

Adsorption–Desorption Behavior of Thiram onto Humic Acid

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The adsorption/desorption behavior of pure thiram (Thi-P) and formulated thiram (Thi-F) onto commercial humic acids (HA) was studied using a batch equilibration procedure. Results of adsorption kinetic experiments showed that thiram adsorption is a fast process since 85% of the equilibrium concentration is reached within two hours. Experimental K_D values between 0.110 to 0.210 L g⁻¹ were obtained for the adsorption of both Thi-P and Thi-F onto HA, suggesting that thiram is strongly sorbed by humic acids. In general, for both Thi-P and Thi-F, the lower the initial thiram concentration, the stronger is its adsorption (higher K_D and percentage adsorption values). The adsorption isotherms were found to match the BET model. The results show that thiram adsorption onto condensed humic acids cannot be explained only in terms of specific interactions, such as those identified in studies of adsorption of thiram with humic acids in solution. The comparison of sorption and desorption results allowed the observation of hysteresis phenomena. Desorption K_D values were consistently higher than those for adsorption at the same equilibrium concentration. Hysteresis was lower for the formulated thiram suggesting that adsorption is more reversible in the presence of the formulation components turning the pesticide more susceptible to be leached.

KEYWORDS: Thiram; humic acids; adsorption–desorption; hysteresis; batch equilibrium

INTRODUCTION

With the intensive application of chemicals in agriculture, the contamination of soil, ground water, and surface water has become a subject of environmental concern. As the fate of chemicals and the potential risk of contamination of aquatic systems depend on the distribution of contaminants between the aqueous and solid phases, it is important to understand the interaction mechanisms with soil, by establishing the influence of each individual component of the soil system.

Humic substances are one of the major and important components of soil organic matter; they are the most ubiquitous natural component in the environment accounting for 50–80% of the carbon in soil, natural water, and sediments. Because of their characteristics, such as polyfunctionality, polydispersive nature, and polyelectrolytic character, combined with their content of hydrophobic active sites, such as aliphatic side chains and aromatic lignin derived moieties, those substances can interact with both metal ions and organic contaminants by different modes (1, 2).

Recently, our interest has been focused on thiram, particularly as a pesticide (3, 4). Thiram or tetra-methyl-thiuram disulfide is a dithiocarbamate compound that has been used as a contact fungicide with preventive action, registered in Annex I of the Council Directive 91/414/CEE (15th July, 1991) regarding the placing of plant protection products on the market (5). Although thiram is one

of the most used fungicides in Portugal (5) and all over the world (6), little data is available about the sorption behavior of thiram onto soils or onto some specific adsorbents. The literature reports adsorption studies of thiram onto soils of Almeria (Spain), lignins, and specific adsorbents (e.g., waste resulting from a coal mine or SiO₂ particles) (7–10). Recently, Stathi et al. (11) have studied the mechanism of thiram interaction with natural humic acids (HA), either in aqueous solution or immobilized onto SiO₂ particles, and emphasized the role of carboxylate groups of the humic macromolecules on interaction. That type of specific interaction was properly modeled by Langmuir sorption isotherms (see Supporting Information from ref (11)).

However, either in the condensed form or in the soil system, humic substances may form aggregates providing an organophilic medium for sorption of hydrophobic molecules from water (12). It is recognized, in the literature, that soil organic matter acts as a partition medium for nonionic organic contaminants (13). Linear sorption isotherms would be expected if partition was the only interaction mechanism, but deviations from linearity have been observed by several authors (12–15). Several hypotheses have been forwarded to explain the nonlinear solute sorption observed at equilibrium concentrations under the contaminant solubility level (13). Those deviations are higher for more polar organic contaminants (13), and one possible cause for these deviations is the existence of specific interactions with functional groups of the organic matter (15). Stathi et al. (11) emphasized the role of specific interactions on thiram adsorption, but, as referred to

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above, these authors have studied the interactions of thiram with humic substances in solution or immobilized at the surface of silica, and other mechanisms of interaction may be present when condensed humic substances, isolated or in the soil system, are considered (12). Thus, in the present work, the sorption–desorption behavior of thiram onto solid humic substances is investigated using the standard batch equilibration procedure, which has been applied for studying the sorption of many other organic contaminants onto humic substances (16–20). Different models for fitting adsorption–desorption isotherms were compared. Results are compared with other similar studies involving humic substances and other than thiram organic contaminants. Batch adsorption–desorption experiments were made using commercial formulations containing thiram in order to compare the adsorption phenomena when using thiram in its pure form (Thi-P) or in a commercial formulation (Thi-F).

MATERIALS AND METHODS

Chemicals. All chemicals were of analytical grade. Pure thiram, Thi-P, (pure substance, 97%) was purchased from Aldrich, and commercial humic acids (Ash 10–15%, M_r 600–1000) were supplied by Fluka. A commercial formulation of thiram, Thi-F, was obtained from Bayer (Pomarsol ultra D, 80% thiram active substance). Methanol and acetonitrile (HPLC grade) were obtained from Riedel-de Haen and LabScan, respectively. An aqueous 0.01 mol L⁻¹ CaCl₂ solution was prepared from anhydrous CaCl₂ (Fluka, p.a.). Ultra pure water for aqueous solutions was obtained with a Milli-Q water purification system (Millipore).

Standard stock solutions of Thi-P and Thi-F (~20 mg L⁻¹) were prepared by previous dissolution of the solids in acetonitrile, followed by dilution with 0.01 mol L⁻¹ CaCl₂ aqueous solution (percentage of acetonitrile in the final solution was always under 1%). Further dilutions were made in 0.01 mol L⁻¹ CaCl₂. Both stock solutions were prepared just before application to solid humic acids.

A stock solution of 100 mg L⁻¹ thiram in acetonitrile was used to prepare more diluted standard aqueous solutions of thiram for the HPLC-UV method calibration.

Adsorption Studies. Each batch adsorption experiment was carried out using the standard batch equilibration technique, performed according to an OECD guideline (21). A 0.01 mol L⁻¹ solution of CaCl₂ was used as aqueous phase, making the phase separation easier and simulating the ionic strength of a soil solution. Portions of commercial HA of 30 mg each, previously ground, were taken into 10 mL Pyrex centrifuge tubes. Then, 6 mL of thiram solutions (Thi-P or Thi-F), within the concentration range of 2–20 mg L⁻¹, were added. The tubes were stoppered and shaken on an end-over-end shaker (Heidolph Reax) at 100 rpm, during 15 h at 21 ± 1 °C. The time needed to reach equilibrium was based on the study of the adsorption kinetics, described in kinetic section. After reaching equilibrium, suspensions were centrifuged at 4000 rpm for 30 min, and the supernatant was filtered using a 0.2 μm filter and cleaned up using solid phase extraction (SPE) as described by Filipe et al. (3). The concentration of thiram in the supernatant was determined by HPLC-UV at 270 nm. The difference of pesticide concentration between the initial and the final equilibrium solutions was assumed to be due to adsorption, and the amount of thiram adsorbed was then calculated. In order to test reproducibility, at least two batch experiments have been done in different occasions. In each batch experiment, triplicates have been done for each initial concentration and for the blank (without thiram). Control samples (only thiram, without HA) have been performed for every sample batch.

Desorption Studies. Desorption studies were also carried out in triplicate and were performed immediately after adsorption equilibrium. After the adsorption period and centrifugation of the aqueous suspensions, the supernatant was decanted; the residual supernatant that could not be removed was determined by gravimetry. Thiram concentration in this residual solution was considered to be the same as that measured in the bulk supernatant. Six milliliters of fresh 0.01 mol L⁻¹ CaCl₂ solution (without thiram) was added to the centrifuge tubes. The tubes were shaken for another 15 h, centrifuged at 4000 rpm for 30 min, and the supernatants collected and submitted to the same procedure as that described in the adsorption experiment. The CaCl₂ desorption cycle was repeated once more. At last, a

desorption cycle using 5 mL of methanol instead of 0.01 mol L⁻¹ CaCl₂ was also performed. All experiments were done at 21 ± 1 °C. In order to confirm that thiram does not degrade during all the adsorption–desorption processes, thiram solutions 4.6 and 22.9 mg L⁻¹, without HA, were shaken during four days at the same temperature of the adsorption/desorption studies, and the recoveries of thiram obtained were always higher than 94%.

Kinetic Study. Aliquots of 6 mL of approximately 3 or 12 mg L⁻¹ Thi-P solution in 0.01 mol L⁻¹ CaCl₂ were added to 30 mg of commercial humic acids in the pyrex centrifuge tubes and shaken at 100 rpm, during 0, 0.5, 1, 2, 4, 8, 12, 20, 24, and 36 h. For each equilibration time, triplicate assays were conducted and processed as described above for the adsorption studies.

SPE Cleanup Procedure. The SPE cartridges used in this work were purchased from Supelco (500 mg commercial supelclean envi-18 cartridges, 75 Å pore diameter and 56 μm particle size). The cartridges were set up in a 12-place manifold from Phenomenex and preconditioned with 6 mL of methanol, 6 mL of Milli-Q water, and 6 mL of 0.01 mol L⁻¹ CaCl₂ aqueous solution (to match the sample matrix). Finally, an aliquot of 5 mL of the CaCl₂ supernatant was percolated through the cartridge at a flow rate of 2 mL min⁻¹ under vacuum at 6 kPa. Before elution, the SPE cartridge was rinsed with 3 mL of milli-Q water in order to remove any residual sample and subsequently dried under nitrogen, during 30 min. Thiram was then eluted with 5 mL of acetonitrile and collected in a 5 mL volumetric flask, and the respective thiram concentration was determined by HPLC-UV at 270 nm.

HPLC-UV Analysis of Thiram. Thiram was determined by a Jasco HPLC apparatus equipped with a PU-980 Pump, an UV–vis Barspec detector operating at 270 nm, a Phenomenex C18 column (150 × 4.60 mm, 5 μm, 110 Å), and a Rheodyne injector with a 20 μL loop. The mobile phase was acetonitrile/water 70:30 (v/v) flowing at 0.7 mL min⁻¹, previously filtered by a 0.2 μm NL16 membrane filter (Schleicher & Schuell). Details about calibration and limits of detection (LOD) were described elsewhere (4).

Calculation of the Distribution of Thiram. The amount of thiram adsorbed by unit mass of humic acids during the equilibration time (Q ; mg g⁻¹) was calculated from the difference between initial aqueous phase concentration (C_0 ; mg L⁻¹) and the thiram equilibrium concentration after adsorption (C_{eq} ; mg L⁻¹),

$$Q = \frac{(C_0 - C_{eq}) \times V_0}{m_{HA}} \quad (1)$$

where V_0 is the initial volume of the aqueous phase in contact with HA during the adsorption experiments, and m_{HA} is the mass of humic acids used in each assay. C_0 was obtained from the control sample (only thiram, without HA).

The percentage of thiram adsorbed onto HA was calculated according to the following equation:

$$\% Ads = \frac{(C_0 - C_{eq})}{C_0} \times 100 \quad (2)$$

The distribution coefficient (K_D ; L g⁻¹) was calculated as the ratio of the adsorbed concentration of thiram onto HA and its equilibrium concentration after adsorption.

$$K_D = \frac{Q}{C_{eq}} \quad (3)$$

The amount of thiram desorbed (m_{des} ; mg) after the first desorption cycle was calculated using the following equation:

$$m_{des} = C_{eq}^{Des} \times (V_0 + V_r) - m_r \quad (4)$$

where, C_{eq}^{Des} (mg L⁻¹) is the thiram equilibrium concentration in solution after desorption, and m_r (mg) is the amount of thiram in the residual solution after the adsorption experiment, calculated from

$$m_r = C_{eq} \times V_r \quad (5)$$

where V_r is the residual volume of the supernatant that could not be removed prior to desorption and that was gravimetrically determined.

The percentage of thiram desorbed from HA was calculated according to the following equation:

$$\% Des = \frac{m_{des}}{m_{ads}} \times 100 \quad (6)$$

where m_{ads} is the mass of thiram adsorbed onto HA during the adsorption experiment.

The adsorption–desorption hysteresis was quantified using the Hysteresis Index (HI) (22, 23) as follows:

$$HI = \frac{Q^{Des} - Q^{Ads}}{Q^{Ads}} \Big|_{C_{eq}} \quad (7)$$

where, Q^{Ads} and Q^{Des} refer to the solid phase thiram concentrations (mg g^{-1}) after adsorption and after a single desorption cycle experiment, respectively, corresponding to a predetermined aqueous solute concentration C_{eq} .

Models for the Isotherms of Adsorption–Desorption. The adsorption and desorption data were fitted to the Linear isotherm (eq 8) by linear regression analysis as follows:

$$\text{Linear equation } Q = K_D C_{eq} \quad (8)$$

where K_D , the distribution coefficient, is assumed as constant.

The experimental data were also fitted to the Freundlich, Langmuir and Brunauer–Emmett–Teller (BET) isotherms, eq 9 to 11, using the nonlinear regression analysis from the program GraphPadPrism5 (trial version) (24) as follows:

$$\text{Freundlich equation } Q = K_F C_{eq}^N \quad (9)$$

$$\text{Langmuir equation } Q = \frac{Q_{\max} K_L C_{eq}}{1 + K_L C_{eq}} \quad (10)$$

$$\text{BET equation } Q = \frac{Q_{\max} K C_{eq}}{(C_S - C_{eq}) \left[1 + (K - 1) \frac{C_{eq}}{C_S} \right]} \quad (11)$$

where K_F and K_L are the Freundlich and Langmuir constants, respectively, which are a measure of sorption capacity, N reflects the degree of linearity, Q_{\max} is the maximum adsorption (mg g^{-1}), which corresponds to the maximum of adsorption of the first layer in the BET isotherm model, C_S is the saturation concentration for adsorbate in solution (mg L^{-1}), and K is an empirical constant. The BET equation can be rearranged and simplified (25) to eq 12 in order to facilitate nonlinear fitting as follows:

$$Q = \frac{K_1 C_{eq}}{(1 + K_2 C_{eq}) \times (1 - K_3 C_{eq})} \quad (12)$$

where, $K_1 = Q_{\max} K / C_S$, $K_2 = (K - 1) / C_S$, and $K_3 = 1 / C_S$.

We are aware of the need of using statistical tools to predict which isotherm model is the most adequate (26). In the present work, we decided to use R^2 adjusted (R_{Adj}^2), which evaluates the goodness of fitting, taking into account the degrees of freedom of each model and is defined as follows (27):

$$R_{Adj}^2 = 1 - \left(\frac{SS_{residual}}{SS_{total}} \right) \frac{n-p}{n-1} \quad (13)$$

where, $SS_{residual} = \sum (Q_{exp} - Q_{est})^2$, $SS_{total} = \sum (Q_{exp} - \bar{Q})^2$; Q_{exp} is the amount of thiram adsorbed by unit mass of humic acids obtained experimentally, Q_{est} is the amount of thiram adsorbed by unit mass of humic acids estimated from the model, \bar{Q} is the mean of the Q_{exp} values, n is the number of data points, and p is the number of adjustable parameters in the model.

RESULTS AND DISCUSSION

Kinetic Studies. Figure 1 shows the adsorption percentages of thiram onto solid HA (% Ads, calculated according to eq 2) for different equilibration times, for thiram initial concentrations of

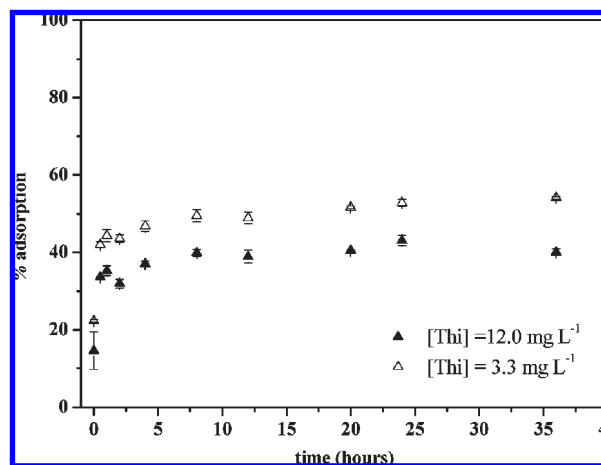


Figure 1. Effect of equilibrium time on the % of adsorption of Thi-P onto humic acids.

3.3 mg L^{-1} and 12 mg L^{-1} . According to these results, thiram is quickly adsorbed during the first two hours since, for both initial concentrations of thiram, 85% of the equilibrium concentration is reached within this contact time. The equilibrium state was considered attained after 15 h of equilibration since the variations in adsorbed percentages did not change more than 5%, when the equilibration time was increased from 12 h until 35 h (28). On the basis of such results, further studies for the establishment of both adsorption and desorption thiram behavior were conducted for 15 h of equilibrium time (overnight equilibration). In previous studies, other authors observed a similar kinetic behavior for the adsorption of atrazine and some of its metabolites onto soil (29).

Adsorption Isotherms. Adsorption isotherms for both Thi-P and Thi-F onto commercial HA are presented in Figure 2. Also in the same Figure 2, the distribution coefficients (K_D ; L g^{-1}) are plotted against thiram equilibrium concentration. Those K_D values are within the range 0.110–0.210 L g^{-1} , decreasing with the increase of thiram concentration in solution. Those values are quite comparable to the K_D values for thiram adsorption onto natural lignin (0.15–0.20 L g^{-1} , as calculated from Figure 4 in ref (8)). Besides, K_D values for Thi-P are not significantly different from those for Thi-F ($p < 0.05$). The experimental K_D values obtained in this work, compared to values for the adsorption of other organic contaminants onto other humic acid samples (Table 1) suggest that thiram is strongly sorbed by humic acids. As referred, K_D values are not constant, decreasing as the equilibrium concentration of thiram increases up to approximately 6 mg L^{-1} , remaining approximately constant for higher concentrations. This behavior is confirmed by the values of the percentage of adsorption, which follow the same trend, varying between 52 and 35%. This deviation from linearity for low thiram concentrations suggests that adsorption can not be explained only by a partition mechanism (14).

Several types of isotherm equations have been used for fitting the experimental adsorption data of pesticides onto soils and humic substances. The Linear, Langmuir, and Freundlich isotherm equations are the most frequently applied (16–20, 28–33). According to Hinze (25), in order to choose the isotherm equation to fit a given adsorption data set, it is useful to begin by identifying the class and subgroup of the isotherm, according to the Giles classification. Following the qualitative approach recommended by Hinze (25), it was concluded that the sorption isotherm of thiram onto humic acids is an L3 type (class L, subgroup 3). L type isotherms are characterized by an initial

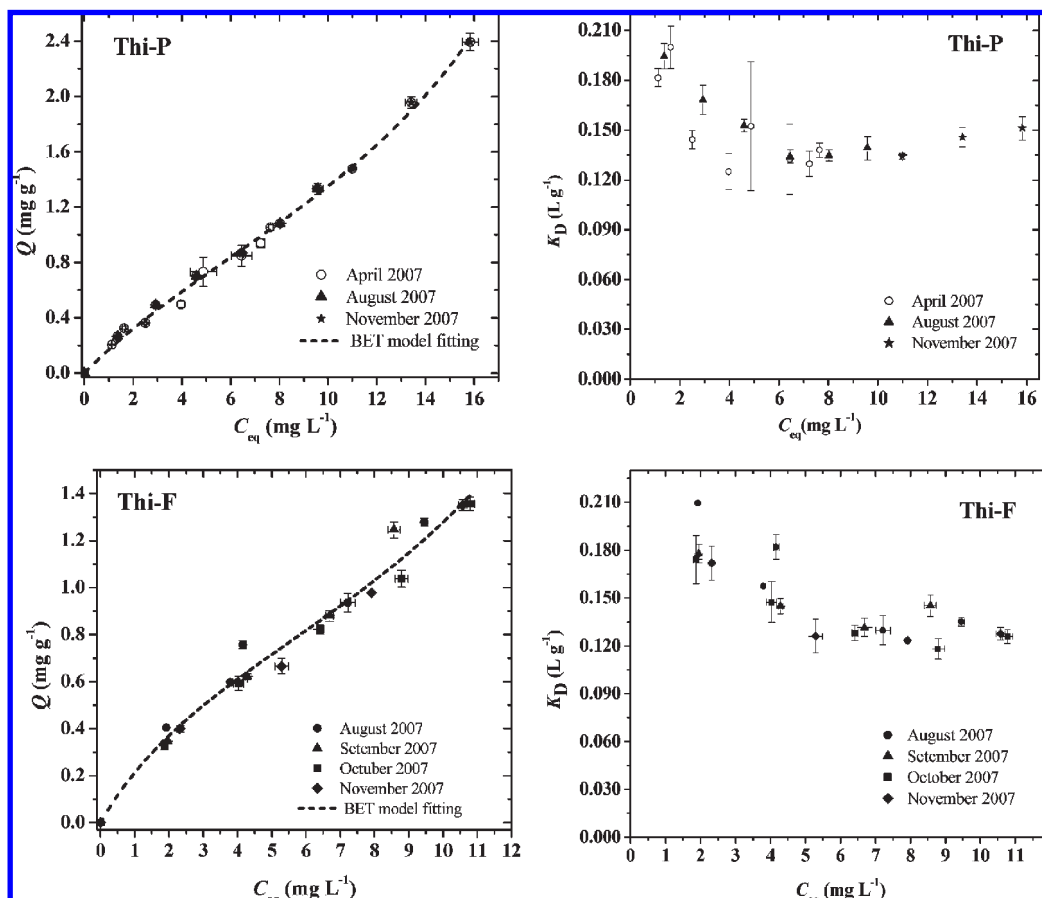


Figure 2. Adsorption isotherm of both Thi-P and Thi-F onto humic acids and respective distribution coefficients (K_D).

Table 1. K_D Values for the Adsorption of Various Pesticides onto Humic Acids

| pesticide | adsorbent | K_D ($L g^{-1}$) | water solubility ($mg L^{-1}$) | ref |
|--------------------------------|--------------------------|----------------------|----------------------------------|-----------|
| glyphosate | soil humic acid | 0.006–0.057 | very soluble | (16) |
| 2,4-dichlorophenoxyacetic acid | soil humic acid | 0.080 | 900 (25 °C) | (17) |
| imidacloprid | soil humic acid | 0.005 | 510 (20 °C) | (18) |
| imazaquin | soil humic acid | 0.088–0.922 | 60 (25 °C) | (19) |
| thiram | commercial humic acid | 0.110–0.210 | 30 (21 °C) | this work |
| 2,4,6-trichlorophenol | soil and peat humic acid | 0.100–0.200 | negligible | (20) |

decrease of K_D as the solution concentration increases, and subgroup 3 is characterized by the existence of a plateau followed by an inflection point in the Q versus C_{eq} plot. Thus, the Brunauer–Emmett–Teller model (BET model), which describes multilayer Langmuir adsorption and is classified as an L3 isotherm, was also tested to fit the experimental sorption data of thiram onto HA. Thus, in the present work, the four isotherm equations have been tested to fit the data.

The parameters for each isotherm equation were determined by nonlinear curve fitting and are presented in Table 2, considering adsorption data for both pure (Thi-P) and formulated thiram (Thi-F). Ambiguous is a GraphPad term to describe a fit that does not really nail down the values of all of the parameters and when many combinations of parameter values lead to curves that fit equally well (24).

According to R^2 adjusted values, the BET equation is the most suitable to model the adsorption of thiram onto commercial humic acids, clearly discarding the Langmuir isotherm. Such a result highlights that the sorption of thiram onto condensed humic substances cannot be explained only in terms of a

Table 2. Adsorption Equilibrium Data of Thi-P and Thi-F Fittings to Linear, Freundlich, Langmuir, and BET Isotherm Models^a

| | Thi-P | Thi-F |
|---------------------|---|--|
| Linear isotherm | $K_D = 0.141 \pm 0.004 L g^{-1}$ $R_{Adj}^2 = 0.987$ | $K_D = 0.117 \pm 0.005 L g^{-1}$ $R_{Adj}^2 = 0.963$ |
| Freundlich isotherm | $K_F = 0.130 \pm 0.011$ $N = 1.04 \pm 0.04$ $R_{Adj}^2 = 0.988$ | $K_F = 0.199 \pm 0.019$ $N = 0.80 \pm 0.05$ $R_{Adj}^2 = 0.968$ |
| Langmuir isotherm | ambiguous fit | $K_L = 0.037 \pm 0.013 L mg^{-1}$ $Q_{max} = 4.63 \pm 1.26 mg g^{-1}$ $R_{Adj}^2 = 0.962$ |
| BET isotherm | $C_S = 28.2 \pm 1.83 mg L^{-1}$ $Q_{max} = 1.27 \pm 0.351 mg g^{-1}$ $K = 3.99 \pm 1.01$ $R_{Adj}^2 = 0.992$ | $C_S = 22.7 \pm 4.13 mg L^{-1}$ $Q_{max} = 0.839 \pm 0.467 mg g^{-1}$ $K = 6.93 \pm 3.35$ $R_{Adj}^2 = 0.970$ |

^a Fitting parameters and their respective errors for a 95% confidence interval are presented.

Table 3. Experimental Data of Adsorption–Desorption Isotherms of Both Thi-P and Thi-F onto Humic Acids

| C_i (mg L ⁻¹) | % Ads | desorption | | | | | | total (%) ^a |
|-----------------------------|------------|---|----------------------------|--|----------------------------|------------------------|------------|------------------------|
| | | first cycle (0.01 mol L ⁻¹ CaCl ₂) | | second cycle (0.01 mol L ⁻¹ CaCl ₂) | | third cycle (methanol) | | |
| | | (% Des) ^a | K_D (L g ⁻¹) | (% Des) ^a | K_D (L g ⁻¹) | (% Des) ^a | | |
| Thi-P | | | | | | | | |
| 2.155 | 47.8 ± 0.8 | 19.9 ± 1.8 | 0.626 ± 0.050 | <LOD | <LOD | nd | | |
| 2.708 | 49.4 ± 1.0 | 30.9 ± 0.6 | 0.399 ± 0.016 | <LOD | <LOD | 25.5 ± 0.9 | 56.4 ± 0.8 | |
| 4.309 | 41.9 ± 0.9 | 33.2 ± 1.0 | 0.339 ± 0.011 | <LOD | <LOD | nd | | |
| 5.417 | 45.9 ± 1.3 | 34.5 ± 1.7 | 0.337 ± 0.030 | 12.9 ± 0.0 | 0.729 ± 0.035 | 21.0 ± 2.7 | 68.4 ± 2.6 | |
| 6.464 | 38.5 ± 2.0 | 38.4 ± 0.4 | 0.271 ± 0.007 | 10.9 ± 1.9 | 0.810 ± 0.170 | nd | | |
| 8.125 | 43.5 ± 0.6 | 36.4 ± 2.4 | 0.312 ± 0.029 | 13.8 ± 1.0 | 0.651 ± 0.065 | 22.4 ± 0.7 | 72.6 ± 2.8 | |
| 8.619 | 43.4 ± 6.3 | 35.2 ± 0.0 | 0.299 ± 0.000 | 10.0 ± 0.0 | 0.901 ± 0.000 | nd | | |
| 10.77 | 40.2 ± 4.0 | 38.2 ± 1.1 | 0.269 ± 0.014 | 12.2 ± 0.2 | 0.705 ± 0.005 | 23.7 ± 1.5 | 74.1 ± 2.4 | |
| 10.83 | 40.4 ± 0.7 | 36.8 ± 0.6 | 0.296 ± 0.011 | 13.1 ± 1.3 | 0.678 ± 0.072 | 22.3 ± 2.4 | 72.2 ± 3.9 | |
| 12.93 | 40.9 ± 0.7 | 35.6 ± 1.1 | 0.302 ± 0.013 | 12.7 ± 0.3 | 0.720 ± 0.039 | 28.5 ± 1.6 | 76.8 ± 1.2 | |
| 13.54 | 40.7 ± 0.6 | 36.5 ± 0.9 | 0.291 ± 0.007 | 15.1 ± 0.4 | 0.579 ± 0.005 | 24.4 ± 2.5 | 76.0 ± 2.6 | |
| 16.25 | 41.1 ± 1.3 | 36.3 ± 0.8 | 0.313 ± 0.010 | 14.8 ± 1.3 | 0.583 ± 0.015 | 25.8 ± 0.1 | 76.9 ± 1.1 | |
| Thi-F | | | | | | | | |
| 3.512 | 46.6 ± 2.1 | 32.8 ± 1.9 | 0.365 ± 0.027 | <LOD | <LOD | 32.9 ± 6.1 | 65.7 ± 5.2 | |
| 4.332 | 46.4 ± 1.6 | 34.9 ± 1.7 | 0.327 ± 0.016 | 15.8 ± 1.4 | 0.559 ± 0.077 | 21.0 ± 1.8 | 71.7 ± 4.8 | |
| 7.023 | 42.6 ± 2.1 | 36.9 ± 0.9 | 0.297 ± 0.015 | 14.6 ± 3.2 | 0.628 ± 0.003 | 24.4 ± 0.0 | 75.9 ± 0.5 | |
| 8.665 | 39.0 ± 2.3 | 39.9 ± 1.3 | 0.250 ± 0.011 | 17.2 ± 1.5 | 0.437 ± 0.057 | 28.3 ± 0.1 | 85.5 ± 2.8 | |
| 10.54 | 39.1 ± 0.9 | 39.1 ± 1.1 | 0.270 ± 0.010 | 18.4 ± 1.5 | 0.476 ± 0.065 | 22.0 ± 6.2 | 79.6 ± 6.8 | |
| 13.00 | 39.1 ± 0.3 | 37.1 ± 1.4 | 0.273 ± 0.08 | 16.2 ± 1.1 | 0.472 ± 0.081 | 27.7 ± 4.2 | 81.0 ± 6.3 | |
| 14.05 | 37.4 ± 1.3 | 39.2 ± 0.2 | 0.261 ± 0.007 | 17.6 ± 0.6 | 0.442 ± 0.032 | 27.6 ± 1.1 | 84.4 ± 1.8 | |
| 17.33 | 39.0 ± 0.7 | 36.6 ± 2.6 | 0.280 ± 0.044 | 16.3 ± 0.7 | 0.526 ± 0.066 | 29.1 ± 1.4 | 82.1 ± 4.6 | |
| 17.56 | 38.6 ± 0.8 | 37.1 ± 1.0 | 0.294 ± 0.016 | 17.8 ± 1.3 | 0.475 ± 0.039 | 26.9 ± 2.0 | 81.8 ± 2.2 | |

^a Desorption value represents the % of the amount initially adsorbed. LOD, limit of detection; nd, not determined.

specific interaction with the carboxyl groups as proposed by Stathi et al. (11) for the interaction with dissolved humic acids or humic acids immobilized on the surface of silica particles since that would give rise to a Langmuir isotherm (see Supporting Information from ref (11)). Also the Linear model is rejected on the basis of R^2 adjusted values. Several authors attributed the nonlinearity of adsorption isotherms to a dual mode adsorption mechanism (13, 23). In the present case, as the adsorption data are described by a BET isotherm, the mechanism may include specific adsorption with a limited number of adsorption sites, and the occurrence of pesticide–pesticide interactions after saturation of those sites (multilayer adsorption). As referred above, specific interactions between thiram and carboxyl groups of humic substances have been identified by others (11) and may be responsible for the concave downward shape of the sorption isotherm at low concentrations, while the upward shape of the isotherm for high concentrations can be due to pesticide–pesticide interactions (multilayer adsorption). A similar behavior was observed for the adsorption of Thifluzamide onto soil, and the upward nature of the isotherm for higher concentrations was also attributed to pesticide–pesticide interactions (30).

Desorption Isotherms. The extent of desorption of both pure and formulated thiram was determined using two consecutive desorption cycles of 15 h in an aqueous solution of 0.01 mol L⁻¹ CaCl₂ and a desorption cycle of 15 h in methanol. % Des and desorption K_D results for each desorption cycle are presented in **Table 3**. The results show that the percentage of thiram that is desorbed (% Des) decreases as the initial thiram concentration decreases, suggesting, once more, a stronger adsorption for low concentrations (in agreement with the results obtained in the adsorption studies). However, the adsorption–desorption isotherms for both Thi-P and Thi-F, which are compared in **Figure 3**, show that desorption behavior is deviated from that corresponding

to the adsorption isotherm, which indicates that thiram sorption onto humic acids was not completely reversible. The desorption K_D values after each desorption cycle were consistently higher than those for adsorption at the same equilibrium concentrations, which strongly suggests the irreversibility of the thiram adsorption onto HA, i.e., hysteresis phenomena.

The experimental desorption data of the first cycle were fitted to Linear, Freundlich, Langmuir, and BET isotherms, and the results are shown in **Table 4**.

The results obtained point out that the Langmuir model should be discarded and indicate the BET equation as the best fitting method for the first desorption cycle. The irreversibility of adsorption onto soils and humic acids has been attributed by several authors to micropore deformation at high concentration levels due to penetration of adsorbate molecules and entrapment when the solution concentration is abruptly decreased during desorption (34–36). Hysteresis due to a capillary phase separation mechanism (37, 38) may also occur in humic acid mesopores.

For comparing the irreversibility of adsorption–desorption for both Thi-P and Thi-F, the HI indices at 21 °C and at some equilibrium concentrations were calculated using eq 7 (**Table 5**). For each C_{eq} value, the values of Q_{ads} and Q_{des} used in eq 7 were calculated by application of the isotherm equation that best fitted the adsorption and the first desorption data, i.e., the BET equation. HI values for Thi-P are consistently higher than for Thi-F. Applying the paired *t*-test to the HI data, it was concluded that hysteresis was significantly higher for Thi-P than for Thi-F ($p < 0.0001$), i.e., desorption of thiram is more facilitated in its formulation form than in its pure form. These results suggest that thiram formulation components have an influence on the desorption process of thiram from humic acids, turning the pesticide more susceptible to be leached. Such a conclusion highlights the need for performing adsorption–desorption

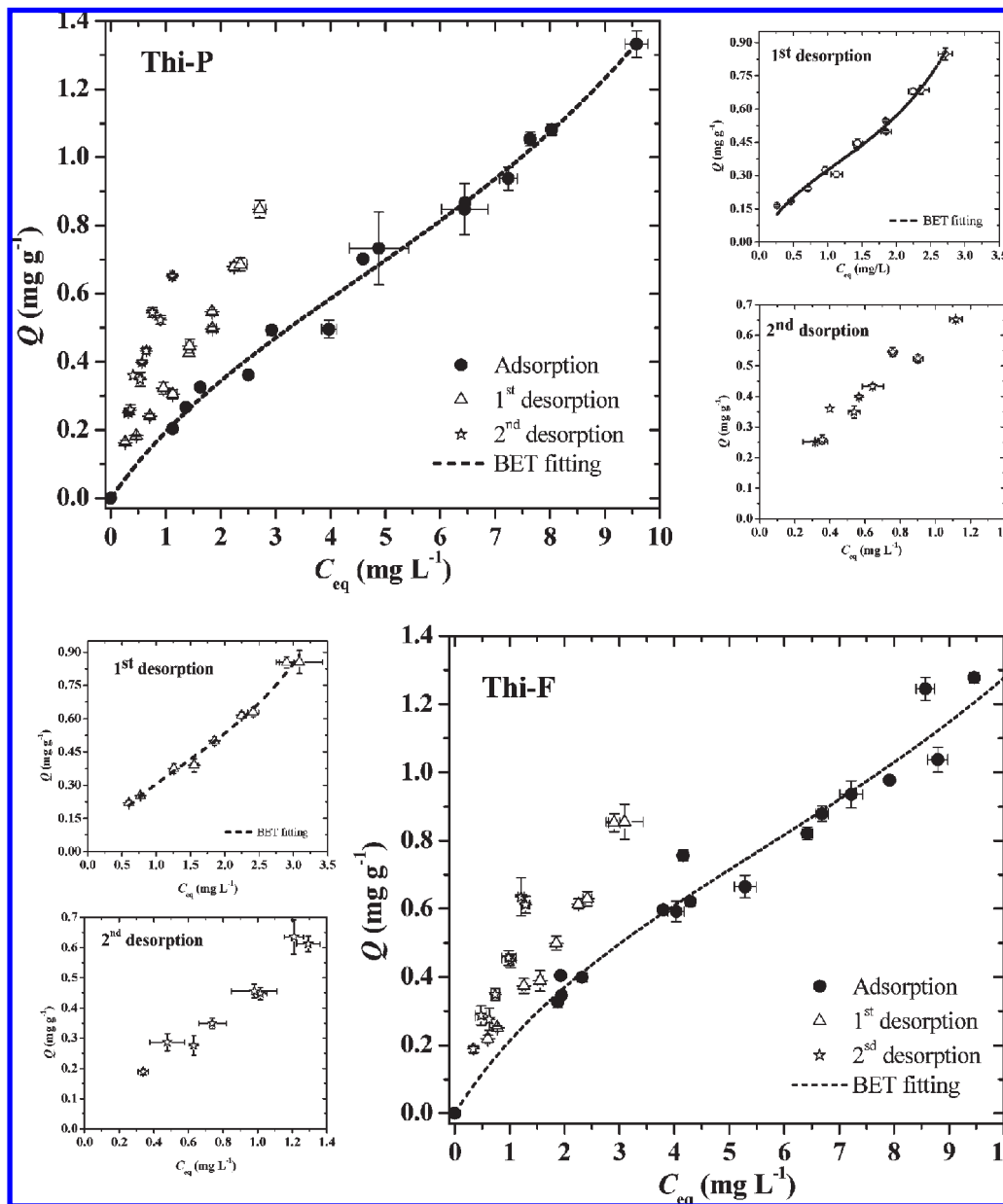


Figure 3. Adsorption–desorption isotherms of Thi-P and Thi-F onto commercial humic acids

Table 4. First Desorption Equilibrium Data of Thi-P and Thi-F Fitting to Linear, Freundlich, Langmuir, and BET Isotherm Models^a

| | Thi-P | Thi-F |
|---------------------|---|---|
| Linear isotherm | $K_D = 0.274 \pm 0.0134 \text{ L g}^{-1}$ $R_{Adj}^2 = 0.974$ | $K_D = 0.263 \pm 0.015 \text{ L g}^{-1}$ $R_{Adj}^2 = 0.976$ |
| Freundlich isotherm | $K_F = 0.316 \pm 0.016$ $N = 0.923 \pm 0.067$ $R_{Adj}^2 = 0.966$ | $K_F = 0.287 \pm 0.018$ $N = 0.962 \pm 0.070$ $R_{Adj}^2 = 0.973$ |
| Langmuir isotherm | ambiguous fit | ambiguous fit |
| BET isotherm | $C_S = 4.48 \pm 0.314 \text{ mg L}^{-1}$ $Q_{max} = 0.366 \pm 0.162 \text{ mg g}^{-1}$ $K = 7.70 \pm 2.91$ $R_{Adj}^2 = 0.983$ | $C_S = 5.51 \pm 0.629 \text{ mg L}^{-1}$ $Q_{max} = 0.440 \pm 0.258 \text{ mg g}^{-1}$ $K = 5.91 \pm 3.06$ $R_{Adj}^2 = 0.984$ |

^a Fitting parameters and their respective errors are for a 95% confidence interval.

studies in soils using commercial formulations of the pesticides and not only the active ingredient.

Table 5. Hysteresis Indices (HI) for Both Thi-P and Thi-F onto Humic Acids

| $C_{eq} \text{ (mg L}^{-1}\text{)}$ | HI | |
|-------------------------------------|-------|-------|
| | Thi-P | Thi-F |
| 1.0 | 0.927 | 0.434 |
| 1.2 | 0.847 | 0.415 |
| 1.5 | 0.781 | 0.407 |
| 1.8 | 0.767 | 0.421 |
| 2.0 | 0.785 | 0.441 |
| 2.2 | 0.824 | 0.471 |
| 2.5 | 0.928 | 0.535 |

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