Controlled Release of Imidacloprid from a Lignin Matrix: Water Release Kinetics and Soil Mobility Study

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Formulations of the insecticide imidacloprid were made using a commercially available pine kraft lignin. The release kinetics of imidacloprid from granules with variation in the loadings of the insecticide and granule sizes were evaluated in water under dynamic flow conditions. The release data were fitted to the generalized model $M_t/M_z = kt^n + c$, where M_t/M_z is the percentage of insecticide released at time t, k and c are constants, and n is another constant that indicates the mechanism of release. The results indicated that the release of imidacloprid was diffusion-controlled. The time taken for 50% of the active ingredient to be released into water, T_{50}, was also calculated for the comparison of formulations. The results showed that the formulation with the higher loading of imidacloprid had the higher value of T_{50}, which means a slower release of the active ingredient. In a related experiment, it was found that as the size of this formulation decreased, the release of the active ingredient was faster. In addition, mobilities of technical and formulated imidacloprid were compared by using soil columns simulating a layered bed system commonly used under a plastic greenhouse. The use of formulated imidacloprid produced a less vertical distribution of the active ingredient compared to the technical product. Sorption capacities of the various soil constituents for imidacloprid molecules were also calculated by using batch experiments. The results obtained were in agreement with those for sorption in dynamic conditions.

Keywords: *Controlled release; imidacloprid; lignin; leaching*

INTRODUCTION

Controlled-release (CR) formulations have several advantages over standard pesticide formulations, including lower application rates, ease and safety in handling, and reduced leaching potentials (Lewis and Cowsar, 1977; Bahadir and Pfister, 1990). Lignin is a naturally biodegradable polymer that is readily available, cheap, and a currently underutilized resource that has shown potential in formulating controlled-release formulations (Wilkins, 1990). The use of the byproduct lignin produced in the pulping of soft wood (kraft lignin) has been reported in other papers (DelliColli, 1977; Wilkins, 1984; Ali and Wilkins, 1992). Imidacloprid [1-(6-chloro-3-pyridinylmethyl)-*N*-nitroimidazolidin-2-ylideneamine] is a new systemic insecticide with novel modes of action (Kagabu et al., 1992; Moriya et al., 1992). This insecticide is effective for controlling aphids, whiteflies, thrips, scales, psyllids, plant bugs, and other various harmful pest species including resistant strains. It is used as seed dressing, soil treatment, and foliar treatment in different crops (Tomlin, 1994). This insecticide is widely applied in the region of Almería, in Andalucía (southeastern Spain), where an intensive horticulture is presented. The agricultural practice is based on a raised layered bed system under plastic greenhouses irrigated from underground aquifers. Pesticide usage has possibly resulted in residues occurring in well waters (Bosch et al., 1991; Chiron et al., 1995). Controlled-release formulations can ameliorate pesticide losses including those by leaching, evaporation, and degradation (Wilkins, 1990). The use of columns composed of uniform layers of the various soil constituents of the layered bed system (i.e., native soil, amended soil, peat, and sand) to assess leaching processes in greenhouses is considered valid as each of the layers in the greenhouses is disturbed and mixed as much as those in a laboratory layered soil column. Preliminary use of such columns combined with an appropriate leaching model supported this view (Blanco et al., 1994).

The aim of this study is to evaluate the potential of controlled-release formulations to reduce leaching of imidacloprid. Therefore, controlled-release formulations were prepared by mixing the insecticide with kraft lignin under melt conditions (Chanse and Wilkins, 1987; Cotterill et al., 1996). The release rate of the active ingredient from CR granules was studied in water under dynamic flow conditions by using a continuous flow-through system (Wilkins and Cotterill, 1993). The mobilities of technical and formulated imidacloprid were compared by using columns of soil layers taken from the greenhouse.

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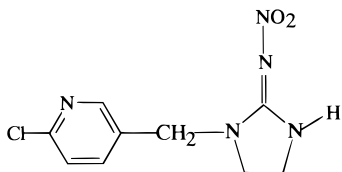
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Figure 1. Chemical structure of imidacloprid.

MATERIALS AND METHODS

Chemicals. The lignin used in this study was a commercially available pine kraft lignin, Indulin AT (Westvaco Corp., Charleston, SC). Technical grade imidacloprid (99%) was kindly supplied by Bayer Hispania. Its molecular formula and selected properties are as follows (Tomlin, 1994): molecular formula, $C_9H_{10}ClN_5O_2$; molecular weight, 255.7; melting point, 143.8 °C; vapor pressure (20 °C), 0.2 μPa; water solubility (20 °C), 0.51 g L^{-1}. The structure is shown in Figure 1.

Formulations. The CR granules were formed by mixing the lignin and imidacloprid in three different ratios [1:1, 1.5:1, and 2.3:1 (w/w)] and heated under melt conditions at 155–160 °C for 15 min (Chanse el at., 1987). On cooling, the glassy matrixes were crushed in a hammer mill and then sieved to obtain granules of size between 0 and 0.25 mm, between 0.25 and 0.50 mm, between 0.50 and 0.71 mm, and between 0.71 and 1.00 mm. A code for the formulations was used, ILY[X], where I represents the active ingredient (imidacloprid), L is the pine kraft lignin, Y is the percentage of active ingredient in the formulation (w/w), and X represents the size range (mm).

Analysis of Imidacloprid in the Granules. Granules (20 mg) were treated with methanol (25 mL) in an ultrasound bath for 10 min. This led to the complete disintegration of the granules. After 24 h at room temperature, the mixture was sonicated for a further 10 min and was then filtered quantitatively through a syringe filter (0.2 μm). The volume was made up to 50 mL with methanol, and the resulting solution was diluted 1:4 with methanol and analyzed for imidacloprid using an HPLC provided with a diode array detector and a data station. Using a mobile phase of acetonitrile (35%) and water (65%) at a flow rate of 1 mL min^{-1}, imidacloprid was analyzed at its wavelength of maximum absorption, 269 nm, by injecting a volume of 20 μL. Separation by isocratic elution was performed on an ODS 2 column, 150 × 3.2 mm, 5 μm packing.

Flow-Through System. Glass flow cells, with sintered glass disks at the top and bottom of a cylindrical cavity of length 40 mm and diameter 18 mm, were set up in an open system, immersed in a water bath at 20 °C (Wilkins and Cotterill, 1993). The CR granules (150 mg) were supported in the flow cells using glass wool; distilled water at 20 °C was then pumped through at a constant flow rate of 2.5 mL min^{-1}, using a multichannel peristaltic pump. The eluate from the flow cells was taken for analysis by HPLC using the conditions above indicated. Three replicates were carried out for each formulation. The same experiment was carried out with technical imidacloprid without lignin to compare the behavior of formulated and unformulated imidacloprid.

Soil Studies. Mobilities of technical and formulated imidacloprid were compared by using soil columns, simulating the typical arrangement of the different layers in a greenhouse, which are composed of sand, peat, and amended and native soils. Sorption experiments were also carried out for determining the K_d parameter.

Soil Characterization. The soils used were a native calcareous soil (Camborthids) and an amended soil (Xerosol-Luvic), both from the Almeria region (southeastern Spain). A commercial peat was used as the organic matter layer (Hydro del Báltico, Navasa S.A.). The sand was obtained from a unused commercial greenhouse. The individual layers of the soil from the greenhouse were characterized in terms of their physical properties. Air-dried samples, <2 mm particle size, were analyzed according to standard methods. The pH was deter-

Table 1. Characteristics of the Four Layers of the Greenhouse Soil

layer	pH	org matter (%)	clay content (%)	field capacity (% v/v)	water satn (% v/v)	CEC[a] (mequiv/ 100 g)
sand	9.39	0.02		5.80	40	10.00
peat	3.28	81.32		77.0	128	116.25
amended soil	8.44	0.08	53.00	38.0	52	10.63
native soil	8.87	0.51	8.00	48.0	51	12.50

[a] Cation exchange capacity.

mined in a 1:2.5 soil/water suspension using a glass electrode (Jackson, 1982); organic matter content by the Walkley–Black method (Walkley and Black, 1934); clay content by the hydrometer method (Black et al., 1982); cation exchange capacity by the barium acetate method (Primo-Yúfera and Carrasco-Dorrien, 1981); and water saturation and field capacity following the guidelines by Hall et al. (1977). All of these characteristics are shown in Table 1.

Sorption Experiments. Sorption experiments of imidacloprid were carried out for obtaining the K_d values as follows: 0.01 M $CaCl_2$ aqueous solutions containing initial pesticide concentrations (C_0) between 1.45 and 31.23 mg L^{-1} were used. Aqueous suspensions of the samples were prepared by adding 25 mL of each insecticide solution to 3 g of soil (native and amended soil), 3 g of sand, and 0.5 g of peat. They were then placed in several stoppered conical flasks and shaken for 24 h (the time required for equilibrium to be reached between imidacloprid adsorbed and imidacloprid in solution) in a thermostatic shaker bath at 25 °C. After shaking, the solutions were centrifuged at 9251g for 10 min, and the concentration of imidacloprid in the supernatant liquid was determined by high-performance liquid chromatography (HPLC) as above indicated. The difference in pesticide concentration between the initial and final equilibrium solutions was assumed to be due to sorption, and the amount of imidacloprid retained per kilogram of sorbent was calculated.

Blanks containing no imidacloprid were used for each series of experiments, and three replicates were analyzed at each pesticide concentration for each sorbent.

Column Preparation. The columns were made using PVC tubes (10 cm diameter, 60 cm length) and designed following the arrangement of the layers in a typical greenhouse, that is, a layer of 20 cm of native soil in the bottom, then a layer of 20 cm of amended soil, then a layer of peat (2 cm), and a top layer of sand (8.5 cm).

Nylon mesh with an effective pore diameter of 60 μm was sealed to the base of the column, minimizing the dead-end volume (Fleming et al., 1992). Each component of the column was added in small increments to the tube to minimize particle size segregation.

The columns were packed to an appropriate bulk density, that is, 1.46 (native soil), 1.69 (amended soil), 0.22 (peat), and 1.86 g cm^{-3} (sand). The columns were covered with cling film to prevent evaporation.

The columns were then saturated in distilled water by capillarity for 3 days. After saturation was completed, the columns were left to drain for 1 day.

Chemical Preparation and Application. All insecticide treatments were applied to triplicate soil columns. A methanol solution containing 10 mg of technical imidacloprid was added to an amount of sand equivalent to 1.5 cm height of the column. The sand/insecticide mixture was left to dry overnight at room temperature before being added to the top of each column. For the imidacloprid granules, 22.83 mg of the IL50 [0.25–0.50] matrix was evenly distributed on the sand layer. In all cases, acid-washed sand (1 cm) was added to the top of the columns. The active ingredient concentration was selected to allow for adequate detection of imidacloprid in all systems.

Leaching and Leachate Collection. The leaching solution used in all experiments was 0.01 M $CaCl_2$. This was done to simulate the soil solution and to prevent dispersion of the soil during the leaching procedure (Johnson and Pepperman, 1995). The columns were leached with 3 L of solution at a

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Table 2. Extraction of Imidacloprid from Granules[a]

formulation	initial imidacloprid (%)	imidacloprid extracted (%)	efficiency of the preparations (%)
IL30 [0.71−1.00]	30	26.42 (0.24)	85.7
IL40 [0.71−1.00]	40	33.76 (0.69)	84.4
IL50 [0.71−1.00]	50	44.70 (0.33)	89.4

[a] Standard deviation of three replicates shown in parentheses.

Table 3. Constants from Fitting the Generalized Model, $M_t/M_z = kt^n + c$, to the Release Data of Imidacloprid in Water[a]

formulation	k	n	c	r	T_{50} (days)
IL30 [0.71−1.00]	27.12 (3.40)	0.40 (0.05)	−3.35 (2.73)	0.9883	5.40
IL40 [0.71−1.00]	22.79 (2.23)	0.48 (0.04)	−2.21 (1.73)	0.9941	5.69
IL50 [0.71−1.00]	13.58 (0.86)	0.53 (0.03)	−0.34 (0.66)	0.9977	11.88

[a] Standard errors shown in parentheses.

Table 4. Constants from Fitting the Generalized Model, $M_t/M_z = kt^n + c$, to the Release Data of Imidacloprid in Water for the IL50 Matrix with Different Granule Sizes[a]

granule size (mm)	k	n	c	r	T_{50} (days)
IL50 [<0.25]	59.67 (9.31)	0.32 (0.06)	−8.57 (7.71)	0.9785	0.94
IL50 [0.25−0.50]	37.95 (4.33)	0.48 (0.05)	−3.97 (3.27)	0.9932	2.08
IL50 [0.50−0.71]	19.50 (1.09)	0.65 (0.03)	0.01 (0.80)	0.9988	4.26
IL50 [0.71−1.00]	13.58 (0.86)	0.53 (0.03)	−0.34 (0.66)	0.9977	11.88

[a] Standard errors shown in parentheses.

flow rate of 0.25 mL min^{-1} using a Gilson Minipuls 3 peristaltic pump over a period of 8 days. The time and volume of each leachate were recorded. Aliquots were taken from the leachate and analyzed for imidacloprid content by passing each 10 mL fraction through a prepared C-18 solid-phase extraction cartridge and eluting the imidacloprid from the cartridge using 1 mL of methanol. After this, the fractions were injected directly in the HPLC system. At the end of the leaching procedure, the columns were allowed to drain for 48 h.

Soil Analysis. Soil columns were sliced following the established division for the different layers of the column, obtaining four fractions corresponding to the native soil, amended soil, peat, and sand. In addition, for the native soil and amended soil, a partition was made in two 10 cm portions labeled (1) and (2), representing the upper and lower fractions, respectively. Each fraction was dried at room temperature and homogenized. Subsamples of soil, sand, and peat were extracted in an ultrasound bath for 15 min with 25 mL of a mixture of methanol/water (80:20), filtered through Whatman No. 42 paper, and analyzed by HPLC, as described above.

The extraction efficiencies of imidacloprid were 89% for the sand, 84% for the peat, and 82% and 83% for the amended and native soils, respectively.

RESULTS AND DISCUSSION

Compatibility of Imidacloprid and Lignin. The solubility parameter of imidacloprid was estimated as being 33.9 mPa$^{1/2}$ by using a group contribution method (Meusberger, 1988). This value is close to that of kraft lignin (~23.5 mPa$^{1/2}$); hence, compatibility was predicted. Imidacloprid was found to be compatible with the kraft lignin, which was all dissolved when heated with the insecticide under melt conditions. Table 2 shows the percentage of imidacloprid in the melt initially, which extracted from granules and the efficiency of the preparations. The actual imidacloprid content determined by extraction was used when the percentage of imidacloprid released in the flow-through system was calculated.

Release Kinetics. The cumulative release of imidacloprid from IL30, IL40, and IL50 granules [0.71−1.00] is shown in Figure 2. The study carried out with technical imidacloprid showed that, in this case, imidacloprid was completely dissolved in <2 h. As can be seen from Figure 2, the slowest release of imidacloprid is from IL50 granules. The release data were analyzed by applying the generalized model $M_t/M_z = kt^n + c$, where M_t/M_z is the percentage of imidacloprid released at time t and k, n, and c are constants. The exponent n indicates the mechanism of release (Ritger and Peppas, 1987). The n values ranged from 0.40 for the IL30 [0.71−1.00] formulation to 0.53 for the IL50 [0.71−1.00] formulation (see Table 3). Values close to 0.5 indicate the release is diffusion-controlled (Ritger and Peppas, 1987). From the constants in Table 3, the T_{50} value (the time taken for 50% of the imidacloprid to be released) was calculated for the formulations. These values are also shown in Table 3.

As can be seen, the higher value of T_{50} corresponds to the IL50 [0.71−1.00] matrix, which means that this preparation produces the slowest imidacloprid release. To analyze the influence of the granule size on the release profile, the IL50 formulation was used. The results are shown in Figure 3. The smaller granule size (IL50 [<0.25]) results in a faster release of imidacloprid. This was as expected due to a higher surface area of the matrix being exposed to water, along a smaller distance over which the imidacloprid must diffuse from the center of the granule. Similar results were obtained for the release of diuron from granules based on a lignin matrix system (Cotterill et al., 1996).

The data were fitted to the generalized model (Ritger and Peppas, 1987); the constants obtained from this model and T_{50} values are given in Table 4. The n values ranged from 0.32 for the IL50 [<0.25] formulation to 0.65 for the IL50 [0.50−0.71] formulation. The T_{50} values ranged from 0.94 day for the smaller granule size (IL50 [<0.25]) to 11.88 days for the higher granule size [0.71−1.00]. The formulation can be ranked in order of increasing T_{50} values:

$$\text{IL50 } [<0.25] < \text{IL50 } [0.25-0.50] < \text{IL50 } [0.50-0.71] < \text{IL50 } [0.71-1.00]$$

The variety shown for T_{50} values in Tables 3 and 4 for the preparations used in this study might be useful for selecting the most appropriate formulation depending on the type of soil.

Soil Studies. *Sorption Studies.* Figure 4 shows the sorption isotherms of imidacloprid on the different sorbents: amended soil and sand (a) and native soil and peat (b).

According to the slope of the initial portion of the curves, these isotherms may be classified as L-type of the Giles classification (Giles el al., 1960) which suggests both that the samples have an average affinity for the insecticide imidacloprid and that there is no strong competition from the solvent for sorption sites. Nevertheless, an increase of the slopes of the initial portion of each adsorption isotherm can be noted as the sample is changing from sand to peat. This fact indicates an increasing affinity of the active sites in the samples surface for the imidacloprid molecules (Giles et al., 1960).

To evaluate the sorption capacities of the different layers of the soil columns, the experimental data points
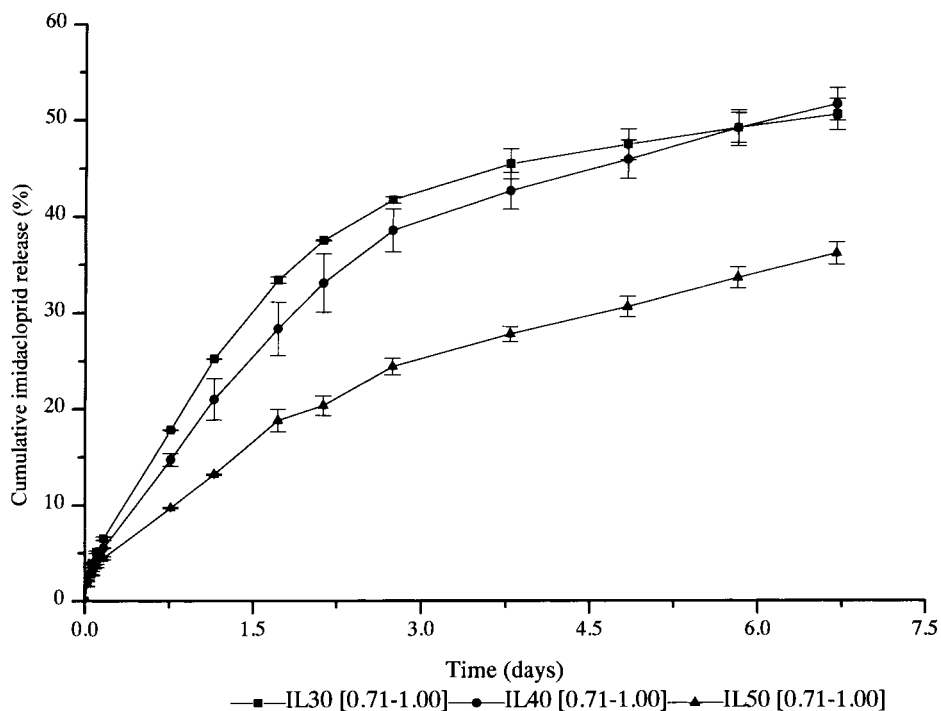
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Figure 2. Cumulative release of imidacloprid from granules with various active ingredient contents (error bars represent the standard deviation of three replicates).
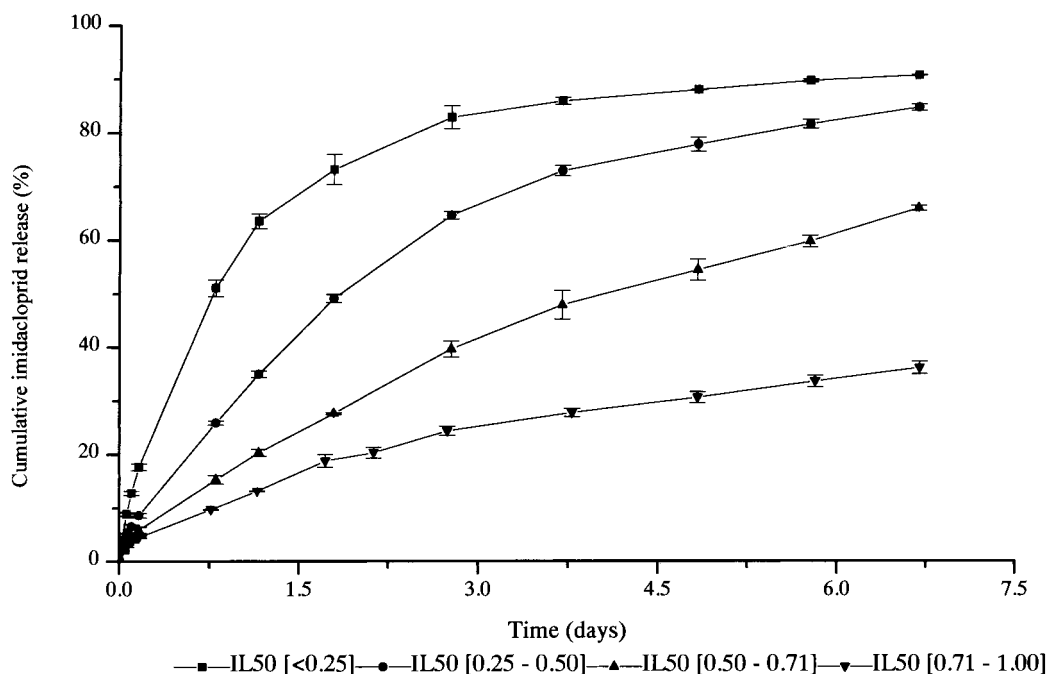

Figure 3. Cumulative release of imidacloprid from IL50 granules with different sizes (error bars represent the standard deviation of three replicates).

were fitted to the Henry equation (Voice et al., 1983)

$$X = K_d C \qquad (1)$$

where X is the pesticide adsorbed per kilogram of sorbent (mg kg^{-1}), K_d is a parameter related with the solute partitioning between the sorbent and solvent (L kg^{-1}), and C is the equilibrium solution concentration (mg L^{-1}).

The K_d values are shown in Table 5. As can be seen from this table, the K_d values increase from 0.10 L kg^{-1}

for the sand to 72.01 L kg^{-1} for the peat sample, the variation order being

sand < amended soil < native soil ≪ peat

To know the factors that affect sorption of imidacloprid by soil layers, the sorption capacities of the four layers, represented by K_d values, were correlated with layers properties. The analysis shows that K_d values are all correlated with the organic matter content and the cationic exchange capacity, the correlation coefficients being >0.999 in both cases.
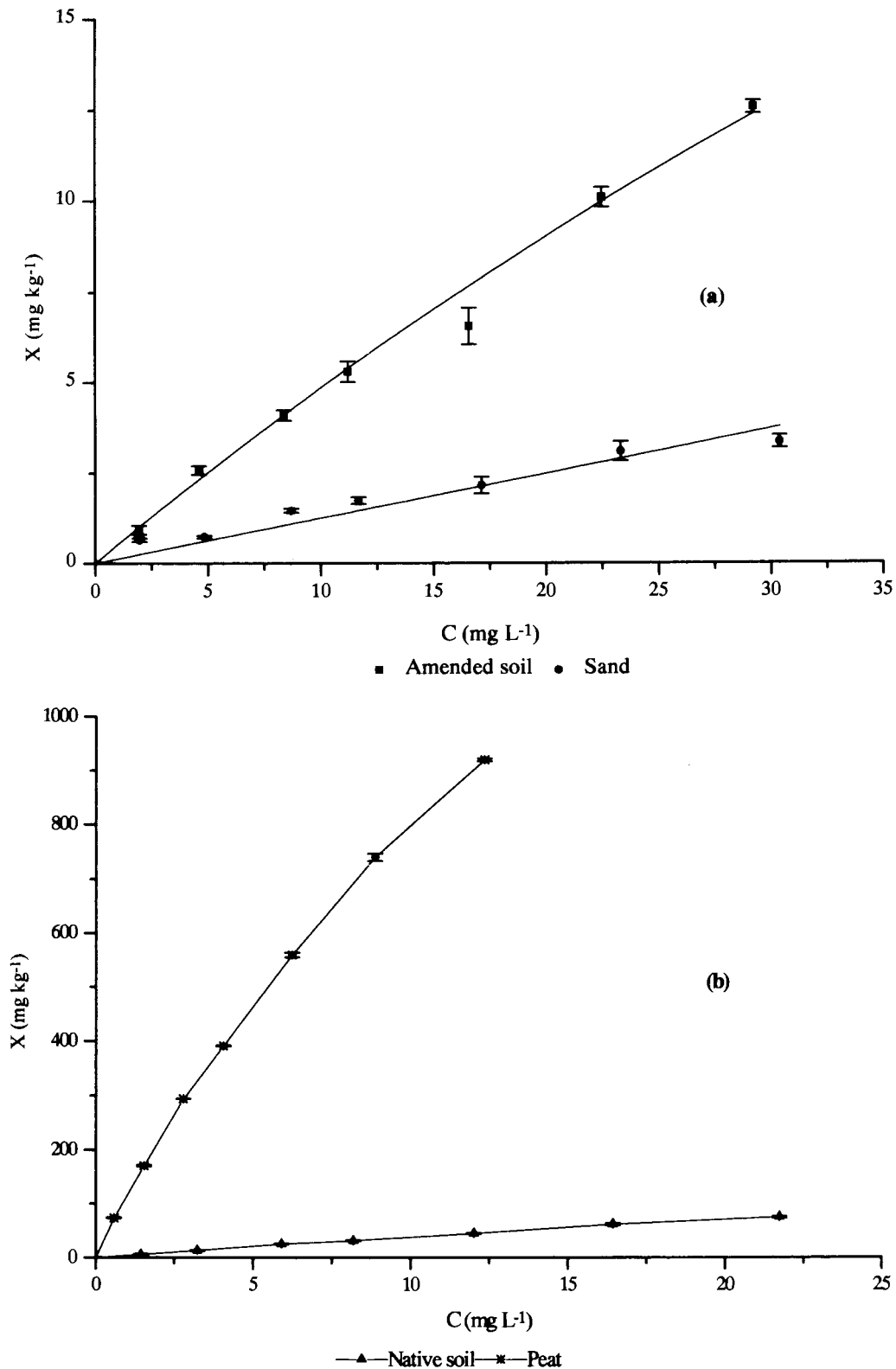
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Figure 4. Sorption isotherms of imidacloprid on the different layers of a greenhouse soil (error bars represent the standard deviation of three replicates): (a) amended soil and sand; (b) native soil and peat.

Mobility Studies. The amount of imidacloprid recovered per kilogram in each portion of the columns is presented in Table 6. In addition, the total percentages of imidacloprid recovered in the soil and leachates referred to the total amount of the insecticide applied in the experiments are also indicated in Table 6.

As can be seen, 95.33% of the total amount is recovered in the soil when imidacloprid is applied as

technical product, whereas 2.90% of the total imidacloprid is present in the leachate. The presence of imidacloprid in the leachate was as expected according to its relatively high solubility in water (0.51 g L^{-1} at 20 °C) and the low value of K_{ow} (3.7), which means a potential mobility capacity in soil.

No imidacloprid was found in the leachate when this insecticide was applied as the IL50 [0.25−0.50] matrix.

Table 5. Parameter of the Henry Equation and Correlation Coefficients[a]

layer	K_d (L kg^{-1})	r
sand	0.10 (0.01)	0.988
peat	72.01 (4.54)	0.994
amended soil	0.42 (0.01)	0.997
native soil	3.42 (0.08)	0.998

[a] Standard errors shown in parentheses.

Table 6. Mean Values of Extracted Imidacloprid from the Soil Layers and Total Percentages of Imidacloprid Recovered from the Soil and Leachates[a]

layer	technical imidacloprid (mg kg^{-1})	IL50 [0.25−0.50] (mg kg^{-1})
sand	0.22 (0.02)	0.13 (0.01)
peat	92.50 (0.32)	59.25 (0.56)
amended soil (1)[b]	0.38 (0.03)	0.44 (0.04)
amended soil (2)	0.42 (0.02)	0.36 (0.07)
native soil (1)	12.29 (0.15)	
native soil (2)	2.33 (0.09)	
% imidacloprid recovered in soil	95.33	53.69
% imidacloprid recovered in leachate	2.90	

[a] Standard deviation of three replicates shown in parentheses.
[b] (1) and (2) represent the upper and lower fractions in amended and native soil.

In addition, the amount of imidacloprid recovered from the soil was less in the columns treated with these granules, reaching only the amended soil layer, indicating a less vertical distribution of the active ingredient.

The amount of imidacloprid recovered per kilogram is higher for the peat layer than for the rest of the soil layers. In all cases, the results obtained are in agreement with those discussed for the K_d parameter. Thus, the amount retained per kilogram increases in the same order as was indicated for K_d values, the order being

sand < amended soil < native soil ≪ peat

The release of imidacloprid from IL50 [0.25−0.50] granules in soil is much slower than that observed in water. The time taken for 50% of the active ingredient to be released in the flow-through system studies was 2.08 days, whereas the time necessary for release of 53.69% of imidacloprid in the soil was 8 days. This fact might be explained if we consider that an occlusion of the formulation surface by soil particles takes place, as well as a slower diffusion within the soil as compared to water (Ali and Wilkins, 1992; Wilkins, 1989). Soil water solutes may also retard movement of pesticides into the aqueous phase (Sharm et al., 1985).

Conclusions. The mix of imidacloprid and kraft lignin was appropriate to prepare a formulation of CR according to the close values of the solubility parameters. The release of imidacloprid from the various formulations into water has been shown to be diffusion controlled. The release rate of the active ingredient from CR granules under dynamic conditions is affected not only by the loading of imidacloprid but also, and to a greater extent, by the size of the granules. Mobility studies indicate that the use of the controlled-release lignin matrixes clearly reduces the vertical mobility of imidacloprid into the soil layer columns, the peat layer showing the highest sorption capacity. From these results, it could be inferred that the use of formulations such as those described in this paper would reduce the possibility of imidacloprid to reach and contaminate the groundwater resources.

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