Sorptive Behavior and Kinetics of Carbendazim in Mineral Soils

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Abstract

Studies on adsorption, desorption and reaction kinetics of carbendazim in grey-brown podzolic soil derived from loamy sand (Albic Luvisls), grey-brown podzolic soil derived from silt (Haplic Luvisols) and brown soil derived from sandy clay loam (Haplic Cambisols) were carried out. Five concentrations of carbendazim (5.0, 3.8, 2.6, 1.0 and 0.2 $\mu g \cdot cm^{-3}$) in $0.01\ mol \cdot dm^{-3}$ $CaCl_2$ were used for the 24 h batch adsorption experiments; the desorption experiments were performed by replacing equilibrium solutions with $0.01\ mol \cdot dm^{-3}$ $CaCl_2$ and shaking again for the same period of time. The experimental data showed a good fit to the Freundlich equation (r^2 in the range 0.988-0.997 for adsorption and 0.980-0.999 for desorption). The values of K_F^{ads} varied from 5.45 in the sandy to 11.81 in the loess soil, the K_F^{des} from 7.82 in the sandy to 17.87 in the loamy soil; the $1/n$ values for adsorption and desorption were in the range 0.636-0.812. Adsorption/desorption kinetics were investigated for 1, 2, 4, 6, 8, 10, 24 and 48 h reaction times. The adsorption process in all soils and the desorption process in sandy soil was time-dependent, initially proceeding quickly but within approximately one hour it slowed and ran slowly. Useful models for the description of presented experimental kinetic data were the two-site model (r^2 in the range 0.727-0.994) and the pseudo second-order model (r^2 in the range 0.636-0.988).

Keywords: carbendazim, soils, adsorption, desorption, kinetic models

Introduction

Carbendazim is a systemic benzimidazole fungicide that is used on a large scale in agriculture throughout Europe [1]. It has fungicidal and fungistatic activities against a wide spectrum of soil fungi [2, 3]. Inhibitory effects on some bacterial processes have also been shown [4]. Carbendazim is a basic compound which in the acid reaction accept a proton and becomes a conjugated acid with pK_a of 4.2 [5, 6]. In soils this compound is retained both by nonionic and ionic sorption processes [6]. The most important soil fraction related to carbendazim adsorption is organic matter [7]. Aharonson and Kafkafi [5] showed also that clay minerals play a prominent role in adsorp-

tion of this compound. Due to its slow rate of degradation and low solubility in water, this fungicide may remain for a long time in an immobilized state in the soil due to interaction with soil colloids [6]. Numerous residue studies have shown that the compound is detectable in fruits and plant foliage well after harvest [8, 9]. Moreover, carbendazim has been documented as mutagenic and having teratogenic effects on mammals in single, low-level doses [10, 11]. Carbendazim is in a priority list for preventing the contamination of ground- and drinking waters by pesticides in Europe, which considers pesticides used in quantities over 50 tons per annum and their capacities as portable or transient leachable substances [12].

Understanding the processes involved in the binding of pesticides in soil is necessary to predict their behavior in the soil system and, consequently, the potential risk

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for contamination of water resources and environmental health [6]. Such studies in soils with small contents of organic matter and clay are necessary because they have a larger potential for substance translocation in the soil profile. Therefore, studies on carbendazim were undertaken whose aim was to compare the courses of adsorption, desorption as well as kinetics of these processes.

Materials and Methods

Soils

Studies were carried out using the samples taken up from the A_p level of grey-brown podzolic soil derived from loamy sand (Albic Luvisols), grey-brown podzolic soil derived from silt (Haplic Luvisols) and brown soil derived from sandy clay loam (Haplic Cambisols). Due to the character of bed-rock they are called sandy, loess and loamy soils in the paper. The soil samples were air-dried, sieved using a 1 mm mesh diameter sieve and averaged. The basic physicochemical properties of sandy, loess and loamy soils were as follows: clay content – 2.0, 3.5 and 24.0%, pH in 1 mol·dm^{-3} KCl – 3.9, 4.3 and 5.6, specific surface area (total) – 8.67, 20.05 and 49.09 m^2·g^{-1}, C_{org} content – 0.72, 0.88 and 1.13%, hydrolytic acidity – 33.4, 40.5 and 22.2 mmol$_c$·kg^{-1}, sum of basic cations – 8.0, 37.0 and 154.0 mmol$_c$·kg^{-1}.

Batch Adsorption/Desorption Experiments

The experiments were performed according to the OECD guideline [13]. In the preliminary study for each soil the 2 g/2 cm^3, 2 g/10 cm^3 and 2 g/50 cm^3 soil/solution (5.0 μg · cm^{-3} carbendazim in 0.01 mol · dm^{-3} CaCl$_2$) ratios and 12 h, 24 h and 48 h equilibrium adsorption/desorption times were examined. As appropriate the 24 h equilibrium time and 1/5 soil/solution ratio were chosen.

Five concentrations of carbendazim (50.0, 38.0, 26.0, 10 and 2 μg·cm^{-3}) in 0.01 mol·dm^{-3} CaCl$_2$ were used for the adsorption experiments. The air-dried 2 g soil samples were placed in 50 cm^3 polypropylene tubes sealed with screw caps and equilibrated by shaking with a volume of 9 cm^3 of 0.01 mol·dm^{-3} CaCl$_2$ overnight (12 h) before the day of the experiment. Afterwards, 1 cm^3 of the appropriate solution was added in order to adjust the final volume to 10 cm^3. The tubes were agitated on a rotary shaker for 24 h at 20 ± 1°C to achieve equilibrium and then centrifuged (10 min, 4500 rpm). The aqueous phase was recovered as completely as possible (9.2 cm^3 for the sandy, 8.9 cm^3 for loess and loamy soils) and analyzed by HPLC. The amount of carbendazim adsorbed by the soil was calculated from the difference between the initial and equilibrium substance concentrations in solution [13].

In the next step performed to examine the desorption process, the volume of solution removed was replaced by an equal volume of 0.01 mol·dm^{-3} CaCl$_2$. The new mixture was agitated for 24 h, then centrifuged to separate the liquid phase for analyses. The amount of pesticide remaining adsorbed by the soil was calculated as the difference between the initial adsorbed amount and the desorbed amount [13].

All adsorption/desorption experiments, including the controls (9 cm^3 of 0.01 mol·dm^{-3} CaCl$_2$ and 1 cm^3 of 50.0 μg·cm^{-3} carbendazim in 0.01 mol·dm^{-3} CaCl$_2$) and blanks (2 g of soil and 10 cm^3 of 0.01 mol·dm^{-3} CaCl$_2$) were performed in triplicate.

Kinetic Adsorption/Desorption Experiments

In the kinetic adsorption experiments tubes with 2 g of soil and 9 cm^3 of 0.01 mol·dm^3 CaCl$_2$ were shaken overnight and 1 cm^3 of 50.0 μg·cm^{-3} carbendazim in 0.01 mol·dm^{-3} CaCl$_2$ was added. Afterwards the tubes were agitated for 1, 2, 4, 6, 8, 10, 24 or 48 h, centrifuged and the liquid phase was sampled for analyses.

In the kinetic desorption experiments the tubes with 2 g of soil and 9 cm^3 of 0.01 mol·dm^3 CaCl$_2$ were shaken overnight, then 1 cm^3 portions of 50.0 μg·cm^{-3} carbendazim in 0.01 mol·dm^{-3} CaCl$_2$ were dosed and tubes were shaken for 24 h, centrifuged and the aqueous phase was recovered (9.2 cm^3 for the sandy, 8.9 cm^3 for loess and loamy soils) and analyzed. The volume of solution removed after 24 h was replaced by an equal volume of 0.01 mol·dm^{-3} CaCl$_2$, agitated for 1, 2, 4, 6, 8, 10, 24 or 48 h and centrifuged to separate the liquid phase for analyses. The amounts of adsorbed/desorbed carbendazim as a function of time were calculated in a similar way as for batch adsorption/desorption experiments. All kinetic experiments, including controls and blanks, were performed in triplicate.

Analytical Methods

For carbendazim analysis, the portion of solution (20 μl) was injected into a WellChrom (Knauer, Berlin, Germany) HPLC equipped with two K-500 pumps, a K-2500 UV-VIS detector and a Hypersil Gold C$_{18}$ column (100 × 3.0 mm i.d., 3 μm particle size, Thermo Electron Corporation, Runcorn, United Kingdom) preceded by a Hypersil Gold C$_{18}$ guard column (10 × 3.0 mm i.d., 3 μm particle size). The mobile phase was 26:74 (v/v) acetonitryle/citrate buffer (pH 6.5). The flow rate of the mobile phase was 0.5 cm^3·min^{-1} with a run time of 6 min per sample and detection wavelength of 225 nm. The retention time was 2.9 min. All measurements were performed at least in duplicate. The detection limit was 0.5 μg·dm^{-3}, reproducibility of results with the relative standard deviation lower than 5%.

The control samples did not show adsorption of carbendazim on the surface of polypropylene tubes. The analysis of blank samples did not exhibit the influence of soil constituents on the results of carbendazim measurements by HPLC.

The experimental data for the adsorption/desorption equilibrium studies and adsorption/desorption kinetics were substituted into an Excel spreadsheet. The parameters of the fitted equations were determined by minimizing the distance between the experimental data points and the model predictions. The sum of the errors squared (*SSE*) was the objective function in the minimization scheme [14],

$$SSE = \sum_{i=1}^{n} (S_{\exp, i} - S_{fit, i})^2 \qquad (1)$$

where $S_{exp,i}$ and $S_{fit,i}$ are the experimental and fitted adsorption/desorption values [$\mu g \cdot cm^{-3}$]. A value for *SSE* close to zero indicates a good fit whereas large values indicate a relatively poor description of the observed data by the selected model.

Adsorption/Desorption Isotherms

The adsorption/desorption isotherms were described for each soil using the Freundlich equation:

$$S^{ads/des} = K_F^{ads/des} C_{eq}^{1/n} \qquad (2)$$

where $S^{ads/des}$ is the amount of adsorbed/desorbed solute per unit mass of soil [$\mu g \cdot g^{-1}$], C_{eq} is the equilibrium solute concentration in solution [$\mu g \cdot cm^{-3}$] and $K_F^{ads/des}$ and $1/n$ are empirical constants.

Kinetic Models

Pseudo First-Order Model

The pseudo-first order rate equation of Lagergren [15] is widely used for the adsorption of solutes from a solid solution [16]. It is expressed as

$$\frac{dS_t^{\text{ads}}}{dt} = k_1 (S_e^{\text{ads}} - S_t^{\text{ads}}) \qquad (3)$$

where k_1 is the rate constant of first order reaction, S_e^{ads} is the amount of solute adsorbed at equilibrium [$\mu g \cdot g^{-1}$] and S_t^{ads} is the amount of solute on the surface of the adsorbent at any time [$\mu g \cdot g^{-1}$]. After integration equation (3) is expressed as

$$S_t^{ads} = S_e^{ads}(1 - \exp(-k_1 t)) \qquad (4)$$

For the desorption process equation (3) can be written as

$$-\frac{dS_t^{\text{des}}}{dt} = k_1 (S_t^{\text{des}} - S_e^{\text{des}}) \qquad (5)$$

where S_e^{des} is the amount of solute adsorbed when desorption equilibrium is achieved [$\mu g \cdot g^{-1}$] and S_t^{des} is the amount of solute adsorbed at any time [$\mu g \cdot g^{-1}$]. After separating the variables and integrating assuming that $S_t^{des} = S_e^{ads}$ at $t=0$ equation (5) becomes

$$S_t^{des} = S_e^{des} + (S_e^{ads} - S_e^{des})\exp(-k_1 t) \qquad (6)$$

Pseudo Second-Order Model

Many authors report successful application of the pseudo-second order equation for kinetics of adsorption of substances in soils (the review was made by Ho and McKay [17]). The pseudo-second order equation based on adsorption equilibrium capacity [17] is expressed as

$$\frac{dS_t^{\text{ads}}}{dt} = k_2 (S_e^{\text{ads}} - S_t^{\text{ads}})^2 \qquad (7)$$

where k_2 is the rate constant of second order reaction. The integrated form of this equation can be written

$$S_t^{ads} = S_e^{ads} - \frac{1}{\frac{1}{S_e^{ads}} + k_2 t} \qquad (8)$$

The desorption process is described by the equation

$$-\frac{dS_t^{\text{des}}}{dt} = k_2 (S_t^{\text{des}} - S_e^{\text{des}})^2 \qquad (9)$$

Integration of Eq. (9) for the boundary conditions as in equation (5) gives

$$S_t^{des} = S_e^{des} - \frac{1}{\frac{1}{(S_e^{ads} - S_e^{des})} + k_2 t} \qquad (10)$$

Elovich Model

The Elovich model [14] is generally expressed as

$$\frac{dS_t^{\text{ads}}}{dt} = \alpha \exp(-\beta S_t^{ads}) \qquad (11)$$

where α and β are empirical constants. One of the two rate constants (α) may be regarded as the rate of the instantaneous rapid reaction not governed by the exponential law. The other rate constant (β) provides the rate of the exponential first-order reaction that took place simultaneously but extended over a period of time [18]. The integrated form of Eq (11) becomes

$$S_t^{ads} = \frac{1}{\beta}\ln(1 + \alpha\beta t) \qquad (12)$$

The desorption process can be described as

$$-\frac{dS_t^{\text{des}}}{dt} = \alpha \exp(-\beta S_t^{des}) \qquad (13)$$

The integrated form of Eq. (13) for the boundary conditions $S_t^{des} = S_e^{ads}$ at $t = 0$ is

$$S_t^{des} = S_e^{ads} - \frac{1}{\beta}\ln(1 + \alpha\beta t) \qquad (14)$$

Two-Site Model

The two-site model was proposed by Willis et al. [19] on the basis of the first order rate law expression. The adsorption process in this model can be expressed as

$$\frac{dS_t^{ads}}{dt} = k_1(S_1^{ads} - S_{1t}^{ads}) + k_2(S_2^{ads} - S_{2t}^{ads}) \qquad (15)$$

where S_{1t}^{ads} and S_{2t}^{ads} [μg · g⁻¹] are the amounts of solute adsorbed at the time t to the sites with the first order adsorption rate constants k_1 and k_2 respectively. It was assumed that at equilibrium $S_e^{ads} = S_1^{ads} + S_2^{ads}$. The integrated form of Eq. (15) is

$$S_t^{ads} = S_1^{ads}(1 - \exp(-k_1 t)) + S_2^{ads}(1 - \exp(-k_2 t)) \qquad (16)$$

For the desorption process Eq. (15) can be written as

$$-\frac{dS_t^{des}}{dt} = k_1(S_{1t}^{des} - S_1^{des}) + k_2(S_{2t}^{des} - S_2^{des}) \qquad (17)$$

The integrated form of Eq. (17) for the boundary conditions $S_t^{des} = S_e^{ads}$ at $t = 0$ becomes

$$S_t^{des} = S_e^{des} + S_1^{des}\exp(-k_1 t) + S_2^{des}\exp(-k_2 t) \qquad (18)$$

It was assumed in Eq. (18) that $S_e^{ads} = S_e^{des} + S_1^{des} + S_2^{des}$. The above equation is similar to McLaren et al. [20] and bi-exponential [21] equations, but the authors of those equations assumed that at $t = \infty$ all amount of adsorbate would desorb ($S_e^{ads} = S_1^{des} + S_2^{des}$). It does not seem to be true in the case of the presented data.

Results

The adsorption isotherms of carbendazim in the three studied soils are shown in Fig. 1. The calculated values of K_F^{ads}, $1/n$, K_d^{ads} and K_{oc}^{ads} are given in Table 1. The values of K_d^{ads} in Table 1 were obtained by fitting the adsorption data into the linear equation ($1/n = 1$ in Eq. 2).

The smallest values of K_F^{ads}, K_d^{ads} and K_{oc}^{ads} were in the sandy soil, the largest in the loess soil. The adsorption process was more concentration dependent in the loess ($1/n = 0.663$) and sandy soils ($1/n = 0.670$) than in the loamy soil ($1/n = 0.795$).

Consecutive desorption experiments (Fig. 2 and Table 1) were carried out not only to obtain the information about quantity desorbed from the soil but also to study the intensity of soil-carbendazim interaction involved. The smallest K_F^{des},
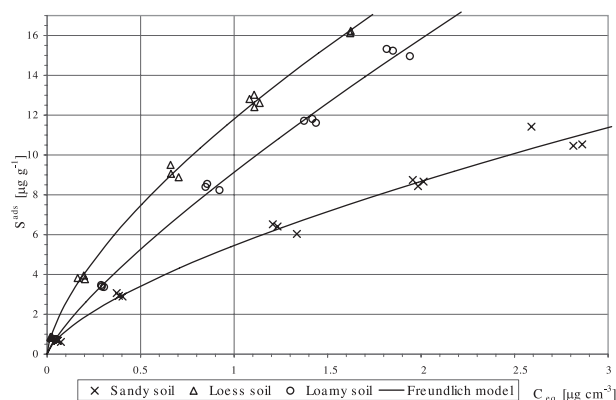

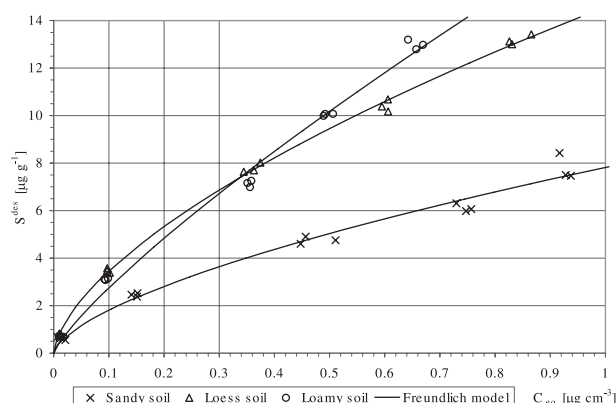Fig. 1. Adsorption isotherms of carbendazim in soils.

Fig. 2. Desorption isotherms of carbendazim in soils.

Table 1. Adsorption/desorption parameters for carbendazim in soils.

	Adsorption				Desorption		
Parameter	Sandy soil	Loess soil	Loamy soil	Parameter	Sandy soil	Loess soil	Loamy soil
K_F^{ads}	5.45	11.81	9.13	K_F^{des}	7.82	14.58	17.87
$1/n$	0.670	0.663	0.795	$1/n$	0.636	0.625	0.812
r^2	0.988	0.997	0.996	r^2	0.980	0.999	0.992
K_d^{ads}	4.21	11.12	8.40	K_d^{des}	8.67	16.96	20.13
r^2	0.929	0.937	0.979	r^2	0.920	0.924	0.981
K_{oc}^{ads*}	584.96	1263.07	743.22	K_{oc}^{des*}	1204.44	1926.93	1781.03

*$K_{oc}^{ads/des} = 100\, K_d^{ads)\,des}/C_{org}$ where C_{org} is the organic carbon content in %.

K_d^{des}, K_{oc}^{des} values were again in the sandy soil, but the largest in the loamy soil; the desorption process was less concentration dependent in the loamy soil than in the sandy and loess soils. Desorption of carbendazim from the sandy, loess and loamy soils, expressed as a percentage of initially adsorbed substance was in the range 5-29, 5-19 and 5-14% respectively. In each of the soils the percentage of desorption was increasing along with the amount of carbendazim adsorbed.
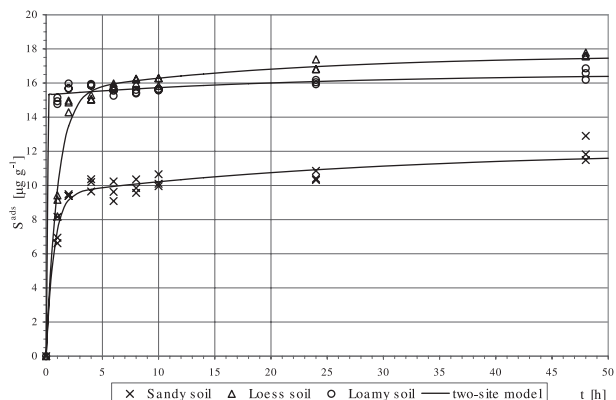

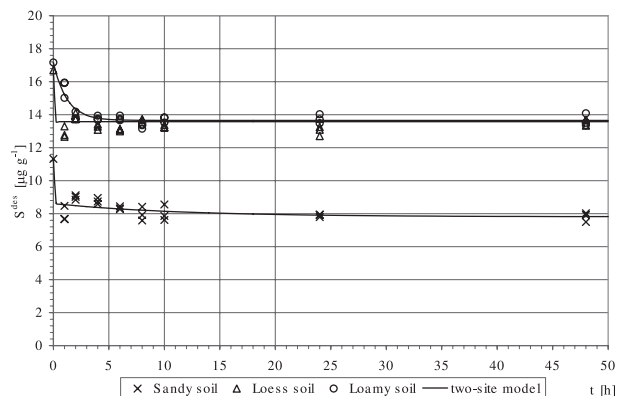Fig.3. Carbendazim adsorption in soils as a function of reaction time.

Fig.4. Carbendazim desorption in soils as a function of reaction time.

Table 2. Kinetic adsorption/desorption parameters for carbendazim in soils.

	Adsorption				Desorption		
Parameter	Sandy soil	Loess soil	Loamy soil	Parameter	Sandy soil	Loess soil	Loamy soil
Pseudo first-order model							
k_1	1.168	0.864	2.878	k_1	15.921	38.400	0.787
$S_e^{ads}*$	10.437	16.518	15.838	$S_e^{des}*$	8.217	13.328	13.609
r^2	0.889	0.959	0.987	r^2	0.623	0.782	0.870
Pseudo second-order model							
k_2	0.180	0.076	0.946	k_2	2.643	631.235	0.338
$S_e^{ads}*$	11.084	17.790	16.000	$S_e^{des}*$	8.200	13.329	13.358
r^2	0.917	0.956	0.988	r^2	0.636	0.782	0.806
Elovich model							
α	$3.63 \cdot 10^3$	$1.12 \cdot 10^3$	$3.55 \cdot 10^{21}$	α	$5.03 \cdot 10^5$	$1.00 \cdot 10^{20}$	$3.51 \cdot 10^2$
β	1.024	0.549	3.355	β	5.383	15.060	2.719
r^2	0.923	0.882	0.950	r^2	0.699	0.682	0.667
Two site model							
k_1	1,474	0.983	0.031	k_1	0.087	29.261	0.810
k_2	0.034	0.049	3.311	k_2	18.621	28.132	0.810
S_1^{ads}	9.464	15.428	1.043	S_1^{des}	0.802	1.560	1.755
S_2^{ads}	2.608	2.220	15.499	S_2^{des}	2.710	1.561	1.757
r^2	0.954	0.976	0.994	r^2	0.727	0.782	0.870
Experimental parameters							
S_e^{ads}	12.072	17.648	16.542	S_e^{des}	7.811	13.576	13.654

$S_e^{ads}*$, $S_e^{des}*$, S_1^{ads}, S_2^{ads}, S_1^{des} and S_2^{des} – values obtained by fitting the appropriate model [µg · g⁻¹]; S_e^{ads} and S_e^{des} – values obtained from the experimental data [µg · g⁻¹].

The results of experiments on kinetics of carbendazim adsorption in soils are presented in Fig. 3 and the parameters of fit models are given in Table 2. The course of adsorption was similar in all soils: in the first stage in a very short time (approximately 1 h), soils adsorbed 52-89% of appropriate S_e^{ads} value, then a stage of slow adsorption followed. Therefore kinetics is best described by the two-site model. In the loamy soil the first stage was the fastest and the second one was the slowest. Therefore the r^2 value for the two-site model differ insignificantly from the r^2 values for the pseudo first-order and pseudo second-order models. The fit amounts of carbendazim adsorbed at equilibrium ($S_e^{ads}*$ in Table 2) are more reasonable for the pseudo second-order model than those of the pseudo first-order model when comparing predicted results ($S_e^{ads}*$) with experimental data (S_e^{ads}), because all $S_e^{ads}*$ values for the pseudo first-order model are lower than experimental results. The Elovich model described kinetics of carbendazim adsorption in the poorest way in the loess and loamy soils, but in the sandy soil only the r^2 value for the two-site model was larger.

Carbendazim desorption in the sandy soil (Fig. 4) was very fast at first, then slowed down rapidly and the stage of slow desorption started; desorption kinetics is best described by the two-site model. In the loess soil the first stage also progressed very quickly but the stage of slow desorption practically did not take place. The r^2 values in this soil are identical for the two-site, pseudo first-order and pseudo second-order models. In the loamy soil desorption also preceded in one stage and is best described by the pseudo first-order model. The results of two-site model fit confirm lack of a slow desorption stage in the loess and loamy soils: in both soils $k_1 \approx k_2$ and $S_1^{des} \approx S_2^{des}$. The Elovich model described the desorption kinetics well in the sandy soil but in the poorest way in the loess and loamy soils.

Discussion of Results

The experimental data on carbendazim adsorption for all three soils (Fig. 1) showed a good fit to the Freundlich equation (values of r^2 in Table 1 are in the range 0.988-0.997). The Freundlich adsorption coefficient was highest in the loess soil ($K_F^{ads} = 11.81$), indicating that this soil adsorbed carbendazim more strongly than the other soils. The $1/n$ values of the isotherms (smaller in sandy and loess soils, the largest in loamy soil) might be explained by an increased difficulty in accessing the adsorption sites when carbendazim concentrations are elevated (loamy soil has the largest amount of organic carbon and clay). The linear equation gave a good fit (r^2 range 0.929-0.979), but not as good as the Freundlich equation. The curve fitting of the adsorption data also could not be improved by using the Langmuir equation (data not presented). The non-applicability of the Langmuir equation could be explained by the heterogeneity and surface acidity of the soils [22, 23].

The desorption data (Fig. 2) conformed well to the Freundlich equation (r^2 in Table 1 are in the range 0.980-0.999) and slightly smaller to the linear equation (r^2 range 0.920-0.981). The Langmuir equation also did not provide a good fit line. The $1/n$ values in the Freundlich equation were almost the same as in the adsorption experiments, but K_F^{des} values were consistently larger. Also K_d^{des} and K_{oc}^{des} values were larger than K_d^{ads} and K_{oc}^{ads}. Berglöf et al. [6] made similar observations for carbendazim in Vietnamese soils and also Monkiedje and Spiteller [24] and Sukul and Spiteller [25] in their studies on metalaxyl. This could be explained by a possible hysteresis effect taking place during desorption, involving various forces that caused the amount of carbendazim retained to be higher after desorption than after adsorption at the unit equilibrium concentration [24, 26].

The $K_{oc}^{ads/des}$ values obtained in this study (Table 1) were smaller in comparison to those of Berglöf et al. [6] (K_{oc}^{ads} in the range from 960 to 2700, K_{oc}^{des} from 438 to 2700) and Nemeth-Konda et al. [27] ($K_{oc}^{ads} = 2805$). It could be explained on the basis of physico-chemical properties of the soils used for the study (smaller amounts of organic carbon and clay). The distribution coefficients K_{oc}^{ads} and K_d^{ads} are not directly related to the total clay content or the total organic matter content in a straightforward manner [28]. In this study K_{oc}^{ads} and K_d^{ads} were larger in the loess soil than in the loamy soil; the same is found in the study of Berglöf et al. [6]. The explanation is that associations between silicate clays, Fe and Al oxides and organic matter will affect pH, and also the sorption properties. The maximum adsorption of carbendazim on the variable charge organic matter surfaces would occur at a pH close to the pK_a value, i.e. 4.2 [6]. In the presented study the loess soil has nearly the same value of pH.

Degradation of carbendazim in soils is a slow process with a half-life in anaerobic conditions usually about 3 months [29]. The desorption process in the loess and loamy soils was very quick and was over within an hour's time. This appears to be evidence that kinetics of adsorption and desorption in these soils was not influenced by degradation. In the sandy soil a certain influence of degradation on the slower stage of adsorption and desorption processes cannot be excluded.

As follows from analysis of the data presented in Table 2, the two-site model proved to be the most universal for description of kinetics of carbendazim adsorption and desorption. It also can be applied for description of pesticide degradation in soils when the first-order kinetics model fails [21].

The current studies also showed great applicability of the pseudo second-order model for description of experimental data. Contrary to the pseudo first-order model it can be successfully used when the adsorption/desorption process slows down after some time and is very slow in the final stage.

The pseudo first-order model showed limited applicability for description of kinetic of carbendazim adsorption/desorption in soils. However, when adsorption/de-

sorption proceeded very quickly not followed by a stage of slow kinetics, the model proved to be sufficient (e.g. for carbendazim desorption in loess and loamy soils).

The Elovich model was successfully applied by many authors for description of kinetics of adsorption/desorption of various substances in soils [14, 30]. However, other models were better for description of the presented experimental data.

Conclusions

1. Carbendazim was strongly adsorbed in the selected soils and only partly capable of desorption. Both the adsorption and the desorption data conformed very well to the Freundlich equation.
2. Adsorption of carbendazim was dependent on the pH of soils and indirectly on the total organic matter content and total clay content. The highest value was found for the soil with pH 4.3, which may have resulted from the partial protonation of carbendazim.
3. The adsorption process in sandy, loess and loamy soil and the desorption process in sandy soil were time-dependent: initially they proceeded very quickly, and within approximately one hour they slowed down and ran slowly. The desorption process in loess and loamy soils was quick and finished within an hour.
4. Kinetics data fitted very well to the two-site model and the pseudo second-order model and, to a lesser extent, to the Elovich model, providing evidence that in certain cases soil reaction occurred in two distinct stages: the fast initial one followed by the slower one.

References

1. CUPPEN J.G.M., VAN DEN BRINK P.J., CAMPS E., UIL K.F., BROCK T.C.M. Impact of the fungicide carbendazim on freshwater microcosms. I. Water quality, breakdown, of particulate organic matter and responses of macroinvertebrates. Aquat. Toxicol. **48**, 233, **2000**.
2. JONES S.E., WILLIAMS D.J., HOLLIMAN P., TAYLOR N., BAUMANN J., FÖRSTER B.,VAN GESTEL C.A.M., RODRIGUES J.M.L. Ring-testing and Field-validation of a Terrestrial Model Ecosystem (TME) – An Instrument for Testing Potentially Harmful Substances: Fate of the Model Chemical Carbendazim. Ecotoxicol. **13**, 29, **2004**.
3. VENEDIKIAN N., CHIOCCHIO V., MARTINEZ A., MENENDEZ A., OCAMPO J.A., GODEAS A. Influence of the fungicides carbendazim and chlorothalonil on spore germination, arbuscular mycorrhizal colonization and growth of soybean plants. Agrochimica. **43**, 105, **1999**.
4. CHALAM A.V., SASIKALA C., RAMANA C.V., RAO P.R. Effect of pesticides on hydrogen metabolism of *Rhodobacter sphaeroides* and *Rhodopseudomonas palustris*. FEMS Microb. Ecol. **19**, 1, **1996**.
5. AHARONSON N., KAFKAFI U. Adsorption of benzimidazole fungicides on montmorillonite and kaolinite clay surface. J. Agric. Food Chem. **23**, 434, **1975**.
6. BERGLÖF T,, VAN DUNG T., KYLIN H., NILLSON I. Carbendazim sorption-desorption in Vietnamese soils. Chemosphere. **48**, 267, **2002**.
7. DIOS CANCELA G., ROMERO TABOADA E., SANCHEZ-RASERO F. Carbendazim adsorption on montmorillonite, peat and soils. J. Soil Sci. **43**, 99, **1992**.
8. CHIBA M., VERES D.F. HPLC method for simultaneous determination of residual benomyl and methyl 2-benzimidazole carbamate on apple foliage without cleanup. J. Assoc. Off Anal. Chem. **63**, 1291, **1980**.
9. KIIGEMAGI U., INMAN R.D., MELLENTHIN W.M., DEINZER M.R. Residues of benomyl (determined as carbendazim) and captan in postharvest-treated pears in cold storage. J. Agric. Food Chem. **39**, 400, **1991**.
10. NAKAI M., HESS R.A., MOORE B.J., GUTTROFF R.F., STRADER L.F., LINDER R.E. Acute and long-term effects of a single dose of the fungicide carbendazim (methyl 2-benzimidazole carbamate) on the male reproductive system in the rat. J. Androl. **13**, 507, **1992**.
11. SARRIF A.M., ARCE G.T., KRAHN D.F., O'NEIL R.M., REYNOLDS V.L. Evaluation of carbendazim for gene mutations in the *Salmonella*/Ames plate-incorporation assay: the role of aminophenazine impurities. Mutat. Res. **321**, 43, **1994**.
12. ABOUL-KASSIM T.A.T., SIMONEIT B.R.T. Pollutant-solid phase interactions: mechanism, chemistry and modeling. The handbook of environmental chemistry Vol. 5, Part E, Springer-Verlag, Berlin, Heidelberg, **2001**.
13. OECD. Adsorption-desorption using batch equilibrium method. OECD guideline for the testing of chemicals pp. 106, **2000**.
14. CHEUNG C.W., PORTER J.F., MCKAY G. Sorption kinetic analysis for the removal of cadmium ions from effluents using bone char. Wat. Res. **35**, 605, **2001**.
15. LAGERGREN S. Zur Theorie der sogenannten Adsorption gelöster Stoffe. Kungliga Svenska Vetenskapsakademiens. Handlingar. **24**, 1, **1898**.
16. HO Y.S., MCKAY G. The sorption of lead(II) ions on peat. Wat. Res. **33**, 578, **1999**.
17. HO Y.S., MCKAY G. Pseudo-second model for sorption processes. Process Biochem. **34**, 451, **1999**.
18. SINGH A.K., PANDEYA S.B. Sorption and release of cadmium-fluvic acid complexes in sludge treated soils. Bioresource Technol. **66**, 119, **1998.**
19. WILLIS B.G., WOODRUFF W.H., FRYSINGER J.R., MARGERUM D.W., PARDUE H.L. Simultaneous kinetic determination of mixtures by on-line regression analysis. Anal. Chem. **42**, 1350, **1970**.
20. MCLAREN R.G., BACKES C.A., RATE A.W., SWIFT R.S. Cadmium and cobalt desorption kinetics from soil clays: effect of sorption period. Soil Sci. Soc. Am. J. **62**, 332, **1998**.
21. BEULKE S., BROWN C.D. Evaluation of methods to derive pesticide degradation parameters for regulatory modelling. Biol. Fertil. Soils. **33**, 558, **2001**.

22. BAILEY G.W., WHITE J.L. ROTHBERG T. Adsorption of organic herbicides by montmorillonite: role of pH and chemical character of adsorbate. Soil Sci. Soc. Am. Proc. **32**, 222, **1968**.

23. WEBER W.J., MCGINLEY P.M., KATZ P.E. A distribution model for sorption by soils and sediments. I. Conceptual basis and equilibrium assessments. Environ. Sci. Technol. **26**, 1955, **1992**.

24. MONKIEDJE A., SPITELLER M. Sorptive behavior of the phenylamide fungicides, mefenoxam and metalaxyl, and their acid metabolite in typical Cameroonian and German soils. Chemosphere. **49**, 659, **2002**.

25. SUKUL P., SPITELLER M. Sorption study on metalaxyl in soils of different physico-chemical properties. Fresenius Environ. Bull. **9**, 701, **2000**.

26. GRAHAM J.S., CONN J.S. Sorption of metribuzin and metolachlor in Alaska sub-arctic agricultural soils. Weed Sci. **40**, 155, **1992**.

27. NEMETH-KONDA L., FÜLKEY Gy., MOROVJAN Gy., CSOKAN P. Sorption behaviour of acetochlor, atrazine, carbendazim, diazinon, imidacloprid and isoproturon on Hungarian agricultural soil. Chemosphere. **49**, 659, **2002**.

28. CELIS R., CORNEJO J., HERMOSIN M.C., KOSKINEN W.C. Sorption of atrazine and simazine by model associations of soil colloids. Soil Sci. Soc. Am. J. **62**, 165, **1998**.

29. AHARONSON N., KAFKAFI U. Adsorption, mobility and persistence of thiabendazole and methyl 2-benzimidazolecarbamate in soils. J. Agric. Food Chem. **23**, 720, **1975**.

30. INOUE M.H., OLIVEIRA R.S., REGITANO J.B., TORMENA C.A., CONSTANTIN J., TORNISIELO V.L. Sorption kinetics of atrazine and diuron in soils from southern Brazil. J. Environ. Sci. Health. **39**, 589, **2004**.