

SORPTION AND DESORPTION OF SUFLAFENACIL IN TWO SOILS IN THE STATE OF SÃO PAULO WITH DIFFERENT PHYSICAL AND CHEMICAL ATTRIBUTES¹

Sorção e Dessorção do Saflufenacil em Dois Solos do Estado de São Paulo

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ABSTRACT - A study was conducted to evaluate the sorption and desorption of ¹⁴C herbicide saflufenacil (pyrimidinedione) in two soils in the State of São Paulo, classified as Red Yellow Latosol with clayey texture (LVA-1) and medium texture (LVA-2), using the batch method through isotherms. The soils were air dried and sieved a 2 mm mesh. The radioactivity was determined by liquid scintillation spectrometry in acclimatized room (25 ± 2 °C). Sorption isotherms were conducted for 5 concentrations of saflufenacil (5.0; 2.5; 1.0; 0.5 and 0.05 µg mL⁻¹) and the results were adjusted to the Freundlich equation, thus obtaining the parameters of sorption followed by two extractions with 0.01 M CaCl₂ to determine desorption parameters similarly to sorption. The results showed that saflufenacil sorption was low for both soils studied, being greater for the LVA with higher organic matter content. The desorption coefficients were greater than their sorption coefficients, suggesting the occurrence of hysteresis. The sorption and desorption isotherms (classified as type C isotherms), hysteresis and the t-test between the angular coefficient of the respective isotherms showed that both the sorption and desorption occur with equal intensity.

Keywords: isotherms, hysteresis, herbicides.

RESUMO - Foi conduzido um estudo para avaliar a sorção e dessorção do herbicida saflufenacil em dois solos do Estado de São Paulo: um Latossolo Vermelho-Amarelo com textura argilosa (LVA-1) e outro com textura média (LVA-2), classificados como argiloso e franco-argiloarenoso, respectivamente, através de isotermas, utilizando o método em batelada. Os solos foram secos ao ar e peneirados em malha de 2 mm. A molécula radiomarcada com ¹⁴C foi o saflufenacil, herbicida do grupo das pirimidinadionas. A radioatividade foi determinada por espectrometria de cintilação líquida. Os ensaios foram realizados em sala climatizada (25 ± 2 °C). Para determinação de sorção e isotermas de sorção, foram empregadas cinco concentrações do saflufenacil (5,0; 2,5; 1,0; 0,5; e 0,05 µg mL⁻¹), sendo os resultados ajustados à equação de Freundlich, obtendo-se assim os parâmetros de sorção. Na sequência, foram realizadas duas extrações com 0,01 M de CaCl₂, determinando-se os parâmetros de dessorção de forma similar à sorção. Os resultados mostraram que a sorção do saflufenacil foi baixa para ambos os solos, sendo maior para o LVA com maior teor de matéria orgânica. Os coeficientes de dessorção foram maiores do que os respectivos coeficientes de sorção, sugerindo a ocorrência de histerese. As isotermas de sorção e dessorção foram classificadas como isotermas tipo C; o índice de histerese mostrou que tanto a sorção como a dessorção ocorreram com igual intensidade.

Palavras-chave: isotermas, histerese, herbicidas.

INTRODUCTION

The behavior of herbicides can be influenced by the complex system of the soil and its interaction with the environment, affecting its absorption by the crop, transport

and degradation. The bioavailability of a herbicide and thus its effectiveness depends primarily on the sorption capacity of the soil and the affinity of the molecule to the exchange sites existing on the colloidal surface (Harper, 1994).

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Several papers have studied the effect of organic matter (OM), humic substances, clays, pH, specific surface area, water storage capacity and cation exchange capacity on the activity of herbicides. Allister et al. (2008) positively correlated the values of the coefficient of linear sorption (K_d) found for flumioxazin, inhibiting herbicide protoporphyrin IX oxidase (PPO), with organic carbon and clay content in soils of the Chilean Andes, depending on location and depth of collection. Among soil properties, OM has been the most consistently linked to the bioactivity of herbicides. Assis et al. (2011) found that the sorption of picloram, an acid herbicide, was higher in a podzolic soil with higher organic matter content and less pH than a Latosol. Alonso et al. (2013) showed a positive correlation between the content of organic matter and clay in Brazilian oxisols and indaziflan sorption. Now Kerr et al. (2004) reported that the bioactivity of the herbicides 2,4-D, oryzalin, chlorsulfuron, metsulfuron and sulfentrazone correlated inversely with OM and directly with the soil pH.

Saflufenacil, N'-[2-chloro-4-fluoro-5-(3-methyl-2,6-dioxo-4-(trifluoromethyl)-3,6-dihydro-1(2H)-pyrimidinyl)benzoyl]-N-isopropyl-N-methyl sulfamide, is a pre-emergent selective herbicide of the chemical group pyrimidinones, systemic, inhibitor of protoporphyrin IX oxidase (PPO), recommended for control of dicotyledons in various cultures and characterized by having low acute toxicity to humans, fish, birds and insects (Knezevic et al., 2010).

The sorption of saflufenacil has been directly correlated with soil organic matter content and soil humic acid content, while its desorption has been inversely related to clay content, thus affecting its bioavailability (Hixson, 2008). This author observed a highly positive correlation of its bioactivity with soil organic matter ($r^2 = 0.85$), and humic acid ($r^2 = 0,81$), but less correlated with CTC ($r^2 = 0.49$) and even less with the sand content ($r^2 = -0.32$). Studying the sorption of saflufenacil at different depths in eroded soils, Papiernik et al. (2012) found lower K_d values at greater depths, where organic matter content was lower.

The sorption and desorption parameters of saflufenacil in tropical soils are scarce, as well

as information about the environmental performance of this new herbicide. Monquero et al. (2012), studying the leaching of saflufenacil in latosols with distinct textural characteristics, beyond the effect of drought on the residual activity, reported a high leaching in these soils, being more pronounced in soils of more sandy texture, with liming, with sharp fall in control levels after 28 days of drought. Studying the persistence of saflufenacil in sandy soils, Robinson & McNaughton (2012) found symptoms of injuries in various crops, such as carrots and onions, one year after application of saflufenacil, varying according to the applied dose and culture.

Thus, additional information is needed to assess the control potential of saflufenacil, its persistence, leaching and *run-off* in tropical soils where it will be used, as recommended by Papiernik et al. (2012). Thus, the objective was to evaluate the sorption and desorption of saflufenacil in Red-Yellow Latosols with different chemical and physical characteristics, using the batch method, through isotherms, also featuring hysteresis in the sorption-desorption process.

MATERIAL AND METHODS

Deformed samples of two Red-Yellow Latosols (LVA) were used, with no vegetation cover, with different textural classification (LVA-1 and LVA-2). Soil samples were collected in the municipality of Engenheiro Coelho, SP. The samples were collected in the surface layer (0 - 0.2 m depth), air-dried and sieved with 2 mm mesh. The physical and chemical characteristics of the soils are presented in Table 1.

The molecule saflufenacil technical grade (purity = 99.6%) was used in the study, as well as its respective radioactive isotope ^{14}C -saflufenacil (99.5% of radiochemical purity and specific activity = 4.26 MBq mg^{-1}). Saflufenacil is a moderately acid herbicide, with pKa value of 4.41 and water solubility of 30 mg L^{-1} at pH 5 and 2.100 mg L^{-1} at pH 7 (Grossman et al., 2010).

The sorption/desorption experiment was carried out using the batch method, with the two soil samples in triplicate. The saflufenacil solutions were made by dissolving both

Table 1 - Chemical and physical attributes of soils

Soil	pH (CaCl ₂)	C _{org}	Sand	Silt	Clay	Texture class
		%				
LVA -1	4.8	2.56	26.0	22.5	51.5	clayey
LVA -2	4.9	2.00	66.3	7.7	26.0	sandy clayey

the technical product and ¹⁴C-saflufenacil in acetonitrile. Five different herbicide concentrations were used, diluted in 0.01 M CaCl₂: 5.0; 2.5; 1.0; 0.5; and 0.05 µg mL⁻¹.

The five solutions were added to samples of dry soil in a ratio of 1/1 (10 g soil to 10 mL of solution). After the time of equilibrium under constant stirring (24 h) and centrifugation, an aliquot was collected from the supernatant. The radioactivity in the supernatant was determined by liquid scintillation spectrometry (LSS), to calculate the sorbed saflufenacil. We considered the sipped herbicide concentration as the difference between the initial concentration of saflufenacil in the solution and the concentration present in the solution after the equilibration time elapses. The sorption results were adjusted to the linearized Freundlich-Van Bemmelen equation in its logarithmic form (Weber, 1991), expressed as $\log S = \log K_f + (1/n) \log C_e$, where S is the amount of saflufenacil sorbed per soil mass unit (µg g⁻¹), C_e is the concentration of saflufenacil in the supernatant after equilibrium (µg mL⁻¹) and K_f and 1/n are empirical constants, K_f being the sorption constant (µg g⁻¹) (mL µg⁻¹)^{1/n} and 1/n at isotherm slope. The linear sorption coefficient (K_d) was calculated assuming 1/n = 1, which was normalized for the soil's of organic carbon (OC) content, thus obtaining the estimated value of K_{oc} (K_{oc} = K_d/CO). The coefficients of linear sorption were determined for each concentration using the average to obtain an estimated K_d. The percentage of organic carbon was calculated from the organic matter content, using the equation:

$$\% \text{ CO} = \% \text{ MO} / 1.724.$$

After collection of the supernatant and determination of radioactivity in the sorption test, the desorption test was performed, reusing of the same containers with the soils that were used in the sorption test. Aliquots

of 15 mL 0.01 M CaCl₂, without saflufenacil, were added to centrifuge tubes containing the remaining soil. After the time of equilibrium under stirring and centrifugation, an aliquot of the supernatant was sampled and added to the scintillation solution. Radioactivity was determined by ECL. This procedure was repeated twice (desorption 1 and desorption 2), and calculating the desorbed fraction identical to the sorption test. The data were fitted to the linearized Freundlich equation.

The temperature during the agitation period in both the sorption and the desorption experiments was maintained at 25 ± 2 °C in the dark.

The experiment was conducted in a completely randomized design with two replicates for each concentration in each soil. Regression analysis was applied to the data to calculate K_{f(sor)}, K_{f(des)}, 1/n_{sor} e 1/n_{des}. The comparison between the isotherms was done by applying t test to the values of the angular coefficient of the straight lines at 1% probability (Centeno, 2001).

RESULTS AND DISCUSSION

Saflufenacil sorption (reported as K_{f(sor)}) differed for LVA with different particle sizes, being equal to 0.43 for LVA-1 and 0.52 for LVA-2 of medium and clayey texture classes, respectively (Table 2). Within the range of concentrations evaluated in the study, the Freundlich equation adequately described the saflufenacil sorption by the two soils with R² e" 0.9996, showing a strong relationship between the variables (Table 2 and Figures 1 and 2). The values of 1/n were 0.94 and 0.95 for LVA-1 and LVA-2, respectively, assume that the data were well-fitted to a linear model. Since the values of 1/n are close to 1, the sorption is linearly proportional to the concentration of the solution in equilibrium.



Table 2 - Freundlich coefficient for sorption ($K_{f(sor)}$), degree of linearity ($1/n_{sor}$), coefficient of determination (R^2), linear sorption coefficient (K_d) and distribution coefficient normalized to organic carbon (K_{oc}), determined in samples of Red-Yellow Latosol

Soil	$K_{f(sor)}$ ($\mu\text{g g}^{-1}$) ($\text{mL } \mu\text{g}^{-1}$) ⁿ	$1/n_{sor}$	R^2	K_d (L kg^{-1})	K_{oc} (L kg^{-1})
LVA - 1	0.52	0.94	0.9996	0.84	0.33
LVA - 2	0.43	0.95	0.9997	0.61	0.31

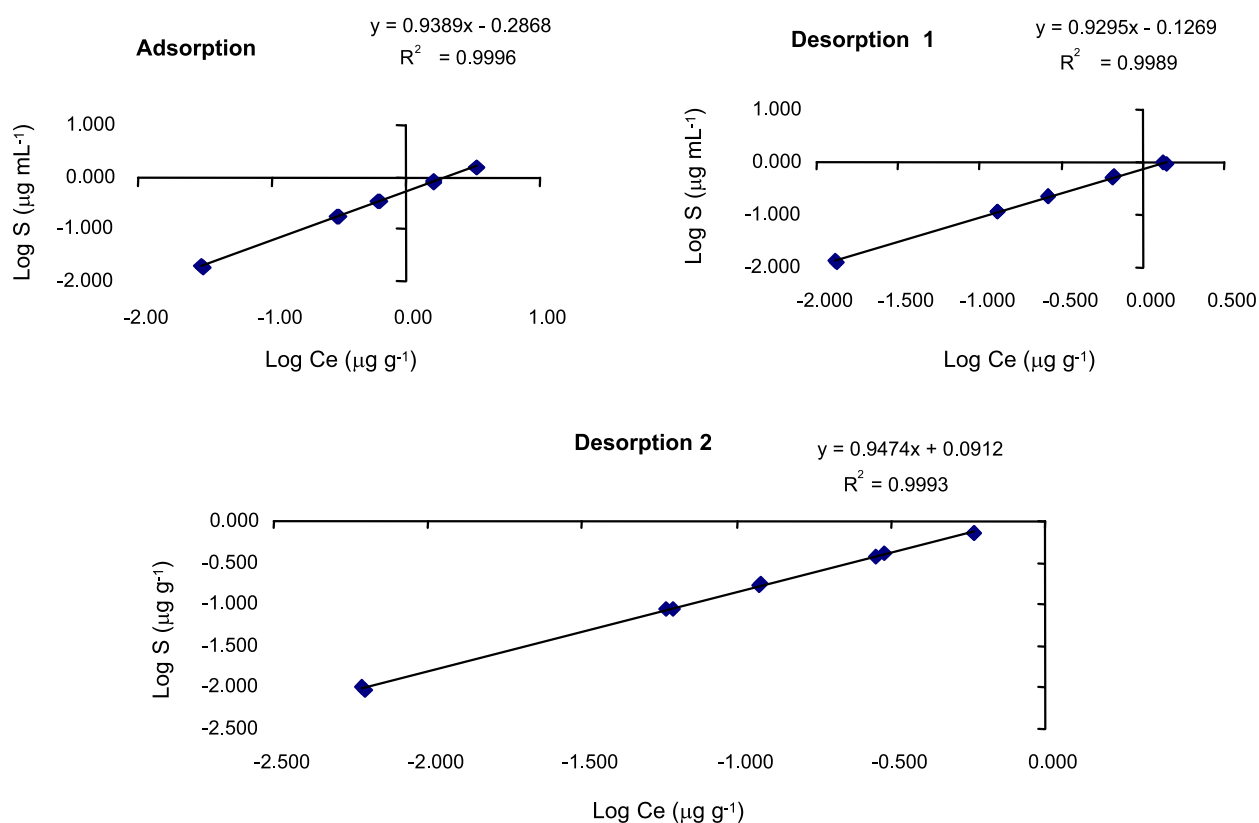


Figure 1 - Sorption (adsorption) and desorption isotherms of saflufenacil in sample of clayey Red-Yellow Latosol (LVA-1).

It was found that sorption of saflufenacil was low in both soils with K_f values equal to 0.52 and 0.43 and estimated K_d of 0.84 and 0.61 L kg^{-1} (Table 2), indicating weak energy binding molecule with soil colloids. These values are consistent with those presented by Papiernik et al. (2012), who reported K_d values ranging from 0.02 to 0.2 L kg^{-1} in sandy soils. Saflufenacil is a weak acid herbicide with pK_a of 4.4, its anionic form predominating in the pH values of the soils used in this study (Table 1). This causes repulsion between molecules of the herbicide and load sites of soil colloids, both negatively charged.

K_{oc} values were similar: 0.33 and 0.31 for soils LVA-1 and LVA-2, respectively (Table 2). According to Hixson (2008), organic matter is the main factor controlling the sorption of herbicides. The values of organic carbon used for the calculation of K_{oc} were obtained from the organic matter content. Thus, K_{oc} values are indicative of the role of organic matter in the saflufenacil sorption process. The highest sorption capacity of weak acid herbicides in soils with higher organic matter is reported by D'antonino et al. (2009). In addition of organic matter, the type and quantity of iron and aluminum oxides present are extremely

Table 3 - Freundlich Desorption Coefficient ($K_{f,des}$), degree of linearity ($1/n_{des}$), coefficient of determination (R^2) and hysteresis index, determined in samples of Red-Yellow Latosol

Desorption	$K_{f(des)}$ ($\mu\text{g g}^{-1}$) (mL μg^{-1})	$1/n_{des}$	R^2	$1/n_{sor}/1/n_{des}$
LVA-1				
1	0.75	0.93	0.9989	1.01
2	1.23	0.95	0.9993	0.99
LVA-2				
1	0.55	0.94	0.9993	1.01
2	2.95	0.94	0.9865	1.01

important in herbicide sorption in highly weathered tropical soils of widespread occurrence in Brazilian Latosols (Assis et al., 2011; DaSilva et al., 2013.).

The Freundlich model also fitted well to the saflufenacil desorption isotherms for both soils, as shown by the high R^2 values (Table 3 and Figures 1 and 2). The values $K_{f,des}$ in the first cycle of desorption were lower than those of the second cycle, suggesting slow release of saflufenacil to the soil solution. In both

cycles the $K_{f,des}$ values were greater than their respective $K_{f,sor}$ (Tables 2 and 3), characterizing hysteresis, indicating that the process of saflufenacil desorption involves mechanisms with greater bonding energy than the sorption. The “hysteresis index” (Table 3) establishes a relationship between the degree of linearity of sorption and desorption. The higher this ratio, the greater the irreversibility of the sorption process and therefore the less the herbicide will be available in the soil solution (Andrade et al., 2010).

The hysteresis index value was approximately equal to 1 in both soils (Table 3), indicating that the process of saflufenacil desorption occurs in the same intensity of the sorption process. This is also evidenced by the isotherms of Figures 1 and 2, classified as type C according to Giles et al. (1960), characterized by a constant partition of the solute (saflufenacil) of the soil solution and the soil colloids, such that the number of sorption sites remains constant. Comparison by *t* test between the angular coefficients of the sorption isotherms with the respective desorption isotherms, both in LVA-1 and

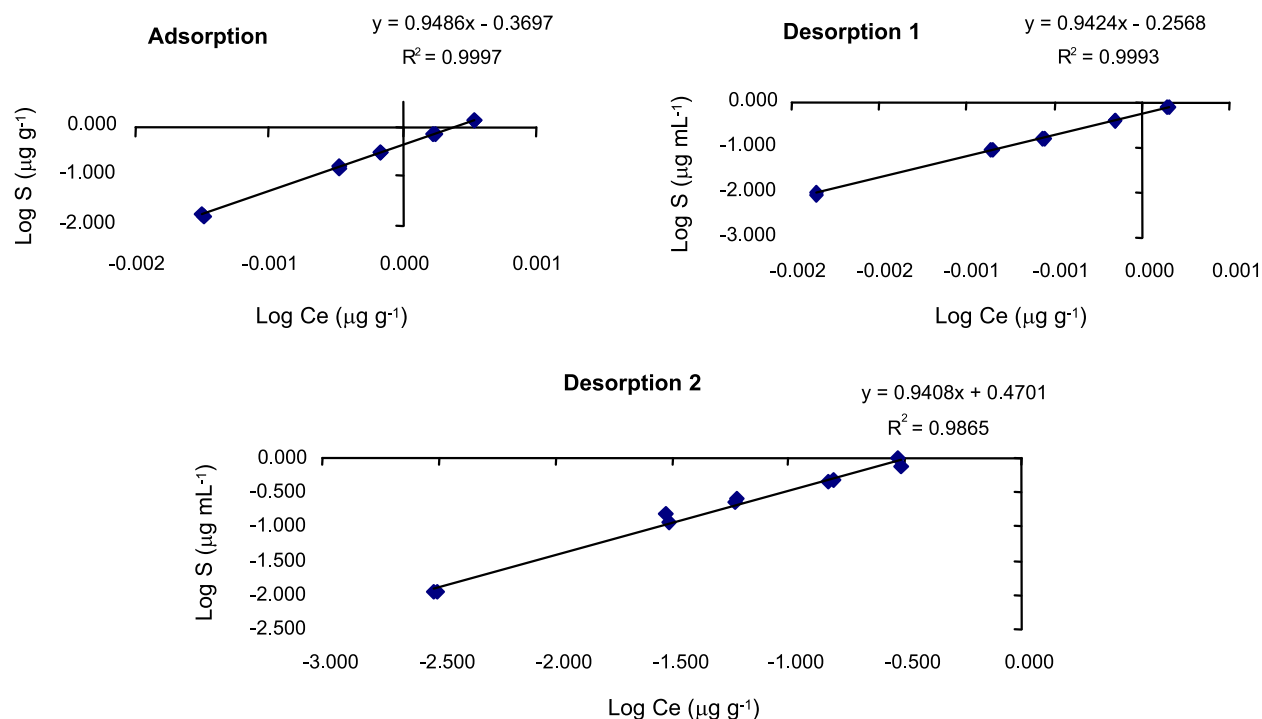


Figure 2 - Sorption (adsorption) and desorption isotherms of saflufenacil in sample of medium texture Red-Yellow Latosol (LVA-2).



LVA-2, always showed $|t| < t$, which leads to assert that the sorption and desorption isotherms are not different from each other; therefore, the response of saflufenacil was the same for both sorption and desorption.

Although the occurrence of hysteresis in the sorption-desorption process of herbicides by soil colloids is a common natural phenomenon (Alonso et al., 2011; Bakhtiary et al., 2013; Ghosh & Singh, 2013), there is no definitive explanation for its occurrence; formation of precipitates, changes in desorption solution composition, degradation, volatilization and irreversible bonds are some factors mentioned by Calvert (1980) and Ma et al. (1993) that contribute to this phenomenon. The mismatch between the sorption capacity of saflufenacil and the hysteresis index in soils appears to be related to the active mechanisms in the process of saflufenacil sorption by soils, as described by Andrade et al. (2010) and Vivian et al. (2007). Working with ametryn, these authors observed that the sorption capacity differs from the hysteresis index, attributing this to the fact that the desorption depends not only on the sorption coefficient, but on the way the herbicide interacts on the adsorbent surface. According to Weber & Snain (1993), in acid conditions, acid herbicides when in its molecular form, can be sorbed by physical interactions such as hydrogen bonds and Van der Waals forces, all with low binding energy conditions, contributing for saflufenacil desorption in the soils.

The results show that the sorption of saflufenacil was low for both soils, being higher for the LVA with higher organic matter content. The desorption coefficients were greater than the corresponding sorption coefficients, suggesting the occurrence of hysteresis. The sorption and desorption isotherms (type C isotherms), the index of hysteresis and the t test between the angular coefficients of the respective isotherms showed that both sorption and desorption occur at equal intensity. The low sorption constants found indicate weak saflufenacil sorption to soil colloids, predisposing the molecule to its release to the soil solution. The occurrence of heavy rain after the application of saflufenacil in soils with the characteristics of those studied here, can contribute to the leaching

of the herbicide, reducing its bioavailability and hence its control effectiveness, increasing the possibility of groundwater contamination.

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