Research Article

Dynamics of Adsorption - Desorption of Cyalotrin in Soils of Rice Culture in Currents

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Abstract The adsorption-desorption processes of herbicides in crop soils are of primary interest because of the possible entry of this element into the food chain. In this work, the adsorption of lambdacialotrin (LC) is studied in a rice cultivation soil in the central area of streams in the town of Perugorria. A previous kinetic study was carried out that shows that the adsorption process is relatively rapid in the first phase, reaching a pseudo-equilibrium in a few hours. The adsorption isotherms obtained indicate an irreversibly linked fraction, a fact that is consistent with the high hysteresis that is later evident in the desorption process. The effect of the presence of habitual ions in agricultural production scenarios was evaluated, quantifying the effect on the adsorption isotherm of LC. The presence of calcium significantly decreased the adsorption of LC thereby increasing its bioavailability, while potassium had the opposite effect. Adsorption-desorption was characterized by applying the Batch method (OECD 1995). The isotherms were fit to the logarithmic form of the Freundlich equation ($R^2 = 0.996$). In general, the magnitude of adsorption was low, $K_{fa} = 0.644 \pm 0.005$ and $1/n_a = 0.74 \pm 0.01$. Desorption is not fully effective as 37% is retained, indicating an irreversibility of the process ($K_{fd} = 0.754 \pm 0.006$ and $1/n_d = 0.708 \pm 0.006$, $R^2 = 0.999$). The values obtained after the modeling of the experiments in this work represent the first basis for the establishment of future production strategies in areas with high organic matter content.

Keywords Pesticide, soil, isotherm model, sorption, clay

Introduction

The high demand for food by the population has led to the use of a wide variety of agrochemicals, so it has been necessary to understand the dynamics of these products in the environment to efficiently manage crops. The systematic application of agrochemicals results in the possible contamination of soils and, depending on the characteristics of this, surface and underground water could be contaminated, being a risk to the environment and health [1-6]. One of the phenomena that occur in the arrival of pesticides to the soil and that has a great influence on their mobility, bioavailability and final destination, is adsorption-desorption [7]. The adsorption of agrochemicals in the soil depends on the physicochemical characteristics of the molecules and their constituents, the most important in this process are organic matter and mineral compounds. The content of organic matter represents a natural

retainer that will adsorb the agrochemical preventing its transport to surface or underground waters [8-10]. Agrochemicals are mostly ionic and non-ionic organic compounds that interact with soil constituents, where various studies attach importance to the interactions of non-ionized pesticides with both organic materials and the mineral constituents of this [11,12]. The adsorption and desorption coefficients of the pesticides describe their behavior in the soil, the inherent mobility of the compound in the soil, if a compound is reversibly or irreversibly adsorbed which will influence its biological availability, its toxicity to terrestrial and aquatic organisms and their bioaccumulative potential.

In the central area of streams in the town of Perugorria de Corrientes, there is a large number of rice crops in addition to other crops, both fruit and cereals, so that in their agricultural management there is the application of agrochemicals, being necessary to know their behavior in the soil and agricultural management controlling their destiny.

The objective of this work was to determine the adsorption-desorption isotherms for lambdacialotrin (LC), in an agricultural soil of the centro-stream region to know its behavior with the soil under study.

Materials and Methods
Soil
The soil samples come from Perugorría a city in the province of Corrientes, Argentina. It is located south of the province, in the fifth section of the department of CuruzúCuatiá, and 228 kilometers from the provincial capital. The soil texture is clay loam, brown, whose composition is 24.7% clay, 8.0% silt and 67.3% sand, is classified as a Vertisol. 0-10 cm deep soil samples were taken in a 10 m transept with a 1 m interval, obtaining a composite sample, which was homogenized, air dried and screened at 2 mm.

Agrochemical
Lambdacialotrin (LC) the commercial grade formulation (10 % LC) was purchased from the group. All other reagents, chemicals, and solvents used for adsorption studies were procured in Argentina. Aqueous solutions of LC were prepared in 0.01 M $CaCl_2$ for the sorption experiments.

Adsorption Test
Adsorption curves were obtained using the equilibrium batch technique (OECD, 1995, 13) 4. 1 g of soil was weighed in triplicate and 30mL of agrochemical solution in $CaCl_2$, 0.01M, were added, the concentrations were 0.017, 0.033, 0.50 and 0.067mg L^{-1} Then, the suspensions were stirred for 24 hours, at 25°C. Adsorption equilibrium time was determined in previous experiments (data not shown). After stirring, the samples were centrifuged at 3500 rpm for 15 minutes. From the supernatant solution the equilibrium concentration of the agrochemical was determined by the gas chromatography method.

Desorption Test
Desorption curves were obtained at the same concentration points as adsorption. All supernatant was removed and replaced with 30 mL of 0.01M $CaCl_2$ solution, stirred for 24 hours at 25°C, then centrifuged for 15 minutes at 3500 rpm. From the supernatant solution the equilibrium concentration of the agrochemical was determined by the gas chromatography method.

Results and Discussion
The amount of LC absorbed by the soil or sediment was determined by the difference between initial and equilibrium concentrations of LC in solution:

$$q_e = \frac{(C_0 - C_e)V}{m}$$

where: q_e is the amount in the equilibrium of LC adsorbed by the solid phase (mg $L^{-1}g^{-1}$), C_0 is the initial concentration LC in solution (mg L^{-1}), C_e is the equilibrium LC concentration in solution (mg L^{-1}), V is the volume of solution (L) and m is the mass of the soil (g).

Adsorption and Desorption Isotherms

The mathematical fit of the Freundlinch equation is used.

$$q_e = K_f C_e^{1/n}$$

Where the linear expression: $\log q_e = \log K_f + \frac{1}{n} \log C_e$

Represented by: q_e as the amount of pesticide adsorbed by the soil (mg $L^{-1}g^{-1}$) C_e as the equilibrium concentration of the pesticide in the solution (mg L^{-1}) K_f where it expresses the amount adsorbed by the soil (L mg $^{-1}g^{-1}$) y1 / n represents the variation of adsorption with concentration.

Thus the adsorption (K_{fa}) and desorption (K_{fdes}) constants are calculated.

Adsorption Isotherms

The experimental isotherm in this work is a type L classification of Giles, [14] which means that as the concentration in the liquid phase increases, the amount absorbed increases more slowly. This means that the adsorbate molecule is not disposed vertically on the surface of the adsorbent and that there is no competition from the solvent. This result indicates that there are multiple interactions between the solute and the adsorbent. There is a strong molecular attraction between solute molecules and little competition between solvent and solute adsorption sites (Figure 1a). The experimental data fit the Freundlich equation with an R^2 value of 0.991 for adsorption (Figure 2a) and 0.990 for desorption (Figure 3), which represents a linear response for both adsorption and for desorption, this indicates that the soils have an affinity for pesticides in the concentration range evaluated, therefore it is confirmed that the adsorption and desorption of pesticides in the soil Vertisol presents adjustment to said model. The empirical parameter, 1 / n, indicates the intensity of the adsorption process and indicates the affinity of the molecules for the soil adsorbent. It also shows that adsorption depends on the initial concentration of the solution, with higher adsorption rates at lower concentrations. The value of 1 / in (slope) <1 Indicated non-linear relationship between the concentration and the adsorption herbicide (Figure 1a, Table 1). Figure 1 shows how the Freundliuch isotherm fits the experimental data. The adsorption of LC in the soil can be correlated with the amount of clay and organic matter present in the soil.

Desorption isotherm

The mobility of a compound in the soil can be evaluated with studies of desorption. The experimental isotherm as well as that of adsorption is of type L (Figure 2b3). They were adjusted to the Freundlich model (Figure 1b), the value of 1 /n of the desorption equilibrium was <to 1, indicating that the desorption percentages were negatively correlated with the adsorbed amount of the herbicide.

Desorption is not fully effective as 37% is retained, indicating an irreversibility of the process ($K_{fd} = 0.754 \pm 0.006$ and $1 / n_d = 0.708 \pm \pm 0.006$, $R^2 = 0.999$). The values obtained after the modeling of the experiments in this work represent the first basis for the establishment of future production strategies in areas with high organic matter content.

Conclusions

It was found that the adsorption of lambdacialotrin can be positively correlated with soil clay and organic carbon content. The adsorption isotherm demonstrated a relatively higher affinity of lambdacialotrin for adsorption sites at low equilibrium concentrations in the soil. Therefore, in normal equilibrium, it cannot be easily desorbed, with which it presents hysteresis and it can be concluded that lambdacialotrin is retained in the soil, a moderately strong adsorption in the soil and therefore, less mobility towards sources of underground water

Table 1: Parameters of the Freundlich isotherm

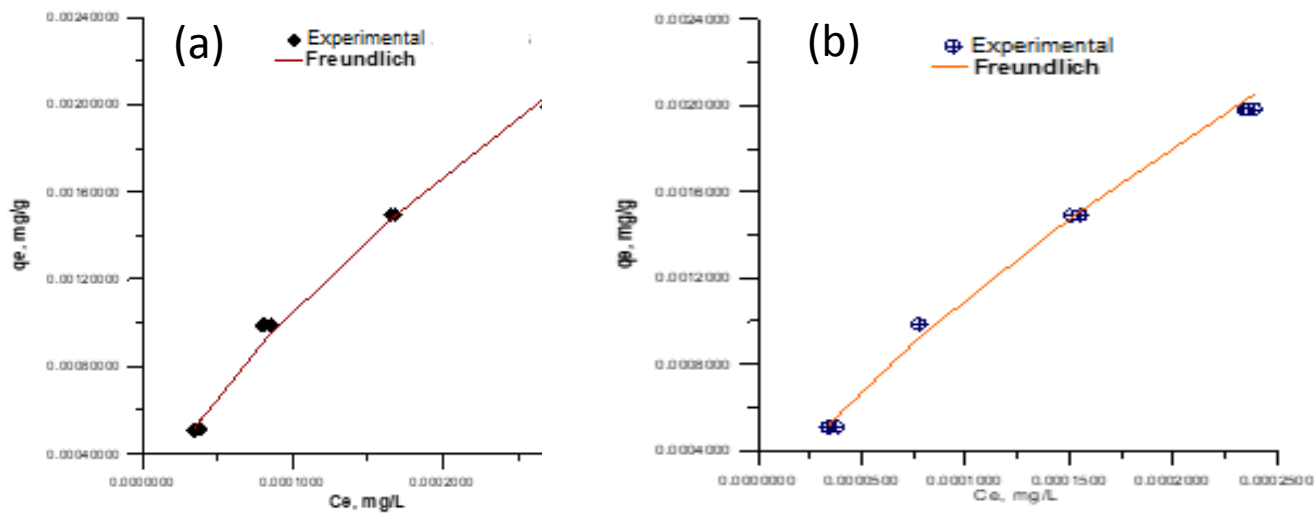| Freundlich Isotherm			
$1/n_a$	n_a	K_{fa} (mg g^{-1})	R^2
0.664	1.506	0.664	0.996
$1/n_d$	n_d	K_{fd} (mg g^{-1})	R^2
0.708	1.412	0.754	0.999

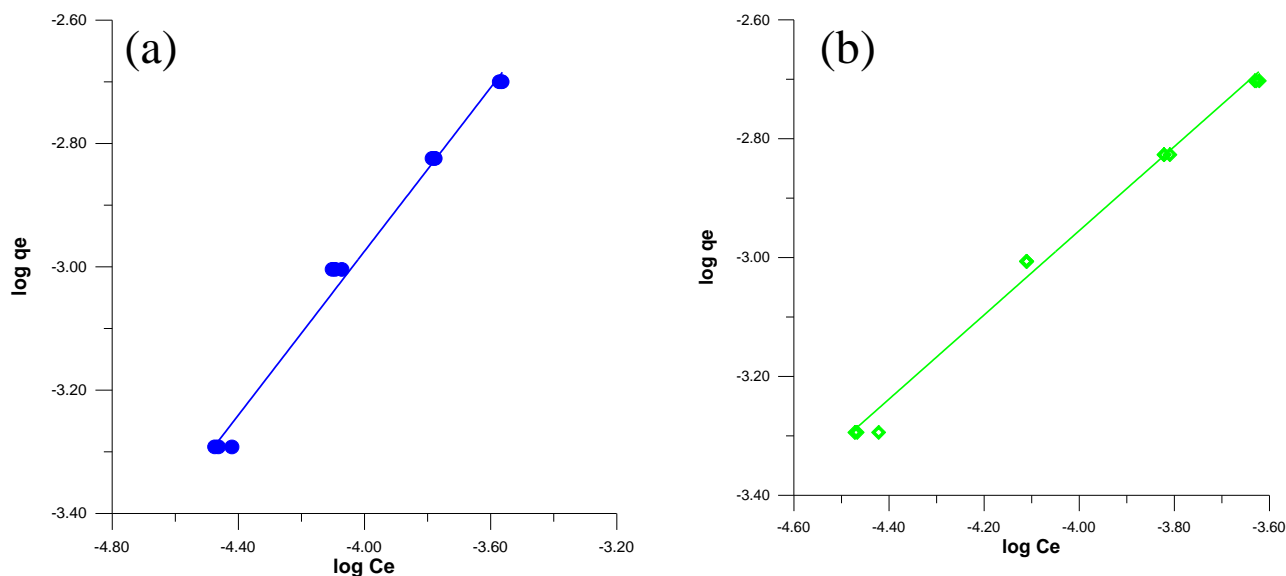*Figure 1: Sorption isotherms of LC in soil. (a) Adsorption; (b) Desorption*

Figure 2: Sorption isotherms of LC using the Freundlich equation. (a) Adsorption; (b) Desorption

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