



Adsorption and desorption characteristics of lindane, carbofuran and methyl parathion on various Indian soils

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ABSTRACT

Adsorption and desorption characteristics of three insecticides on four Indian soils were studied. Insecticides used were representative of organochlorine, organophosphate, and carbamate groups. The order of adsorption of pesticides on soils was: lindane > methyl parathion > carbofuran. Compost soil had shown the maximum adsorption capacity. The order of adsorption capacity of various soils were: compost soil > clayey soil > red soil > sandy soil. Adsorption isotherms were better fitted to Freundlich model and K_f values increased with increase in organic matter content of the soils. Thermodynamic parameters indicated favorable adsorption of all the three pesticides in four different soils. Adsorption was exothermic in nature. Distilled water desorbed 30–60% of adsorbed pesticides whereas; organic solvents were able to affect 50–80% of sorbed pesticides. Clay content and organic matter played a significant role in pesticide adsorption and desorption processes. Hysteresis effect was observed in red, clayey and compost soils. Hysteresis effect increased with increase in organic matter and clay content of the soils.

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1. Introduction

Increasing use of pesticides in agriculture and domestic activities for controlling pests is polluting the environment day by day [1]. The contamination of soils, groundwater and surface water by pesticide is currently a significant concern through out the world because these compounds are detrimental to both human life and environment [2]. Toxicity of parent pesticides and their degradation products is making these chemical substances a potential hazard. When these pesticides are introduced into the environment through spraying on crops, droplets of pesticides fall on soil, plant and water. While some part of these chemicals stays in the area where it is applied, major part gets transported to various environmental compartments [3]. The adsorption/desorption phenomena of pesticides in soils are of great importance from environmental point of view. Pesticide sorption affects other processes like transport, degradation, volatilization and bioaccumulation, which influence the final fate of these compounds in the soil [4,5].

Plenty of literatures are available regarding the strong relationship between total organic carbon and the mobility of pesticides in the soil. Calderbank [6] reported that physical and chemical characteristics of the soil influence the rate of adsorption and leach-

ing of carbofuran. The adsorption characteristics of carbamates in different soils were studied by Lalah and Wandiga [7]. They have reported that organic matter and clay content influenced the adsorption/desorption process significantly. Kumar and Philip [5] reported that adsorption of endosulfan was more in clayey soils followed by red soil and composted soil. However, the adsorption was insignificant in sandy soil.

Desorption process of pesticides is also important since it determines the release rate and potential mobility of pesticides in soil [8]. Adsorption and desorption of atrazine in various Indian soils was studied by Raman et al. [9]. They have reported that adsorption and desorption isotherms followed Freundlich equation. In case of lindane adsorption, Van der Waals forces and hydrogen bonding were considered as the most probable adsorption mechanisms [10]. Adsorption of insecticides by soils and lake sediments has been shown to vary with type of insecticide, pH, temperature, clay and organic matter content [11]. Yazgan et al. [12] studied the sorption behavior of carbofuran and imidacloprid in batch and centrifugation method and reported that batch method over-estimate sorption in comparison to the centrifugation method.

Among all pesticides, lindane (1 α ,2 α ,3 β ,4 α ,5 α ,6 β -hexachloro-cyclohexane), an organo chlorine compound; methyl parathion (O,O-dimethyl-O-4-nitrophenyl phosphorothioate), an organo phosphate chemical; and carbofuran (2,3-dihydro-2,2-dimethylbenzofuran-7-yl methylcarbamate), a carbamate group pesticides are most commonly used in India. Consumption of these pesticides in India, in various sectors, is presented in Table 1 [13].

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Table 1
Consumption of various pesticides (tones technical grade) in India

Pesticide	2000–2001	2001–2002	2002–2003	2003–2004
Endosulfan	8500	8500	3700	3100
Lindane	600	500	300	200
Methyl parathion	2000	2200	1900	1600

Source: Department of Chemicals & Petrochemicals (India), Annual Report 2002–2003 and <http://www.ncipm.org.in/databases.html>.

Though the production of lindane in India is reduced as compared to its earlier production, India is the highest lindane contaminated country in the world [14,15].

Though many works have been carried out on adsorption of lindane, methyl parathion and carbofuran on various Indian soils individually and under various conditions, only limited work has been carried out to understand the desorption characteristics of these pesticides on various Indian soils [1,9,16]. Moreover, various adsorption studies were conducted under different experimental conditions which make the comparison of adsorption behavior difficult.

The aim of the present work was to evaluate the adsorption and desorption characteristics of various groups of pesticides on different Indian soils. These studies were carried out using different soils having various concentrations of organic matter, clay minerals, and humic substances. An attempt was also made to delineate the mechanism of adsorption and desorption of these pesticides on the selected soils. This work is a part of pesticide contaminated soil remediation study.

2. Materials and methods

2.1. Soil characterization

Four commonly found soils in India were used for the present study. All soils, except sandy soil, were collected from agricultural fields of various parts of Tamilnadu, India. Sandy soil was collected from a riverbed and was washed before using it for experiments. The soil pH was measured using a direct reading type pH meter with glass electrode and a calomel reference electrode (Eutech, Singapore). The specific gravity was determined by pycnometer method [17]. The electrical conductivity was measured using conductivity meter (Eutech, Singapore). Total soluble solids were estimated from electrical conductivity [18]. The organic matter content of the soil was determined by chromic acid method [19]. All the soils were sterilized before starting the experiment in order to avoid any biodegradation of applied pesticides.

The soils were identified and classified based on sieve analysis and Atterbergs limit analysis as clayey soil (CL—lean clay with sand), red soil (GM—silty gravel with sand), compost soil (PT—peat) and sandy soil (SM—silty sand with gravel) as per American Society for Testing and Materials (ASTM) standards. The characteristics of different soils employed in the present study are given in Table 2. Similar soils were used for our earlier studies also [5]. The red soil is also classified as red loam. *Luvisol* is the other name of this type of soils. Clayey soil comes under the classification of black soils. These soils are also called as *Vertisols*. Compost soils are a mixture of red and alluvial soils. These soils are also called as *Histosols* soils [20,21].

2.2. Pesticides and chemicals

High grade (purity 99.7%) lindane, methyl parathion and carbofuran were purchased from Occua Standards, USA. Technical grade lindane and methyl parathion were supplied by Tamilnadu Pollution Control Board (TNPCB), Chennai, India. Commercial grade

carbofuran (carbofuran 3G) was purchased from the local market. Stock solutions of lindane (1%) in ethanol, methyl parathion (1%) in acetone and carbofuran (300 mg/L) in distilled water were prepared. Other chemical reagents and solvents used were of HPLC grade procured from Ranbaxy, India.

2.3. Adsorption experiments

2.3.1. Kinetic study

Five grams of sterilized soil (<2 mm size) samples were added to 250 mL conical flasks containing 100 mL of solution having 100 mg/L of lindane, methyl parathion or carbofuran. All studies were conducted in duplicate. The reaction mixture was kept in an orbital shaker at 150 rpm for a period of 24 h at room temperature (28 °C). From the flasks, 5 mL of samples were collected at pre-determined time intervals of 0.25, 0.5, 0.75, 1, 2, 4, 6, 8, 10, 12, 16, 20 and 24 h. Collected samples of lindane and methyl parathion were extracted with different organic solvents. Extracted samples were filtered through anhydrous sodium sulfate to remove the moisture content and were analyzed for residual pesticide concentrations [22].

2.3.2. Equilibrium studies

Adsorption equilibrium studies were conducted for all the four soils with an adsorbent quantity of 5 g with respective pesticide concentrations of 1, 2, 5, 10, 20, 50, 100, 200 and 500 mg/L in identical conical flasks of 250 mL capacity containing 100 mL solution. A blank was also maintained to assure the quality control of the experiments. After the addition of soil samples, the reaction mixtures were agitated in an orbital shaker at 150 rpm at 28 °C until the equilibrium was established (based on kinetic study, 10 h for lindane, 8 h for methyl parathion and 6 h for carbofuran). After the desired time, 5 mL of sample was collected from each conical flask, centrifuged at 9600 rpm for 4 min and the supernatant was extracted, filtered through anhydrous sodium sulfate to remove moisture content and was analyzed for residual pesticide concentrations.

2.4. Desorption experiments

2.4.1. Kinetic study

Desorption kinetic study was conducted for lindane, methyl parathion and carbofuran adsorbed on various soils. For this, adsorption kinetic study was conducted as described earlier. When the system reached equilibrium, supernatant liquid was decanted and the adsorbents were washed twice with tap water. Washed adsorbents were used for the desorption study. Decanted supernatant was replaced with equal volume of eluents like distilled water and a solvent (15%, v/v of ethanol for lindane; 15%, v/v acetone for methyl parathion and 15%, v/v acetonitrile for carbofuran) [23]. The reaction mixture was kept in an orbital shaker at 150 rpm for a period of 24 h at room temperature (28 °C). From the flasks, 5 mL samples were collected at pre-determined time intervals of 0.25, 0.5, 0.75, 1, 2, 4, 6, 8, 10, 12, 16, 20 and 24 h. Collected samples of lindane and methyl parathion were extracted with different organic solvents. Extracted samples were filtered through anhydrous sodium sulfate to remove moisture content and were analyzed for residual pesticide concentrations

2.4.2. Equilibrium studies

Adsorption equilibrium study was conducted as described earlier. Once the system reached equilibrium, the supernatant liquid was decanted and the adsorbents were washed twice with tap water. The washed adsorbents were used for desorption equilibrium study. Decanted supernatant was replaced with equal volume of eluents like distilled water and a solvent (15%, v/v of ethanol

Table 2
Soil characterization/properties

Soil	Parameter							
	pH value	Total dissolved solids (mg/L)	Electrical conductivity ($\mu\text{mhos/cm}$)	% clay content	% organic matter	CEC (mequiv./100 g)	% organic humic substance	Fe (mg/L)
Sandy soil	8.48	212.2	330	0.2	0.575	0	0	–
Red soil	7.2	33.92	53	7.6	4.13	4.1	0.9	25
Clayey soil	8.46	299.52	468	56	3.29	48	0.2	16
Compost soil	7.37	76.8	120	3.6	9.51	2.3	2.1	21

for lindane; 15%, v/v acetone for methyl parathion and 15%, v/v acetonitrile for carbofuran). The reaction mixtures were agitated in an orbital shaker at 150 rpm at 28 °C until the equilibrium was established. After the desired time (10 h for lindane, 8 h for methyl parathion, and 6 h for carbofuran), 5 mL of sample was collected from each conical flask, centrifuged at 9600 rpm for 4 min and the supernatant was extracted, filtered through anhydrous sodium sulfate to remove moisture content and was analyzed for residual pesticide concentrations.

2.5. Effect of pH on adsorption of pesticides

The initial pH of red soil was in the range of 8.4 and it was adjusted to pH 2, 5, 8 and 10 with concentrated hydrochloric acid (HCl) and sodium hydroxide (NaOH). Five grams of acid- and alkali-treated red soil sample at various pHs was used for kinetic study. Adsorption kinetic study was conducted with an initial concentration of 10 mg/L of each pesticide. The supernatant was decanted and replaced with equal volume of distilled water with pH values of 2, 5, 8 and 10 (adjusted using HCl/NaOH) and desorption kinetic study was conducted as described earlier.

2.6. Analytical methods

2.6.1. Extraction of pesticides

Aliquots of 5 mL of homogenized liquid samples were collected at different time intervals and centrifuged at 9600 rpm for 4 min and supernatant sample of 4 mL was transferred to a 15 mL volumetric tube and mixed with 4 mL of 1:1 hexane–acetone solution [24]. The tubes were sealed and shaken for 10 min in vortex mixture in order to transfer of pesticides and waited for 5 min until the clear organic phase was separated from the liquid phase. The average extraction efficiencies (%) were of 89.4 ± 3.8 , and 91.8 ± 1.8 , for lindane and methyl parathion, respectively. Carbofuran was injected directly to the HPLC along with water.

2.6.2. Analysis of lindane and methyl parathion

Samples of lindane and methyl parathion were analyzed using PerkinElmer Clarus 500 gas chromatograph with electron capture detector (GC-ECD) and nitrogen phosphorus detectors (GC-NPD), respectively. GC was equipped with an auto sampler, an on-column, split/split less capillary injection system, and a capillary column (PerkinElmer (PE)-35, 30 m \times 0.53 mm \times 0.5 mm film thickness). During the analysis, the column was held initially at a temperature of 130 °C for 1 min, then the temperature was raised at a rate of 10 °C/min to 200 °C and held at 200 °C for 11 min. The temperature of injector and detector were maintained at 250 and 290 °C, respectively. Nitrogen was used as the make-up and carrier gas at a flow rate of 60 and 0.85 mL/min, respectively. The injections were made in the split mode with a split ratio of 1:20. The retention time for lindane, under these conditions, was 16.0 min.

During the analysis of methyl parathion, the column temperature was initially kept at 90 °C for 1 min then raised at a rate of 10 °C/min to 180 °C and held at 180 °C for 5 min. The temperature

of injector and detector were maintained at 200 and 290 °C, respectively. A mixture of hydrogen and air (ratio of 2:100) was used as the make up gas and helium was used as the carrier gas at a flow rate of 0.85 mL/min, respectively. The injections were made in the split mode with a split ratio of 1:20. Under these conditions, the retention time for methyl parathion was 4.75 min.

2.6.3. Analysis of carbofuran

Samples of carbofuran were analyzed using high pressure liquid chromatography (HPLC) (Jasco, UK) with UV detector (MD 2010, PDA) equipped with packed column (Agilent C18) of 15 cm length with a pore size of 5 μm . Operating conditions were as follows: mobile phase was a mixture of water and acetonitrile (at a ratio of 60:40) and a flow rate of 1 mL/min. was maintained throughout the run. Under these conditions, the retention time for carbofuran was 14.81 min.

2.6.4. Humic substance

Humic substance in the soil fraction was extracted by sodium extraction method as suggested by Stevenson [25]. One gram of soil was dissolved in 5 mL of 0.5N of NaOH and mixed thoroughly and the supernatant was filtered. The filtered samples of humic substance were analyzed using HPLC. During the analysis of humic substance, mobile phase was a mixture of water and acetonitrile (at a ratio of 70:30) and a flow rate of 1 mL/min was maintained throughout the run. Under these conditions, the retention time for carbofuran was 1.74 min.

3. Results and discussion

The prediction of sorption rate gives important information about the availability of pesticides in the liquid phase. The transport and transformation of pesticides depends on this concentration. Information on the kinetics of pesticide sorption is required for selecting optimum operating conditions and design parameters for full-scale remediation system. Nature of the sorption processes depends on physical and chemical characteristics of the adsorbent as well as the characteristics of the system.

3.1. Adsorption kinetic study

Kinetics of adsorption of lindane, methyl parathion and carbofuran on four Indian soils were studied and the results are presented in Fig. 1a–c. The adsorption kinetics exhibited two distinct stages, a very rapid adsorption in the initial stages (within 1 h) followed by a slow adsorption. The pseudo-equilibrium was reached within 10 h for lindane, 8 h in case of methyl parathion and 6 h in case of carbofuran in compost soils. However, in sandy soils the pseudo-equilibrium was reached within 2 h for all three pesticides. Similar trend was observed while studying the adsorption characteristics of endosulfan [5], lindane [26], and carbofuran [27] in different soils.

More than 70% of lindane was adsorbed on compost and clayey soil within 1 h whereas, the adsorption of lindane on sandy soil was only 35%. Lindane is more hydrophobic as compared to methyl

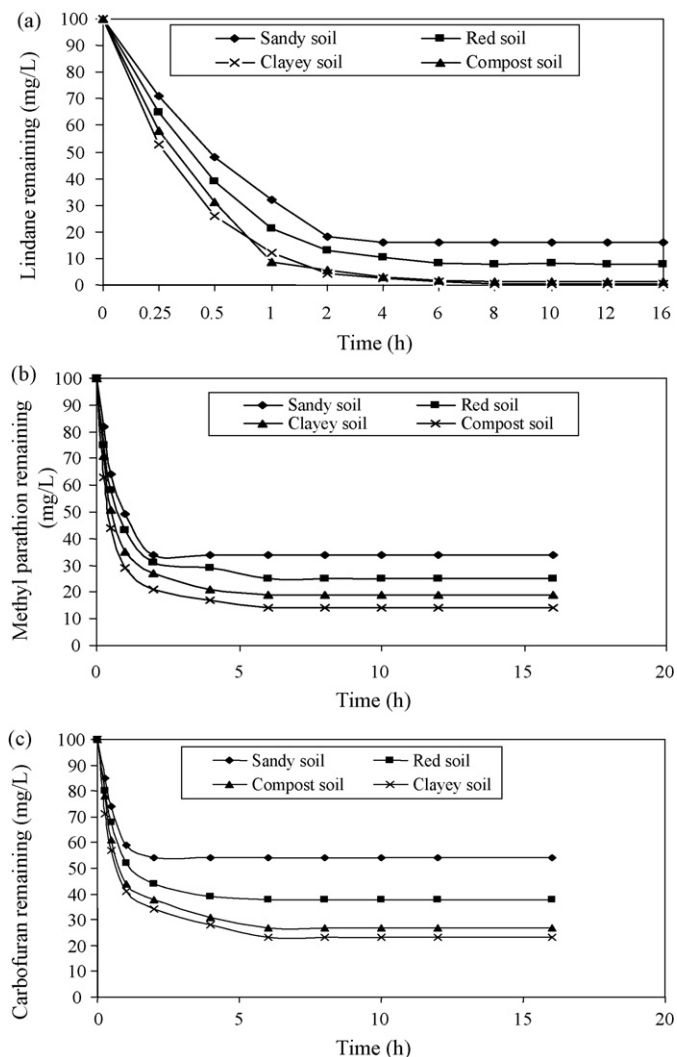


Fig. 1. Adsorption kinetics of (a) lindane, (b) methyl parathion and (c) carbofuran on various Indian soils.

parathion and carbofuran. Lindane must have occupied the available surface sites at a faster rate and migration and diffusion of lindane molecules to other sites must have taken a long time as reported by other researchers [4,28]. The equilibrium time was decreased as the hydrophilicity increased. From these results, it can be inferred that the contribution of rapid adsorption (surface phenomena) is more significant as compared to the slow/long-term sorption. This is important information for the remediation studies involving these pesticides. A control was maintained in all the adsorption studies to account for the loss due to volatilization. The concentration variation in the blank with respect to time was insignificant (<1%) in all the cases.

In order to find out the mechanism involved in the sorption process, several researchers used different kinetic models such as Lagergren pseudo-first-order model [29] and Ho's pseudo-second-order reaction rate models [30]

$$\log(q_e - q_t) = \log q_e - k_t \quad (1)$$

$$\frac{1}{q_t} = \frac{1}{h} + \frac{1}{q_t} t \quad (2)$$

where q_e is the amount of adsorbate sorbed at equilibrium; q_t is the amount of adsorbate sorbed on the surface of the sorbent at time, t ; k is the rate constant of sorption; t is the time and $h = kq^2$.

In the present study, applicability of the pseudo-first-order and pseudo-second-order model has been tested for the sorption of different pesticides on various soils. The best-fit model was selected based on the linear regression correlation coefficient (r^2 values).

However, neither of the models fitted the experimental results well. Hence, the data were fitted for intra-particle diffusion model by plotting square root of time ($t^{1/2}$) versus equilibrium concentration (q_e) to predict the intra-particle diffusion effect on adsorption. The rate of adsorption was calculated as the slope of the tangent drawn from the origin. The calculated rate constants for lindane varied from 0.4355 to 1.2375 $\text{mg g}^{-1} \text{h}^{-1/2}$, for methyl parathion, it varied from 0.4069 to 0.9971 $\text{mg g}^{-1} \text{h}^{-1/2}$ and for carbofuran the rate constant values varied between 0.2552 and 0.9266 $\text{mg g}^{-1} \text{h}^{-1/2}$. The kinetic rate constants for different soils are given in Table 3. Irrespective of the pesticide, the diffusion rate constant was high for compost soil followed by clayey soil.

3.2. Adsorption equilibrium study

Adsorption isotherm studies were conducted at 28 °C for lindane, methyl parathion and carbofuran using different soils. Langmuir (equation (3)) and Freundlich (equation (4)) isotherm models were used to calculate the isotherm constants and maximum adsorption capacity of different pesticides on various soils.

$$\frac{x}{m} = \frac{q_{\max} b C_e}{1 + b C_e} \quad (3)$$

$$\frac{x}{m} = K_f C_e^{1/n} \quad (4)$$

where x/m is adsorbed amount (mg/g), C_e is the equilibrium concentration (mg/L), K_f is the Freundlich constant, n represents energy distribution of sorption sites. q_{\max} (mg/g) maximum adsorption capacity of the adsorbent, and b is Langmuir constant. Adsorption isotherms for the soils are presented in Fig. 2a–c. Shape of adsorption isotherms is an important characteristic, because it provides information about the adsorption mechanisms [31]. Adsorption isotherms for carbofuran and methyl parathion were of S-shape on sandy and clayey soil with a slight concavity in the initial stage of adsorption. It may be due to a marked localization of the forces of attraction over the carbonyl group of carbofuran and phosphate group of methyl parathion leading to an interaction with soil cations. S-shape is a common feature for the adsorption of organic chemicals (OCs) on soils with low organic matter or clay contents [9]. C-shape was observed for equilibrium curves for methyl parathion and carbofuran on red soil and compost soil whereas; lindane isotherms followed L-shape for all the soils. L-shape corresponds to a constant partition of the solute between bulk solution and the adsorbent. Similar type of results was reported by Chiou et al. [32], while studying the adsorption behavior of chlorinated organic compounds on soils. The correlation coefficient values (r^2) show that the data fitted well with Freundlich isotherm model ($r^2 > 0.97$) than Langmuir model ($r^2 > 0.88$). These results are presented in Table 4. The maximum adsorption capacity of lindane, methyl parathion and carbofuran was exhibited by compost soil followed by clayey soil. Sandy soil showed the least adsorption for all the three pesticides. Among the three pesticides studied, maximum adsorption (48.42 mg/g) occurred for lindane on compost soil. The organic matter content of compost soil was much higher as compared to other soils. This must be the reason for high adsorption capacity of compost soil.

In the present study, K_f value increased with increase in the organic matter content and highest adsorption was observed on compost soil. When Freundlich constant n is close to 1, adsorption would be linearly proportional to equilibrium solution concentration and this value would be used as distribution coefficient K_f . In

Table 3
Kinetic rate constants of adsorption and desorption of lindane, methyl parathion and carbofuran on four soils

Pesticide	Soil type	Adsorption rate constants		Desorption rate constants	
		mg g ⁻¹ h ^{-1/2}	r ²	mg g ⁻¹ h ^{-1/2}	r ²
Lindane	Sandy soil	0.435 ± 0.015	0.877	0.604 ± 0.025	0.943
	Red soil	0.761 ± 0.005	0.893	0.5105 ± 0.02	0.998
	Clayey soil	1.0139 ± 0.01	0.965	0.4162 ± 0.01	0.943
	Compost soil	1.237 ± 0.025	0.973	0.255 ± 0.015	0.876
Methyl parathion	Sandy soil	0.4069 ± 0.01	0.998	0.7990 ± 0.02	0.96
	Red soil	0.5331 ± 0.02	0.98	0.557 ± 0.015	0.922
	Clayey soil	0.8139 ± 0.02	0.998	0.3495 ± 0.02	0.96
	Compost soil	0.997 ± 0.025	0.999	0.2163 ± 0.01	0.927
Carbofuran	Sandy soil	0.255 ± 0.005	0.943	0.8871 ± 0.03	0.943
	Red soil	0.5105 ± 0.01	0.943	0.842 ± 0.025	0.82
	Clayey soil	0.765 ± 0.015	0.943	0.5212 ± 0.01	0.908
	Compost soil	0.9266 ± 0.02	0.976	0.2808 ± 0.02	0.98

the present study, it was observed that the n values varied from 0.93 to 0.99 for various soils. Calvet [31] observed that low values of n are frequently associated with a high soil organic matter content. Similar trend was observed in the present study also.

3.3. Effect of soluble organic content

The ratio of humic substance to organic matter plays a major role in the adsorption and desorption of pesticides. As this ratio increases, the binding nature of the soil also increases. Out of 9.52% of organic matter in the compost soil, 2.18% was humic substance. For soils that have higher organic matter (>5%), the mobility of the pesticides has been related to the total organic matter content [33]. Red soil contained 4.13% of total organic matter out of which 0.9% was humic substance. Except organic matter, other parameters were almost the same in red soil and compost soils. The organic matter content as well as the ratio between humic substances and organic matter was less in red soils as compared to compost soil. This might be the reason for the less adsorption of pesticides on red soil. Similar type of results were observed in the adsorption of 2,4-D and isoproturon by Spark and Swift [34]. Not only the organic matter content, but also the nature of the organic matter (humic substance) plays a significant role in pesticide adsorption [35]. However, in clayey soil, the total organic and humic fraction were 3.29 and 0.2%, respectively. For soils, which have low organic matter contents (<5%), the mobility of the pesticide is often related to the active components of the inorganic fraction, which is predominantly the clay-sized fraction [33]. An increase in the clay content results in decreasing mobility of the pesticide. The mobility of pesticides also depends on the

composition of clay and the nature of the major cations in the soil solution [36]. High clay content also increases the adsorption capacity due to the availability of large surface area/surface charge. On percentage wise (w/w), organic matter seems to have high affinity to pesticides as compared to clay. Though clay content in red soil (7.6%) was almost double that of compost soil (3.6%), the adsorption of pesticides was more in compost soil. K_{OM} values of these three pesticides on various soils were given in Table 5.

$$K_{OM} = \left(\frac{K_f}{\%OM} \right) \times 100 \quad (5)$$

From the experimental data it was observed that K_{OM} of compost soil was higher than that for other three soils. A direct correlation between adsorption capacity and K_{OM} values were observed. The K_{OM} values of various soils for different pesticides followed the order, K_{OM} compost > K_{OM} clayey > K_{OM} red > K_{OM} sandy soils. K_{OM} value for compost soil (509) was higher than that for other soils and maximum K_{OM} value was observed for lindane. Pesticides with low K_{OM} value below 500 are considered as mobile with respect to leaching [37]. According to the K_{OM} values obtained in the present study, carbofuran and methyl parathion are mobile and have potential to contaminate the ground water in sandy and red soils.

The change in the partial molar free energy, ΔG° as a result of adsorption process, was calculated from the thermodynamic relationship:

$$\Delta G^\circ = -RT \ln K_{OM} \quad (6)$$

where ΔG° is free energy change (kcal/mole), R is gas constant (1.986 cal/K mole) and T is the absolute temperature. The value of ΔG° may be used as a measure of the extent of the driving force of the reaction. The greater the absolute magnitude of ΔG° value,

Table 4
The adsorption isotherm constants of pesticides on different soils by Langmuir and Freundlich models

Pesticide	Soil type	Langmuir constants			Freundlich constants		
		q_{max} (mg g ⁻¹)	b	R^2	K_f (mg g ⁻¹)	n	R^2
Lindane	Sandy soil	1.2 ± 0.8	0.059	0.845	1.41 ± 1.2	1.12	0.93
	Red soil	4.22 ± 1.1	0.046	0.836	12.43 ± 1.5	1.04	0.98
	Clayey soil	11.1 ± 2.4	0.034	0.877	15.89 ± 2.1	0.99	0.98
	Compost soil	23.4 ± 1.8	0.04	0.875	48.42 ± 1.8	0.98	0.98
Methyl parathion	Sandy soil	0.84 ± 0.2	0.031	0.873	1.15 ± 1.12	1.1	0.97
	Red soil	2.28 ± 0.55	0.046	0.868	8.61 ± 2.14	0.99	0.99
	Clayey soil	3.49 ± 0.75	0.016	0.879	12.41 ± 2.14	0.9	0.98
	Compost soil	6.45 ± 0.35	0.023	0.893	37.83 ± 1.8	0.89	0.99
Carbofuran	Sandy soil	0.87 ± 0.2	0.024	0.809	0.91 ± 0.34	1.05	0.87
	Red soil	1.23 ± 0.30	0.042	0.975	3.53 ± 0.18	0.99	0.99
	Clayey soil	4.85 ± 0.3	0.076	0.863	8.29 ± 0.54	0.93	0.96
	Compost soil	3.32 ± 0.5	0.054	0.843	11.41 ± 0.25	0.88	0.95

Table 5
 K_{OM} , ΔG° and hysteresis index (HI) values of lindane, methyl parathion and carbofuran on various Indian soils

Pesticide	Soil type	K_{OM}	ΔG° (kcal/mole)	Hysteresis index
Lindane	Sandy soil	245.22	-3.26	0.80
	Red soil	300.97	-3.38	0.77
	Clayey soil	482.98	-3.66	0.73
	Compost soil	509.15	-3.69	0.66
Methyl parathion	Sandy soil	200.00	-3.14	0.78
	Red soil	208.47	-3.16	0.84
	Clayey soil	377.20	-3.51	0.73
	Compost soil	397.79	-3.54	0.71
Carbofuran	Sandy soil	83.48	-2.62	0.77
	Red soil	109.69	-2.78	0.76
	Clayey soil	234.98	-3.27	0.67
	Compost soil	276.43	-2.83	0.64

the greater is the extent to which the adsorption reaction may take place. The small negative value of free energy change indicates the exothermic nature of the reaction. In such cases, it can be inferred that adsorption is physical in nature involving weak forces of attraction. Further, the negative ΔG° values indicate spontaneous process. The ΔG° values obtained in the present study indicate that the adsorption capacity of the soils would be in the order of com-

post soil > clayey soil > red soil > sandy soils. All ΔG° values were negative which represents the adsorption was exothermic and an increase in temperature will result a decreased sorption and favors the desorption process.

3.4. Effect of pH on adsorption of pesticides

An attempt was made to investigate the significant role played by pH in the adsorption process. Red soil was selected for the study because it was having considerable amount of organic matter and clay content as compared to other soils. Red soil was digested with acid solution of varying concentrations to disrupt the soil structure. pH of the red soil was adjusted to 2, 5, 8 and 10 using concentrated HCl and NaOH. Adsorption kinetic studies of lindane, methyl parathion and carbofuran were carried out using the treated red soil. Adsorption of lindane, methyl parathion and carbofuran on red soil adjusted to various pHs is shown in Fig. 3.

Adsorption of carbofuran and methyl parathion was significant at pH 2. However, adsorption of lindane was very minimal at this pH. As pH increased from 2 to 8, there was an increase in adsorption of all pesticides. It is reported that adsorption of neutral molecules increases with increase in pH. Among the three pesticides, carbofuran showed maximum adsorption followed by methyl parathion and lindane. From pH 8 to 10, there was a slight reduction in adsorption capacity for all three pesticides. This may be due to the masking of functional groups at elevated pH. Effect of pH on carbofuran adsorption was studied by Gupta et al. [38]. They have reported that when pH was lower, carbofuran adsorption on the soils was higher. Similarly, higher adsorption was observed at pH 5 for atrazine and metalochlor pesticides. Adsorption decreased when pH decreased to 3 and increased to 11 [39]. Maximum adsorption of alachlor and trifluralin was observed at a pH range of 3–6.5 [40].

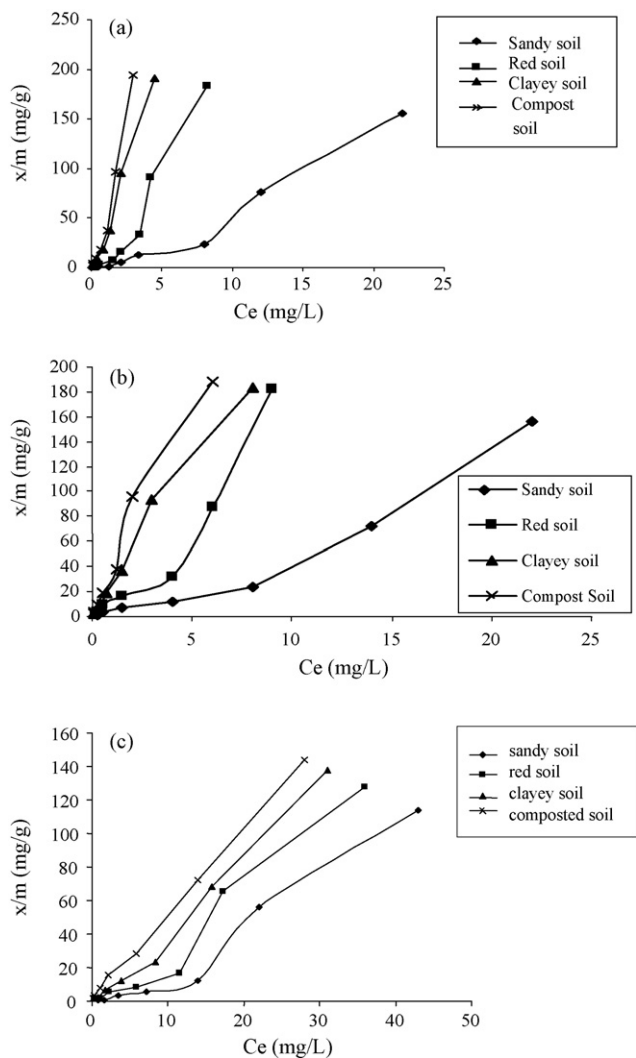


Fig. 2. Adsorption isotherms of (a) lindane, (b) methyl parathion and (c) carbofuran on various Indian soils.

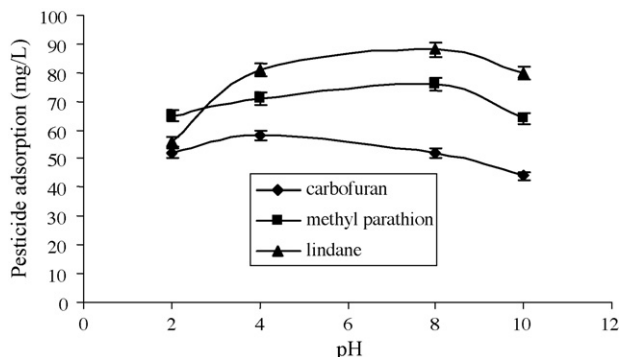


Fig. 3. The effect of pH on adsorption of lindane, methyl parathion and carbofuran.

3.5. Desorption

3.5.1. Kinetic study

Desorption is a key process affecting the mobility of pesticide molecules in soils. This is one of the important factors considered for selecting the treatment options for the contaminated sites and aquifers. Before the desorption study, the soil samples were washed with distilled water. During the washing process, removal of carbofuran was around 5–12%, methyl parathion was 4–8% and lindane was 2–6%. During washing, maximum percentage of pesticide removal was observed in sandy soil and minimum loss in compost and clayey soils. Desorption kinetic studies were conducted to assess the desorption potential of adsorbed lindane, methyl parathion and carbofuran in various soils. In sandy soil, 50% of desorption was taken place within first 15 min whereas, in other soils it took more than 2 h to desorb 50% of the adsorbed pesticides. The rate of desorption was quite high in sandy soils as compared to other three soils. In case of pesticides, lindane took more time to desorb as compared to methyl parathion and carbofuran. Red soil and sandy soils exhibited considerably high desorption rates as compared to compost soil and clayey soil. Minimum desorption rate was observed for compost soil irrespective of the pesticide. As observed in the adsorption studies, maximum desorption occurred for carbofuran followed by methyl parathion and lindane. Desorption rate constants were determined by intra-particle diffusion model by plotting $t^{-1/2}$ and equilibrium concentrations of pesticides for different soils. These results are shown in Fig. 4a–c. The maximum desorption rate was observed for sandy soil. The values were 0.79, 0.61 and 0.88 $\text{mg g}^{-1} \text{h}^{-1/2}$ for methyl parathion, lindane and carbofuran, respectively. Desorption rate constants of various pesticides in different soils are presented in Table 4.

3.5.2. Equilibrium study

Desorption equilibrium studies were conducted separately for all soils loaded with lindane, methyl parathion and carbofuran of 1, 2, 5, 10, 20, 50, 100, 200 and 500 mg/L by providing a pseudo-equilibrium time of 10 h using different organic solvents, and distilled water. Desorption isotherms also followed Freundlich model ($r^2 = 0.91\text{--}0.98$). Desorption isotherms for the low concentrations of adsorbed pesticides were similar to the adsorption isotherms. Similar results were observed by Raman et al. [9], while studying the desorption behavior of atrazine in Indian soils. However, in the desorption process of higher concentrations of adsorbed pesticides, desorption isotherms varied significantly from adsorption isotherms. This is due to the changes taken place in the soil (hysteresis). The Freundlich desorption equilibrium constant (n) value for all soils were lesser than Freundlich adsorption equilibrium constants (Table 6). But desorption values (K_{des}) were higher than adsorption values (K_{ads}) for all soils and all pesticides. K_{des} value was maximum for compost soil followed by clayey soil and red soil. Sandy soils exhibited the least K_{des} . A higher K_{des} value indicates a stronger affinity for the pesticide. Large proportion of pesticides were retained by soil (especially compost and clayey soil) during desorption as compared to adsorption at equilibrium. Soils with high organic matter and clay content have greater affinity to lindane, methyl parathion and carbofuran.

3.6. Sorption–desorption hysteresis

Hysteresis index (HI) was calculated according to the ratio of Freundlich exponents [41]

$$\text{Hysteresis index} = \frac{n_{\text{des}}}{n_{\text{sorp}}} \quad (7)$$

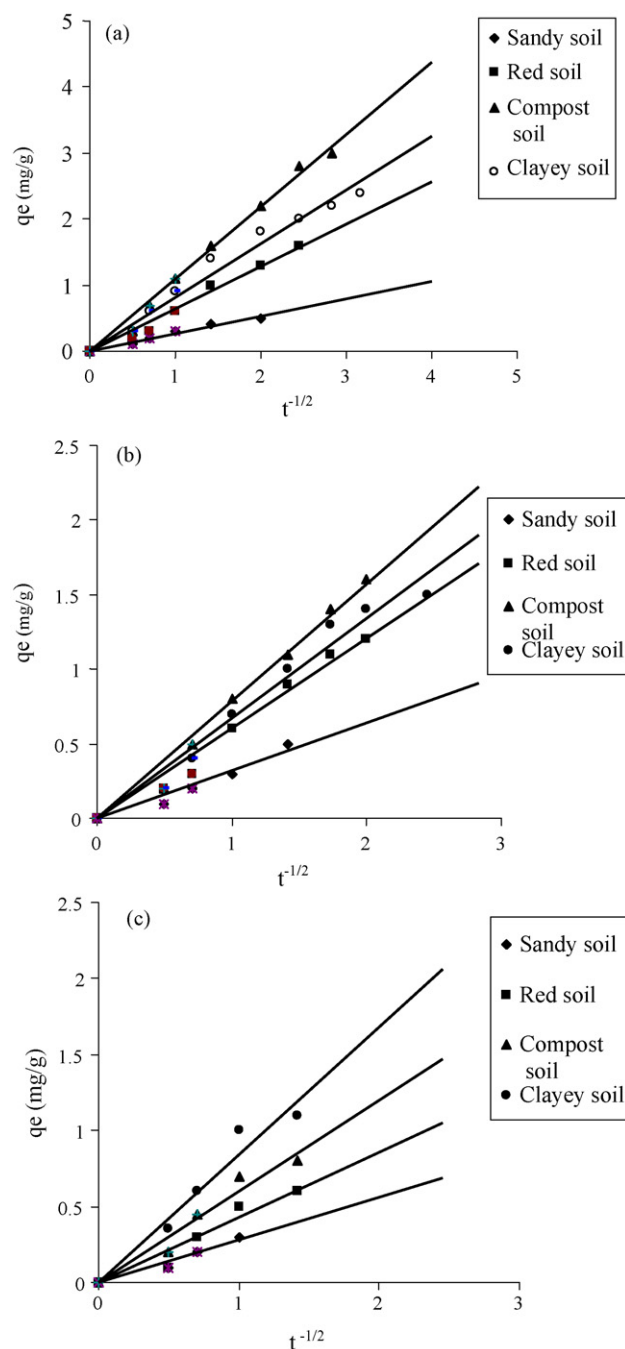


Fig. 4. Desorption kinetics of (a) lindane, (b) methyl parathion and (c) carbofuran from various Indian soils.

where the n_{des} and n_{sorp} are desorption and sorption exponents, respectively. Among the three pesticides, maximum hysteresis effect was observed for lindane. The HI was the highest for sandy soils and the least for compost soil. Highest hysteresis effect (the lowest HI) was observed in compost soils. Entrapment of sorbent molecules within the condensed soil organic matter (SOM) matrices contributes significantly to sorption–desorption hysteresis [8]. It shows that lindane was strongly sorbed on compost soils. So, desorption was more difficult. Soils with high organic matter content, the sorption–desorption hysteresis is mainly controlled by organic matter. But in soils with low organic matter, clay content plays an important role in the hysteresis [8].

Table 6
The desorption isotherm constants for lindane, methyl parathion and carbofuran on different soils by Freundlich models

Pesticide	Soil type	Freundlich constants		
		K_f (mg g ⁻¹)	n	R^2
Lindane	Sandy soil	1.48 ± 0.3	0.89	0.91
	Red soil	14.14 ± 1.1	0.8	0.965
	Clayey soil	29.07 ± 1.6	0.72	0.943
	Compost soil	58.13 ± 1.35	0.65	0.985
Methyl parathion	Sandy soil	1.15 ± 1.12	0.86	0.975
	Red soil	9.30 ± 1.14	0.83	0.934
	Clayey soil	22.36 ± 2.0	0.66	0.988
	Compost soil	36.87 ± 1.8	0.63	0.946
Carbofuran	Sandy soil	0.89 ± 0.34	0.81	0.91
	Red soil	5.21 ± 0.75	0.75	0.943
	Clayey soil	12.67 ± 0.81	0.62	0.989
	Compost soil	16.07 ± 1.25	0.56	0.965

3.7. Effect of solvents on desorption

Distilled water was used as a common eluent to quantify how much pesticides can be desorbed during precipitation (rainfall) and irrigation, which are very common phenomenon in agricultural fields. Most commonly used solvents for each pesticide was used as the second eluent, i.e., acetone for methyl parathion, ethanol for lindane and acetonitrile for carbofuran to assess the maximum desorption potential under the worst scenario. Distilled water affected 40–50% of adsorbed lindane in sandy soil, 30–40% in red soil and 25–30% in compost soil and clayey soils. But in case of carbofuran and methyl parathion, the desorption was more in all the soils as compared to lindane. Desorption by distilled water was least for lindane irrespective of the soils. As expected, desorption by respective solvents were higher for all the pesticides and all soil matrices tested. The solvents could desorb 75–80% of the adsorbed pesticides in sandy soils whereas; it was only 50–65% for other soils. Desorption efficiency followed the order sandy soil > red soil > clayey > compost soil. The above findings indicated that adsorption of lindane, carbofuran and methyl parathion on various soil matrices has occurred by the influence of physical and chemical forces. However, the contribution of them varied from soil to soil.

In sandy soil, the influence of physical adsorption was more as compared to chemisorption. However, the extent of physical sorption also varied from pesticide to pesticide. The contribution of physical sorption was more in case of methyl parathion and carbofuran as compared to lindane. For the treatment of pesticide contaminated sandy soils, flushing followed by pump and treat may be a feasible option in most of the cases. As the organic matter and clay content increased, the contribution of chemisorption became more predominant. The functional groups available in clay particles and organic matter must have provided enough adsorption/reaction sites for the pesticides. Though the solvent could affect considerable amount of sorbed pesticides, it may not be a feasible option for remediation of pesticide-contaminated sites due to the associated cost and environmental problems. By increasing the clay and organic matter content, the pesticide immobilization in the soil matrix can be improved. However, one should be cautious about the long-term behavior of such immobilized systems.

4. Conclusions

The adsorption/desorption characteristics of lindane, methyl parathion and carbofuran, on four Indian soils were studied. Batch kinetic and equilibrium experiments were carried out to assess

the adsorption rates and maximum adsorption capacity of these selected pesticides on different Indian soils. Adsorption rate constants were highest for compost soil whereas, it was the least for sandy soil. Lindane exhibited maximum rate of adsorption followed by methyl parathion and carbofuran. The maximum adsorption capacity was exhibited by compost soil for lindane (48.42 mg/g). Freundlich isotherm fitted the adsorption data well. It was found that organic matter and clay content played a significant role in pesticide adsorption. It was also noticed that nature of organic matter influenced the pesticide adsorption. Distilled water was able to desorb 30–60% of adsorbed pesticides whereas, the solvents were able to affect 50–80% of the sorbed pesticides. For sandy soil, soil flushing followed by pump and treat may be an appropriate remediation technology. However, high clay and organic matter content can immobilize the pesticides effectively in the soils.

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