

## Modeling of Single-Step and Multistep Adsorption Isotherms of Organic Pesticides on Soil

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The aim of this study was to investigate the sorption behavior and mechanisms of the organic pesticides on soil. To establish the sorption isotherms of six commonly used pesticides (acetochlor, atrazine, diazinon, carbendazim, imidacloprid, and isoproturon), laboratory equilibrium studies were performed at extended concentration ranges on brown forest soil using the batch equilibrium technique. The pesticide concentrations in the equilibrated liquid phase were quantified with high-performance liquid chromatograph by ultraviolet detection. The adsorption processes could be described by a single-step (Langmuir) isotherm for acetochlor and carbendazim, by a two-step curve for diazinon, isoproturon, and atrazine, and by a three-step curve for imidacloprid. A nonlinear mathematical model—derived from the Langmuir equation—has been developed that represents well the detected single-step and multistep shaped adsorption isotherms. The interpreted model was found to fit the experimental data well and allows the description of the adsorption profile with great precision. The altered adsorption activity, which was indicated by the step arising on the plot, may represent the existence/occurrence of a different specific type of adsorption mechanism. This binding force starts to operate simultaneously at a critical concentration of solute in the studied soil–pesticide system. The parameters calculated from the equation provide an opportunity to estimate the extent of absorption constant, adsorption capacity, and concentration limit characteristic to the measured stepwise isotherms.

**KEYWORDS:** Pesticides; soil; adsorption; isotherms; binding mechanism

### INTRODUCTION

With progressive increases in the production and application of chemicals for agricultural activities, the contamination of soil, ground, and surface waters has become a problem throughout the world (1–4). Efforts to preserve the environment and to reduce the risk of contamination have established the need to understand the behavior of pesticides in the natural environment. The fate and behavior of pesticides in the environment involve several different and often simultaneous phenomena, such as chemical and biological transformation processes, runoff, leaching, volatilization, and wind erosion. Although various physicochemical processes affect the fate of agrochemicals in contact with soil, the sorption to the solid matrix of soil is one of the most important phenomena, which controls other processes such as pesticide transport, persistence, bioavailability, and degradation (5–12).

Many theories and models have been presented in the literature to simulate the sorption processes (13–18). Derivation of a scientifically based adsorption isotherm was first achieved by Langmuir. The Langmuir isotherm model assumes monolayer adsorption on an energetically homogeneous surface, where the adsorption takes place only at specific localized sites and the saturation coverage corresponds to complete occupancy of these sites. Each site can accommodate one and only one molecule or atom, and there is no interaction between neighboring adsorbed molecules or atoms (19). Nevertheless, the soil has a polydisperse nature with polyelectrolytic character, surface activity properties, and various chemically reactive functional groups and hydrophilic and hydrophobic sites, which is possibly reflected in great differences in adsorption energy. The nature of the binding forces in soil is determined by the different types of mechanisms such as ionic, hydrogen, and covalent bonding, charge-transfer and electron donor–acceptor mechanisms, van der Waals forces, ligand exchange, and hydrophobic bonding or partitioning (20–22). In some instances, especially when organic compounds are adsorbed, the S-shaped isotherms are the results of cooperative interactions among the adsorbed molecules. These interactions (e.g., surface polymerization,

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multilayer sorption, or stereochemical interactions) cause the adsorbate to become stabilized on a solid surface, and thus they produce an enhanced affinity of the surface for the adsorbate as its surface excess increases (23). The variety of chemical heterogeneity of soil components is further complicated by the colloidal structure of the soil, such as its micro- or mesoporous heterogeneity besides the existence of macropores.

Using more realistic assumptions, modifications have been made to the Langmuir isotherm, which are summarized in the monographs of Ruthven (24), Yang (25), Adamson (26), and Rudzinski and Everett (27). Another concept derived from the models for saturated media takes into account the chemical heterogeneity of the soil by considering two (or possibly more) sites of different adsorption capacities (28). Several more complex equations such as that of Brunauer, Emmett, and Teller have been proposed to describe multilayer adsorption (29–31). Gregg and Sing have given a detailed discussion of the various models used to interpret each type of isotherm (32). Numerical methods presented during recent years, however, could not be easily handled because of the large number of parameters required, which make the model too complex for practical calculation from a reasonable number of experiments (33–37).

The most commonly used adsorption isotherm equations for organic contaminants on soil are the Langmuir and Freundlich isotherms. In many cases, the sorption of pesticides has been well described using these empirical models (38–41). These commonly used equations have the advantage of the possibility of linearization yielding the adsorption parameters by the slope and intercept of the fitted line. These equations have been found to fit some pesticide adsorption results moderately well and have occasionally been used to estimate the capacity for adsorption.

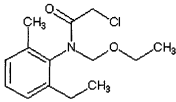
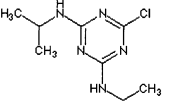
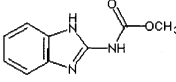
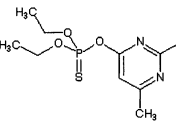
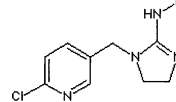
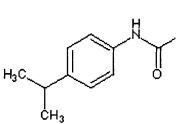
The objective of the present work was to investigate the sorption behavior of the organic pesticides atrazine, acetochlor, carbendazim, diazinon, imidacloprid, and isoproturon at extended concentration ranges to understand their binding mechanisms to soil colloids. These chemicals have been used in plant production and animal health intensively for the past several years. Their biological effects and utilization are detailed in the literature (42, 43). They represent a wide range of chemical and functional classes capable for the investigation of the behavior of organic pesticides in a soil environment.

Our secondary aim was to develop a valid mathematical model to allow the description of the adsorption processes of the investigated compounds and to calculate physicochemical parameters of equilibrium derived from adsorption isotherms as well.

## MATERIALS AND METHODS

**Chemicals, Reagents, and Standards.** Acetochlor, atrazine, carbendazim, diazinon, imidacloprid, and isoproturon, all with purity >99%, were obtained from Sigma Aldrich Kft. (Hungary, Budapest). The structures of the chemicals are shown in **Figure 1**. Their physicochemical properties are presented in **Table 1**. HPLC grade methanol, acetone, tetrahydrofuran, and acetonitrile and analytical grade citric acid monohydrate and calcium chloride dihydrate were purchased from Merck (Darmstadt, Germany). Extraction cartridges used were Waters Sep-Pak octadecyl (C<sub>18</sub>, 500 mg) columns (Waters Corp., Milford, MA). HPLC disposable membrane filters (0.45 μm) were purchased from Millipore (Bedford, MA). HPLC grade water was obtained using a Milli-Q system (Millipore Corp. Stock standard solutions of each pesticide (1000 μg/mL) were prepared by dissolving the required amount in acetonitrile and were stored under refrigeration. Dilutions were made with 0.01 M calcium chloride solution to the desired final concentrations.

**Experimental Soil.** All sorption experiments were conducted on representative Hungarian brown forest soil with clay alluviation (Luvisol

| Common name  | Molecular  | IUPAC name  | MW     |
|--------------|--|---|--------|
| ACETOCHLOR   |  | 2'-ethyl-6'-methyl-N-(ethoxymethyl)-2-chloroacetanilide                             | 269,77 |
| ATRAZINE     |  | 2-chloro-4-ethylamino-6-isopropylamine-s-triazine                                   | 215,69 |
| CARBENDAZIM  |  | 1H-Benzimidazol-2-ylcarbamic acid methyl ester                                      | 191,19 |
| DIAZINON     |  | Phosphorothioic acid O,O-diethyl O-[6-methyl-2-(1-methylethyl)-4-pyrimidinyl]-ester | 304,35 |
| IMIDACLOPRID |  | 1-[(6-Chloro-3-pyridinyl)methyl]-4,5-dihydro-N-nitro-1H-imidazol-2-amine            | 255,66 |
| ISOPROTURON  |  | N,N-Dimethyl-N'-[4-(1-methylethyl)phenyl]urea                                       | 206,29 |

**Figure 1.** Chemical structures of the six pesticides studied.

**Table 1.** Physicochemical Properties of the Six Pesticides Examined

| pesticide    | log $P_{ow}$ <sup>a</sup> | water solubility <sup>b</sup> (mg/L) | dissociation coefficient <sup>c</sup> |
|--------------|---------------------------|--------------------------------------|---------------------------------------|
| acetochlor   | 3.37                      | 223 (25 °C)                          |                                       |
| atrazin      | 2.82                      | 33 (20 °C)                           | 2.75                                  |
| carbendazim  | 1.55                      | 8 (24 °C, pH 7)                      | 5.52                                  |
| diazinon     | 3.86                      | 60 (20 °C)                           | 1.64                                  |
| imidacloprid | 0.56                      | 510 (20 °C)                          | 5.94                                  |
| isoproturon  | 2.84                      | 65 (22 °C)                           |                                       |

<sup>a</sup> Logarithm of estimated octanol–water partition coefficients based on chemical structure using Environmental Science Centre estimation software (U.S. EPA's Office of Pollution and Toxics). <sup>b</sup> Listed solubility values are cited in *Pesticide Manual*, 10th ed. (43). <sup>c</sup> Predicted dissociation coefficients using Pallas 2.0 expert system (Compu Drug, Budapest, Hungary).

according to classification of the Food and Agriculture Organization of the United Nations), which has the following composition and characteristics: 1.16% organic matter, 21.8% silt, 15.4% clay, and 62.8% sand, with cation-exchange capacity of 16.8 mequiv/100 g of soil and pH 6.1. Mineralogical composition determined by X-ray diffraction of the soil was the following: 59% quartz, 12% plagioclase, 11% phyllo silicate, 6% chlorite, 4% potash feldspar, 3% kaolinite, 3% pyroxene, 1% smectite, and 1% siderite.

**Adsorption of Pesticides.** All experiments have been performed under isotherm condition at 20 ± 1 °C. The soil was air-dried, homogenized, and sieved to a grain size fraction <2 mm. Pesticide solutions were prepared in 0.01 M calcium chloride to maintain constant ionic strength. Concentration ranged between 1 and 15.0 mg/L for atrazine, acetochlor, diazinon, imidacloprid, and isoproturon and between 1.0 and 8.0 mg/L for carbendazim because of its limited solubility. Each sample consisted of 2.5 g of soil mixed with 25 mL of the pesticide solution in a 50 mL polypropylene centrifuge tube sealed with a screw cap except for diazinon, in which case adsorption was found to the plastic. Because of that, the diazinon sorption experiment was performed using glass tubes and screw caps with Teflon lining.

The tubes were agitated on a rotary shaker for 24 h to achieve equilibrium. The amount of pesticide adsorbed by the soil was calculated from the difference between the initial and equilibrium pesticide concentrations in solution. The adsorption equilibration process was made in three replicates for each concentration.

**Pesticide Analysis.** After equilibration, 15 mL aliquots of suspension were centrifuged at 6000 rpm for 20 min. Cleanup of the supernatant was performed via a C<sub>18</sub> solid phase extraction (SPE) method. Ten milliliters of supernatant was loaded onto the previously activated extraction column and was washed subsequently with 2 mL of water. Elution was performed with 2 mL of acetone. The organic solvent was evaporated to dryness under a gentle stream of nitrogen, and the residue was dissolved in a 1.0 mL mixture of acetonitrile/water (1:1 v/v). Prepared samples were passed through disposable membrane filters and analyzed using high-performance liquid chromatography (HPLC) with and UV detection. Above an initial pesticide concentration of 5 mg/L no SPE was used. Soil supernatants were centrifuged as described above, filtered, diluted if necessary, and injected into the HPLC.

The HPLC system was a JASCO liquid chromatograph (JASCO, Kyoto, Japan) equipped with a UV-vis detector. A Symmetry C<sub>18</sub> column (75 × 3.9 mm i.d., 4 μm particle size, Waters, Milford, MA) preceded by a guard column (BST C<sub>18</sub> 20 × 4 mm, Budapest, Hungary) was used. Samples were eluted and analyzed using the following two mobile phases: for imidacloprid, carbendazim, isoproturon, and atrazine 10:20:70 (v/v/v) tetrahydrofuran/methanol/0.1% (m/v) citrate buffer (pH 5.8); for acetochlor and diazinon 40:60 (v/v) acetonitrile/0.1% (m/v) citric acid solution, respectively. The flow rate was 1 mL/min and the injected volume was 50 μL in all cases. The analytes were quantitatively determined with a UV detector at 220 nm wavelength.

Linearity (regression coefficients 0.978–0.999 up to 5 mg/L) and reproducibility (2.1–4.9%) of the methods were appropriate in all cases. Recoveries ranged from 92.9 to 101.7%. Detection limits were 0.2 μg/L for atrazine, acetochlor, carbendazim, and imidacloprid and 0.4 μg/L for isoproturon and diazinon.

## RESULTS AND DISCUSSION

The sorption isotherms for acetochlor and carbendazim obtained from our experimental equilibrium data have been found to fit well to the Langmuir equation. By visual inspection of the stepwise isotherms obtained for atrazine, diazinon, imidacloprid, and isoproturon similarities were observed to the characteristic types IV described by Brunauer, Deming, and Teller for vapor and gas adsorption on solids (30). Excellent reviews are available in the field of life sciences and colloid interface chemistry regarding multiple equilibria (44–46) as well. Nevertheless, the publication of stepwise shape isotherms in the field of soil science is rather limited (47, 48). We have not found adequate mathematical descriptions in the reviewed literature, which could represent well the multistep-shaped plot measured in the case of the compounds examined. Hence, we derived a nonlinear mathematical model—obtained from the sum of Langmuir-type isotherms with the additional assumption that sterically or energetically heterogeneous adsorption sites exist in the soil, and there are potential interactions among the adsorbed molecules. Each step on the curve thus represents different existing specific types of adsorption mechanisms, which could be described by the Langmuir equation

$$q = \frac{akc}{1 + kc} \quad (1)$$

where  $q$  is the amount of adsorbed pesticide per unit mass of soil (mg/kg),  $c$  is the equilibrium pesticide concentration in solution (mg/L),  $a$  represents the adsorption capacity (mg/kg), and  $k$  is the adsorption equilibrium constant (mg<sup>-1</sup>).

Furthermore, a critical concentration of the substance on the sorbent depending on the adsorbate–sorbent interaction has been

introduced. Above this concentration, the next, new adsorption mechanism becomes effective. This parameter could be interpreted, if the processes separated energetically and temporally. Using the limit concentration, eq 1 can be modified as

$$q = \frac{ak(c - b)}{1 + k(c - b)} \quad (2)$$

where  $b$  is the concentration limit of the adsorption mechanism in question (mg/L). In a physical and mathematical approach, the function can be used only if  $c > b$ . Thus, the equation must be modified using the function below:

$$\left[ \frac{(c - b) + abs(c - b)}{2} \right] = c - b \quad \text{if } c - b > 0 \quad (3)$$

$$\left[ \frac{(c - b) + abs(c - b)}{2} \right] = 0 \quad \text{if } c - b < 0$$

Thus, eq 2 could be rearranged

$$q = \frac{ak \left[ \frac{(c - b) + abs(c - b)}{2} \right]}{1 + k \left[ \frac{(c - b) + abs(c - b)}{2} \right]} \quad (4)$$

After transformation, eq 4 yields

$$q = \frac{ak[(c - b) + abs(c - b)]}{2 + k[(c - b) + abs(c - b)]} \quad (5)$$

This mathematical formula describes the model of one step for one type of adsorption mechanism.

For calculating the second and further steps, it is assumed that the total adsorption capacity is the sum of the adsorption capacities of the effective adsorption sites above the critical concentration. The common features of this theory are the adsorption equilibrium constant ( $k$ ), the adsorption capacity ( $a$ ) provided by the adsorption mechanism in question, and the limit concentration ( $b$ ). The mathematical expression is the same in all cases. The  $i$ th step can be calculated from eq 5 using the formula

$$q_i = \frac{a_i k_i [(c - b_i) + abs(c - b_i)]}{2 + k_i [(c - b_i) + abs(c - b_i)]} \quad (6)$$

where  $i$  is the index of a given step.

Multistep isotherms can be calculated additively from the adsorption isotherms of the individual “steps” (eq 6)

$$q = \sum_{i=1}^s \left\{ \frac{a_i k_i [(c - b_i) + abs(c - b_i)]}{2 + k_i [(c - b_i) + abs(c - b_i)]} \right\} \quad (7)$$

where  $s$  is the total number of steps in the isotherms.

The two-step isotherm is as follows:

$$q = \frac{a_1 k_1 c}{1 + k_1 c} + \frac{a_2 k_2 [(c - b_2) + abs(c - b_2)]}{2 + k_2 [(c - b_2) + abs(c - b_2)]} \quad (8)$$

The parameter  $b_1$  is implicitly equal to zero in the first step.

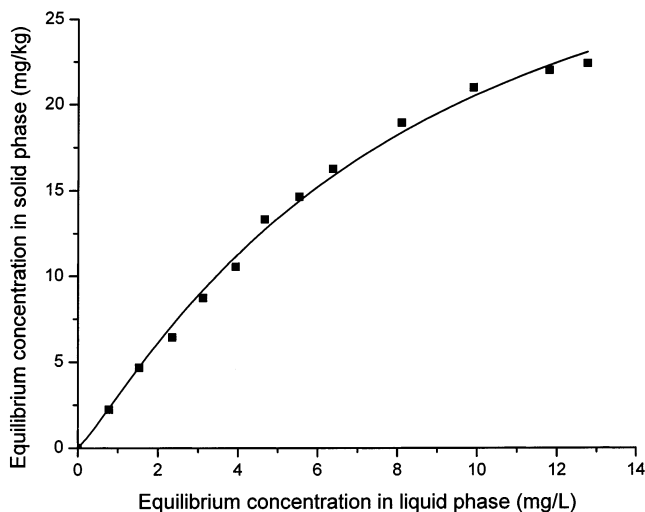


Figure 2. Adsorption isotherm of acetochlor.

The three-step isotherm is

$$q = \frac{a_1 k_1 c}{1 + k_1 c} + \frac{a_2 k_2 [(c - b_2) + \text{abs}(c - b_2)]}{2 + k_2 [(c - b_2) + \text{abs}(c - b_2)]} + \frac{a_3 k_3 [(c - b_3) + \text{abs}(c - b_3)]}{2 + k_3 [(c - b_3) + \text{abs}(c - b_3)]} \quad (9)$$

The maximum sorption capacity is defined by  $S_{\max} = \sum a_i$ . Each  $a_i$  value is the convergence limit for the corresponding step. Using the derived function, the parameters of a given isotherm can be calculated by nonlinear curve fitting. Modifying eq 7 by an empirical power constant ( $n > 0$ ), the error of fitting could be significantly decreased.

$$q = \sum_{i=1}^s \left\{ \frac{a_i k_i [(c - b_i) + \text{abs}(c - b_i)]^n}{2^n + k_i [(c - b_i) + \text{abs}(c - b_i)]^n} \right\} \quad (10)$$

Unfortunately no evident physical explanation could be attributed to  $n$ . For calculations presented in this paper eq 9 was used.

The mathematical equation detailed above has been applied to describe adsorption isotherms for all of the examined compounds. We found that the experimental adsorption data could be simulated with a single-step (Langmuir) model for acetochlor and carbendazim, with a two-step model for diazinon, isoproturon, and atrazine, and with a three-step model for imidacloprid. The adsorption isotherms of the six pesticides studied are shown in Figures 2–7. Cumulated adsorption capacities ( $S_{\max}$ ) were decreased in the order diazinon (77.67 mg/kg), carbendazim (46.91 mg/kg), acetochlor (36.78 mg/kg), imidacloprid (22.79 mg/kg), and isoproturon (14.05 mg/kg). The adsorption capacities calculated for the first step ( $a_1$ ) are  $\sim 2$  times lower than for the second ( $a_2$ ) in the cases of atrazine, isoproturon, and imidacloprid, whereas they are approximately equal in the case of diazinon. The similarity of the  $b_2$  parameters determined for atrazine, diazinon, and isoproturon might indicate that the first interactions between soil and pesticides are closely similar to each other. The  $k$  constant dependent on temperature characterizes the adsorption equilibrium. Interpretation of individual  $k_i$  values is rather difficult without information regarding the energetic background of the adsorption processes. In the case of isoproturon the explanation of  $k_i$  is further complicated by the relatively larger errors of estimation due to limited number of experiments. The shape of the sorption

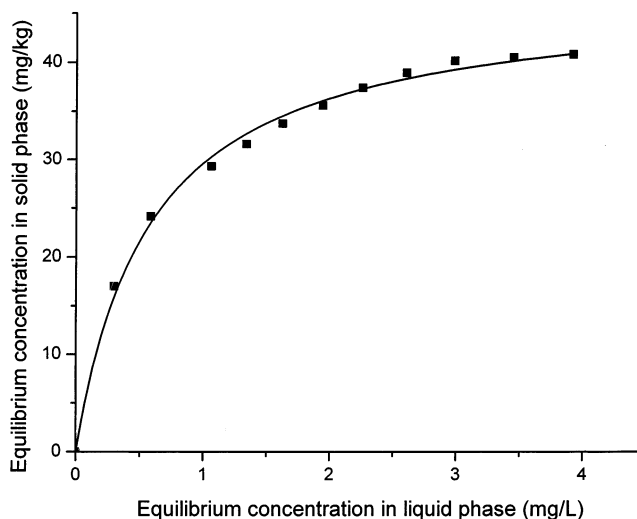


Figure 3. Adsorption isotherm of carbendazim.

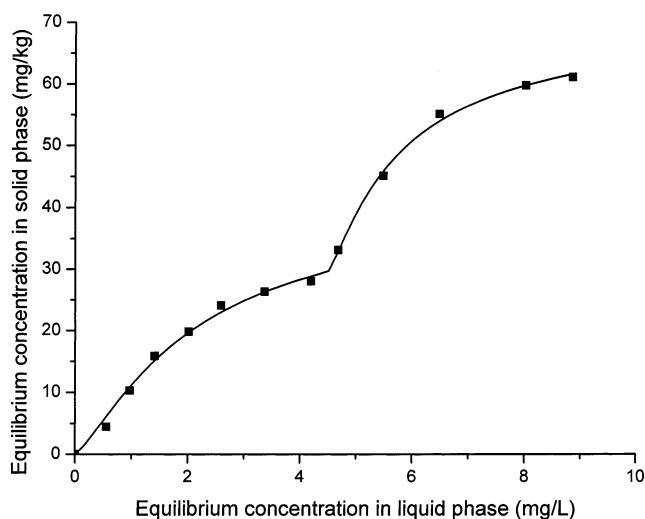


Figure 4. Adsorption isotherm of diazinon.

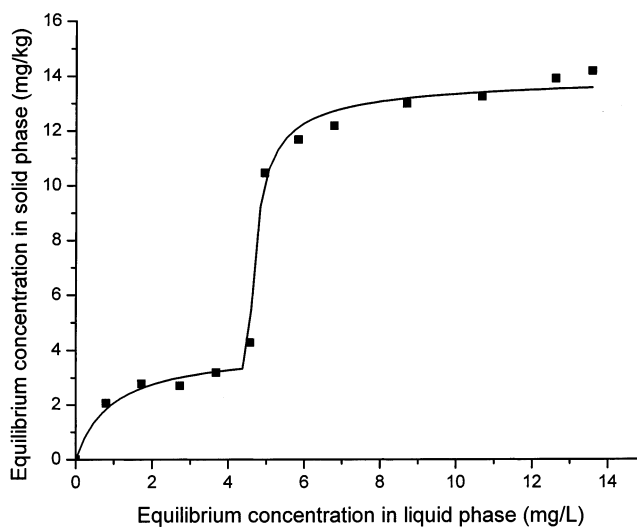


Figure 5. Adsorption isotherm of isoproturon.

isotherm line suggests but does not confirm information about the sorbate–sorber interaction. We assume that the steps arising on the isotherms indicate the inhomogeneity of adsorbent surface activity. A smaller part of the active sites may have increased activity, and they have been saturated at relatively low concentration. Additionally, interactions between the pesticide

Table 2. Calculated Parameters from Adsorption Isotherms of the Selected Pesticides<sup>a</sup>

| pesticide    | $a_1$        | $a_2$        | $a_3$       | $k_1$       | $k_2$       | $k_3$       | $b_2$       | $b_3$       |
|--------------|--------------|--------------|-------------|-------------|-------------|-------------|-------------|-------------|
| acetochlor   | 36.78 (1.46) |              |             | 0.09 (0.01) |             |             |             |             |
| carbendazim  | 46.91 (0.74) |              |             | 1.71 (0.11) |             |             |             |             |
| atrazine     | 6.28 (1.27)  | 13.93 (1.11) |             | 0.41 (0.18) | 1.16 (0.29) |             | 4.77 (0.11) |             |
| diazinon     | 41.19 (2.61) | 30.71 (2.60) |             | 0.37 (0.05) | 0.88 (0.22) |             | 4.49 (0.08) |             |
| isoproturon  | 4.06 (0.88)  | 9.99 (0.66)  |             | 1.04 (0.73) | 4.95 (1.15) |             | 4.55 (0.01) |             |
| imidacloprid | 5.64 (1.27)  | 9.36 (0.81)  | 7.79 (0.86) | 0.87 (0.28) | 1.22 (0.31) | 0.73 (0.17) | 3.43 (0.18) | 6.70 (0.84) |

<sup>a</sup> Standard deviations are given in parentheses. Regression coefficients were 0.991–0.999.  $a_i$  values represent the adsorption capacity provided by the adsorption mechanism in question,  $k_i$  are the equilibrium constants, and  $b_i$  are the limit concentrations in the  $i$ th step.

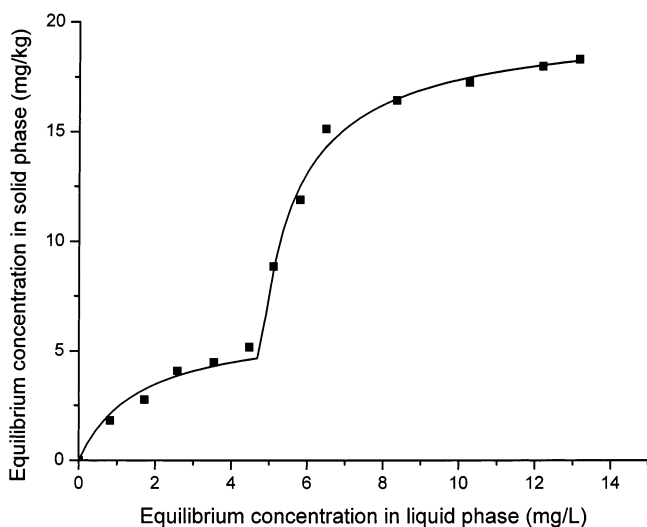


Figure 6. Adsorption isotherm of atrazine.

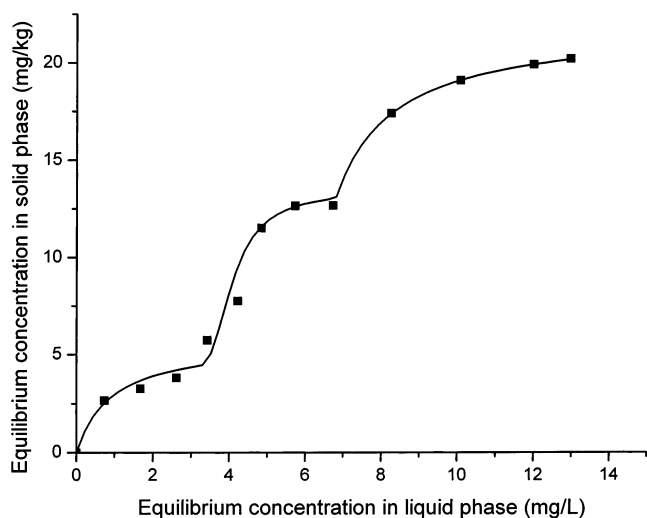


Figure 7. Adsorption isotherm of imidacloprid.

molecules may occur on the surface or in the solution as well, because most of the pesticides consist of functional groups with different chemical and hydrophobic character. The calculated parameters from the isotherms are given in Table 2.

## CONCLUSIONS

On the basis of the results obtained from the present study it can be concluded that the developed mathematical model described the measured experimental adsorption data well. The model gives an exact implementation of the description of adsorption processes for those compounds, which provide plots with a one-step or multistep shape. It also makes it possible to extend the description of the adsorption processes with great

precision. The parameters calculated from the new equation provide estimates for the absorption constant, adsorption capacity, and concentration limit for different adsorption mechanisms existing often simultaneously in soil–pesticide environmental systems. Determination of the sorption isotherm type and characteristic adsorption parameters provides information about solute mobility in soil and allows prediction of environmental behavior such as runoff and leaching properties of the pesticide.

However, further experiments have been initiated to study the energetic background of the multistep adsorption nature of the studied pesticides on soil. Examination of the desorption feature of these pesticides may provide additional information concerning the intensity of soil–pesticide interactions involved.

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