



Sorption – desorption of imidacloprid insecticide on Indian soils of five different locations

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Abstract

Sorption-desorption processes govern the movement of all chemicals including pesticides in soils. The present investigation was undertaken to study the sorption-desorption of imidacloprid, using a batch method, on soils of five different location of India. Sorption data were fitted to Freundlich isotherm. The log K value was the highest for loam type soil (1.830) and the lowest for clay type soil (1.661). The value of $1/n$ was the maximum for silt loam soil (0.909) but minimum for loam soil (0.723). Simple correlation analysis indicated that among soil properties only electrical conductivity showed a higher but marginally non-significant negative correlation with log K ($r = -0.826$) indicating that higher concentration of solutes solutes are conducive to low sorption capacity of soil. The desorption data conformed to two surfaces Freundlich desorption isotherm. The values of $1/n_1'$ corresponding to easily desorbed fraction of imidacloprid showed significant negative correlation with soil pH ($r = -0.886$, significant at $p \leq 0.05$) but significant positive correlation with clay content ($r = 0.980$, significant at $p \leq 0.01$). The desorption index for easily desorbed fraction of imidacloprid (n_1'/n) also had significant negative correlation with soil pH ($r = 0.953$, significant at $p \leq 0.05$). From cumulative desorption data, it appeared that bioavailability of imidacloprid would be lower in neutral soil than acidic or alkaline soils.

Article Info

Received : 10.01.2013

Accepted : 30.04.2013

Keywords: sorption-desorption, imidacloprid, soil, loam, clay, Freundlich isotherm

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Introduction

Imidacloprid, [1-(6-chloro-3-pyridylmethyl)-N-nitroimidazolidin-2-ylidene amine] is a neonicotinoid group of a systemic insecticide, introduced by Bayer India Ltd. in 1993. It has a broad spectrum activity and low mammalian activity (Elbert et al., 1991) and a unique property of excellent translaminar activity. It is highly effective against a wide variety of sucking and chewing insects, termites and is also effective in controlling certain household pests in the public health and animal health sectors (www.main.co.il). Investigation of sorption phenomena of pesticides in soils is of great importance from environmental point of view as pesticide sorption affects processes like transport, degradation, volatilization, bioaccumulation, etc. which influence the final fate of the compounds in the soil environment (Gao et al., 1998). All these processes influence the extent of surface water and ground water contaminations too. Since, soils are a heterogeneous mixture of several components, many of which are organic and inorganic compounds of varying composition

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ISSN: 2147-4249

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and surface activity, they can bind pesticides and reduce their bioavailability (Torrents and Jayasundera, 1997).

Thus, knowledge of the pesticide sorption- desorption characteristics of soil is necessary for predicting their mobility and fate in soil environments and also to understand whether bioremediation is a feasible option for the cleanup of contaminated soil. Numerous studies have been reported on the strong relationship between total organic carbon in the soil and the mobility of pesticides. However, only a few studies are being conducted on sorption-desorption characteristics of pesticides from various soils though they are of fundamental importance to quantify the transport of pesticides and the selection of proper remediation technique. The importance of organic matter, particle size, as well as pH of the soil for sorption has been emphasized by many workers (Huang and Mckercher, 1984; Barriuso et al., 1992; Gao et al., 1998).

Sorption is mainly affected by the physical and chemical properties of the pesticide and soil (Koskinen and Harper, 1990). The objectives of present investigation were to determine the physico-chemical properties of soils in which studies have to be conducted, to study the kinetics of imidacloprid sorption in different soils and investigate the concentration dependant sorption-desorption characteristics of imidacloprid on soils of varying properties.

Material and Methods

Soil Characterization

Surface (0-15cm) soils samples were collected from five different locations of Uttarakhand and Uttar Pradesh states of India viz. Lohaghat (LOH 2 & LOH 5), Badaun (BD 2), Garh Mukteshwar (GM 1) and Rampur (RM 2). Soil properties were analyzed following the standard procedures outlined by Page (1982). General properties of soil samples are presented in Table 1.

Table 1. General properties of soil samples

Soils	Sand (%)	Silt (%)	Clay (%)	Textural class	pH (1:2)	E.C. (1:2, dS m ⁻¹)	Organic Carbon (g kg ⁻¹)
LOH 2	6.2	22.6	71.2	Clay	5.37	0.022	3.63
LOH 5	15.6	38.0	46.4	Clay	5.36	0.927	13.91
BD 2	38.1	36.0	25.9	Loam	8.71	0.228	5.94
GM 1	30.8	61.0	8.2	Silt loam	8.53	0.565	18.23
RM 2	55.1	22.0	22.9	Sandy clay loam	7.03	0.151	2.89

Pesticides and chemicals

High grade (purity 98.0%) imidacloprid was obtained from Aryan Chemical Sciences, Faridabad, Haryana (India). Other chemical reagents and solvents used were of HPLC grade procured from Merck and S.D. Fine-chemical Ltd., India.

Kinetics of Sorption

The experiment was carried out as per OECD guidelines (OECD). Two g of each type of characterized soil were taken separately in each centrifuge tube of capacity, 50 mL. Then 1 mL of 0.01M CaCl₂ solution was added to it. The volume in each tube was made to 20 mL by addition of double distilled water. Thereafter the suspensions were kept for shaking on mechanical shaker for different time intervals of 0.5, 2, 4, 6, 8, 12, 24, 36, 48 and 72 h. The suspensions were then centrifuged at 7000 rpm for 20 minutes. Imidacloprid was extracted for HPLC analysis as mentioned below.

Extraction and clean up of insecticide

Twenty mL of the supernatant of the soil solutions was taken in separating funnel and 20 mL of organic solvent dichloromethane was also added to it. The mixture was shaken vigorously and the layers were allowed to separate. The organic layer was collected and the process was repeated thrice. The pooled CH₂Cl₂ layer was passed through anhydrous sodium sulphate packed in the column to remove the water and evaporated to dryness on a rotatory evaporator at 40°C. The residue was dissolved in HPLC grade acetonitrile and filtered through 0.45µm Millipore prior to HPLC analysis.

Analysis of imidacloprid residue

The samples obtained after extraction and cleanup were subjected to HPLC analysis. The amount of residues was analyzed by Dionex Ultimate 3000, HPLC system equipped with the C-18 column (250×4.6mm), mobile

phase acetonitrile: water (60:40 v/v) at a flow rate of 0.5 mL/minute and a UV-VIS detector. Detection of imidacloprid was done at 270 nm. The retention time (R_t) of imidacloprid under the above conditions was 6.7 min.

A calibration curve was plotted between different concentrations of imidacloprid and peak area and the concentrations of imidacloprid in replicates of different samples were calculated with the help of the calibration curve.

The equilibrium time after complete analysis was found to be 24 h.

Sorption – desorption study

Sorption study was carried out by equilibrations of 2 g soil sample with 2, 4, 6, 8, 10, and 20 μg imidacloprid in 20 mL of 0.01 M CaCl_2 . The mixture was equilibrated for 24 h (equilibration time), centrifuged at 7000 rpm for 20 minutes. The clear supernatants were decanted in clear glass vials (20ml capacity) and the pesticide concentrations was determined after extraction and clean up by HPLC as mentioned above.

The desorption study of sorbed imidacloprid was carried out using the soil sample equilibrated with highest amount (20 μg) of imidacloprid in the sorption study. The soil samples were equilibrated with 20 mL of 0.01M CaCl_2 solution for 24 h (equilibration time) and centrifuged as described earlier. This process was repeated four times till imidacloprid amount in the supernatant could be detected. The supernatant collected at each desorption step was extracted and analysed as mentioned in the preceding paragraphs.

Recovery studies

The recoveries of imidacloprid from different soil samples were carried out at two concentrations (1 and 0.1 $\mu\text{g/g}$). The samples were extracted, cleaned up and analysed as per the procedure mentioned in earlier section. The percentage recovery varied from 86.2 to 93.6% (mean 89.9 ± 0.8) at 1 $\mu\text{g/g}$ and 80.4 to 88.8% (mean 84.6 ± 0.6) at 0.1 $\mu\text{g/g}$ fortification level. The LOQ and LOD were 0.05 and 0.02 $\mu\text{g/g}$ respectively.

Results and Discussion

Sorption of Imidacloprid

The sorption data of imidacloprid were fitted to Freundlich adsorption isotherm mathematically expressed as:

$$\log x/m = \log K + (1/n) \log C$$

where,

x is the quantity of imidacloprid sorbed, m is the mass of the adsorbent and C is the concentration of imidacloprid, K and n are empirical constants at a given temperature.

From the data presented in Fig. 1 it was apparent that clay soil LOH 2 sorbed higher amount of insecticide than the soil LOH 5; the former had higher clay content than the latter. In alkaline soils (GM 1 and BD 2), sorption of insecticide was higher in GM 1 than in soil BD 2. Soil GM 1 was less alkaline in nature but had high organic content carbon content than the soil BD 2. Thus the adsorption of imidacloprid was dependent both on clay and organic carbon content of the soil. The neutral soil RM 2, sorbed imidacloprid in an intermediate range. The sorption data of imidacloprid fitted well in Freundlich adsorption isotherm and the values of the coefficient of determination (R^2) varied from 0.875 to 0.949; all significant at $p \leq 0.05$ (Fig.2). The computed values of $\log K$ and $1/n$ are depicted in Table 2. The values of $\log K$ varied from 1.661 to 1.830 while that of $1/n$ ranged from 0.723 to 0.909. Amongst acidic soils, the soil LOH 2 had higher value of $1/n$ than the soil LOH 5 whereas, in alkaline soils, GM 1 had higher value of $1/n$ as compared to BD 2 soil. A higher value of $1/n$ indicated the involvement of sites of relatively higher bonding energy in the sorption process.

Table 2. Freundlich sorption parameters of imidacloprid in five Indian soils

Soil Samples	log K	1/n	R^2
LOH 2	1.806	0.817	0.875
LOH 5	1.661	0.791	0.945
BD 2	1.768	0.909	0.949
GM 1	1.800	0.738	0.888
RM 2	1.830	0.723	0.938

All R^2 values were significant at $p \leq 0.05$.

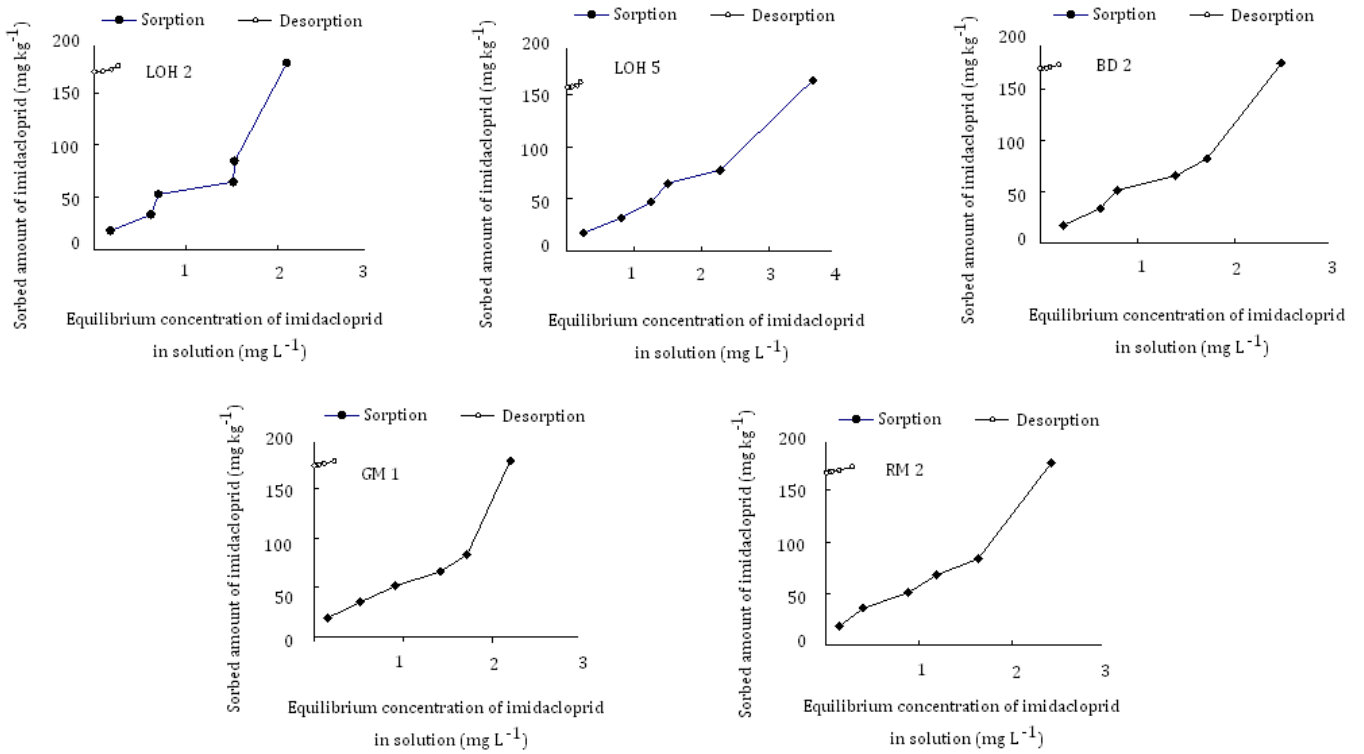


Figure 1. Sorption-desorption of imidacloprid in five Indian soils

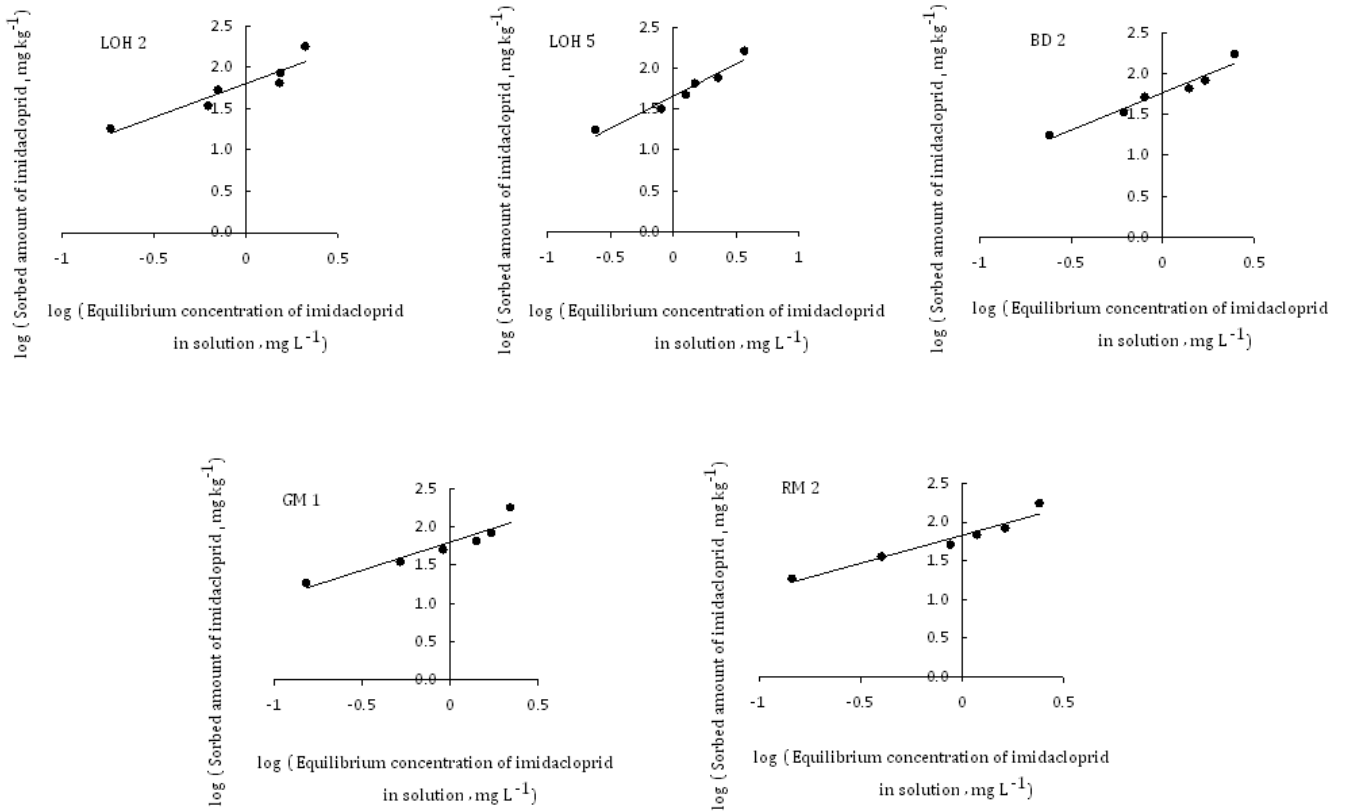


Figure 2. Freundlich sorption isotherms of imidacloprid in five Indian soils

Desorption study

The obtained desorption data were also fitted to Freundlich desorption isotherms model mentioned below.

$$\text{Log } x'/m = \log K' + (1/n') \log C'$$

where,

x' is the quantity of imidacloprid remaining sorbed on soil after desorption, m is the mass of the adsorbent and C' is the concentration of imidacloprid, K' and n' are empirical constants at a given temperature.

The distribution of points revealed at least two patterns of varying slope (Fig. 3), therefore, two surfaces Freundlich desorption model, one representing an initial easily desorption phase and the other subsequent relatively difficultly desorption phase. The computed values the relevant constants for one surface ($\log K'$ and $1/n'$) and two surfaces ($\log K_1'$, $1/n_1'$, $\log K_2'$ and $1/n_2'$) along with coefficients of determination are presented in Table 3.

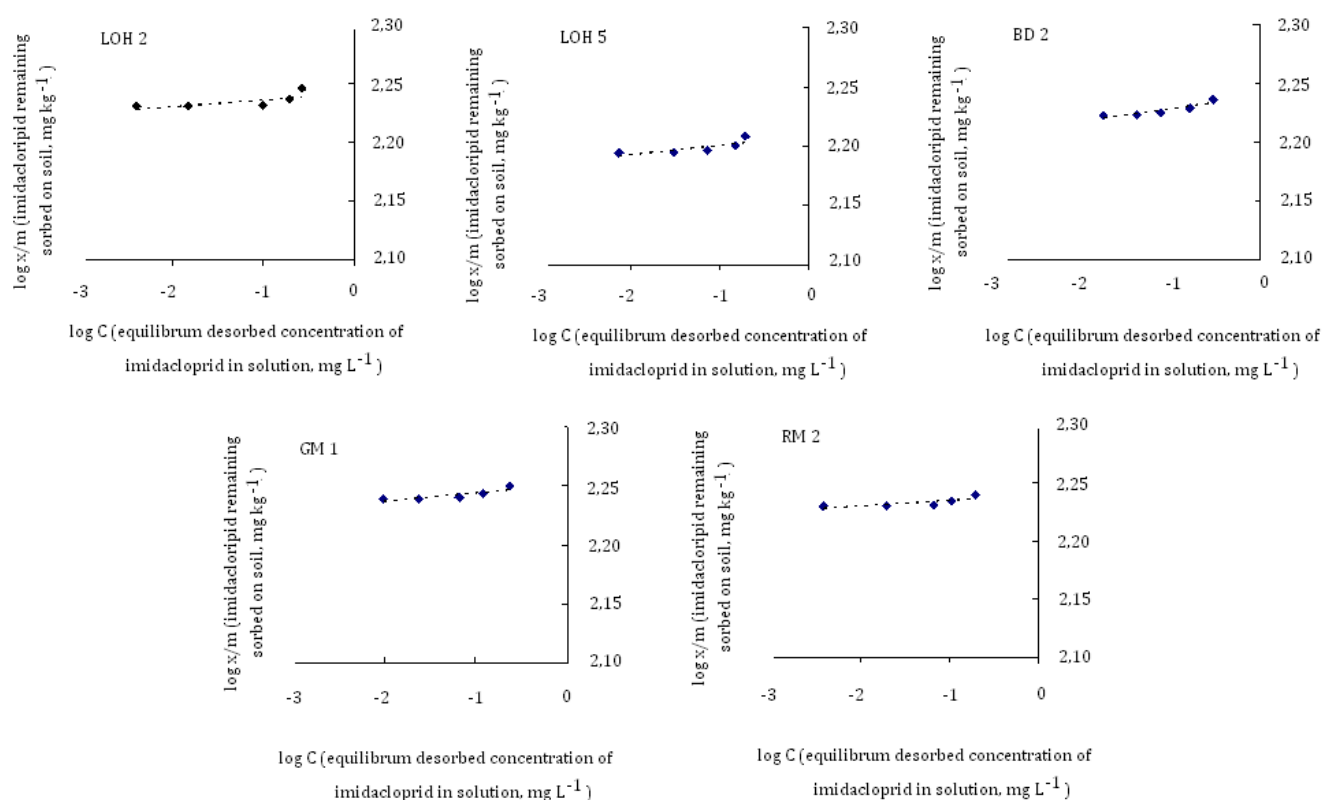


Figure 3. Freundlich desorption isotherms of imidacloprid in five Indian soils

Table 3. Single surface and two surfaces Freundlich desorption parameters, desorption indices (DI) and desorbed content of imidacloprid in five Indian soils.

Soil Samples	Single surface Freundlich Des. parameters				Two surfaces Freundlich Des. parameters								Desorption (mg/kg)		
	Log K'	$1/n'$	R^2	DI (n'/n)	Log K_1'	$1/n_1'$	R^2	DI (n_1'/n)	Log K_2'	$1/n_2'$	R^2	DI (n_2'/n)	Initial	Later	Total
LOH 2	2.242	0.006	0.527	143.4	2.262	0.031	0.853	26.0	2.232	0.001	0.952	1135.6	11.21	0.38	11.59
LOH 5	2.209	0.008	0.615	98.9	2.24	0.025	0.806	31.6	2.198	0.002	0.790	405.7	8.24	0.75	8.99
BD 2	2.239	0.010	0.826	90.1	2.245	0.018	0.928	51.0	2.229	0.004	0.899	240.0	10.04	1.01	11.05
GM 1	2.252	0.007	0.774	101.2	2.260	0.017	0.982	43.7	2.243	0.002	0.961	356.7	8.44	0.68	9.12
RM 2	2.24	0.005	0.624	147.6	2.254	0.019	0.998	38.5	2.233	0.001	0.808	769.3	7.41	0.48	7.88

The desorption data of imidacloprid conformed well to two surfaces Freundlich desorption isotherms as the values of R^2 varied from 0.527 to 0.826 for single surface isotherm and from 0.853 to 0.998 for two surfaces

isotherm. The values of $\log K'$ and $1/n'$ (single surface model) varied from 2.209 (Loh 5) to 2.252 (GM1) and from 0.005 (RM2) to 0.010 (BD20), respectively. With two surface Freundlich desorption isotherm, the values of $\log K_1'$ and $1/n_1'$ (initial easily desorbed phase) ranged from 2.224 (Loh 5) to 2.262 (Loh2) and from 0.017 (GM1) to 0.031 (Loh2), respectively. The values of $\log K_2'$ and $1/n_2'$ (subsequent difficultly desorbed phase) ranged from 2.198 (Loh 5) to 2.243 (GM1) and from 0.001 (Loh 2 and RM 2) to 0.004 (BD 2), respectively. Initial easily desorbed quantity of imidacloprid varied from 7.41 (RM 2) to 11.21 (Loh 2) mg L⁻¹ while the subsequent difficultly desorbed quantity varied from 0.38 (Loh 2) to 1.01 (BD 2) mg L⁻¹. This indicated that the bioavailability of imidacloprid was likely to be lower in neutral soil as compared to acidic or alkaline soil.

Desorption Index

The computed values of desorption index (n'/n for single surface) varied from 90.1 (BD 2) to 147.6 (RM 2) and that of two surfaces isotherm (n_1'/n for initial easily desorbed imidacloprid) varied from 26.0 (LOH 2) to 51.0 (BD 2). The desorption index value for subsequent difficultly desorbed fraction (n_2'/n) of imidacloprid ranged between 240.0 (BD 2) to 1135.6 (LOH 2). In general, higher values of desorption index (>1) in all the soils indicated poor reversibility of adsorbed imidacloprid insecticide with negligible chances for groundwater pollution through leaching.

Relationships of sorption and desorption parameters with general soil properties

Simple correlation analysis was also done between sorption-desorption parameters of imidacloprid and general properties of soils and the simple correlation coefficients (r) are presented in Table 4. In general, simple correlation coefficients computed between general soil properties and Freundlich isotherm parameters ($\log K$ and $1/n$) were statistically not significant. However, the adsorption capacity of soil ($\log K$) for imidacloprid showed a marginally non-significant yet a high correlation with electrical conductivity of soils signifying that the presence soluble solutes in soil reduced the adsorption capacity of soil for imidacloprid. The order of desorption for the initial easily desorbed fraction of imidacloprid ($1/n_1'$) had a significant negative correlation with pH ($r = -0.886$, significant at $p \leq 0.05$) but positive correlation with clay content ($r = 0.980$, significant at $p \leq 0.01$). The desorption index (n_1'/n) for the initial easily desorbed fraction of imidacloprid also had a significant positive correlation with soil pH ($r = 0.953$, significant at $p \leq 0.05$).

Table 4. Simple correlation coefficients (r) between soil properties and Freundlich sorption-desorption isotherm parameters, desorption index of imidacloprid ** $P < 0.01$, * $P < 0.05$

Freundlich parameters		Soil Properties					
		Sand %	Silt %	Clay %	pH	EC	Organic C
Sorption	$\log K$	0.440	-0.187	-0.223	0.380	-0.826	-0.449
	$1/n$	-0.247	-0.155	0.294	0.157	-0.201	-0.287
Desorption (single surface)	$\log K'$	0.331	0.190	-0.383	0.608	-0.654	-0.128
	$1/n_1'$	-0.106	0.357	-0.148	0.404	0.322	0.256
	D.I.	0.079	-0.708	0.397	-0.469	-0.635	-0.654
Desorption (two surfaces)	$\log K_1'$	0.129	-0.020	-0.088	0.297	-0.743	-0.260
	$1/n_1'$	-0.815	-0.527	0.980**	-0.886*	-0.140	-0.306
	$\log K_2'$	0.366	0.177	-0.402	0.608	-0.655	-0.139
	$1/n_2'$	0.159	0.353	-0.353	0.629	0.158	0.161
	D.I. ₁ (n_1'/n)	0.664	0.455	-0.815	0.953*	-0.019	0.159
	D.I. ₂ (n_2'/n)	-0.316	-0.688	0.694	-0.642	-0.607	-0.602

Discussion

The present investigation were undertaken to study the sorption-desorption phenomenon of imidacloprid in five Indian soils differing in physiochemical properties. Cox et al., (1998) also conducted a study on sorption-desorption of imidacloprid using the batch equilibration method with seven U.S. soils varying in their physicochemical properties. They observed that sorption coefficients K_f and soil properties like organic carbon and CEC gave the higher simple correlation coefficients, due to positive correlation between organic carbon (OC) and cation exchange capacity (CEC). In the present study, electrical conductivity (EC) was the only factor which appeared to influence the adsorption capacity of soil for imidacloprid. Ramakrishnan et al., (2000) also found that the soil properties such as organic matter content, silt and clay proportions, pH, and cation exchange capacity (CEC) affect the bioavailability of imidacloprid on termite feeding. Liu et al., (2002)

reported that soil organic matter and clay minerals are responsible for the adsorption of many pesticides. In the present study, soil LOH 2 having the highest clay content sorbed higher amount of imidacloprid than the soil LOH 5 which had lower clay content but high organic C content. The mechanism may be through either competition between the dissolved organic carbon and the imidacloprid for sorption sites in the soil or from interactions between imidacloprid and the organic carbon in solution. Flores-Céspedes et al., (2002) also reported that the imidacloprid's binding to soil decreased in the presence of dissolved organic carbon in calcareous soil. Fernandez-Bayo et al. (2007) found that desorption of imidacloprid from soil was slower for the soil with the higher OC and clay content.

Thus the sorption of imidacloprid by soils conformed to Freundlich adsorption isotherm while the desorption could be better accounted by two surfaces Freundlich desorption isotherm. Higher clay content was conducive to higher sorption of imidacloprid while high content of soluble solutes decreased sorption. Based desorbed content of imidacloprid in different soils the bioavailability of imidacloprid appeared to be lower in neutral soil as compared to acidic or alkaline soils. Owing to higher values of desorption index in different soils, there appears to be negligible possibility of groundwater pollution due to leaching of imidacloprid.

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