

## **ADSORPTION OF HERBICIDE FLUAZIFOP-P-BUTYL (FPB) BY CLAY AND SANDY CLAY LOAM SOILS**

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### **ABSTRACT**

The tendency of herbicides to be adsorbed by the soil and their affinity to be desorbed are some of the most substantial factors influencing contamination of soil and water. Therefore, a kinetic and adsorption experiments were conducted to evaluate the adsorption of herbicide Fluzifop-P-butyl (FPB) onto two soils clayey and sandy clay loam soils using a batch equilibrium method. The experimental results of kinetic showed that the adsorption process was reaching equilibrium in 60 min, the kinetics of adsorption was well fitted by the pseudo-second order equation ( $R^2 > 0.99$ ). The adsorption coefficients of FPB was positively related with the clay and organic carbon content. Where ( $K_{oc}$ ) were 2142.3 and 1914.3, ( $K_c$ ) 21.14 and 10.67 for clayey and sandy clay loam soils, respectively. Adsorption data was more fitted to linear partition model and to linear Freundlich adsorption model. Freundlich constants ( $K_f$ ) of FPB for the clayey and sandy clay loam were found to be 11.028 and 0.083, respectively. Distribution coefficients ( $K_d$ ) were 11.15 and 2.01, respectively. The adsorption data also represented by Langmuir Isotherm model ( $R^2$  were 0.96 and 0.92), the maximum monolayer coverage ( $q_m$ ) was determined to be 46.65 and 1.038  $mg\ kg^{-1}$  and the separation factor ( $R_l$ ) were 0.0008 and 0.0834 for clayey and sandy clay loam soils, respectively, indicating a favorable sorption experiment. The adsorption isotherm suggested a relatively higher affinity of FPB to the adsorption sites at low equilibrium concentrations. It was found that FPB has lower values of soil organic carbon partition coefficient ( $K_{oc}$ ) in the sandy clay loam soil, referring to its weak adsorption and thus increased its mobility. Hence, herbicide should be applied judiciously to avoid contamination

**Key Words:** Adsorption, Clayey Soil, Fluzifop-P-Butyl, Freundlich Isotherms, Model.

### **INTRODUCTION**

Today, chemical control of weeds is considered one of the most popular methods for controlling weeds as it is important to reduce weeds infestation, cause rapid and desirable control of weeds (Aboali and

**Saeedipour, 2015**). Herbicides are highly efficient in controlling weeds, increasing yield and improving quality of crop (**Murugesan, and Moses, 2023**). On the other hand, widely used pesticides may accumulate in soil leading to negative changes in biological soil properties, (**Romdhane et al., 2019**). In soil system, sorption of pesticide get influenced by soil properties as soil organic matter (SOM), clay content, CEC, metal oxides, metal hydroxides, temperature, pH, moisture content, exchangeable cations and other environmental conditions along with pesticide properties such as solubility, charge distribution, polarity (polar/non-polar), molecular size, basicity (pK<sub>b</sub>), and acidity (pK<sub>a</sub>) (**Yadav, et al., 2021**).

Pesticide residues are found in soil either in free or adsorbed form. The adsorbed form is unavailable state for microbial degradation and biological action whereas; 'free form' of pesticide is submits to movement inside and outside the soil ecosystem. Pesticides can move both vertically (leaching) and horizontally (runoff). Leaching causes groundwater contamination while Runoff causes contamination of surface water The movement of pesticides is greater in coarse-textured soil than in fine soil (**Yadav, et al., 2021**).

Fluazifop-P-butyl is a worldwide selective grass herbicide that well-known for post-emergence application in various broad-leaved crops (**Keulet et al., 1990**). Fluazifop-P-butyl herbicide is used to control both annual and perennial grasses. The herbicide is related to aryloxyphenoxy-propionate (AOPP), which is a class of graminicides that act specifically on inhibiting the enzyme Acetyl CoA carboxylase in susceptible grass species (**Burton et al., 1989**). It kills by inhibiting lipid synthesis (lipids are necessary components of cell membrane), particularly at the sites of active growth. In the environment, Fluazifop-p-butyl is degraded primarily through hydrolysis and microbial metabolism. Fluazifop-butyl is rapidly hydrolyzed in most aerobic soils, with a half-life of < 3 days, to the free acid, Fluazifop (**Bewick, 1986**). Other studies (**Carr, 1986**) have indicated that Fluazifop is the most likely phytotoxic moiety of Fluazifop-butyl. It is not degraded readily by sunlight or other chemical ways. The half-life of Fluazifop-p-butyl in soils ranged from one to two weeks. Because it strongly adsorbs with soil particles and is not water-soluble. Fluazifop-p-butyl does not volatilize readily. It is not highly mobile Fluazifop-p-butyl binds strongly with soils (**Gessa et al., 1987**) stated that Fluazifop-p-butyl can form irreversible bonds with certain clay soils by several different mechanisms. Interaction of

herbicides with soil that has low organic matter content is often related to the other active components of the inorganic fraction i.e., clay minerals, mainly kaolinite and smectite, as well as iron (hydr) oxides that dominate the inorganic fraction of soil and control pesticide adsorption (**Liu *et al.*, 2008**).

**Miceraet *al.*, (1988)**, also demonstrate that the adsorption of fusilade in the interlayer of smectite clays takes place by more than one interaction mechanism. The first mechanism includes the protonation of the pyridinic nitrogen atom by the acidic water connected to the exchangeable cations, analogous to the behavior of pesticides. Another mechanism of adsorption, which is exotic for Fluazifop, is associated with the carboxylate groups coordination to the exchange cations. These mechanisms may be related; in fact, the pyridinium ion formation should consume surface protons and decrease acidity of the surface thereby, promoting the COOH groups dissociation. Thus, several species should be arise from that interactions: (1) Fluazifop molecules having protonated pyridine nitrogens and undissociated carboxyl groups; (2) Fluazifop molecules containing protonated pyridinic, but deprotonated carboxylic groups bound to the cations, and (3) adsorbed molecules containing deprotonated nitrogens and metal-bound carboxylates.

Due to many pesticides are characterized by low water solubility and moderate to high water hydrophobicity, they are bind strongly to soil particles (**Pinheiroet *al.* 2015**). The main factors controlling the mobility and persistence of pesticides in soil are adsorption and desorption. These processes affect the pesticides bioavailability and thus preform a key role in the pollutants sequestration. Knowledge of these two processes is essential to define the environmental risk of agricultural chemicals usage, to conduct treatments to pesticide contamination and to enhance pesticide disposal technologies. However, the information concerning this issue is scattered and. It is difficult to draw conclusions. Therefore, the aim of present work was to identify the main soil parameters affecting the sorption of Fluazifop-P-butyl on agriculturally different soils. And examine the relationships between the experimental parameters, soil properties and physico-chemical characteristics of the herbicide to predict the behavior and availability of the herbicide.

## **MATERIALS AND METHODS**

### **Soil sampling and characterization**

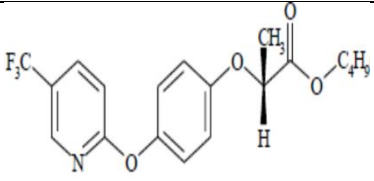
Two surface soil samples (0-30cm) variable in their texture were collected from two locations in Egypt. Clay textured soil was taken from Abis and sandy clay loam soil was collected from El-Hammam area,

north-west coast of Egypt. The samples were air dried, crushed and sieved through a 2 mm sieve. The main characteristics of the studied soils were determined as follows: Soil reaction (pH) was measured in the soil extract (suspension 1:2.5 Soil and water ) using a pH meter, 3320 Jenway, total soil salinity (ECe) was determined in the soil saturation extract using a conductance meter YSI model (35). Cation exchange capacity (CEC) was determined using the method described by **Dawid and Dorota (2014)**. Organic matter content was determined as recommend by **De Voset al., (2007)**. CaCO<sub>3</sub> content was estimated using Collins calcimeter and particle size distribution by the pipette method (**Syvitski, 2007**).

#### Herbicide and chemicals.

Analytical-grade Fusilade (Fluazifop-P-butyl (FPB); (R)-2-[4-(5-trifluoromethyl-2-pyridyloxy) phenoxy] propionate; > 96 % purity), was purchased from Sigma Aldrich Co. Selected physicochemical properties of these compounds are given in Table 1..

**Table (1): Some physical and chemical characteristics of Fluazifop-P-butyl**

Properties	Fluazifop-P-butyl	Reference
Molecular structure		U.S. EPA/OPP (2004)
Chemical formula	R-2-[4-[[5-(trifluoromethyl)-2-pyridinyl]oxy]phenoxy]propanate	Tomlin (2004)
Herbicide Family	Aryloxyphenoxy-propionate	Mallory-Smith and Retzinger (2003)
Molecular formula	C <sub>19</sub> H <sub>20</sub> F <sub>3</sub> NO <sub>4</sub>	Tomlin 2004; U.S. EPA/OPP (2004)
Molecular Weight	383.37 g/mole	EPI-Suite (2011)

#### Kinetic experiment.

Kinetic experiment was carried out at ambient temperature (25 ± 1 °C). 2 g of air-dried soils were mixed with a 10 mL aliquot of an aqueous solution of 5 mgL<sup>-1</sup> FPB (in 0.01 M CaCl<sub>2</sub>), then shake horizontally at the natural pH of soils during 5, 15, 30, 60, 90, 120, 180 and 720 min and then centrifuged at 3000 rpm for 5 min. Each supernatant was filtered

through a 0.22  $\mu\text{m}$  membrane pore-size Millipore filter, then pH was measured. The concentration of FPB in solutions was determined by HPLC (Thermo Ultrimate 3000). Experimental results were analyzed using pseudo-second-order (PSO) kinetic model which defined in Equation (1) (Ho and Mckay 1998).

$$t/q_t = 1/k_2 q_e^2 + (1/q_e)t \quad (1)$$

Where  $K_2$  (g/mg min) is the pseudo-second order rate constant which can be calculated from the intercept of the straight line obtained from plotting  $t/q_t$  vs.  $t$ .  $q_t$  and  $q_e$  ( $\text{mg g}^{-1}$ ) are amount of FPB adsorbed on soil at different time and at equilibrium respectively.

#### Adsorption studies.

Fluazifop-P-butyl (FPB) sorption isotherm experiments on soils were carried by the equilibration technique described in OECD Guideline 106 was used (OECD, 2000) to determine the soil sorption coefficients  $K_d$  ( $\text{mlg}^{-1}$ ) using glass centrifuge tubes closed with Teflon caps. Triplicate soil aliquots (1 g) were pre-equilibrated with 3.6 ml 0.01 M  $\text{CaCl}_2$  (containing 0.01 M  $\text{NaN}_3$  to avoid microbial degradation during incubation) and rotated overnight in the dark before being combined with Fluazifop-P-butyl solution (6.4 ml) to provide a final soil dry-weight: solution  $\text{CaCl}_2$  ratio of 1:10 (w/v). Initial FPB solutions (5, 10, 15, 20 and 25  $\text{mgL}^{-1}$ ) from a stock 100  $\text{mgL}^{-1}$  were prepared in acetone. gently rotating on a horizontal shaker (30 rpm.) at room temperature ( $25 \text{ }^\circ\text{C} \pm 1^\circ\text{C}$ ) for 60 min. A preliminary kinetic experiment showed that equilibrium was reached within 60 min.  $\text{CaCl}_2$  (0.01 M) was used as background electrolyte in order to minimize ionic strength changes and to promote flocculation. After equilibration, the suspensions were centrifuged at 5000 rpm for 5 min and filtered. Samples were analyzed by high-pressure liquid chromatography HPLC (Thermo Ultrimate 3000) to measure the concentration of pesticide remaining in solution after adsorption ( $C_e$ ). The amount of FPB adsorbed ( $C_s$ ) was calculated from the difference in concentration between the initial ( $C_i$ ) and the equilibrium FPB ( $C_e$ ) concentrations in solution. Initial solutions without soil were also shaken for 180 min and served as control.

$$C_s = V (C_i - C_e) / m \quad (2)$$

Where ( $m$ ) is the mass of soil(g) and ( $V$ ) is the volume of the solution (mL).

Several mathematical models can be applied to describe experimental data of adsorption isotherms (Foo and Hameed 2010).

**Linear model.**

A simple linear model is the most widely used adsorption isotherm equation. Such an adsorption isotherm equation is generally expressed in terms of the sorption coefficient or partition coefficients between the solution and solid phase,  $K_d$  ( $L\ g^{-1}$ ) is represented by Equation (3).

$$C_s = K_d C_e \quad (3)$$

Where  $C_s$  is the adsorbed amount per unit mass ( $mg\ g^{-1}$ ) and  $C_e$  is the equilibrium concentration of the solute in the bulk solution ( $mgL^{-1}$ )

**Langmuir isotherm model.**

The Langmuir isotherm model supposes the monolayer coverage of adsorbate over a homogeneous adsorbent surface where all adsorption sites are identical and energetically equivalent. There is no interaction between the adsorbed molecules on neighboring sites. The expression of the Langmuir isotherm is represented by Eq.(4) Vermeulan, *et al.*, (1966).

$$q_e = q_{max} K_L C_e / (1 + K_L C_e) \quad (4)$$

Where  $q_e$  is the amount of solute adsorbed per unit weight of adsorbent at equilibrium,  $C_e$  the equilibrium concentration of the solute in the bulk solution ( $mgL^{-1}$ ),  $q_m$  maximum monolayer coverage capacity ( $mg.g^{-1}$ ) and  $K_L$  is the Langmuir constant related to the free energy of adsorption ( $Lmg^{-1}$ ). Langmuir adsorption parameters were determined by transforming the Langmuir Equ. (4) into linear form:

$$C_e/q_e = C_e/q_{max} + 1/k_l q_{max} \quad (5)$$

The values of  $q_{max}$  and  $K_L$  are calculated from the slope and intercept of the Langmuir plot of  $C_e/q_e$  versus  $C_e$  (Langmuir, 1918). The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter  $R_L$ , which is a dimensionless constant referred to as separation factor or equilibrium parameter (Webber and Chakravarti, 1974).

$$R_L = 1/1 + K_L C_0 \quad (6)$$

Where  $C_0$  = initial concentration,  $K_L$  = the constant related to the energy of adsorption (Langmuir Constant).  $R_L$  value indicates the adsorption nature to be either unfavorable if  $R_L > 1$ , linear if  $R_L = 1$ , favorable if  $0 < R_L < 1$  and irreversible if  $R_L = 0$ .

**Freundlich isotherm model**

Freundlich isotherm model is the oldest relationship describes the non-ideal and reversible adsorption. This empirical model can be applied to multilayer adsorption on a heterogeneous adsorbent surface. The Freundlich adsorption was defined in: Equation (7)

$$C_s = K_f C_e^{1/n} \quad (7)$$

and fitted to the logarithmic form of the Freundlich Equation (8)

$$\log C_s = \log K_f + n_f \log C_e \quad (8)$$

Where  $C_s$  is the adsorbed amount per unit mass,  $K_f$  is a Freundlich constant indicative of the relative adsorption capacity of the adsorbent ( $\text{mgL}^{-1}$ ) and ( $n_f$ ) is the adsorption intensity describes the degree of curvature of the isotherms.  $C_e$  is the equilibrium concentration of the solute in the bulk solution ( $\text{mgL}^{-1}$ ).

The affinity of Fluazifop-P-butyl (FPB) towards organic carbon was evaluated by  $K_{oc}$  values which calculated by normalizing adsorption constant  $K_d$  with the organic carbon (OC) content of the sorbate using Equ.(9).

$$K_{oc} = K_d \cdot 100 / \%OC \quad (9)$$

The affinity of Fluazifop-P-butyl (FPB) towards the clay content of the soils is also evaluated by calculating  $K_c$  using Equation (10).

$$K_c = (K_f / \%C) \times 100 \quad (10)$$

Where  $K_f$  is the Freundlich constant and C is the percent of clay content in soil.

## RESULTS AND DISCUSSION

### Soil characterization

Table (2) showed that the soil textures of Abis and El-Hammam soils were clay and sandy clay loam, respectively. This is due to the difference in their clay content. As shown in the Table (2), the soil reaction (pH) was slightly alkaline (7.52) in the Abis soil, while it was alkaline (8.04) in the El-Hammam soil. Electrical conductivity (EC dS/m) of Abis soil showed that soil was non-salin (1.52 dS/m), but the soil of the El-Hammam was lightly saline (2.85 dS/m). The results also showed that the organic matter content of Abis and El-Hammam soils, were 8.9 and 1.8  $\text{gkg}^{-1}$ , respectively. Total content of calcium carbonate ( $\text{CaCO}_3$ ) was 85.8  $\text{gkg}^{-1}$  in Abis. While it was 411.2  $\text{gkg}^{-1}$  in El-Hammam which was classified as calcareous soil. Cation exchange capacity (CEC) of Abis and El-Hammam soils was 45.27 and 16.58  $\text{CmolcKg}^{-1}$ , respectively. This difference may be due to the difference in clay minerals in the two studied soils.

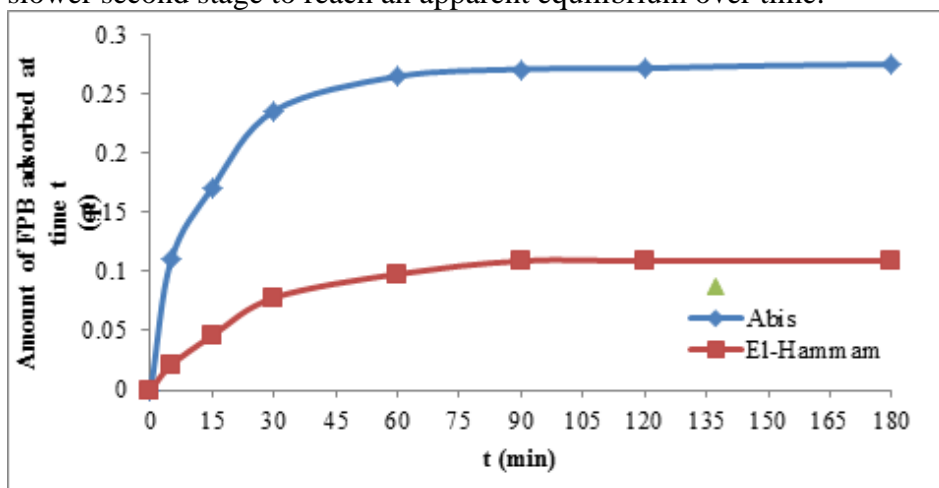
**Table (2): Some initial physical and chemical properties of the experimental soils.**

Soils	Soil separates %				Textural Class	Chemical properties					
	C. sand	F. sand	Silt	Clay		pH 1:2.5	EC dS/m	O.C %	O.M gkg <sup>-1</sup>	CaCO <sub>3</sub> gkg <sup>-1</sup>	CEC CmolcKg <sup>-1</sup>
Abis	6.60	31.52	9.72	52.16	Clay	7.52	1.52	0.52	8.9	85.8	45.27
El-Hammam	7.24	53.35	19.88	19.53	Sandy Clay Loam	8.04	2.85	0.105	1.8	411.2	16.58

O.C = organic carbon    O.M = organic matter

### Effect of contact time on FPB adsorption

It is clear in Figure (1) that the adsorption efficiency of two studied soils increased with increasing the equilibrium contact time up to 180 min. The adsorption process was fast reaching equilibrium in 60 min with variable magnitudes. For clay soil of Abis, adsorption of FPB rapidly increased with increasing equilibrium time from 5 to 30 min but increases slowly upon increasing time up to 60 min and remains constant up to 180 min. Likewise, for sandy soil adsorption of FPB was progressively increased upon increasing time from 5 to 15 min, then increases slowly up to 60 min and remains constant to 180 min. FPB adsorption processes were done with a rapid initial stage followed by a slower second stage to reach an apparent equilibrium over time.



**Figure (1).** Effect of contact time on FPB adsorption onto two studied soils.

### Adsorption kinetics.

Kinetic models help to investigate potential rate-controlling mechanisms. The pseudo-second-order equation analyzes the equilibrium



adsorption. This model assumes that the sorption capacity could be proportional to the number of active soil sites, where  $q_t$  and  $q_e$  have the same definition. Also, the initial sorption rate  $h$  can be calculated using the relation (Koynucu, 2008).

$$h = K_2 q_e^2$$

The pseudo-second-order model shows a good fit with the experimental data, with correlation coefficient  $R^2$  values  $> 0.99$  for two soils as shown in Figure (2). The  $q_e$  values obtained are consistent with experimental values. The highest kinetic rate constant ( $k_2 = 14.386$ ) for sandy soil undergoes faster sorption kinetic than for clayey soil ( $k_2 = 0.5433$ ). There are marked differences in the first stage of the adsorption process according to the values of the initial rate constant ( $h = K_2 q_e^2$ ), obtained from the intercept of pseudo-second-order equation. In general,  $h$  showed greater amount of neutral molecules of herbicide in sandy soil,  $h$  values were approximately  $0.0458$  and  $0.1187 \text{ mg g}^{-1} \text{ min}^{-1}$  for clayey and sandy soils respectively (Table 3).

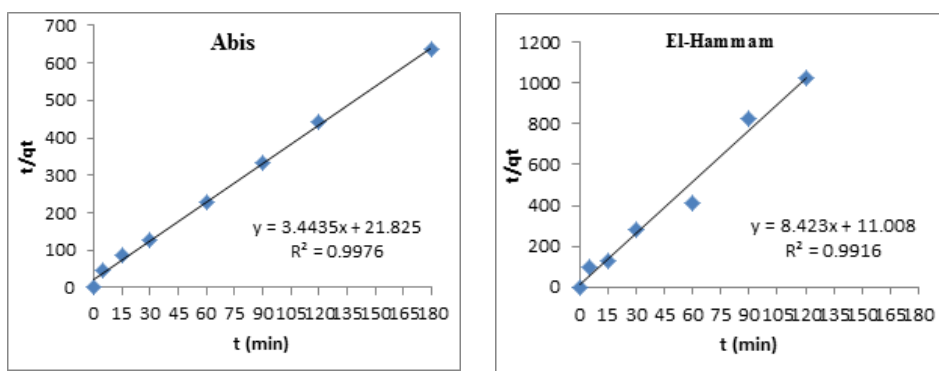


Figure (2). Pseudo-second-order kinetics adsorption for FPB onto two studied soils.

Table (3). Parameters and constants of the kinetic models of the pseudo-second-order .

Soils	$q_e$ ( $\text{mg g}^{-1}$ )	$K_2$ ( $\text{mg}^{-1} \text{ min}^{-1}$ )	$h$ ( $\text{mg g}^{-1} \text{ min}^{-1}$ )	$R^2$
Abis	0.5433	0.5433	0.0458	0.9976
El-Hammam	0.008	14.386	0.1187	0.9816

### Adsorption equilibrium

Adsorption amplitude of the pesticide under any particular soil type and soil solution conditions will depend on the nature and properties of

the soil and the pesticide. Adsorption isotherm studies of the two investigated soils were conducted at ambient temperature ( $25 \pm 1^\circ\text{C}$ ) as shown in Figure (3). The adsorption isotherm of Abis soil was seen to be L-type isotherm which are characterized by the reduction in the adsorption at higher aqueous compound concentrations. This indicates higher competition for adsorption sites which get limited as concentration of solute in solution increased (Akçay and Yurdakoc2000). So L-type adsorption called as high-affinity adsorption reaching a constant saturation value. While El-Hammam soil exhibit S-type adsorption isotherm where mainly parabolic in nature with the S- type shaped curvature mainly confined to the initial stages of adsorption. This indicated a greater initial competition of water molecules to the adsorbent as compared to the herbicide, until a certain level of adsorbed herbicide is composite. This is a general sorption process of organic molecules on the soils of low organic matter or on clay (Raman and Rao 1987).

Based on linear model isotherms the  $K_d$  parameter is more significant for comparison. The extent of the partition coefficient  $K_d$  values found for the adsorption of FPB on the two soils are shown in Table (4) and Figure (3), where  $K_d$  values were  $11.15 \text{ Lkg}^{-1}$  and  $2.01 \text{ Lkg}^{-1}$ . A high  $K_d$  value reflects high adsorption capacity and was commonly associated with clayey Abis soil which presented the highest organic matter ( $8.9 \text{ gkg}^{-1}$ ) and clay content (52.16%). In contrast, the lowest  $K_d$  value was found in sandy clay loamy El-Hammam soil. The correlation coefficient ( $R^2$ ) measured the strength of the linear relationship as shown in Table (4) and Figure (3). The  $R^2$  values are 0.9961 and 0.9916 for Abis and El-Hammam respectively, proving that the sorption data fitted well to linear isotherm model.

Related to Langmuir isotherm model data shown in Table (4) and Figure (4), the maximum monolayer coverage capacity ( $q_m$ ) from Langmuir Isotherm model was determined to be 46.65 and 1.038  $\text{mg. g}^{-1}$ , for Abis and El-Hammam respectively and  $K_L$  (Langmuir isotherm constant) was  $2.63 \cdot 10^2$  for Abis while El-Hammam exhibited  $0.51 \cdot 10^2 \text{ Lmg}^{-1}$ .  $R_L$  (the separation factor) from the data calculated in Table (3) were 0.0008 and 0.0834.  $R_L$  is greater than 0 and less than 1 indicating that the equilibrium sorption was favorable and the  $R^2$  value is 0.9607 and 0.9241 for Abis and El-Hammam respectively. This proving

that the sorption data less fitted to Langmuir Isotherm model compared to linear isotherm model.

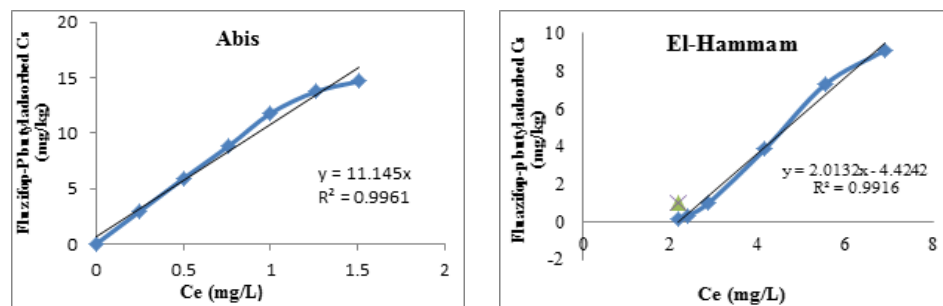


Figure (3). Linear model adsorption isotherms of Fluazifop-P-butyl onto Abis and El-Hammam soils.

Table (4). Linear and Langmuir Isotherm constants for the adsorption of FPB in investigated soil samples.

Soils	Linear model		Langmuir model			
	$K_d$ ( $L \cdot kg^{-1}$ )	$R^2$	$q_{max}$ $mg \cdot g^{-1}$	$K_L \cdot X10^{-2}$ $L \cdot mg^{-1}$	$R_L$	$R^2$
Abis	11.15	0.9961	46.65	2.63	0.0008	0.9607
El-Hammam	2.01	0.9916	1.038	0.51	0.0834	0.9241

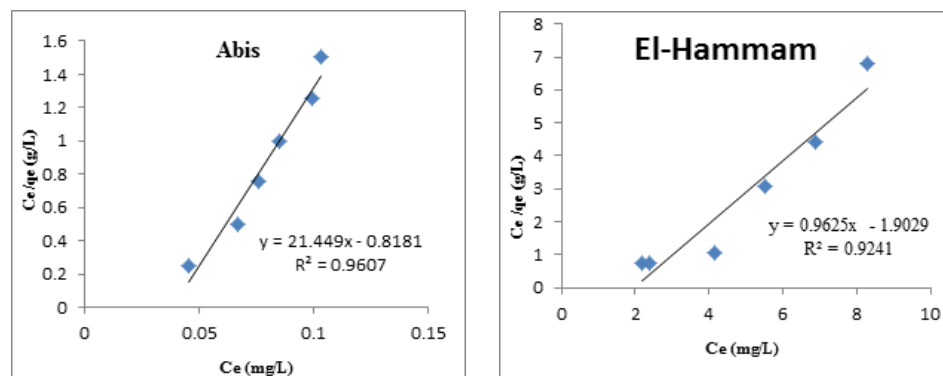
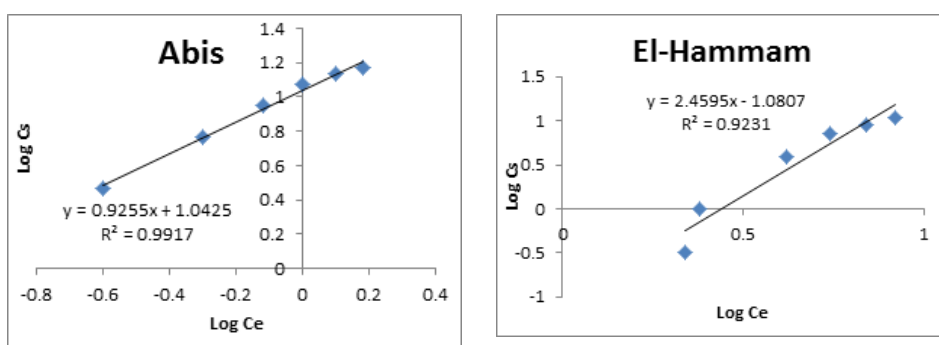


Figure (4). Langmuir model adsorption isotherms of fluazifop-P-butyl onto Abis and El-Hammam soil samples.

The Freundlich model was perhaps the most common adsorption model for a single solute system (Huang *et al.* 1996). Adsorption isotherms for sandy clay loam and clayey soils of El-Hammam and

Abisare given in Figure (5). Data in Table (5) showed that Freundlich adsorption coefficient values obtained of FPB was high in the clayey soil of Abis ( $K_f = 11.028$ ). Whereas it was low in the sandy clay soil of El-Hammam ( $K_f = 0.083$ ). A small  $K_f$  value reflects low adsorption capacity and is commonly associated with a higher permeability of soils and thus higher leaching potential (Spark and Swift, 2002). The value of  $1/n$  represented variation in the FPB adsorption with varying concentrations of herbicide. (slope)  $< 1$  in sandy clay loam soil of El-Hammam (0.41) indicated a nonlinear relationship between the herbicide concentration and adsorption (Giles et al., 1960). Higher values of Freundlich  $K_f$  in clayey Abis soil than in sandy clay loam soil of El-Hammam may be related with high soil clay contents. An increase  $K_f$  value with increasing adsorbed concentration is symptomatic of difficult desorption. Hence; a portion of adsorbed herbicide was resistant to desorb. As the herbicide may be bound to the soil sites and may not have been readily released into the solution (Clay and Koskinen, 1990). The correlation coefficient ( $R^2$ ) was used to determine how well the Freundlich model represents the data. The correlation coefficient ( $R^2$ ) in Table (5) showed that Freundlich model describes the adsorption data of Fluazifop-P butyl better than the Langmuir model. Freundlich equation provided a good fit as shown in Figure (5) where  $R^2 = 0.9917$  in clayey soil;  $R^2 = 0.9231$  in sandy clay loam to the adsorption data in both the soils proving the Freundlich model isotherm was better in describing the sorption data.



**Figure (5).** Freundlich adsorption isotherms of Fluazifop-P-butyl onto Abia and El-Hammam soil samples.

The sorption coefficient ( $K_{oc}$ ) was a good measure of pesticide sorption, which, in assembly with soil organic matter, is commonly supposed to be a main mechanism of pesticide sorption in soils. Data in Table (5) showed that sorption coefficients ( $K_{oc}$ ) were 1914.3 and 2142.3 in sandy clay loam soil of El-Hammam and clayey soil of Abis, respectively. The clayey soil adsorbed a greater amount of fluazifop-P-

butyl per unit organic carbon; therefore, a higher  $K_{oc}$  was found in clay soil than in sandy clay loam soil it has been observed that the adsorption of Fluazifop-P butyl from solution by sandy clay loam soil of El-Hammam was relatively low.

Data in Table (5) also showed that the affinity of Fluazifop-P-butyl towards clay content ( $K_c$ ) was found to be 10.67 and 21.14 in sandy clay loam and clayey soils of El-Hammam and Abis respectively. The ratio of clay content to the organic carbon content is a useful parameter to predict adsorption of herbicides in soil (Liu *et al.*, 2008). The clay content of the soil has been seen to have a great effect on the adsorption of herbicides applied to the soil as mentioned by Liu *et al.* (2008). Clays, as organic matter, have charges and large surface areas. Thus, they have large potentials for adsorption. Inorganic and organic surfaces cause the soil adsorption complex (Calvert 1980). The highest clay and organic carbon content of the clayey soil compared to the sandy loamy soil may be responsible for increased amounts of Fluazifop-P-butyl on clayey soil. The same results were reported earlier by Reddy *et al.* (1995).

**Table (5). Freundlich Isotherm constants  $K_c$  (clay constant) and  $K_{oc}$  (organic carbon constant) values for the adsorption of FPB in investigated soil samples**

Soils	Freundlich model					$K_c$	$K_{oc}$
	$C_s = K_f C_e^{1/n}$	$K_f$ ( $\text{mgkg}^{-1}$ )/( $\text{mgL}^{-1}$ ) <sup>1/n</sup>	$n_f$	$1/n_f$	$R^2$		
Abis	$C_s = 11.028 C_e^{1.08}$	11.028	0.9255	1.08	0.9917	21.14	2142.3
El-Hammam	$C_s = 0.083 C_e^{0.41}$	0.083	2.459	0.41	0.9261	10.67	1914.3

## CONCLUSION

The adsorption of Fluazifop-P-butyl was positively correlated with the soil organic carbon and clay content. The adsorption isotherm demonstrated a relatively higher affinity of the Fluazifop-P-butyl for the adsorption sites at low equilibrium concentrations in the clayey soil. Thus, it is assumed that Fluazifop-P-butyl strongly bound to the clayey soil than the sandy clay loam soil. Hence, at normal equilibrium, it cannot be easily desorbed. The adsorption process was fast reaching equilibrium in 60 min with variable magnitudes. Three adsorption isotherm models were studied. The sorption data was more represented by Linear, Langmuir and Freundlich isotherms where Freundlich adsorption model and linear model describe the adsorption of Fluazifop-P-butyl on soil better than the Langmuir model. It was found that Fluazifop-P-butyl has lower values of soil organic carbon partition coefficient ( $K_{oc}$ ) in the sandy clay loam soil, referring to its weak adsorption in soil and thus increased its mobility into soil. Hence, herbicide should be applied judiciously to avoid the contamination.

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## ادمصاص مبيد الأعشاب فلوزيفوب-ب-بوتيل (FPB) بواسطة التربة الطينية

### والرملية الطينية الطمبية

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يعد ميل مبيدات الحشائش إلى الادمصاص بواسطة التربة وقابليتها للانتزاز من أهم العوامل التي تؤثر على تلوث التربة والمياه ولذلك، أجريت تجربة الادمصاص لتقييم ادمصاص مبيد الأعشاب فلوزيفوب-ب-بوتيل (FPB) في تربتين مختلفتين في القوام، التربة الطينية والرملية الطينية الطمية باستخدام طريقة الاتزان ووجد أن ادمصاص فلوزيفوب-ب-بوتيل مرتبط بشكل إيجابي مع محتوى الطين والكربون العضوي في التربة. تم تحديد الحد الأقصى للادمصاص الأحادية الطبقة ( $q_m$ ) من نموذج لانجمير أيزوثرم لتكون 46.65 و 1.038 ملليجرام لكل كيلوجرام للتربة الطينية والرملية الطينية الطمية على التوالي، وعامل الفصل ( $R_f$ ) الذي يشير إلى ان تجربة الادمصاص مناسبة هو 0.0008 و 0.0834 للتربة الطينية والرملية الطينية الطمية ، على التوالي. حيث ان قيم  $R_f$  تقع بين الصفر والواحد وقد وجد أن ثابت فريندليتش ( $K_f$ ) لفلوزيفوب-ب-بوتيل للتربة الطينية والرملية الطينية الطمية هي 11.028 و 0.083 على التوالي. أما معاملات الادمصاص ( $K_d$ ) ومعاملات الادمصاص المرتبطة بمحتوي الكربون العضوي في التربة (KOC) فقد بلغت 11.15 و 2.01 و 2142.3 و 1914.3 للتربة الطينية والرملية الطينية الطمية على التوالي. اقترحت أيزوثرم الامتزاز قابلية كبيرة نسبياً لـ فلوزيفوب-ب-بوتيل إلى مواقع الادمصاص عند تراكيزات توازن منخفضة. يصف نموذج ادمصاص فريندليتش والنموذج الخطي نتائج تجربة الادمصاص لـ فلوزيفوب-ب-بوتيل بشكل أفضل من نموذج لانجمير لقد وجد أن فلوزيفوب-ب-بوتيل لها قيم أقل للمعامل المرتبط الكربون العضوي في التربة (KOC) في التربة الرملية الطينية الطمية ، مما يشير إلى ضعف ادمصاصها للمبيد وبالتالي زيادة حركيته في التربة ومن ثم، ينبغي استخدام مبيدات الحشائش بحكمة لتجنب حدوث التلوث.