the use of activated carbon [14]. Adsorption of pesticides from aqueous solutions using activated carbon has been reported [15-23]. Conventional activated carbon adsorption has been reported to be very expensive [24]. Hence, the search for low cost, readily available agricultural by-products for waste decontamination have been reported such as cocoa pod husk for endosulfan, Chlorpyrifos and monocrotophos [25], cocoa pod husk for heavy metals [26]; coconut fibre for adsorption of heavy metals [27,28], magnetic molecularly imprinted polymer for chlorpyrifos adsorption [29] and so on. Boiler fly ash has been reported for the adsorption of Glyphosate and paraquat dichloride pesticide [30], adsorption of heavy metals [31] and dyes [32]. Maize cob has been reported for the adsorption of copper fungicide [33] and heavy metals [34].

Adsorption isotherms are important for the description of how molecules or ions of adsorbate interact with adsorbent surface sites and also, are critical in optimizing the use of adsorbents [35]. The successful representation of the dynamic adsorptive separation of solute from solution onto an adsorbent depends upon a good description of the equilibrium separation between the two phases [36]. An adsorption isotherm is characterized by certain constant values, which express the surface properties and affinity of the adsorbent and can also be used to compare the adsorptive capacities of the adsorbent for different pollutants [37]. Hence, the correlation of equilibrium data using either a theoretical or empirical equation is essential for the adsorption interpretation and prediction of the extent of adsorption [35].

The kinetics of adsorbate sorption is an important parameter for designing sorption systems. In addition to the uptake capacity, the rate of uptake of the adsorbate by the biosorbent is also critical as far as the reactor configuration is concerned [38]. A rapid kinetics will facilitate smaller reactors (lower retention time for effective adsorbate uptake) whereas a slow rate of uptake will necessitate long columns or series of columns to utilize maximum potential of the biosorbent. The rate of sorption onto a sorbent surface depends upon a number of parameters such as structural properties of the sorbent, initial concentration of the solute and the interaction between the solute and the active sites of the sorbent [38].

Therefore, in this paper, the results of the adsorption of chlorpyrifos onto boiler fly ash and maize cob is reported. The effect of adsorption contact time, initial concentration of pesticide and activation of the adsorbents were investigated. Comparison of the sorption capacity of the adsorbents was also investigated and the experimental results were fitted to some known isotherm models and some kinetic equations. This will serve as a cost effective as well as an environmental sound alternative to the conventional methods of pesticide decontamination.

Material and Methods

Material

Boiler fly ash was obtained from an oil mill located at Uturu, Abia State, while maize cob was obtained from a refuse dump site at Eke market Okigwe Imo State Nigeria. All reagents used were of analytical grade, purchased and used without further purification. Active force Chlorpyrifos ($C_9H_{11}Cl_3NO_3PS$), 400g/L, manufactured by Jabaili Agrotech was purchased and used without further purification. Doubly distilled-deionized water was used in all dissolutions and dilutions.



Methods

Preparation of adsorbents

The maize cob was washed thoroughly with water and then with de-ionized water, ground to powdered form and air dried. Big lumps in the boiler fly ash were removed and both maize cob and boiler fly ash were sieved using a test sieve shaker (EFL IMK3 model made by Endecotts England). The meal retained on the 250 μm was used. The adsorbents were divided into two parts each. One part each was dissolved in 2% (V/V) nitric acid for 24hrs, filtered and air dried. These were stored as activated boiler fly ash (ABFA) and activated maize cob (AMC) for experimental studies. The remaining one part each was left unactivated and labeled as unactivated boiler fly ash (UBFA) and unactivated maize cob (UMC).

Effect of contact time

Batch sorption experiments were performed at various time intervals. 100mL of pesticide concentration of 100mg/L was put in reagent bottles and 1.0g each of ABFA, UBFA, AMC and UMC of 250 μm size were separately added to different reaction mixtures and was monitored in a constant temperature rotary shaker for different time intervals (10 mins to 120 mins) at a constant temperature of 30°C and pH of 7.5. After the required time interval, the reaction mixture was centrifuged and the supernatant was filtered rapidly through a Whatman No. 41 filter paper. The pesticide concentration in the filtrate was determined using a UV visible absorption spectrophotometer model SP-300 at a wavelength of 290 nm.

Effect of Initial concentration

100 mL of different concentrations (10 mg/L to 100 mg/L) of chlorpyrifos were put in reagent bottles and 1.0g each of ABFA, UBFA, AMC and UMC of 250 μm size were separately added to different reaction mixtures and agitated in a constant temperature rotary shaker at 100 rpm, temperature of 30°C and pH of 7.5 for 1 hr. After 1 hr, the reaction mixtures were centrifuged and the supernatants were filtered rapidly through a Whatman No. 41 filter paper. The pesticide concentration in the filtrate was also determined using a UV visible absorption spectrophotometer model SP-300 at a wavelength of 290 nm.

Results and Discussion

The amount of pesticide adsorbed by the adsorbents was obtained as the difference between the initial and final concentrations of the pesticide in solution. This was calculated from a simplified mass balance equation as [39]:

$$q_e = (C_o - C_e) V/m \quad (1)$$

Where q_e is the amount adsorbed (mg/g); C_o is the initial concentration of the pesticide solution (mg/L); C_e is the concentration of the pesticide in solution after adsorption (mg/L), V is the volume of solution used (L) and m is the mass of the adsorbent used (g).

The activation of the boiler fly ash and maize cob with 2% (V/V) nitric acid was to open-up the micro pores of the adsorbents and make them ready for adsorption. Also activation helps to wash off any soluble biomolecules that might interfere with the sorption process. This means that activation of the adsorbents could change the surface characteristics of the adsorbent and this could affect the sorption process.

Adsorption capacity

The amount adsorbed (q_t) as contact time was increased for adsorption of Chlorpyrifos onto ABFA, UBFA, AMC and UMC is shown in Figure 1. As time was increased, the amount adsorbed increased rapidly from contact time of 10 min to 60 min and then decreased. At the initial time of the experiment, the adsorption sites on the adsorbents were unoccupied. From 10 min when sorption process was started, adsorbate molecules started occupying the sorption sites and as time was increasing, more pesticide molecules were being adsorbed on the sorption sites until about 60 min when the sorption sites were saturated and no more pesticide molecule could be adsorbed, hence the sorption process is said to have reached equilibrium. Similar observations have been reported [25, 30]. It could also be observed that the percentage adsorbed also increased as time was increased. Again, the amount of Chlorpyrifos



adsorbed by activated boiler fly ash (ABFA) was higher followed by activated maize cob (AMC), followed by unactivated boiler fly ash (UBFA) and then by unactivated maize cob (UMC). In each case, it could be seen that the activated adsorbents (ABFA and AMC) gave better sorption capacity more than the unactivated adsorbents (UBFA and UMC). Hence activation of the adsorbent increased the sorption capacity of the adsorbent. Other methods of activation have been reported, such as sodium hydroxide and deionized water [40]; hydrogen chloride [41] sulphuric acid [42]. The influence of activation on the sorption capacity of adsorbents have also been reported [25, 42].

The effect of initial concentration of pesticide solutions is shown in Figure 2. The amount adsorbed increased as initial concentration was increased. The increase in amount adsorbed as initial concentration was increased could be explained based on the fact that, as long as the sorption sites are not saturated, the increase in initial concentration increases the available pesticide sorbate molecules for sorption, thereby increasing the amount adsorbed. Clausen *et al* [44] reported that amount adsorbed increased with increasing sorbate concentration for adsorption of 2,4-D on α -alumina. Fontecha-Camera *et al*, [18] reported that rise in initial concentration increased the amount adsorbed at equilibrium for adsorption of diuron and amitrole onto activated carbons.

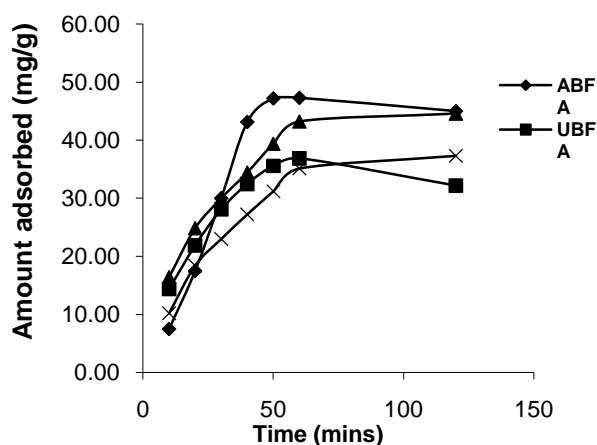


Figure 1: Amount adsorbed (mg/g) against time (min) for adsorption of chlorpyrifos onto boiler fly ash and maize cob

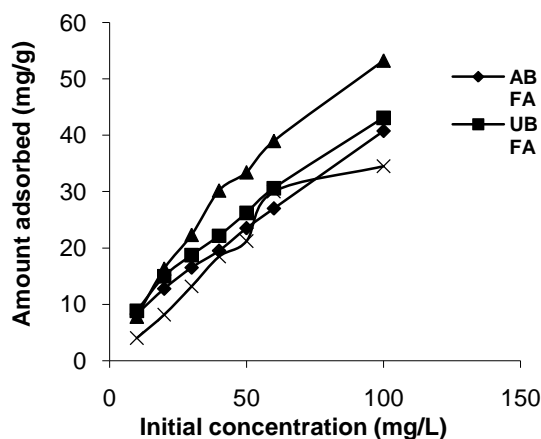


Figure 2: Amount adsorbed (mg/g) against initial concentration (mg/L) for adsorption of chlorpyrifos onto boiler fly ash and maize cob

On a closer look, it could be seen that as amount adsorbed increased, with increase in initial concentration, the percentage adsorbed decreases. For example, for activated boiler fly ash (ABFA) the percentage adsorbed decreased from 82.50% at initial concentration of 10mg/L to 43.13% at initial concentration of 100mg/L. As the initial



concentration increases, the number of pesticide molecules competing for sorption site increases and this competition results in the reduction in percentage adsorbed even when amount adsorbed increases. [45-47].

Sorption Kinetics and Intraparticle Diffusivity

The experimental kinetic data was analyzed using three kinetic equations namely; pseudo-first order, pseudo-second order and Ritchie’s second order equations while the intraparticle diffusivity was analyzed using three intraparticle diffusion equations namely; penetrant transport, Elovich and McKay and Poots equations. The kinetic equations are given below as follows; pseudo-first order (Eq. 2) [48]; pseudo-second order (Eq. 3) [49] and Ritchie’s second order (Eq. 4) [50]:

$$\log (q_e - q_t) = \log q_e - K_1 t / 2.303 \tag{2}$$

$$t/q_t = 1/h_0 + t/q_e \tag{3}$$

$$1/q_t = 1/K_2 q_e t + 1/q_e \tag{4}$$

Where q_e and q_t (mg/g) are the amount of pesticide adsorbed at equilibrium and time t (min) respectively; K_1 is the rate constant for pseudo-first order equation; K is the rate constant for Ritchie’s second order equation and h_0 is the initial sorption rate for pseudo-second order equation given by

$$h_0 = K_2 q_e^2 \tag{5}$$

where K_2 is the rate constant for pseudo-second order equation. The pseudo-first order plot is show in Figure 3, the pseudo-second order plot is shown in Figure 4 and the Ritchie’s second order plot is given in Figure 5.

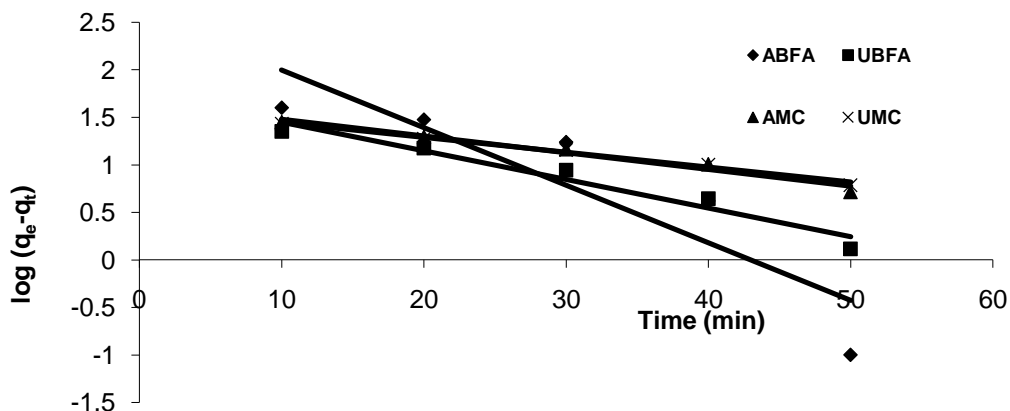


Figure 3: Pseudo-first order plot for adsorption of chlorpyrifos onto boiler fly ash and maize cob

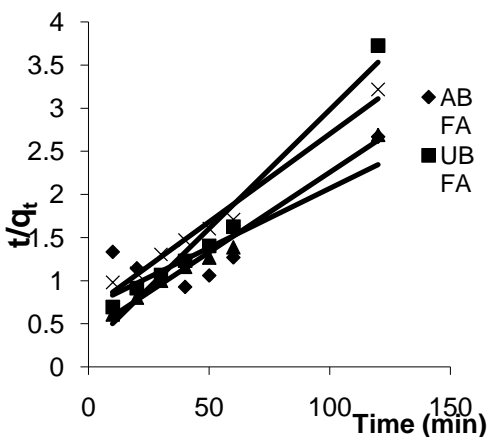


Figure 4: Pseudo-second order plot for adsorption of chlorpyrifos onto boiler fly ash and maize cob

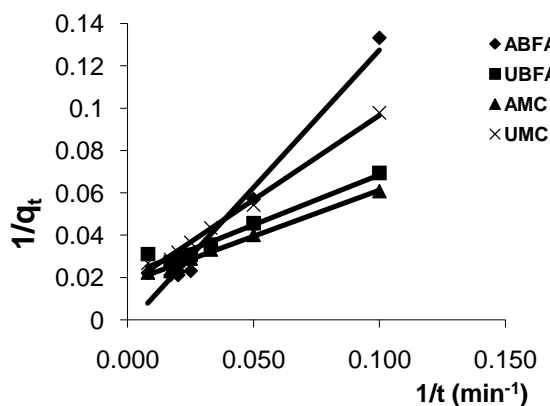


Figure 5: Ritchie's second order plot for adsorption of chlorpyrifos onto boiler fly ash and maize cob

From these figures, it could be seen that all the three equation gave fairly good straight lines to the kinetic experimental data. The values of the kinetic constants were evaluated from the slopes and intercepts of the respective plots and are shown in Table 1.

Table 1: Kinetic constants for Chlorpyrifos sorption on activated and unactivated boiler fly ash and maize cob

<i>Kinetic equation/ constants</i>	<i>ABFA</i>	<i>UBFA</i>	<i>AMC</i>	<i>UMC</i>
Pseudo first order				
K_1	0.139	0.069	0.041	0.036
q_e	400.41	56.08	45.09	39.90
R^2	0.8043	0.9513	0.9716	0.9889
Pseudo Second order				
K_2	2.75×10^{-4}	33.63×10^{-4}	8.69×10^{-4}	6.29×10^{-4}
q_e	72.46	36.36	53.76	49.02
h_0	1.441	4.446	2.510	1.512
R^2	0.6938	0.9668	0.9901	0.9812
Ritchies Second order				
K	1.92×10^{-3}	44.48×10^{-3}	40.65×10^{-3}	21.20×10^{-3}
q_e	400.00	47.39	56.50	59.17
R^2	0.9636	0.9587	0.9921	0.9934

From Table 1, it could be seen that for pseudo-first order model, ABFA had the highest K_1 and q_e values while UMC had the lowest values. For pseudo-second order, K_2 values were highest for UBFA while q_e values were highest for ABFA. Ritchie's second order equation gave highest rate constant (K) values for UBFA and lowest for ABFA while q_e values were highest for ABFA and lowest for UBFA. Other researchers have reported on the use of kinetic equations to model pesticide sorption systems. These includes; kinetics of diuron and amitrole adsorption from aqueous solution on activated carbons [18]; adsorption kinetics and isotherms of pesticides onto activated carbon-cloth [19]; Equilibrium, kinetic and thermodynamic studies on the adsorption of 2-nitroaniline onto activated carbon prepared from cotton stalk fibre [20]; removal of metobromuron pesticide from aqueous solutions by adsorption at high area activated carbon cloth [23]. From the R^2 values for the kinetic models, it can be observed that the Ritchie's second order model gave higher R^2 values, hence gave a better fit to the sorption kinetic data.

The intraparticle diffusion equations used in this study are as shown below; penetrant transport (Eq. 6) [51]; Elovich equation (Eq. 7) [52] and McKay and Poots (Eq. 8) [35]:

$$\log R = \log a + n \log t \quad (6)$$

$$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln t \quad (7)$$

$$q_t = X_i + K^1 t^{0.5} \quad (8)$$

Where R is percent (%) adsorbed, a and n are penetrant transport constants; α and β are Elovich coefficients and represents initial sorption rate and desorption constant respectively. β is also related to the extent of surface coverage and activation energy for chemisorption [35]; X_i is related to the boundary layer diffusion effect and K^1 is the McKay and Poots constant. The plots of penetrant transport is shown in Figure 6; that of Elovich equation is shown in Figure 7 and that of McKay and Poots is shown in Figure 8.

The intraparticle diffusion constants were evaluated from the slope and intercept of the respective plots and are shown in Table 2. The linear coefficient of determination (R^2) is also shown in Table 2.



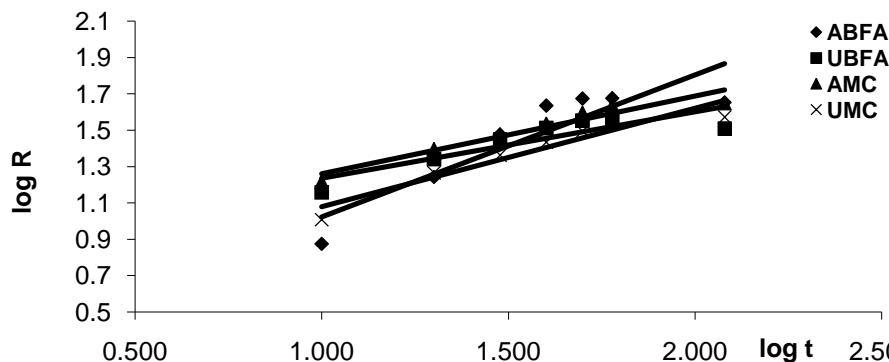


Figure 6: Penetrant transport plot for adsorption of chlorpyrifos onto boiler fly ash and maize cob

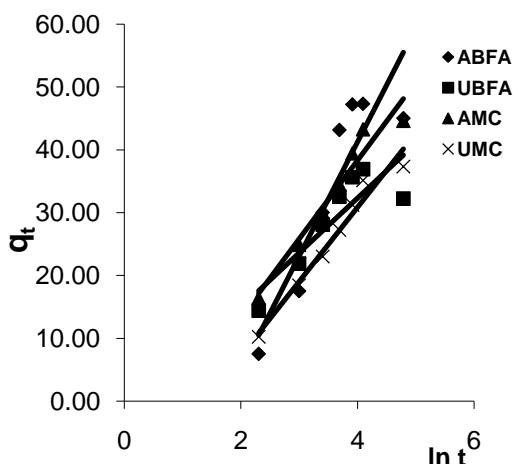


Figure 7: Elovich equation plot for adsorption of chlorpyrifos onto boiler fly ash and maize cob

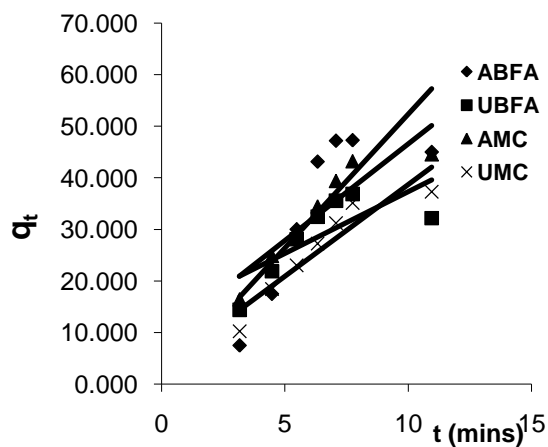


Figure 8: McKay and Poots plot for adsorption of chlorpyrifos onto boiler fly ash and maize cob

Table 2: Intraparticle diffusion constants for adsorption of Chlorpyrifos onto activated and unactivated boiler fly ash and maize cob

Intraparticle diffusion equation/ constants	ABFA	UBFA	AMC	UMC
Penetrant Transport				
a	1.75	3.45	7.45	6.80
n	0.78	0.54	0.36	0.43
R ²	0.8053	0.9191	0.7538	0.9233
Elovich Equation				
α	0.125	0.635	0.315	0.165
β	0.055	0.115	0.080	0.085
R ²	0.8169	0.7420	0.9468	0.9616
McKay & Poots				
X _i	0.420	13.311	9.036	3.038
K ¹	5.191	2.394	3.755	3.567
R ²	0.6633	0.5575	0.8480	0.8711

From Table 2, it could be seen that penetrant ‘a’ values are all > 1, being highest for AMC and lowest for ABFA. Also n values are all < 1. It has been reported that penetrant n-values represent the likelihood and degree of strive. n > 1 indicates the presence of high strive, n=1 depicts moderate strive while for n<1, the adsorption process may not be due to adsorbate core strive [51]. Also, penetrant a-values of adsorption systems are usually <1 for an interaction between adsorbent and adsorbate which is dominated by ion-exchange. If a-value is >1, there is indication that

dipole induced dipole interactions are dominant in the adsorption process [51]. From the results of this work, it means that the sorption process was dominated by dipole induced dipole interactions. This means that penetrant transport did not give a good fit to the sorption process. This is also confirmed by the low values of the R^2 . From Table 2, it could be seen that Elovich equation gave higher R^2 values more than penetrant transport and McKay and Poots equations, hence gave a better fit to the sorption process.

Sorption Isotherm

The experimental equilibrium sorption studies was analyzed by six adsorption isotherms namely; Langmuir, Freundlich, Dubinin-Radushkevich (D-R), Temkin, Harkins and Jura (H-J) and Florry-Huggins (F-H) equations. The Langmuir equation was chosen to estimate the maximum adsorption capacity corresponding to complete monolayer coverage on the biomass surface and is given by [53]:

$$C_e/q_e = 1/q_{\max}K_L + C_e/q_{\max} \quad (9)$$

Where K_L (L/g) is a constant related to the adsorption/desorption energy and q_{\max} is the maximum sorption upon complete saturation of the biomass surface. The experimental data were fitted into the Langmuir equation for linearization by plotting C_e/q_e against C_e and is shown in Figure 9.

The Freundlich model was chosen to estimate the adsorption intensity of the sorbate towards the biomass and was represented by [17]:

$$\log q_e = \log K_F + 1/n \log C_e \quad (10)$$

Where K_F and n are the Freundlich constants. The value of n indicates the affinity of the sorbate towards the biomass. The plot of $\log q_e$ against $\log C_e$ for the Freundlich isotherm is shown in Figure 10.

The D-R isotherm was chosen to estimate the characteristic porosity of the biomass and the apparent energy of adsorption. The model is given by [54]:

$$\ln q_e = \ln q_D - \beta \varepsilon^2 \quad (11)$$

Where q_D is the D-R isotherm constant related to the degree of sorbate sorption by the sorbent surface; ε is the Polyanyni potential given by:

$$\varepsilon = RT \ln (1+1/C_e) \quad (12)$$

and β is related to the free energy of sorption per mole (E) of the sorbate as it migrates to the surface of the biomass from infinite distance in the solution given by

$$E(\text{KJ/mol}) = (2\beta)^{-1/2} \quad (13)$$

The D-R isotherm plot of $\ln q_e$ against ε^2 is given in Figure 11.

The Temkin isotherm assumes that the fall in the heat of sorption is linear rather than logarithmic as implied in the Freundlich equation. The Temkin isotherm model is given as [36]:

$$q_e = B \ln A + B \ln C_e \quad (14)$$

Where $B = (RT/b)$, q_e (mg/g) and C_e (mg/L) are the amount adsorbed at equilibrium and the equilibrium concentration respectively. Also, T is the absolute temperature in K and R is the universal gas constant, 8.314J/mol-K. The constant b is related to the heat of adsorption [52]. The plot of Temkin isotherm is shown in Figure 12.

The other two isotherms, the H-J is shown as Eq. (15) and the F-H isotherm is shown in Eq. (16):

$$1/q_e^2 = (B/A) - (1/A \log C_e) \quad (15)$$

$$\log(\theta/C_e) = \log K_a + n \log (1-\theta) \quad (16)$$

Where A and B are H-J constants; K_a is a measure of the adsorption equilibrium constant and θ is the degree of surface coverage given by:

$$\theta = (1 - C_e/C_0) \quad (17)$$

The H-J accounts for multilayer adsorption and can be explained with the existence of a heterogeneous pore distribution [55]. The F-H isotherm is used to evaluate the degree of surface coverage and the equilibrium constant for the sorption process. The plot of the H-J isotherm is shown in Figure 13 while the plot of the F-H isotherm is shown in Figure 14.



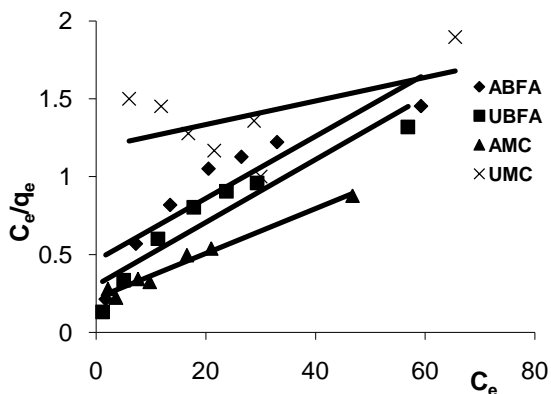


Figure 9: Langmuir isotherm for adsorption of chlorpyrifos onto boiler fly ash and maize cob

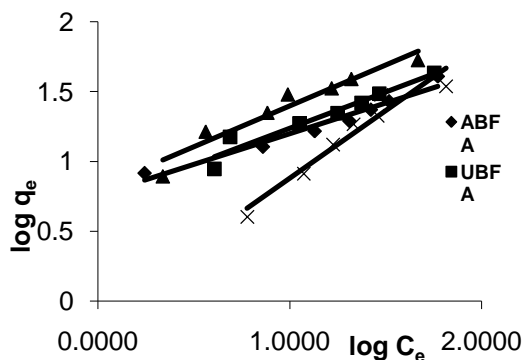


Figure 10: Freundlich isotherm for adsorption of chlorpyrifos onto boiler fly ash and maize cob

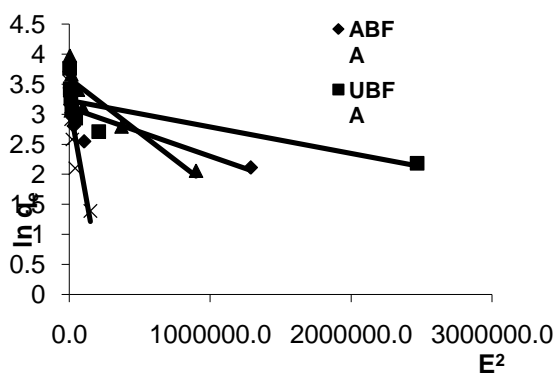


Figure 11: Dubinin-Radushkevich isotherm for adsorption of chlorpyrifos onto boiler fly ash and maize cob

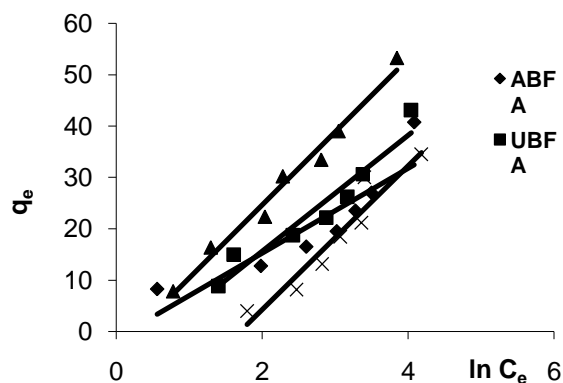


Figure 12: Temkin isotherm for adsorption of chlorpyrifos onto boiler fly ash and maize cob

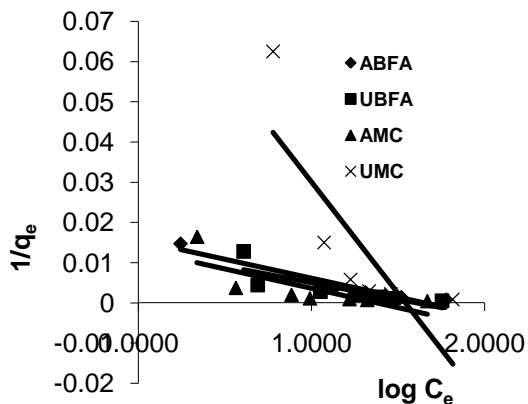


Figure 13: Harkins and Jura isotherm for adsorption of chlorpyrifos onto boiler fly ash and maize cob

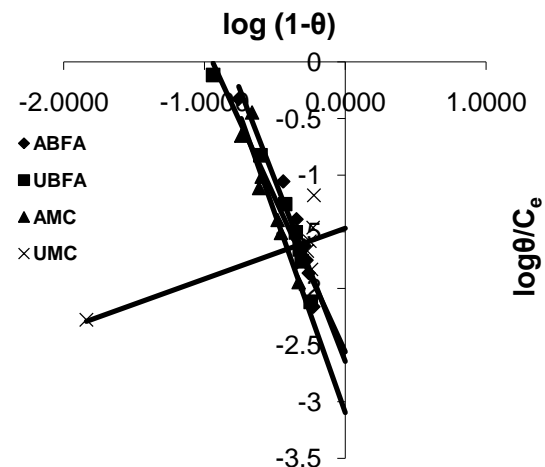


Figure 14: Flurry-Huggins isotherm for adsorption of chlorpyrifos onto boiler fly ash and maize cob

The isotherm constants were calculated from the slope and intercepts of the various linear plots for the different isotherms and are tabulated in Table 3. The linear regression coefficients are also shown in Table 3. The maximum monolayer coverage for the Langmuir isotherm (q_{\max}) are all positive. UMC had the highest q_{\max} value followed by AMC, ABFA and then UBFA. The R^2 values are very poor and this means that Langmuir isotherm did not give a good fit to the sorption of Chlorpyrifos on the adsorbents. The Freundlich isotherm constant (K_F) gave the following values; AMC (6.47), ABFA (5.74), UBFA (5.23) and UMC (1.22). The higher the K_F value the higher the adsorption intensity [25]. The values of n from the Freundlich Isotherm were all > 1 but < 10 . The values of n between 1 and 10 represent beneficial adsorption [56]. Since n values are > 1 , $1/n$ values are < 1 . 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 concentration and vice versa [52, 57-59]. This corroborates the decrease in percentage adsorbed as initial concentration was increased, which was observed earlier. From the R^2 values, Freundlich isotherm gave a better fit than the other isotherms to the sorption process, having R^2 values all $> 93\%$.

Table 3: Isotherm constants for adsorption of Chlorpyrifos onto activated and unactivated boiler fly ash and maize cob

<i>Isotherm models/ constants</i>	<i>ABFA</i>	<i>UBFA</i>	<i>AMC</i>	<i>UMC</i>
Langmuir				
q_{\max}	50.25	49.51	69.44	131.58
K_L	0.043	0.067	0.066	0.006
R^2	0.8247	0.8921	0.9781	0.2687
Freundlich				
K_F	5.74	5.23	6.47	1.22
N	2.28	1.93	1.70	1.04
R^2	0.9593	0.9389	0.9323	0.9301
D-R				
q_D	22.43	25.21	36.40	23.53
β	8.0×10^{-7}	4.0×10^{-7}	2.0×10^{-6}	1.0×10^{-5}
$E(KJ/mol)$	790.57	1118.03	500.00	223.61
R^2	0.5546	0.6187	0.8804	0.8064
Temkin				
A	0.862	0.540	0.766	0.184
B	8.25	11.31	14.24	14.00
R^2	0.8023	0.9270	0.9803	0.9140
H-J				
A	106.38	121.95	104.17	18.02
B	1.649	1.610	1.375	1.541
R^2	0.9398	0.6508	0.5806	0.6659
F-H				
K_a	2.28×10^{-3}	2.76×10^{-3}	0.80×10^{-3}	34.00×10^{-3}
N	-3.21	-2.72	-3.51	0.45
R^2	0.9392	0.9604	0.9012	0.6181

Key: D-R = Dubinin-Raduskevich; H-J = Harkins-Jura; F-H = Florry-Huggins.

The D-R isotherm constants showed that the q_D values were highest for AMC and lowest for ABFA. The apparent energy of sorption $E(KJ/mol)$ gave 223.61 for UMC, 500.00 for AMC, 790.57 for ABFA and 1118.03 for UBFA. It has been reported that physisorption processes usually have adsorption energies less than 40 KJ/mol, above which



chemisorption processes occur [60, 61]. Therefore, from the values obtained in this study, it means that the sorption processes followed chemisorption mechanism. The values of A from the Temkin isotherm are less than the values of A from the H-J isotherm. Again, the values of B from the Temkin isotherm are greater than those from the H-J isotherm. The low values of R^2 for both isotherms indicate that they did not give good fit to the sorption process. The n values from the F-H isotherm were all negative except for UMC and the equilibrium constant (K_a) values obtained were all far less than unity. If F-H isotherm had given a good fit then the amount in solution was > amount adsorbed.

The use of sorption isotherm equations to model pesticides sorption have been reported [19, 21, 30, 33, 62, 63]. Similar to the results of this study, the favourability of the Freundlich isotherm to sorption of pesticides have been reported [17, 19, 23, 33, 44, 63]. Other isotherms not used in this study have been employed such as Redlich-Peterson, Langmuir-Freundlich [20]; Sips and Langmuir [64].

Conclusion

The isotherm and kinetic studies of Chlorpyrifos adsorption onto activated and unactivated boiler fly ash and maize cob have been reported in this paper and the following concluding remarks can be made:

1. Activated and unactivated boiler fly ash and maize cob was successfully utilized to remove Chlorpyrifos from aqueous solution.
2. The adsorption capacity increased with increasing time and initial pesticide concentration but percentage adsorbed increased with time but decreased with increase in initial pesticide concentration.
3. Three kinetic and three intraparticle diffusion equations were used to model the sorption process and Ritchie's second order gave a better fit to the sorption process.
4. The equilibrium data was modeled by six isotherm equations and Freundlich isotherm gave a better fit to the sorption equilibrium data.
5. The sorption process was found to follow chemisorption mechanism probably through hydrophobic pesticide-pesticide interactions.

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