

## **The Study of Adsorption and Desorption of Picloram on six Agricultural Soils**

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**Abstract:** A study was conducted to determine the differences in the adsorption - desorption behavior of picloram [4-amino-3, 5, 6-trichloropicolinic acid] which is an ionic herbicide on six agricultural soil samples. Employing linearized versions of three kinetic models, namely first-order, Elovich, and power function equations, data from batch equilibrium method revealed that the adsorption - desorption of picloram on the selected soil samples followed the first order rate law. Linear and Freundlich models were used to describe the adsorption of the pesticide. Wide variation in adsorption affinities of the soils to the pesticides was observed,  $K_d$  values for picloram varied between 1.406 and 2.151  $\text{mlg}^{-1}$  and  $K_F$  for picloram between 1.078 and 1.189  $\text{mlg}^{-1}$  for adsorption processes. The value of  $K_d$  and  $K_F$  ranged from 0.439 to 0.625  $\text{mlg}^{-1}$ , 1.045 to 1.585  $\text{mlg}^{-1}$  respectively for the desorption processes. The desorption processes exhibited with the percent 26.4-94.3% these percentage from adsorbed, as compared to adsorption processes percentage is 16.8-56.9 %.

Considering the experimental  $k_o / k_o' = k_{eq}$ , the agreement in the comparisons is quite satisfactory. It indicates to a good approximation that adsorption in the systems studied may be viewed as a reaction in which a solute molecule collides with an adsorption site to form the adsorption complex, the desorption constant  $k_o'$  vary by more than an order of magnitude. The large difference in the equilibrium adsorption arise mainly from the difference in the rate of desorption. Values of  $K_o$  by using Bigger equilibrium constant for desorption of picloram on selected soil samples were in the following from 2.673 to 11.395. All desorption isotherms exhibited hysteresis. Higher desorption hysteresis (picloram was less readily desorbed),

**Keywords** picloram Adsorption-desorption kinetics, Adsorption-desorption isotherms, Freundlich, Elovich, power function, HPLC.

### **Introduction**

The desorption is defined as the percentage of the test substance which is desorbed and related to the quantity of the substance which is previously adsorbed under the test condition. Equilibrium was attained for most of the systems in 4-24h. Desorption was slower than sorption. In desorption of pesticides from soils, and soil constituents such as clay minerals and humic substances has generally been characterized by an initial rapid rate followed by a much slower approach to an apparent equilibrium. The initial reaction has been associated with diffusion of the pesticides to and from the surface of the sorbent(1).

The adsorption-desorption of pesticides by the active soil surfaces is one of the main processes that control soil-pesticide interactions (2). The purpose of the desorption kinetics is to investigate whether a chemical is reversibly or irreversibly adsorbed on a soil. This information is important, since desorption

also plays an important role in the behavior of a chemical in field soil. Moreover, desorption data are useful inputs in the computer which model and solve the run-off simulation. If desorption study is desired, it is recommended that the study described below be carried out on each system for which an accurate determination of  $K_{des}$  in the preceding adsorption kinetic experiment was possible (3).

Knowledge of the adsorption behavior of chemical substance is necessary to understand the consequences that may arise from their controlled or uncontrolled distribution in the soil environment. The adsorption and desorption of pesticides in soil which influences their bioefficacy and persistence. It is also an important factor governing the migratory behavior of the pesticide in soil and ground water and may also influence the uptake and metabolism by plants or microorganisms and the other organisms present in soil(4). Changes in solution concentration with time

for pesticides of adsorption and desorption processes in heterogeneous systems continues to attract considerable interest (5).

Desorption isotherms did not coincide with adsorption isotherms to indicate hysteresis which is commonly observed in pesticide adsorption-desorption studies with soils. Once adsorbed, some adsorbates may react further to become covalently and irreversibly bound, while others may become physically trapped in the soil matrix. Moreover, hysteresis may increase with adsorbent-adsorbate contact time (6-8).

Picloram is anionic herbicide is used to control unwanted woody plants and to prepare sites for planting trees and used to control broad-leaf plants and trees (9). Its adsorption involved ionic interaction with positive charges in soil and also the less energetic Van der Waals forces and charge transfer (10, 11), on its adsorption to sterile and non-sterile soils (12) and on modified natural clay (13).

### **Materials and methods**

**Soils:** Fresh soil samples were taken from plough layer (0-15 cm depth), after removal of stones and debris, air dried under shade, ground then sieved through 2mm sieve and stored in black plastic container in dark (14, 15). The six soil samples were collected from six main agricultural, representing a range of physico-chemical properties. Subsamples of homogenized soils were analyzed for moisture content, organic matter content, particle size distribution, texture, pH, loss on ignition and exchangeable basic cations (Table 1 a& b).

#### **Pesticide**

Analytical grade substituted picloram herbicide was purchased from Riedel-de Haen, Sigma-Aldrich company Ltd. With following purities expressed in weight percent picloram >97.4% [CAS-No.1918-02-1] respectively.

All chemicals used were of analytical grade reagents and used without pre-treatments. Standard stock solutions of the pesticides were prepared in deionised water.

#### **Adsorption Experiments**

Adsorption of picloram from aqueous solution was determined at ambient laboratory temperature (25±1 C°) employing a standard batch equilibrium method (16, 17) Duplicate air-dried soil samples were equilibrated with different pesticide concentrations (2, 5, 10, and 15 µg ml<sup>-1</sup>) were for the pesticide at the soil solution ratios 4:8, in 16 ml glass tube fitted with Teflon-lined screw caps. The samples plus blanks (no pesticide) and control (no soil) were thermostated and placed in shaker for 0.5, 1, 3, 6, 9, 12, 24, 48. The tubes were centrifuged for 20 min. at 3500 rpm. One ml of the clear supernatant was removed and analyzed

for the pesticide concentration (18). Pesticide identification was done by PerkinElmer series 200 USA family high performance liquid chromatography (HPLC) equipped with a changed loop (20µl), C18 reversed phase column, flow rate 1.0 ml min<sup>-1</sup>, and a variable wave length UV detector at wavelength 220 nm. Separation of picloram in aqueous phase was achieved with a mobile phase of 40% acetonitrile and 60% water (acidified with 0.1% phosphoric acid).

Each sample was injected twice to determine the pesticide content by integrating the obtained peak with the respective standard pesticides. The pesticide content was average of two measurements, with no more than 5% deviation between the measurements.

#### **Desorption Experiments**

Desorption processes were done as each test tube was placed in a thermostated shaker at 25°C after equilibration for 48 h with different pesticide concentrations (2, 5, 10 and 15 µg ml<sup>-1</sup>) the samples were centrifuged, 5ml of supernatant was removed from the adsorption equilibrium solution and immediately replaced by 5ml of water and was this repeated for four times. The resuspended samples were shaken for 0.5, 1, 3, 6, 9, 12, 24, and 48 for the kinetic study.

#### **Data analysis**

##### **Adsorption-Desorption Kinetics**

The rate constants for adsorption of each pesticide on soils were calculated using the first order rate expression (19):

$$\text{Log } (C_0 - C_t) = \log C_0 - \frac{k}{2.303} t \quad (1)$$

Where k is the rate constant (hour<sup>-1</sup>), t the time (hour), Co the concentration of pesticide added (µg ml<sup>-1</sup>) and Ct the amount adsorbed (µg ml<sup>-1</sup>) at time t. In all cases, first order equation provided satisfactory fit for the data as linear plots of log (Co – Ct) against t (Table 2).

The first order kinetic describes the process of desorption in all experiments and on all soil samples (20, 21 & 22).

$$K_{des} = \log (C_0 / C_t) \cdot (2.303/t) \dots\dots\dots(2)$$

Where Kdes is the desorption rate constant (h<sup>-1</sup>), Ct is the amount of released pesticides at time t and Co is the amount of released pesticides at equilibrium and Kdes is the slope of straight line which is equal to coefficient release rate of Kdes. A plot of log Ct versus t should give a straight line with slope – Kdes/2.303 and intercept of log Co (Table 2).

The Elovich equation was claimed to be superior to other kinetic equations based on higher (R<sup>2</sup>) and low standard error (SE).

A form of the Elovich equation as applied to the adsorptions-desorption is as follows (23,24&25):

$$C_t = (1/K) \ln (C_0 K) + (1/K) \ln t \dots \dots \dots (3)$$

A plot of  $C_t$  versus  $\ln t$  should give a straight line with slope equal to  $1/k$  and logarithmic intercept  $[(1/k) \ln (C_0 K)]$ . The value of slope of straight line is coefficient of release rate (Table 3).

Power function equation used to describe the pesticides adsorption-desorption from soils is given as(26):

$$\ln C_t = \ln C_0 + k \ln t \dots \dots \dots (4)$$

Where  $C_t$  is the amount of the pesticides released at time  $t$ . A plot  $\ln C_t$  versus  $\ln (t)$  should give a straight line with a slope ( $k$ ) and the intercept is  $\ln (C_0)$  where the value of slope of straight line is coefficient of release rate (Table 3).

**Adsorption-Desorption Isotherms**

During adsorption-desorption studies, equilibrium concentration of pesticide in solution ( $C_e$ ) was determined by direct analysis of the solution and amount of pesticide adsorbed on soil ( $C_s$ ) was computed by the difference between the initial and the equilibrium concentration in the aqueous phase. Analysis of control samples showed that, in the absent of soil, pesticide concentration remained constant during the course of the batch experiments. The adsorption data were used to construct the following linear forms of isotherms(19).

**Linear Adsorption -desorption Coefficient (Distribution Coefficient)**

$$C_s = K_d C_e \dots \dots \dots (5)$$

The distribution coefficient ( $K_d$ ) was calculated by taking the ratio of adsorption concentration in soil ( $C_s$ ) and equilibrium concentration in solution ( $C_e$ ), and averaged across all equilibrium concentration to obtain a single estimate of  $K_d$  (Table 4)

**Freundlich Adsorption-desorption Isotherm**

Adsorption isotherm parameters were calculated using the linearized form of Freundlich equation(27):

$$\log C_s = \log K_f + \frac{1}{n} \log C_e \dots \dots \dots (6)$$

$C_s$  and  $C_e$  were defined previously,  $K_f$  is Freundlich adsorption coefficients, and  $n$  is a linearity factor, it is also known as adsorption intensity,  $1/n$  is the slope and  $\log K_f$  is the intercept of the straight line resulting from the plot of  $\log C_s$  versus  $\log C_e$ .

The values of  $K_f$  and  $1/n$  calculated from this regression equation showed that Freundlich adsorption model effectively describes isotherms for the pesticides in all cases. The desorption isotherms of picloram were fitted to the linearized form of the Freundlich equation(26, 28, 29& 30):

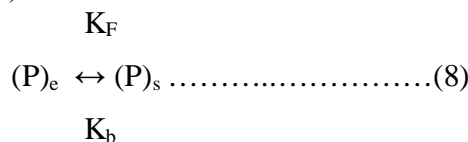
$$\log C_s = \log K_{fdes} + n_{des} \log C_e \dots \dots \dots (7)$$

Where  $C_s$  is the amount of picloram still adsorbed ( $\mu\text{g g}^{-1}$ ),  $C_e$  is the equilibrium concentration of picloram in solution after desorption ( $\mu\text{g mL}^{-1}$ ), and  $K_{fdes}$  ( $\mu\text{g g}^{-1} \cdot \text{mL} / \text{mL} \cdot \text{mL} \cdot \text{g}^{-1}$ ) and  $n_{des}$  are two characteristic constants of picloram desorption(31). The values of the  $K_{fdes}$  and  $n_{des}$  constants of picloram (Table 4).

**Desorption equilibrium constant**

Desorption behavior can provide additional information on the sorbate-sorbent interaction sorption and desorption of the organic chemicals in soils which are not rapid, reversible process, despite the past assumption which was on the contrary(23).

In the equilibrium studies of the adsorption of pesticide on soil, we may consider an adsorption and desorption process taking place simultaneously at equilibrium. At steady state the following condition holds(32).



Where  $(P)_e$  are the free pesticide molecules in the solution and  $(P)_s$  are the adsorbed molecules. The symbols  $K_F$  and  $K_b$  are the rate constants for the adsorption and desorption reactions, respectively. At steady state the following condition

$$a_s/a_e = k_F/k_b = k_0 \dots \dots \dots (9)$$

Where  $k_0$  is the thermodynamic distribution constant or the equilibrium constant for adsorption process. The symbols as described in chapter five. At equilibrium and at sufficient low concentration where the activity can be approximated by concentration and the occupied fraction of the adsorbing surface is very small (the usual case for pesticides in the environment) the following should hold:

$$k_b C_s = k_F C_e (m/v) \dots \dots \dots (10)$$

$$k_F/k_b = k_0 / k' = C_s / C_e (m/v) = (x/m)/C_e = k_{eq} \dots \dots \dots (11)$$

Where  $C_s$  is the amount of picloram per unit volume of solvent ( $\mu\text{g g}^{-1}$ ),  $C_e$  is the equilibrium concentration of picloram ( $\mu\text{g mL}^{-1}$ ),  $m/v$  is the weight adsorbent per unit volume of solvent, and  $x/m$  is the specific adsorption (amount adsorbed per unit weight of adsorbent). Equations 10, and 11 present another description of the system as compared with equation .8, and 9. While the equation 8, and 9, represent a partition between two phases, bulk and surface. Equations 10 and 11 represent an interaction between various species (solute molecules and adsorption sites) in the same phase.

Considering the experimental  $k_o / k_o' = k_{eq}$ , the agreement in the compactions is quite satisfactory. It indicates a good approximation that adsorption in the systems studied may be viewed as a reaction in which a solute molecule collides with an adsorption site to form the adsorption complex. The desorption may be viewed as "unimolecular" process by which the adsorption complex dissociates to a free site and solute molecule. Interestingly, while the adsorption constant  $k_o$  are relatively similar to the three systems, the desorption constant  $k_o'$  vary by more than an order of magnitude. The large difference in the equilibrium adsorption arise mainly from the difference in the rate of desorption. Thus equations 10 and 11 approach the Freundlich isotherm (32&33). (Table 4).

**Hysteresis phenomena**

A study of picloram desorption isotherms show positive hysteresis coefficients H in the six selected soil samples (21, 29&34). Hysteresis coefficients (H), can be determined by using the following equation (21).

$$H1 = N_a / N_{des} \dots\dots\dots(12)$$

Where  $N_a / N_{des}$  ratio for Ferundlich adsorption and desorption constants, respectively, indicating the greater or lesser irreversibility of adsorption in all samples, the highest values corresponding for which the highest adsorption constant was obtained. The coefficient H1 is a simple one and easy to use (21). (Table 5).

The ratio  $N_{des} / N_a$  measuring the degree of irreversibility of adsorption phenomenon, the ratio called the apparent hysteresis index (AHI), H2 (29, 35&36)

$$H2 = (N_{des} / N_a) \times 100 \dots\dots\dots(13)$$

The extent of hysteresis was quantified by using hysteresis coefficient ( $\omega$ ), it was defined on the discrepancy between the sorption and desorption isotherms, and calculated by using Freundlich parameters estimated from sorption and desorption isotherms separately. ( $\omega$ ) can be expressed as(37, 38 &39):

$$\omega = (N_a / N_{des} - 1) \times 100 \dots\dots\dots(14)$$

Recently Zhu et. al (40) proposed an alternative hysteresis coefficient ( $\lambda$ ) based on the difference in the areas between adsorption and desorption isotherms, they derived the following expression for the parameter  $\lambda$  for the traditional isotherms fig 1 as:

$$\lambda = (N_a + 1 / N_{des} + 1 - 1) \times 100 \dots\dots\dots(15)$$

**Results and Discussion**

**Adsorption-Desorption Rate**

Data in Table 2 showed that adsorption of the pesticides in all cases followed first order rate law as reported in literature (41, 42). Values of rate

constants for adsorption and desorption of picloram on selected soil samples were in the range from 0.711 to 1.495 h<sup>-1</sup> and 0.137 to 0.920h<sup>-1</sup> respectively. Thus desorption during the first few hours is likely to come from the or more accessible sites and /or from the low-energy –release sorption mechanisms, whereas picloram sorbed on less accessible sites and/or more strongly adsorbed sites is not susceptible to desorption initially and is subsequently subject to slow release over time(43). The value of R2 for adsorption-desorption of picloram on selected soil samples ranged from 0.721 to 0.983 and from 0.730 to 0.994 respectively.

The Elovich equation is one of the most widely used to describe the kinetics of pesticides adsorption on the selected soil samples during this study revealed the different characteristics of the studied soil samples(23). Data listed in table 3 represent values of K and Kdes together with R2 by Elovich kinetic for adsorption-desorption of picloram on selected soil samples. Values of R2 ranged from 0.702-0.989 and 0.579-0.986 for adsorption and desorption process respectively. Values of K and Kdes were in the following range 2.124 to 12.74 mg l<sup>-1</sup> h<sup>-1</sup> and 1.015 to 32.89 mg l<sup>-1</sup> h<sup>-1</sup> respectively.

The R2 values ranged from 0.752-0.989 and 0.304-0.988 for adsorption-desorption process respectively. Data listed in table 3 represent values of K and Kdes by Power function kinetic for adsorption-desorption of picloram on selected soil samples were in the following from 0.113 to 0.215 mg l<sup>-1</sup> h<sup>-1</sup> and from 0.043 to 0.191 mg l<sup>-1</sup> h<sup>-1</sup> respectively.

**Adsorption-Desorption Isotherms**

Ferundlich desorption isotherms were determined on the soils used in the adsorption isotherms experiment, the KFdes values indicate that a small proportion of the chemical has desorbed into solution. The Ferundlich n<sub>des</sub> value describes nonlinearity curvature in the desorption isotherm and is often used as an index of hysteresis. Results obtained in the present work showed that the values of n<sub>des</sub> values were smaller than the values for the other works. Values of K<sub>d</sub> for picloram varied between 1.406 and 2.151 mlg<sup>-1</sup> and KF for picloram between 1.078 and 1.189 mlg<sup>-1</sup>for adsorption processes. The value of K<sub>d</sub> and KF ranged from 0.439 to 0.625 mlg<sup>-1</sup>, 1.045 to 1.585 mlg<sup>-1</sup> respectively for the desorption processes. The desorption processes exhibited with the percent 26.4-94.3% these percentage from adsorbed, as compared to adsorption processes percentage is 16.8-56.9 %.

Data in table 4 demonstrated the R2 values ranged from 0.655-0.964 and S.E ranged from 0.578-0.812 while the values of Ko by using Bigger equilibrium constant for desorption of picloram on

selected soil samples were in the following from 2.673 to 11.395.

Data in table 5 demonstrated H1 values for picloram from the selected soil samples in the range from 0.223-0.517 for desorption process, indicating an increase in the irreversibility of the adsorption of herbicide as the clay content increases. Data in table 5 Summarized H2 values for picloram from the selected soil samples were in the range from 195.7-447.7 for desorption process. Lower index values indicate the increased difficulty of the sorbed analyte to desorb from the matrix. The calculated values of  $\omega$  for adsorption and desorption of picloram on the selected soil samples were summarized in table 5 ranged from -77.66 to 75.86. Whereas  $\omega$  is only applicable for the traditional type isotherms of the successive desorption as shown in fig 1. The data in table 5 demonstrated  $\lambda$  according to equation 15 for desorption of picloram from the selected soil samples were ranged from -173 to 11.94.

### Conclusion

The batch kinetics experiments were used to differentiate the behavior of two pesticides in six agricultural soil samples. The experimental data were evaluated by employing linearized versions of three kinetic models, namely first-order, Elovich, and power function equations. The regression equations relating that the highest values are in first-order which is the most suitable to be used. We have further found that soil OC and clay content and the chemical nature of the constituents determined the adsorption affinity of the soil. Since the current level understanding the role of the chemical composition of soil OC in determining pesticide fate and behavior in soils of our country is inadequate. Efforts must continue to develop better understanding of role of chemistry of soil organic carbon in governing pesticide adsorption and explaining different types of soil pesticide interactions.

All desorption isotherms exhibited hysteresis. Higher desorption hysteresis (picloram was less readily desorbed), the increasingly difficult desorption with decreasing solute concentration which can be explained by the limited number of the available sites for the high-energy. Most of these sites were occupied at low solute concentrations, whereas at high solute concentrations, more molecules are taken up by low-energy binding sites and therefore they can more readily desorb. This could also be explained by the possible hysteresis effect taking place during desorption involving various forces that caused the amount of compounds retained to be higher after desorption than after adsorption at the unit of equilibrium concentration.

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Table 1 (a): Some physico-chemical properties of the selected soil samples.

Soil	OM %	Moisture%	Loss On ignition%	C EC meq100g <sup>-1</sup>	E.C*10 <sup>2</sup> sm <sup>-1</sup> ind.w	pH	
						In D.W	in CaCl <sub>2</sub>
S <sub>1</sub>	2.799	2.544	7.864	47.760	0.414	7.516	7.501
S <sub>2</sub>	1.039	1.864	3.445	54.276	0.431	6.825	6.805
S <sub>3</sub>	3.196	2.633	6.160	26.780	0.572	6.981	6.906
S <sub>4</sub>	2.356	2.604	4.058	41.133	0.388	7.651	7.621
S <sub>5</sub>	1.914	2.012	5.442	32.488	0.492	6.395	6.305
S <sub>6</sub>	1.509	3.417	2.926	55.121	0.545	6.940	6.900

Table 1 (b): Particle size distribution and the texture of the selected soil samples.

No.	Soil	X (m)	Y (m)	Sand%	Silt %	Clay %	Texture
S1	Halabjh	45 <sup>+</sup> 58.905 <sup>-</sup>	35 <sup>+</sup> 101.166 <sup>-</sup>	4.4	39.4	56.2	Clay
S2	Darbnidikhan	45 <sup>+</sup> 42.31	35 <sup>+</sup> 06.39	37.4	46.1	20.2	Loam
S3	Jamjamal	44 <sup>+</sup> 50.026 <sup>-</sup>	35 <sup>+</sup> 31.355 <sup>-</sup>	11.7	52.2	36.1	Silty Clay Loam
S4	Halabjh	45 <sup>+</sup> 58.786 <sup>-</sup>	45 <sup>+</sup> 10.338 <sup>-</sup>	20.2	48.0	31.8	Clay loam
S5	Kirkuk	44 <sup>+</sup> 21.825 <sup>-</sup>	35 <sup>+</sup> 34.940 <sup>-</sup>	17.6	61.8	20.6	Silt Loam
S6	Duhok	42 <sup>+</sup> 53.944 <sup>-</sup>	36 <sup>+</sup> 51.185 <sup>-</sup>	11.6	45.7	42.7	Silty Clay

Table 2: Adsorption-Desorption rate constants for Picloram on the selected soil samples.

Soil	Conc. ppm	Picloram(ads)			Picloram(des)		
		$K_{ads}$ (calc) (h <sup>-1</sup> )	S.E	R <sup>2</sup>	$K_{des}$ (calc) (h <sup>-1</sup> )	S.E	R <sup>2</sup>
S <sub>1</sub>	2	1.161	0.276	0.879	0.251	0.327	0.888
	5	0.866	0.305	0.903	0.386	0.197	0.994
	10	0.751	0.204	0.805	0.292	0.187	0.909
	15	1.001	0.384	0.829	0.357	0.169	0.815
S <sub>2</sub>	2	1.371	0.204	0.856	0.453	0.244	0.864
	5	0.682	0.311	0.846	0.707	0.056	0.894
	10	0.953	0.184	0.899	0.465	0.243	0.992
	15	1.280	0.351	0.823	0.589	0.203	0.962
S <sub>3</sub>	2	1.495	0.211	0.481	0.179	0.022	0.747
	5	1.145	0.204	0.873	0.332	0.078	0.826
	10	0.870	0.197	0.878	0.401	0.057	0.841
	15	0.711	0.198	0.836	0.439	0.095	0.877
S <sub>4</sub>	2	1.071	0.199	0.852	0.432	0.046	0.848
	5	1.203	0.202	0.848	0.137	0.839	0.822
	10	1.034	0.204	0.873	0.566	0.184	0.931
	15	1.186	0.197	0.983	0.671	0.194	0.955
S <sub>5</sub>	2	1.149	0.149	0.833	0.437	0.145	0.730
	5	0.972	0.197	0.721	0.295	0.199	0.832
	10	1.004	0.196	0.976	0.147	0.231	0.976
	15	1.111	0.186	0.821	0.414	0.199	0.971
S <sub>6</sub>	2	1.454	0.207	0.903	0.951	0.187	0.970
	5	1.470	0.199	0.864	0.137	0.137	0.913
	10	1.469	0.134	0.948	0.920	0.192	0.871
	15	1.458	0.154	0.973	0.876	0.187	0.934



Table 3: Kinetic studies of Picloram desorption and applied models on the selected soil samples.

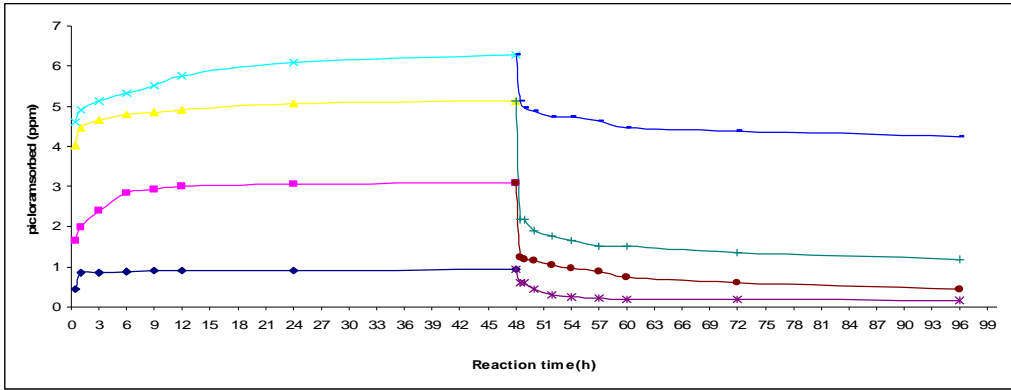
Soil	conc. ppm	Elovich(ads)		Elovich(des)		Power.function (ads)		Power.function (des)	
		K <sup>(calc)</sup> (mg l <sup>-1</sup> h <sup>-1</sup> )	R <sup>2</sup>	K <sup>des</sup> (calc) (mg l <sup>-1</sup> h <sup>-1</sup> )	R <sup>2</sup>	K <sup>(calc)</sup> (mg l <sup>-1</sup> h <sup>-1</sup> )	R <sup>2</sup>	K <sup>des</sup> (calc) (mg l <sup>-1</sup> h <sup>-1</sup> )	R <sup>2</sup>
S <sub>1</sub>	2	12.74	0.962	8.833	0.894	0.113	0.755	0.113	0.784
	5	3.235	0.913	5.907	0.885	0.128	0.881	0.169	0.768
	10	4.523	0.948	5.211	0.983	0.147	0.830	0.191	0.969
	15	2.647	0.973	1.015	0.985	0.167	0.898	0.133	0.964
S <sub>2</sub>	2	10.85	0.916	23.15	0.766	0.147	0.752	0.043	0.984
	5	6	0.975	7.616	0.925	0.159	0.876	0.170	0.977
	10	4.636	0.938	5.875	0.969	0.157	0.881	0.131	0.938
	15	2.469	0.989	5.577	0.986	0.14	0.790	0.076	0.988
S <sub>3</sub>	2	8.651	0.866	32.89	0.965	0.215	0.707	0.031	0.931
	5	2.828	0.908	21.78	0.943	0.180	0.852	0.046	0.925
	10	3.210	0.932	7.651	0.981	0.173	0.891	0.131	0.969
	15	3.408	0.970	5.382	0.579	0.147	0.897	0.186	0.979
S <sub>4</sub>	2	11.71	0.887	14.29	0.954	0.114	0.819	0.070	0.912
	5	2.672	0.885	9.930	0.977	0.195	0.831	0.101	0.304
	10	2.905	0.975	6.596	0.926	0.188	0.875	0.152	0.938
	15	2.124	0.969	3.865	0.969	0.199	0.882	0.119	0.969
S <sub>5</sub>	2	10.02	0.702	21.32	0.903	0.188	0.859	0.047	0.848
	5	3.779	0.824	13.77	0.963	0.125	0.767	0.008	0.979
	10	2.866	0.967	13.19	0.965	0.191	0.894	0.073	0.949
	15	2.679	0.961	9.655	0.967	0.176	0.875	0.043	0.973
S <sub>6</sub>	2	11.79	0.868	19.08	0.942	0.161	0.755	0.051	0.915
	5	5.534	0.821	12.19	0.955	0.173	0.777	0.082	0.964
	10	3.040	0.977	3.235	0.977	0.185	0.989	0.167	0.972
	15	2.972	0.970	2.705	0.951	0.168	0.968	0.128	0.912
Mean K		5.323		10.864		0.173		0.103	

Table 4: Picloram Adsorption-desorption isotherm parameters for the linear, Freundlich and Equilibrium constant models to compare the selected soil samples .

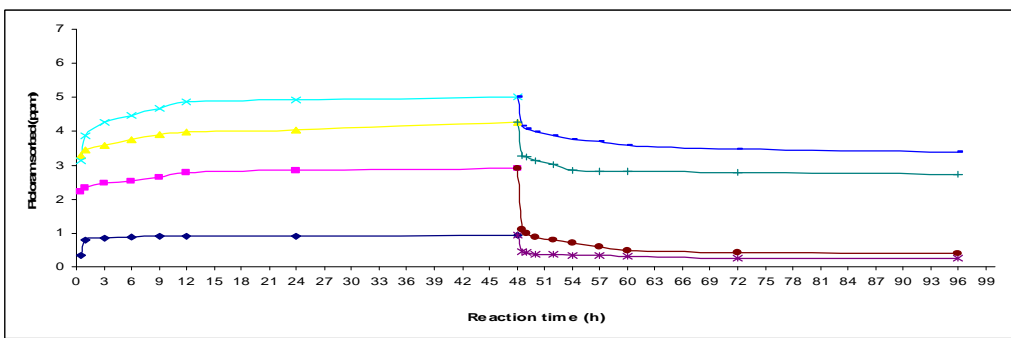
Models	Parameter	Soils					
		S <sub>1</sub>	S <sub>2</sub>	S <sub>3</sub>	S <sub>4</sub>	S <sub>5</sub>	S <sub>6</sub>
Distr. coeff.	K <sub>d</sub> (calc)	2.151	1.764	1.954	1.836	1.737	1.406
	S.E	0.786	0.705	0.437	0.537	0.564	0.579
	R <sup>2</sup>	0.732	0.765	0.977	0.846	0.968	0.852
Freundlich(ads)	K <sub>F</sub> (mL/g)	1.171	1.085	1.211	1.078	1.168	1.189
	S.E	0.361	0.361	0.389	0.380	0.378	0.379
	n <sub>F</sub>	0.397	0.435	0.497	0.344	0.559	0.966
	R <sup>2</sup>	0.933	0.973	0.997	0.999	0.978	0.882
Distr. coeff.	K <sub>d</sub> (calc)	0.625	0.518	0.439	0.522	0.512	0.563
	S.E	0.107	0.183	0.115	0.151	0.142	0.133
	R <sup>2</sup>	0.999	0.936	0.972	0.951	0.937	0.971
Freundlich (des)	K <sub>Fdes</sub> (mL/g)	1.045	1.586	1.066	1.277	1.398	1.493
	S.E	0.317	0.183	0.358	0.356	0.142	0.374
	n <sub>F</sub>	0.718	1.947	1.189	1.425	1.733	1.867
	R <sup>2</sup>	0.999	0.987	0.999	0.992	0.998	0.995
Eq. consta	K <sub>o</sub> (calc)	11.395	3.468	2.704	8.775	3.146	2.673
	S.E	0.718	0.812	0.715	0.776	0.672	0.578
	R <sup>2</sup>	0.655	0.958	0.876	0.964	0.937	0.944

Table 5: Hysteresis effect on desorption of picloram on the selected soil samples.

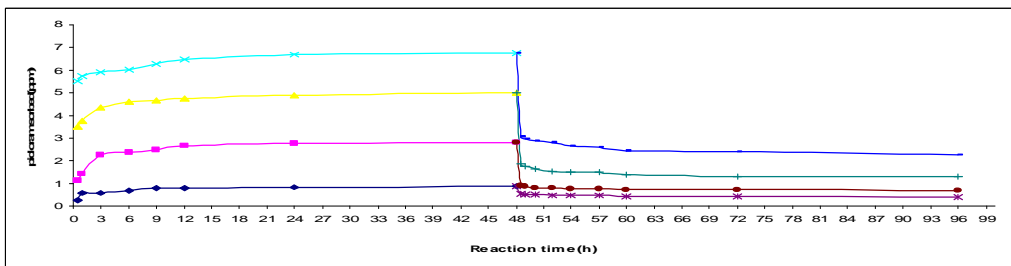
Soil	H <sub>1</sub>	H <sub>2</sub>	ω	λ
S <sub>1</sub>	0.511	195.7	-48.91	-173.9
S <sub>2</sub>	0.223	447.7	-77.66	-46.21
S <sub>3</sub>	0.418	239.4	-58.22	11.94
S <sub>4</sub>	0.241	414.3	75.86	-26.67
S <sub>5</sub>	0.322	309.6	-67.71	-19.68
S <sub>6</sub>	0.517	193.2	-48.25	-25.49



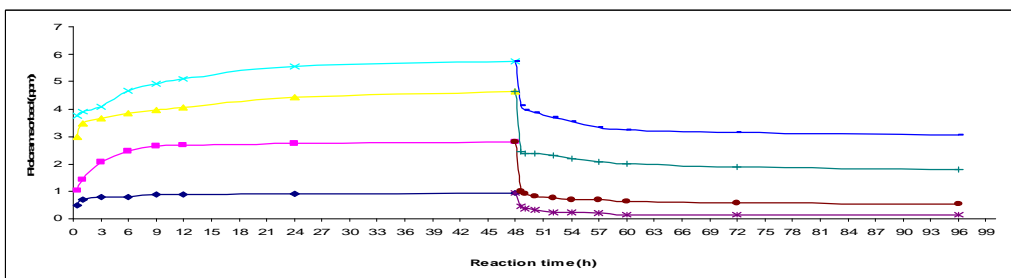
a-



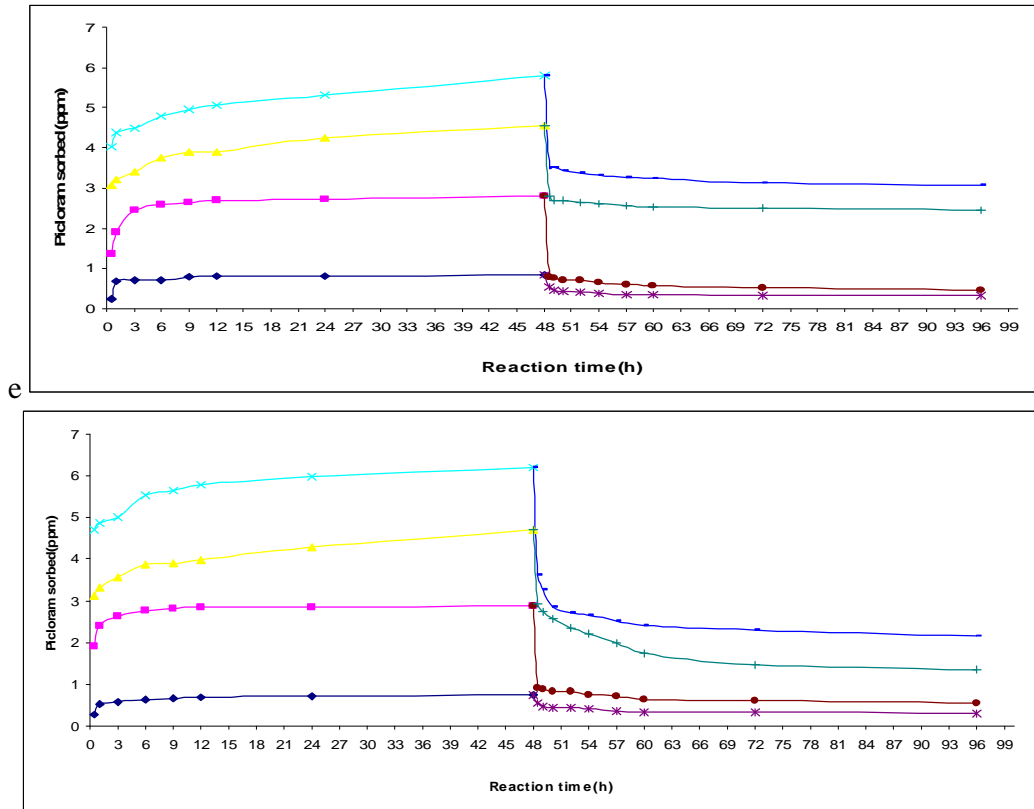
b-



c-



d-



f-  
Fig. 1: Amount of picloram adsorbed-desorbed kinetically with time on selected soil samples (a) S<sub>1</sub>, (b) S<sub>2</sub>, (c) S<sub>3</sub>, (d) S<sub>4</sub>, (e) S<sub>5</sub> and (f) S<sub>6</sub>, (♦ 2, ■ 5, ▲ 10, and x 15 µgml<sup>-1</sup>).

دراسة الد ينمية والحركية لامتزاز - والابتزاز لمبيد بايكلورام على ست ترب الزراعية

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#### الخلاصة

الدراسة أجريت على أظهار الفوارق في سلوك إمتزاز-و إلبتزاز التنافسي للمبيد بايكلورام و البيانات من التجربة طبقت عليها ثلاث نماذج بإستعمال قانون السرعة للمرتبة الأولى- ايلوفج - معادلة القوة لأظهار الفوارق في هذا السلوك على ست نماذج لمواقع مختلفة من ترب زراعية بإستعمال طريقة التوازن الدفعي، اما البيانات من التجربة فقد تطابقت مع نموذجي الخطي وفرندليك و التي حصلنا بموجبها على معامل الإمتزازية الخطية (Kd) تراوحت بين ( 1.406 - 2.151 ) mlg-1 و حين بلغت قيم معامل KF بين (1.078 - 1.189) لعملية إلمتزاز بينما بلغت هذه القيم لعملية إلبتزاز بين ( 0.439 - 0.625 )، (1.045 - 1.585) mlg-1 على التوالي. وإن قيم ثابت الاتزان (K<sub>o</sub>) كذلك قد قيس بإستعمال قانون بايكر للتوازن و قد تراوحت بين ( 2.673 - 11.39). كل تجارب الإبتزاز يزداد او يقل معتمدا في ذلك على ظاهرة التخلف والتي تم وصفها حسب فرندليك .