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## Clomazone Retention in Agricultural Soil

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### Abstract

Clomazone (CLM), is an herbicide from the oxazolidinone chemical group (Carotenoid synthesis inhibitors), is a selective pre- and post-emergence herbicide indicated for application in rice. It is absorbed both by the roots and by the aerial growth points of weeds and therefore can be applied both pre- and post-emergence. Once in the soil, the adsorption-desorption process are the main mechanism that will determine its passage into the groundwater. The objective of this work is to study the adsorption and desorption of CLM in an agricultural soil for vegetable cultivation, carrying out batch type experiments. The results obtained indicate that the adsorption capacity of the soil is high, decreasing with temperature indicating that the process is exothermic. On the other hand, the desorption process is irreversible, reducing the lixiviation and contamination capacity of underground layers.

**Keywords:** Clomazone, retention, agricultural soils, herbicide

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### 1. Introduction

Weed management in the cultivation of rice and other cultures in Argentina has frequently been carried out with herbicides that persist in the soil for a long time [1]. The incorrect and indiscriminate use of these agrochemicals has caused environmental problems, such as soil contamination (impeding crop rotation), groundwater and surface waters [2].

Clomazone [2-(2-chlorobenzyl)-4,4-dimethyl-1,2-oxazolidin-3-one] belongs to the chemical group of isoxazolidinones. The active (toxic) molecule is metabolized (created) in plants. It has a broad spectrum for pre-emergence control of monocotyledons and dicotyledons and a limited post-emergence action in rice, sugarcane, tobacco, peppers and pumpkin cultures [3].

In soil solution, it tends to remain in its molecular form because it is a non-ionizable herbicide [4]. However, the behavior of non-ionic herbicides can be influenced by changes in pH that cause alterations in clay mineral complexes and soil organic matter [5]. Clomazone Inhibits the action of the enzyme 1-deoxy-d-xyulose 5-phosphate



synthetase (DOXP) synthase, a key component in the synthesis of plastid isoprenoids, which is involved in the biosynthesis of carotenoid pigments.

Knowing the processes that interfere with the behavior of herbicides is essential to understand their fate in the environment, especially in relation to the adsorption process to the soil [6,7]. This process is characterized by being the main transport route for herbicides, since from it it is possible to predict the downward movement of molecules of these products towards the soil matrix in mass flow, together with soil water, leaching process. The leaching potential of a herbicide depends on its physical-chemical characteristics and the edaphoclimatic conditions of the growing location [8].

The adsorption process would indicate whether there could be excessive leaching and therefore may contribute to the migration of herbicides from the site of interest to deeper layers of the soil, with the possibility of reaching groundwater. Thus, the adsorption and leaching process are directly related to the effectiveness of weed control and the risks of environmental contamination by herbicides.

The behavior of clomazone in rice crop soils can help make safe recommendations for this herbicide from a technical and environmental point of view. In this work, the adsorption of clomazone was carried out in a soil sample from the province of Chaco, Argentina, cultivated with rice.

## 2. Material and methods

### Soil

Soil samples used in this study was collected in the town of La Leonesa, Chaco Province. Soil samples were collected in areas with no herbicide application history, in the superficial layer (0.0 - 0.20 m depth); subsequently, dried in the shade, sieved in a 2 mm mesh and, later, they were chemically and physically characterized (Table 1).

### Herbicide

The compound used has a purity of 99.8% and purchased from Sigma Aldrich.

### Adsorption study

The adsorption-desorption studies were carried out by batch experiments, in triplicate. Adsorption isotherms were carried out at temperatures of 25, 35 and 45°C by interacting 1 g of soil sieved at 2 mm with 40 mL of a 0.01 M CaCl<sub>2</sub> solution (in order to maintain the ionic strength constant and favor centrifugation of solids), at different initial concentrations (C<sub>i</sub>) of CLM. The initial concentrations (C<sub>i</sub>) used were 0.12, 1.92, 2.4 and 2.88 mg L<sup>-1</sup>, these concentrations being within the solubility range of the herbicide.

The suspensions were placed in 50 mL capacity polypropylene tubes and shaken at 200 rpm for 24 hours at the different temperatures, a sufficient period of time in which it had previously been verified that the equilibrium between the solution and the particles of the medium, with no significant degradation of the active materials studied. Subsequently, the suspensions were centrifuged at 4000 rpm for 10 min, and the supernatant was filtered and analyzed by spectrophotometry to determine the equilibrium concentration (C<sub>e</sub>). The differences between C<sub>i</sub> and C<sub>e</sub> were assumed to be due to adsorption processes, calculating the adsorbed amount (q<sub>e</sub>) per unit weight of soil as follows:

$$q_e = \frac{(C_i - C_e) \cdot V}{m}$$

Where C<sub>i</sub> is the initial concentration, C<sub>e</sub> the equilibrium concentration, V the volume of solvent used and m the mass of the soil. The adsorption isotherms were carried out by representing the adsorbed quantities (q<sub>e</sub>) against the equilibrium concentrations (C<sub>e</sub>) corresponding to each initial concentration.

### Analysis of CLM

The concentrations of unadsorbed CLM in the sorption medium were measured colorimetrically using a spectrophotometer (METASH model UV-5100B). The absorbance of the color was read at 210 nm.

### Adsorption equilibrium

The details of the process equilibrium, generally known as adsorption isotherms, describe the behavior of the adsorbate-adsorbent interaction and provide information on the capacity of the studied adsorbent. Four models,



Langmuir, Freundlich, Temkin and Dubinin Radusevich, each with two characteristic constants, are studied for this adsorption system. [9,10]

The Langmuir isotherm is a valid theoretical model for adsorption in a monolayer on a completely homogeneous surface with a finite number of identical and specific adsorption sites and with a negligible interaction between the molecules, represented by the following equation:

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

Where the parameter  $q_m$  ( $\text{mg g}^{-1}$ ) is a constant that denotes the maximum adsorption capacity, while the constant  $K_L$  ( $\text{L mg}^{-1}$ ) defines the affinity of the adsorbate for the adsorbent.

The Freundlich model is an empirical equation that assumes no homogeneity in the energy of the sites on the surface and no limit on the maximum adsorption load, and shows a consistency of an exponential distribution of active centers characteristic of a heterogeneous surface, represented as the equation given below.

$$q_e = K_F \cdot C_e^{1/n}$$

The parameters  $K_F$  ( $\text{mg g}^{-1} (\text{mg L}^{-1})^{-1/n}$ ) and  $n$  characterize the adsorption capacity and intensity, respectively; Hypothetically,  $K_F$  reaches the value of  $q_e$  when  $C_e$  approaches unity and thus can be considered as an indicator of adsorption intensity.

The Temkin Model, characterized by a uniform distribution of binding energy, up to a certain maximum binding energy, introduces constants whose values depend on the initial heat of adsorption and assumes a linear decrease in the heat of adsorption with the degree of coating, expressed in the following equation.

$$q_e = \beta \cdot \ln C_e + \beta \cdot \ln K_T$$

Where  $\beta$  is a constant that is related to the heat of adsorption and  $K_T$  ( $\text{L mg}^{-1}$ ) is the equilibrium binding constant corresponding to the maximum binding energy.

The Dubinin-Radushkevich model determines the presence of microporous solids in adsorption processes that give rise to the formation of a monolayer. By applying Polany's theory (adsorption potential on non-porous surfaces) and by calculating the average adsorption energy ( $E$ ) it is possible to know whether the nature of the adsorption is chemical or physical [11]. Average adsorption energy values less than  $8 \text{ kJ} \cdot \text{mol}^{-1}$  indicate physical adsorption processes, while values between  $8 - 16 \text{ kJ} \cdot \text{mol}^{-1}$  consider a chemical adsorption process [12].

$$q_e = q_m \cdot e^{-K_{DR}\epsilon^2}$$

Where the parameter  $q_m$  ( $\text{mg g}^{-1}$ ) is a constant that denotes the maximum adsorption capacity, while the  $K_D$  represents a constant;  $\epsilon$  ( $\text{kJ/mol}$ ), symbolizes the Polany potential.

### Thermodynamic parameters

Thermodynamic parameters reflect the feasibility and spontaneous nature of the process; thus, the free energy change, the enthalpy change, and the surface entropy change can be estimated using the change of the equilibrium constant with absolute temperature. The heterogeneous equilibrium that is reached can be represented with the apparent equilibrium constant  $K_D$  defined by the equation:

$$K_D = \frac{q_e}{C_e}$$

Where  $q_e$  is the concentration of the adsorbate adsorbed on the adsorbent, and  $C_e$  is the equilibrium concentration. With the  $K_D$  value, the change in the adsorption free energy  $\Delta G^\circ$  ( $\text{kJ mol}^{-1}$ ) at the respective temperature is calculated.

$$\Delta G^\circ = -R \cdot T \cdot \ln K_D$$

Where  $R$  is the universal gas constant ( $8.314 \text{ J mol}^{-1}\text{K}^{-1}$ ) and  $T$  (K) the absolute temperature. The change in free energy indicates the degree of spontaneity of the process. More negative values reflect a greater favorability of adsorption and its variation can be expressed as a function of the change in the enthalpy  $\Delta H^\circ$  ( $\text{kJ mol}^{-1}$ ).

The enthalpy  $\Delta H^\circ$  and entropy  $\Delta S^\circ$  ( $\text{J mol}^{-1}\text{K}^{-1}$ ) of adsorption were calculated from the graph of  $\ln K_D$  as a function of  $1/T$ , the regression line with slope  $\Delta H^\circ$  and intercept  $\Delta S^\circ$ , as shown the equation:



$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

$$\ln K_D = \frac{\Delta H^0}{R.T} - \frac{\Delta S^0}{R}$$

A negative value of  $\Delta H^0$  reflects that the process is exothermic in nature, while negative values of  $\Delta S^0$  indicate a decrease in randomness at the solution-solid interface during adsorption.

### Error Functions

Error functions (Table 1) are statistics that measure the error between model parameters and experimental values. The model parameters are determined by the slope and ordinate, which are clearly defined as functions of the experimental data. The fitted parameters are determined by regression to minimize the sum of squares errors between the theoretical and experimental values.

Normally by doing least squares the value of  $R^2$ , the determination correlation factor ( $R^2$ ) confirms and supports the model already discriminated by  $R^2$ . High  $R^2$  values correspond to low error statistics in most cases. When the  $R^2$  values are too close to discriminate the models used, it is convenient to resort to other error functions [13]. The most well-known error functions are listed in the table. When its value is closer to unity, it indicates a good fit.

**Table 1:** Error function.

Function name	Abbreviation	Equation	Interpretation
Chi squared	$\chi^2$	$\sum_{i=1}^n \frac{(q_{e,cal} - q_{e,exp})^2}{q_{e,cal}}$	It is an indicator of precision, in which the best fit of the data can be evaluated from the value of the sum of squares. The smaller value for SSE indicates that the data fits the model better.
relative percentage error	$\varepsilon(\%)$	$\sum_{i=1}^n \frac{(q_{e,exp} - q_{e,cal})}{q_{e,exp}} \cdot 100$	The relative error has the mission of serving as an indicator of the quality of a measurement.
Sum of Squares of the Errors	SSE	$\sum_{i=1}^n (q_{e,cal} - q_{e,exp})^2$	The characteristics of this function is that when the concentration of the liquid phase increases with time, the square of the errors also increases, resulting in a better fit of the isothermal parameters.
Sum of the Absolute Errors	SAE	$\sum_{i=1}^n  q_{e,exp} - q_{e,cal} $	Calculates the sum of absolute errors between the calculated and the experimental results. A better adjustment is observed at high concentration.

### 3. Results and discussion

#### Soil parameters

**Table 2:** Parameters physicochemical

Depth (cm)	Physicochemical characteristics					
	Conductivity dS. cm <sup>-1</sup>	pH	Organic matter (%)	K <sup>+</sup> (mEq/ 100g)	Ca <sup>2+</sup> (mEq/ 100g)	Mg <sup>2+</sup> (mEq/ 100g)
0-10	0.41	5.90	3.41	0.35	13.68	5.08

#### Clomazone sorption isotherms

The graphic representation of the equilibrium models for the CLM is seen in Figure 1, at temperatures of 25°C, 35°C and 45°C. In the concentration range studied, there is an increasing behavior of the adsorbed load and a concave curve towards the concentration axis, characteristic of type L in the classification of isotherms proposed by Giles [14], where, in addition, a maximum adsorption limit.



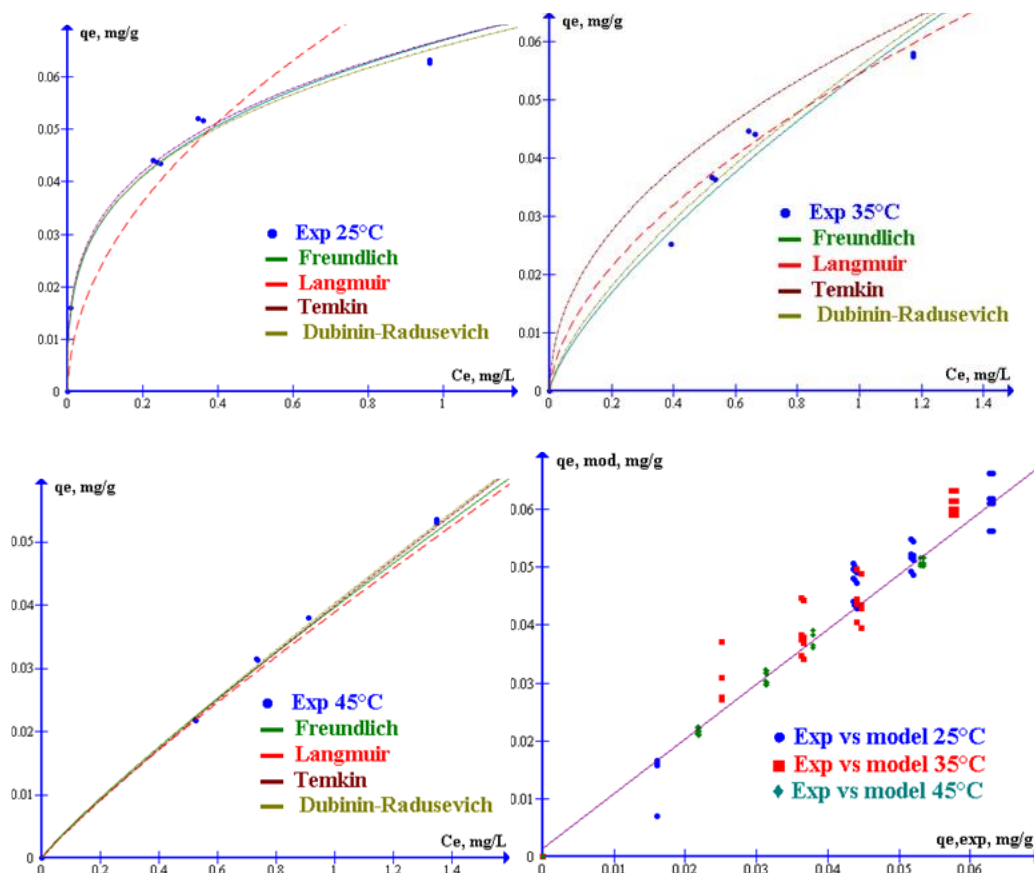


Figure 1: Representation of the models adjusted to the temperature (a) 25°C, (b) 35°C, (c) 45°C and (d) comparison of experimental and theoretical data

The comparison of the estimated values with the experimental ones (Figure 1d) shows the magnitude of the deviation of each model as it moves away from the straight line.

It is observed that the Langmuir model presents the greatest deviation, overestimating the load at medium concentrations, and underestimating it at high concentrations. A similar effect is verified for the Temkin model, but with a much smaller deviation like that of Dubinin-Radusevich. The Freundlich model offers the best fit to the experimental data at all temperatures and concentrations analyzed.

The parameters of each isotherm model are presented in Table 1. The error analysis indicates the Freundlich isotherm as the most appropriate model in representing the equilibrium of the adsorption process as it has excellent correlations ( $R^2 > 0.99$ ) and low values in the percentage of average standard error ( $\varepsilon < 1.5\%$ ) at all evaluated temperatures.

Likewise, the Temkin model, with  $R^2$  correlations greater than 0.98 and  $\varepsilon$  errors less than 4.0%, can acceptably represent the isotherms. On the contrary, Langmuir obtained the lowest correlation and the highest error, ruling it out as an adjustable model for the equilibrium of this system.



**Table 3:** Parameters of the fitted isotherm models (a) Freundlich, (b) Langmuir, (c) Temkin, (d) Dubinin-Radusevich and (d) Thermodynamic parameters.

<b>(a) Freundlich</b>							
T (°C)	$K_F$ ( $\text{mgg}^{-1}/(\text{Lmg}^{-1})$ )	1/n	$R^2$	$\chi^2$	$\epsilon(\%)$	SSE	SAE
25	0.067	0.302	0.994	0.001	0.01	$6.27 \cdot 10^{-5}$	0.021
35	0.054	0.729	0.991	0.003	0.90	$1.10 \cdot 10^{-4}$	0.036
45	0.039	0.889	0.997	0.0004	1.05	$1.74 \cdot 10^{-5}$	0.013
<b>(b) Langmuir</b>							
T (°C)	$K_L$	$q_m(\text{mg}/\text{q})$	$R^2$	$\chi^2$	$\epsilon(\%)$	SSE	SAE
25	12.69	0.067	0.988	0.038	1.97	$3.9 \cdot 10^{-4}$	0.056
35	1.02	0.108	0.985	0.004	3.6	$1.1 \cdot 10^{-4}$	0.028
45	0.14	0.326	0.978	0.001	3.4	$4.1 \cdot 10^{-5}$	0.019
<b>(c) Temkin</b>							
T (°C)	$K_T$	$\beta$	$R^2$	$\chi^2$	$\epsilon(\%)$	SSE	SAE
25	618.48	0.009	0.985	0.001	0.25	$5.9 \cdot 10^{-5}$	0.020
35	11.42	0.024	0.999	0.019	2.73	$8.0 \cdot 10^{-4}$	0.092
45	3.78	0.031	0.991	0.001	3.30	$2.8 \cdot 10^{-5}$	0.009
<b>(d) Dubinin-Radusevich</b>							
T (°C)	$K_{DR} 10^9$	$q_m(\text{mg}/\text{q})$	$R^2$	$\chi^2$	$\epsilon(\%)$	SSE	SAE
25	9.55	0.058	0.975	0.004	2.5	$2.3 \cdot 10^{-4}$	0.025
35	104.8	0.077	0.991	0.001	4.2	$3.3 \cdot 10^{-5}$	0.017
45	170.6	0.158	0.985	0.001	8.0	$3.7 \cdot 10^{-5}$	0.018
<b>(d) Thermodynamic Parameters</b>							
T (°C)	$\Delta G^0$ (J mol <sup>-1</sup> )	$\Delta H^0$ (kJ mol <sup>-1</sup> )	$\Delta S^0$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$R^2$			
25	-5948.95						
35	-4309.37	-68.03	-241.19	0.988			
45	-3811.56						

For equilibrium, by increasing the temperature a decrease in the adsorbed load was observed at the respective concentration, this difference being more pronounced when going from 35 to 45°C. This effect is best represented in the magnitude of the  $K_F$  parameter, which relatively indicates the adsorption intensity; It can be seen that an increase in temperature leads to a decrease in the value of this constant and, therefore, a lower load of clomazone in the soil, especially at a given concentration.

The value of 1/n, also called heterogeneity factor, associated with the adsorption efficiency, at all the temperatures evaluated presents values between 0 and 1, which demonstrates the favorability of the process.

The value of  $K_T$ , corresponding to the maximum binding energy of the Temkin model, shows a notable decrease with increasing temperature, while the value of parameter  $\beta$ , which indicates the heat of adsorption, does not show a clear trend, but it has the highest value at the highest evaluated temperature of 45°C. These two behaviors suggest the exothermic nature of the adsorption process [15]. The negative values obtained for  $\Delta G^0$  confirm the feasibility of the process and its spontaneous nature. On the contrary, the value of the enthalpy change,  $\Delta H^0$ , was negative, indicating the exothermic nature of the process. On the other hand, the negative value of  $\Delta S^0$  reflects the low affinity of the soil for clomazone in solution, indicating a decrease in randomness at the solution-solid interface during adsorption. (table 1(d)).



#### 4. Conclusion

This study also had another objective to statistically establish the "goodness of fit" using adsorption isotherm models for the adsorption of clomazone in soil. In this research, four different isothermal models were used to analyze the equilibrium adsorption data. A complete set of isothermal parameters was optimized using four different error functions. Statistical optimization performed using the statistics revealed that the Freundlich model provided the most accurate representation of the experimental data. Furthermore, the isothermal parameters were consistent with the magnitude of the error analysis.

The results indicate that the prediction of the best-fitting isothermal model depends on the correlation between the errors and the theoretical basis of the isothermal parameters. Importantly, the application of various statistical approaches and isothermal models can improve the understanding of the adsorption process and increase confidence in the accuracy and reliability of the model predictions.

In conclusion, the equilibrium of the clomazone adsorption process is best described by the Freundlich model, where the isotherms with their increasing behavior indicate the formation of multilayers on the adsorbent, typical of physical adsorption systems. Finally, the negative value for the surface Gibbs free energy indicates the favorability and spontaneity of the process that, due to its endothermic nature, is favored by increasing temperature.

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