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Models Sorption of Cyhalofop-Butyl, on Mesopotamic Agricultural Soils

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Abstract The adsorption equilibrium of butyl (2R)-2-[4-(4-cyano-2-fluorophenoxy) phenoxy]propanoate (CB) was studied in rice-growing soil. The equilibrium sorption data were fitted into Langmuir, Temkin and Dubinin–Radushkevich (DRK) isotherms. Of the four adsorption isotherm, the R^2 value of Dubinin–Radushkevich isotherm model was the highest. The maximum monolayer coverage (q_m) from Langmuir isotherm model was determined to be 0.079 mg g^{-1}, the separation factor indicating a favorable sorption experiment is 0.38. The heat of sorption process was estimated from Temkin Isotherm model to be 0.0004 J mol^{-1} and the mean free energy was estimated from DRK isotherm model to be 7.0 KJ mol^{-1} which vividly proved that the adsorption experiment followed a physical process.

Keywords Herbicide, soil, isotherm model, sorption, clay

1. Introduction

Actually increasing attention has been paid to the adverse impact of pesticides on the environment, human health, and life-support systems.

The potential for contamination of water bodies is high in areas where rice is cultivated under flooded conditions [1-6]. The agrochemical products applied to the aquatic environments like the rice-fields are a motive of worry for the potential leaching [7-9] and the persistence in the soil and the water [10]. During the drainage phase, which consists of a forced movement of water of rice towards other chambers of field and finally in courses of surface water, the agrochemical ones they can be mobilized and to spread in the environment. Inversely in not flooded soils, the great one water volume of rice it increases considerably the quantity of agrochemical in the solution and his possible adsorption in the sediment of rice-field is not favored.

Usually, the retention and the mobility of the pesticides in the soil are determinate for the extension and the force of the interactions with the surfaces of the soil and are ruled by the chemical and physical properties of the soil and of the pesticides.

For soils characterized by a low content of organic matter, the interaction with pesticides relates often to the active components of the inorganic fraction (it is to say, clays and clayey minerals [11]). Normally, an increase in the content of clay results in a decrease of the mobility of the pesticide. For the soils with major content of organic matter, the retention of pesticides has related to the organic total content, having the nature of the organic small matter influences in the processes of sorción [12, 13].

The cyhalofop-butyl (butyl (2R)-2-[4-(4-cyano-2-fluorophenoxy) phenoxy]propanoate, CB) is a selective herbicide applied at rates of up 300 g/ha, is an acetyl CoA carboxylase inhibitor for post emergence control of barnyard grass (Echinochloa spp.) and silver top (Lepthochloafusca) in rice [27, 28]. CB is a member of the aryloxyphenoxy propionate class of herbicides. Like the majority of the compounds in this class, cyhalofop -butyl is readily absorbed by plant tissue, is phloem mobile and accumulates in the meristematic región of the plant. The formulation as ésters facilitates the capture across the cuticle of the plant and, as soon as they enter the plant, they transform in a few hours in the acid (That is to say, the active herbicide [29 - 31]). In the soils, the cyhalofop-butyl is transforms rapidly into more soluble negative ionizable acidic form [32].

In previous works of this research group, adsorption kinetics were carried out and the isotherm was adjusted to the Freundlich isotherm, which although it has been adjusted to the experimental data, has done so with a good correlation coefficient. [33].

The present study aimed to identify the main soil parameters affecting the sorption and desorption of cyhalofop-butyl on agriculturally-representative rice soils (Vertisols). The relationships between the experimental parameters, soil properties and physico-chemical characteristics of the compound were examined to predict the availability of the herbicide.

2. Materials and Methods

2.1. Soil Samples

One soil come from Perugorría a town in the province of Corrientes, Argentina, was used, and obtained by collecting the first 10 centimeters of the soil. Soil samples were air-dried, sieved at <2 mm, and stored at room temperature in the dark. The soil pH was determined in 0.01 M $CaCl_2$ solution with a soil/liquid phase ratio of 1:2.5 w/v. The total organic carbon (OC) was determined according to the modified Walkley-Black method [34]. The cation exchange capacity (CEC) was determined according to the procedure of Hendershot and Duquette [35]. A summary of characteristics of the soils is reported in Table 1. The site soil is texture clay loam and considered a Vertisol according to the Soil Classification of FAO 1990 and 2006. In general, the soils used in the study are dark brown of sandy clay loam texture,24.7% clay, silt 8.0% and 67.3% sand. The most important property is the high content of organic matter (CO).

2.2. Herbicide

Cyhalofop-butyl (CyB), analytical reference standard of purity 99.9 %, and the commercial grade formulation (10 % EC) were purchased from the group. All other reagents, chemicals, and solvents used for adsorption studies were procured in Argentina. Aqueous solutions of CyB were prepared in 0.01 M $CaCl_2$ for the sorption experiments.

2.3. Batch equilibrium studies

Forty-milliliter aliquots of aqueous solutions that contained increasing concentrations of the CB compounds were added to 1g portions of the soil in 125 mL flasks. CB concentrations ranged from 0.017, 0.033, 0.050 and 0.067 mg/L. The pH of the soil suspensions was 6.8 the original without any pH adjustment. The flasks were agitated continuously on a laboratory shaker at room temperature (25 °C± 1°C) for 24 hours. The soils were separated then by high speed centrifugation for 20 minutes and the equilibrium concentration of each CB compound was determined in the supernatant by by UV spectrophotometry.

3. Results and Discussion

The physico-chemical parameters of the soil are shown in the table 1. According to the determination of soil texture this was classified as sandy clay loam.

Table 1: Physico-chemical characteristics of the soils.

Depth (cm)	**pH**	**OC (%)**	**CIC (meq/100g)**	**N (%)**	**Ca^{2+} (meq/100g)**	**Mg^{2+} (meq/100g)**	**K^+ (meq/100g)**
0-10	6.53	2.78	21	0.49	8.5	3.0	0.30

3.1. Sorption Isotherms

Adsorption data of CB were expressed as the distribution coefficient: $K_d = C_s/C_e$, where C_s (mg kg^{-1} adsorbent) is the amount of herbicide adsorbed on soil, and C_e (M) is the equilibrium concentration in the liquid phase (Table 2). Different isotherm models have been proposed for describing adsorption processes, including Langmuir, Temkin and Dubinin–Radushkevich. Parameters isotherms were obtained by applying the nonlinear model (Table 3).

Table 2: Parameters for ploting Langmuir, Temkin and Dubinin-Radushkevich Adsorption Isotherms of CB in soil

C_o x 10^2 mg L^{-1}	**C_e x10^3 mg L^{-1}**	**q_e x 10^2 mg g^{-1}**	**lnC_e**	***C_e/q_e g L^{-1}***	**logq_e**	**ε^2 x 10^8**
1.7	6.47	1.05	-5.04	0.61	-1.97	1.57
1.7	6.40	1.06	-5.05	0.60	-1.97	1.56
1.7	6.33	1.06	-5.06	0.59	-1.97	1.57
3.3	13.33	1.96	-4.31	0.67	-1.70	1.15
3.3	13.47	1.95	-4.30	0.68	-1.70	1.14
3.3	13.40	1.96	-4.31	0.68	-1.70	1.14
5.0	22.00	2.80	-3.81	0.78	-1.55	0.90
5.0	22.07	2.79	-3.81	0.79	-1.55	0.90
5.0	22.13	2.78	-3.81	0.79	-1.55	0.90
6.66	32.13	3.44	-3.43	0.93	-1.46	0.74
6.66	32.00	3.46	-3.44	0.92	-1.46	0.74
6.66	32.00	3.46	-3.44	0.92	-1.46	0.74

3.2. Adsorption models

3.2.1. Langmuir Isotherm

The Langmuir isotherm is used for adsorption processes of formation of a monolayer on the homogeneous surfaces in which the adsorption occurs at specific sites of the adsorbent. The expression of the Langmuir isotherm is represented by Equation 3 [27]:

$$q_e = \frac{q_m \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \qquad (1)$$

Where q_e the amount of CB adsorbed per gram of the adsorbent at equilibrium (mg g^{-1}), C_e is the equilibrium concentration of adsorbate (mg L^{-1}), K_L is the Langmuir adsorption constant (L mg^{-1}), related to Adsorption energy and q_m maximum monolayer coverage capacity (mg g^{-1}).

Langmuir adsorption parameters were determined by transforming the Langmuir equation (3) into linear form:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \qquad (2)$$

The values of q_m and K_L were computed from the slope and intercept of the Langmuir plot of C_e/q_e versus C_e. [28] 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 [29].

$$R_L = \frac{1}{(1+K_L C_o)} \qquad (3)$$

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 $R_L=0$. From the data calculated in table 2, the R_L is greater than 0 but less than 1 indicating that Langmuir isotherm is favorable.

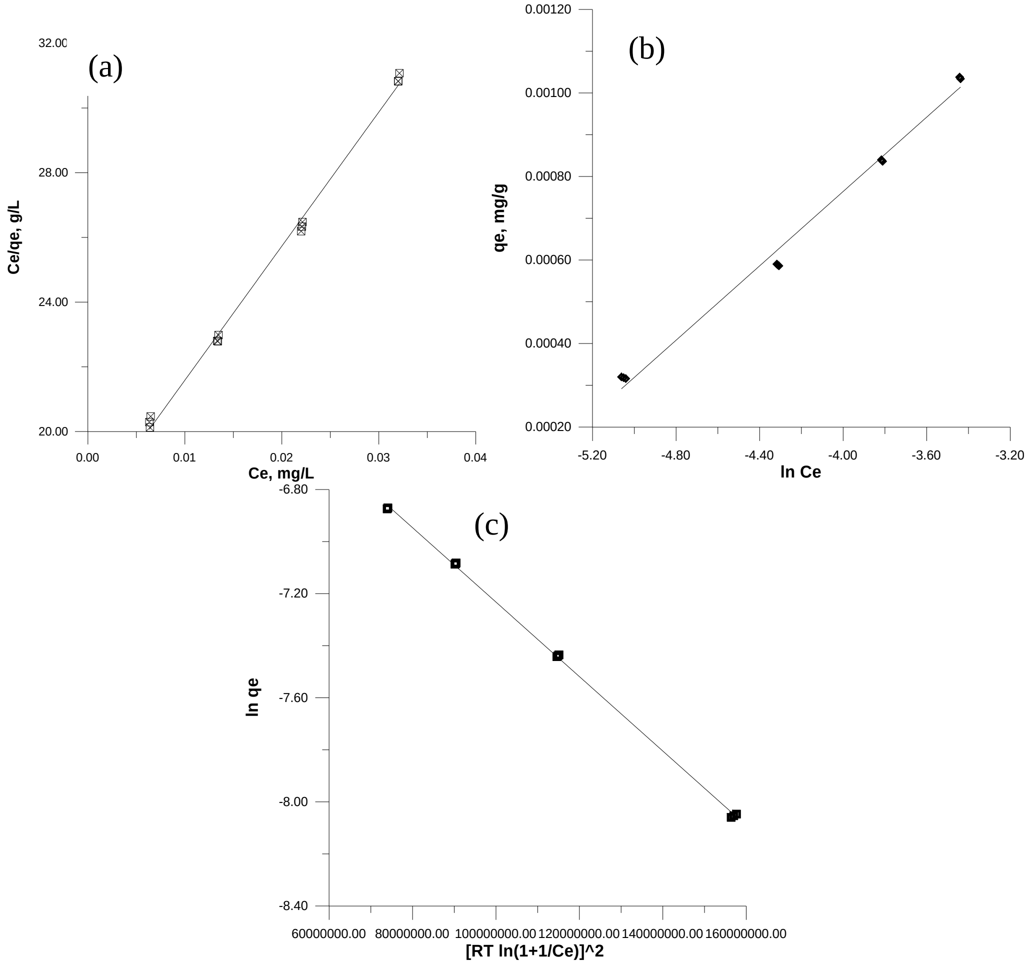

Figure 1: Sorption isotherms of Cyhalofop-butyl using the (a) Langmuir equation; (b) Temkin equation; (c) Dubinin–Radushkevich equation

From this research work, the maximum monolayer coverage capacity (q_m) from Langmuir Isotherm model was determined to be 0.0024 mg g^{-1}, K_L (Langmuir isotherm constant) is 10.25 10^3 L mg^{-1}, R_L (the separation factor) is 0.0002 indicating that the equilibrium sorption was favorable and the R^2 value is 0.997 proving that the sorption data fitted well to Langmuir Isotherm model. (Table 3, Figure 1).

3.2.2. The Temkin Isotherm

This isotherm contains a factor that explicitly taking into the account of adsorbent–adsorbate interactions. By ignoring the extremely low and large value of concentrations, the model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage [30, 31]. As implied in the equation, its derivation is characterized by a uniform distribution of binding energies (up to some maximum binding energy) was carried out by plotting the quantity sorbed q_e against ln C_e and the constants were determined from the slope and intercept. The model is given by the following equation:

$$q_e = \frac{RT}{b}\ln(A_T C_e) \tag{4}$$

$$q_e = \frac{RT}{b}\ln A_T + \frac{RT}{b}\ln C_e \tag{5}$$

If $B = \frac{RT}{b}$

$$q_e = B\,ln\,A_T + B\,ln\,C_e \tag{6}$$

Where A_T is Temkin isotherm equilibrium binding constant (L g^{-1}), b= Temkin isotherm constant R= universal gas constant (8.314 J mol^{-1} K^{-1}), T= Temperature at 298K. B = Constant related to heat of sorption (J mol^{-1})

From the Temkin plot shown in Figure 3, the following values were estimated: A_T = 285.2 L mg^{-1}, B=0.0004 J mol^{-1} which is an indication of the heat of sorption indicating a physical adsorption process and the R^2=0.991.

3.2.3. Dubinin–Radushkevich isotherm

Dubinin–Radushkevich isotherm is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface [32,34]. This isotherm model was chosen to estimate the characteristic porosity of the biomass and the apparent energy of adsorption. The model is represented by the equation below:

$$q_e = q_D\ \exp K_{DB}\,\varepsilon^2 \tag{7}$$

The linear form of equation is given as;

$$\ln q_e = \ln q_D - K_{DB}\,\varepsilon^2 \tag{8}$$

Where K_{DB} is related to the free energy of sorption per mole of the sorbate (mol^2 kJ^{-2}) as it migrates to the surface of the adsorbente from infinite distance in the solution, q_D is the Dubinin-Radushkevich isotherm constant related to the degree of sorbate sorption by the sorbent surface and ε Dubinin–Radushkevich isotherm constant [35, 36].

The apparent energy (E_D) of adsorption from DubininRadushkevich isotherm model can be computed using the relation given as below [35].

$$E_D = \left(\frac{1}{\sqrt{2\ K_{DB}}}\right) \tag{9}$$

Where K_{DB} is denoted as the isotherm constant. Meanwhile, the parameter ε can be calculated as:

$$\varepsilon = RT\ln\left(1 + \frac{1}{C_e}\right) \tag{10}$$

Where R, T and C_e represent the gas constant (8.314 J mol^{-1} K^{-1}), absolute temperature (K) and adsorbate equilibrium concentration (mg L^{-1}), respectively. A plot of ln q_e against ε^2 as shown in Figure 1, yielded straight lines and indicate a good fit of the isotherm to the experimental data.

The coefficient of Regression-R^2, the apparent sorption energy-E, and the values of $q_D$and B_D are summarized in Table 3. The constants q_D and B_D were calculated from the intercept and slope respectively. E_D was calculated using equation 11 when transferred to the surface of the solid from infinity in solution. The value obtained experimentally from the Dubinin Radushkevich parameter q_D indicates a lower adsorption of the CB by the soil. When the value of E_D lies below 20 kJ mol^{-1} it indicates a physical sorption process.

From the linear plot of DRK model, q_D was determined to 0.1006 mg g^{-1}, the mean free energy, E= 5.9 kJ mol^{-1} indicating a physiosorption process and the R^2= 0.999 higher than that of Temkin, Langmuir and Freundlich. The experimental data fit well with the DRK isotherm model. (Figure 1).

Table 3: Langmuir, Temkin and Dubinin–Radushkevich Isotherm constants for the adsorption of CB in soil.

Models Isotherm				**Parameters**
Langmuir	q_m (mg g^{-1})	K_L 10^{-3} (L mg^{-1})	R_L	R^2
	0.0024	10.25	0.0002	0.997
Temkin	A_T (L mg^{-1})	b	B 10^4	R^2

	518.0	6.19 10^6	4.0	0.994
Dubinin – Radushkevich	q_D (mg g^{-1})	K_{DB} (mol^2 J^{-2})	E_D (kJ mol^{-1})	R^2
	0.0030	1.43 10^{-8}	5.9	0.999

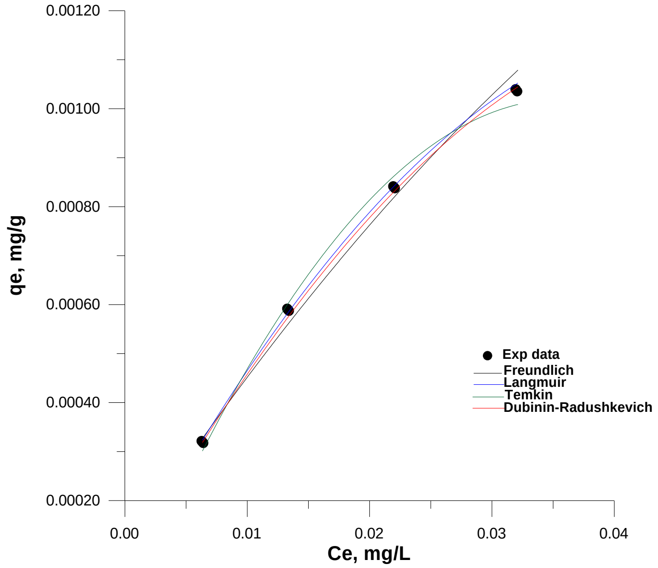

Figure 2: Experimental values according to equilibrium and non-isothermal prediction model adsorption system for the herbicide CB in soil. The graph shows the Freundlich isotherm tested in a previous work by the research group [33]

4. Conclusions

This study indicates that the presence organic matter and other properties of the soil of the mesopotamic region favor the sorption process. The investigation of the equilibrium sorption was carried out at 25°C and pH 6.53. Three adsorption isotherm models were studied. The sorption data fitted into Langmuir, Temkin and Dubunin – Radushkevich isotherms out of which Dubunin – Radushkevich Adsorption model was found to be have the highest regression value and hence the best fit. Adsorption energy of 5.9 kJ mol^{-1} obtained indicate a physical adsorption.

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