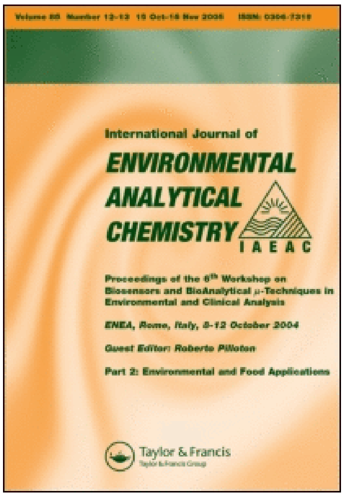

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SORPTION THERMODYNAMICS OF CYPERMETHRIN AT HIGH CONCENTRATIONS ON SOME INDIAN SOILS

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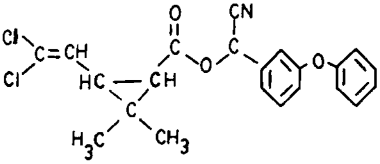
Sorption thermodynamics of cypermethrin on four different type of Indian soils (alluvial, forest, hill and humid) from water/acetone mixtures (f_s = 0.666) at 30°C and 50°C has been investigated through sorption isotherms, Freundlich equation, distribution coefficient and thermodynamic parameters. The measured equilibrium sorption isotherm for all soil-cypermethrin combinations were of non-linear Freundlich type and yielded 'S' shaped curves for soils at both temperatures. The sorption of cypermethrin was higher on hill silt loam soil followed by forest loam, alluvial sandy loam and humid loam soils and lower at higher temperature. The order of sorption was anticipated with K and K_d values. Comparison of the Freundlich coefficient K-values in relation to soil properties suggests that organic carbon, $CaCO_3$, clay content and surface area are the most important factors affecting cypermethrin sorption. From Freundlich sorption constant K values, the organic carbon partition coefficient K_{oc} and clay content partition coefficient K_c values were evaluated and found that cypermethrin sorption was better correlated with clay content than the organic carbon content. The thermodynamic equilibrium constant (K_o), standard free energy ($\triangle G°$), ethalpy ($\triangle H°$) and entropy ($\triangle S°$) changes were calculated in order to predict the nature of sorption.

KEY WORDS: Cypermethrin, sorption isotherms, Freundlich constant, distribution coefficient, organic carbon partition coefficient, soils.

INTRODUCTION

Cypermethirn [(RS)-α-cyano-3-phenoxy benzyl (1RS)-cis, trans-3-(2,2-dichlorovinyl) 2,2-dimethyl cyclopropane carboxylate] (I) is a synthetic pyrethroid widely used as a stomach and contact insecticide. It has been reported that cypermethrin is very effective against a



(I)

number of insects pests particularly belonging to order of Lepidoptera[1,2]. Several workers[3–6] have shown the superiority of cypermethrin over other insecticides. Its behaviour bioefficacy, persistence, movement and degradation in soil, water and sediments have studied by Roberts and Standen[7,8], Kaufman *et al.*[9], Gupta *et al.*[10] and Agnihotri *et al.*[11,12] Rao *et al.*[13], Nkedi-kizza *et al.*[14] and Walters and Gulseppl-Elle[15] have reported the sorption and transport of hydrophobic organic chemicals in aqueous and mixed solvent systems. However, information on cypermethrin sorption on Indian soils is not available in the literature. Hence, in the present study an attempt has been made to study the sorption equilibrium of cypermethrin on four different type of Indian soils at 30°C and 50°C and to evaluate the thermodynamic parameters for the interaction of this insecticide with soils.

MATERIALS AND METHODS

The alluvial, forest, hill and humid (Tarai) soils used for these studies were sampled to a depth of 0–30 cm from Aligarh, Tehri, Dehradun and Pilibhit districts of U.P. (India) respectively. These soils were air dried crushed and sieved. The mechanical composition of soil was estimated by the International pipette method.[16] The pH in 1:2.5 soil-water samples and their $CaCO_3$ contents were determined by usual methods.[17] The values of percentage of organic matter and organic carbon, cation exchange capacity and surface area of the soils were obtained by Walkley and Black,[18] Ganguli's[19] and Dyal and Handrick[20] methods, respectively. The results are given in Table 1.

The technical cypermethrin (92.87%) was obtained from Bharat Pulverising Mills Limited, Bombay (India). All other chemicals used were of AR grade.

The binary solvent used in this study was a mixture of acetone-water. Acetone was used because it is completely miscible with water, highly polar and proton acceptor. Since cypermethrin is extremely hydrophobic and quickly adsorbed on the walls of the containers

Table 1 Physico-chemical properties of the soils.

Physico-chemical properties	*Hill soil*	*Forest soil*	*Alluvial soil*	*Humid soil*
Mechanical composition				
Sand (%)	29.1	50.2	64.1	44.4
Silt (%)	59.9	30.8	26.4	42.1
Clay (%)	11.0	19.0	9.5	13.5
Texture	Silt loam	Loam	Sandy loam	Humid loam
pH	8.7	6.3	7.9	9.0
Organic matter (%)	1.84	1.19	1.06	0.52
Organic carbon (%)	1.06	0.69	0.61	0.30
CEC [cmol(P^+) Kg^{-1}]	5.5	5.9	4.1	4.7
Surface area (m^2g^{-1})	234	200	100	35
$CaCO_3$ (%)	6.25	2.65	0.45	0.25

from aqueous solution, to avoid this, the containers used for these studies were rinsed with hexane thoroughly. A ratio of acetone/water 2:1, was used throughout the experiment to improve the precision of the sorption measurement.

Batch shake testing was used to generate kinetic and equilibrium isotherm data. Experiments were conducted by placing 1 g of soil sample in various 50 ml conical flasks fitted with screw caps containing varying amounts (0,1,2,3 ...... 10 ml) of an acetone solution of cypermethrin (2000 μg/ml). The total volume of each flask was made up to 15 ml with a mixture of acetone/water (2:1). The suspensions were then shaken in a temperature controlled SICO shaker for 3h at 30 ± 1°C for the first set of experiments and at 50 ± 1°C for the second one and left overnight. The suspensions were then centrifuged at 13500 rpm for 10 min using Beckman model L 3–50 ultracentrifuge and supernatants were collected for cypermethrin estimation.

A 5 ml of the supernatant solution was taken in a tube and shaken for one to two minutes with 2g sodium chloride. The supernatant was then transferred into the separatory funnel, and extracted with 1 ml of *n*-hexane. The solvent layer was separated and the hexane extraction was repeated twice (3 × 1 ml). The aqueous layer was discarded and the hexane solution was dried over 2g sodium sulphate to remove the moisture content. The extract was evaporated to near dryness at room temperature and the content transfered to a graduated tube using hexane and concentrated to 2 ml by gentle evaporation with nitrogen at room temperature. The overall recovery of cypermethrin by this method was 98.8%.

The cypermethrin concentration of the resulting solution was estimated by GLC (NUCON 5700, India) equipped with FID and coiled glass column (61 cm × 3 mm i.d.) packed with 3% OV-101 on chromosorb W, 60–100 mesh. The operating temperatures were as follows: injector 270°C, column 260°C and detector 270°C. The carrier gas (nitrogen) flow rate was maintained at 60 ml min^{-1} and the hydrogen and air gas used at the flow rates of 30 and 300 ml min^{-1}, respectively. The 5 μl concentrated extract solution of cypermethrin in hexane was injected on the column for analyte determination. The retention time (RT) of cypermethrin peak under these conditions was 3.15 min. From the retention time (RT) and amounts of cypermethrin used in a calibration run (standard run), the reference factor (RF) value was evaluated. The RF value was then used to calculate the amount of cypermethrin quantitatively in the equilibrium suspensions. The amount of cypermethrin sorbed was determined as the difference between the amount of cypermethrin added and left after sorption. All the analyses were repeated twice.

The distribution coefficient values (K_d) were determined by using the formula

$$\frac{x}{m} = K_d \cdot C_e \qquad \ldots (1)$$

where x/m and C_e were the amount of cypermethrin sorbed (μg g^{-1}) and that present in solution (μg ml^{-1}) after equilibrium, respectively. The statistical average of all the K_d values was calculated by linear regression equation forced through the origin.

$$K_d = \frac{\sum\left(\frac{x}{m} \cdot C_e\right)}{\sum (C_e)^2} \qquad \ldots (2)$$

Evaluation of thermodynamic parameters

The thermodynamic equilibrium constant K_o for the sorption was calculated by the method of Biggar and Cheung[21]

$$K_o = \frac{C_s}{C_e} \cdot \frac{\gamma_s}{\gamma_e} \qquad \ldots (3)$$

where C_s is the amount of cypermethrin sorbed per gram of the solvent in contact with soils, C_e ($\mu g\ ml^{-1}$) is the concentration of cypermethrin in equilibrium suspension, γ_s and γ_e are the activity coefficients of the sorbed solute and solute in equilibrium suspension respectively and assumed to be the unity[22] in the dilute range.

The values of C_s were calculated using the equation proposed by Fu *et al.*[23]

$$C_s = \frac{(p / M)\, A}{S / N \cdot \left(\frac{x}{m}\right)} \qquad \ldots (4)$$

where ρ is the density of the solvent ($g\ ml^{-1}$), M the molecular weight of the solvent ($g\ mol^{-1}$), A is the cross sectional area ($cm^2\ molecule^{-1}$) of the solvent molecule, N is the Avogadro's number, S the surface area of the adsorbent ($m^2 g^{-1}$) and x/m is the amount of cypermethrin sorbed expressed in $\mu g\ g^{-1}$.

The cross sectional area of the solvent is estimated by the equation[24]

$$A = 1.091 \times 10^{-16} \left[\frac{M \times 10^{24}}{N \cdot \rho}\right]^{2/3} \qquad \ldots . (5)$$

The values of K_o were obtained by plotting $1_n \left(\frac{C_s}{C_e}\right)$ Vs C_s and extrapolating C_s to zero.

The standard free energies ($\angle G^\circ$), enthalpies ($\angle H^\circ$) and entropics ($\angle S^\circ$) changes for sorption of cypermethrin were evaluated from equations 6, 7 and 8.

$$\angle G^\circ = -RT \ln K_o \qquad \ldots . (6)$$

$$\ln\left(\frac{k_{oT_2}}{K_{oT_1}}\right) = \frac{-\angle\ H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad \ldots . (7)$$

$$\angle G^\circ = \angle H^\circ - T\,\angle S^\circ \qquad \ldots . (8)$$

RESULTS AND DISCUSSION

The results of the effect of equilibrium time on the sorption of cypermethrin was shown by plotting a graph of K_d values versus time (Figure 1) of soils. The sorption of cypermethrin on soils increased with the increase of the equilibrium time to a certain value after which the process becomes constant for 3 h for hill and forest soils and 2.5 h for alluvial and humid

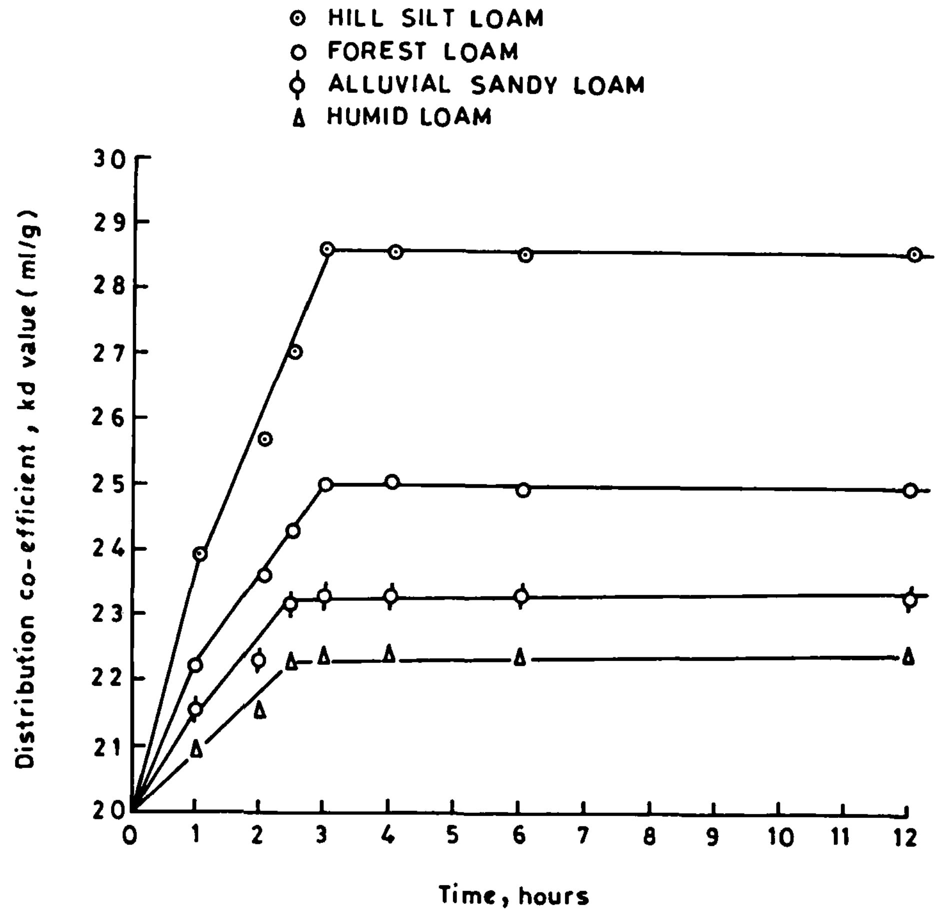


Figure 1 Time dependence of sorption of cypermethrin (10,000 μg) on different type of soils.

soils. Therefore, 3 h shaking period was chosen for cypermethrin sorption studies on soils.

The sorption of cypermethrin by the soils at 30°C and 50°C was represented by the isotherms in Figures 2 and 3. In all the cases the sorption was higher at 30°C than at 50°C and it may be due to the fact that attractive forces of soil sites were weaker at high temperature. The lower K_d values (Table 2) obtained at higher temperature for soils also support the above conclusion. However, the nature of the reaction remained unaffected.

The sorption data were fitted to the Freundlich equation[25], $x/m = K C_e^{1/n}$, where K and 1/n are empirical sorption constants specific to each soil cypermethrin combination being considered, and x/m and C_e are sorbed ($\mu g\ g^{-1}$ soil) and solution phase ($\mu g\ ml^{-1}$) cypermethrin

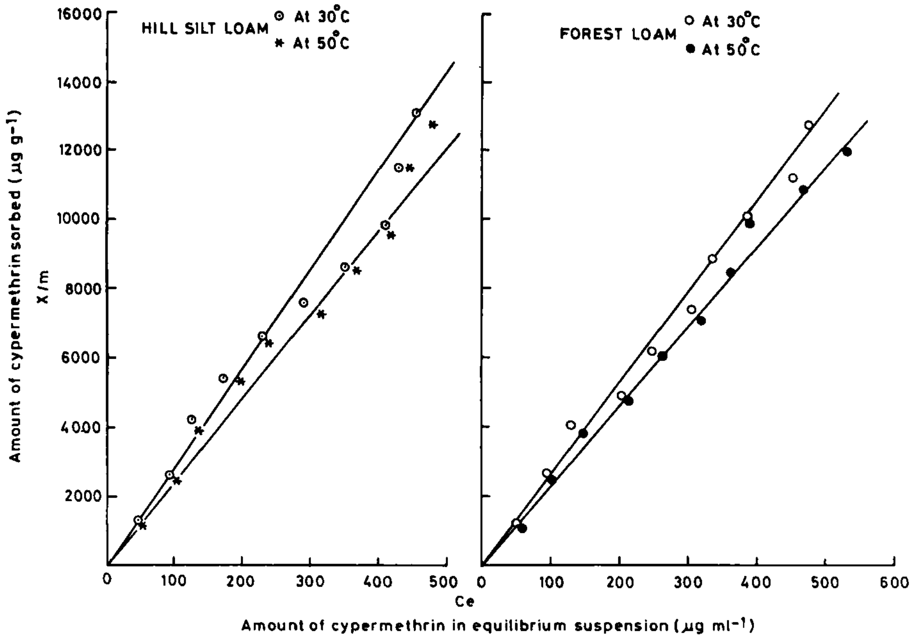


Figure 2 Sorption isotherms of cypermethrin on alluvial sandy loam and humid loam soils at 30°C and 50°C.

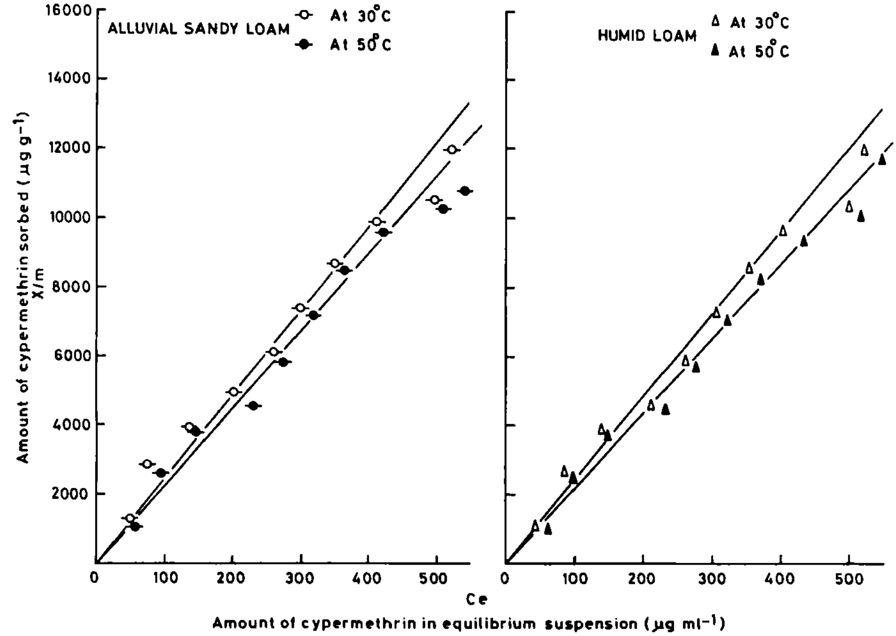


Figure 3 Sorption isotherms of cypermethrin on hill silt loam and forest loam soils at 30°C and 50°C.

Table 2 Freundlich constants calculated from equilibrium sorption isotherms for soil-cypermethrin combinations.

Soils	*K*	*1/n*	K_{oc}	K_c	*Statistical average* K_d *value*	r^2
			At 30°C			
Hill	66.06	0.857	6232	600	26.83	0.985
Forest	50.11	0.882	7262	263	25.14	0.951
Alluvial	45.70	0.896	7491	481	23.34	0.983
Humid	33.11	0.941	11036	245	22.91	0.992
Average ± %CV*	49.33 ± 27.83	0.894 ± 3.94	7234 ± 27.56	397.25 ± 43.43	24.56 ± 7.33	0.997 ± 1.86
			At 50°C			
Hill	45.70	0.885	4311	415	24.69	0.989
Forest	34.67	0.930	5024	182	23.49	0.998
Alluvial	32.35	0.925	5303	340	21.91	0.991
Humid	26.30	0.962	8766	194	21.03	0.994
Average ± %CV*	34.76 ± 23.30	0.925 ± 3.4	6971 ± 31.89	282.75 ± 40.21	22.43 ± 7.19	0.993 ± 0.39

* CV is the coefficient of variation, % CV = (Standard deviation/average) × 100

concentrations, respectively. The sorption coefficient K has units of $\mu g^{(1-n)}\, ml^n g^{-1}$, while 1/n is dimensionless. The values of the Freundlich sorption constants K and 1/n for cypermethrin-soil combination were obtained using a least square fit (Figure 4) of the sorption isotherms (Figure 3) and values are tabulated in Table 2. From the K and 1/n values, it is clear that higher values of 1/n and lower values of K were obtained at higher temperature indicated that cypermethrin was highly sorbed at lower temperature on soils. On the basis of K values (Table 2) the extent of cypermethrin sorption on soils was in the order of hill silt loam > forest loam > alluvial sandy loam > humid loam soils at both the temperatures. This order of sorption is directly proportional to the percentages of organic matter, surface area, and $CaCO_3$ contents of the soils[26]. To determine the sorptive capacity for organic carbon and clay content of soils, the organic carbon partition coefficient K_{oc} and clay content partition coefficient K_c were computed by dividing the Freundlich constant K value by soil organic carbon content and soil clay content, respectively. These values are summarized in Table 2. As indicated by the values of the coefficient of variation (CV), the K_{oc} values for cypermethrin are much less variable among these soils studied than are the K values uncorrected for organic carbon. Similar observations were reported by Hamaker[27] that the K_{oc} values for pesticides were nearly independent of soil type. In the present study cypermethrin sorption was slightly better correlated with clay content than the organic carbon content of the soils, because K_{oc} values were by and large higher than K_c values (Table 2). This tendency is due to the fact that mineral phases or presence of clay colloidal particles (non settling micro particles) may be responsible for making a significant contribution of cypermethrin sorption. The results are in accordance with the work of Hamaker and Thompson[28]. Wahid and Sethunathan[29] demonstrated that beyond the organic matter 2% in soils, the sorption of parathion takes place almost entirely on organic surfaces but at organic

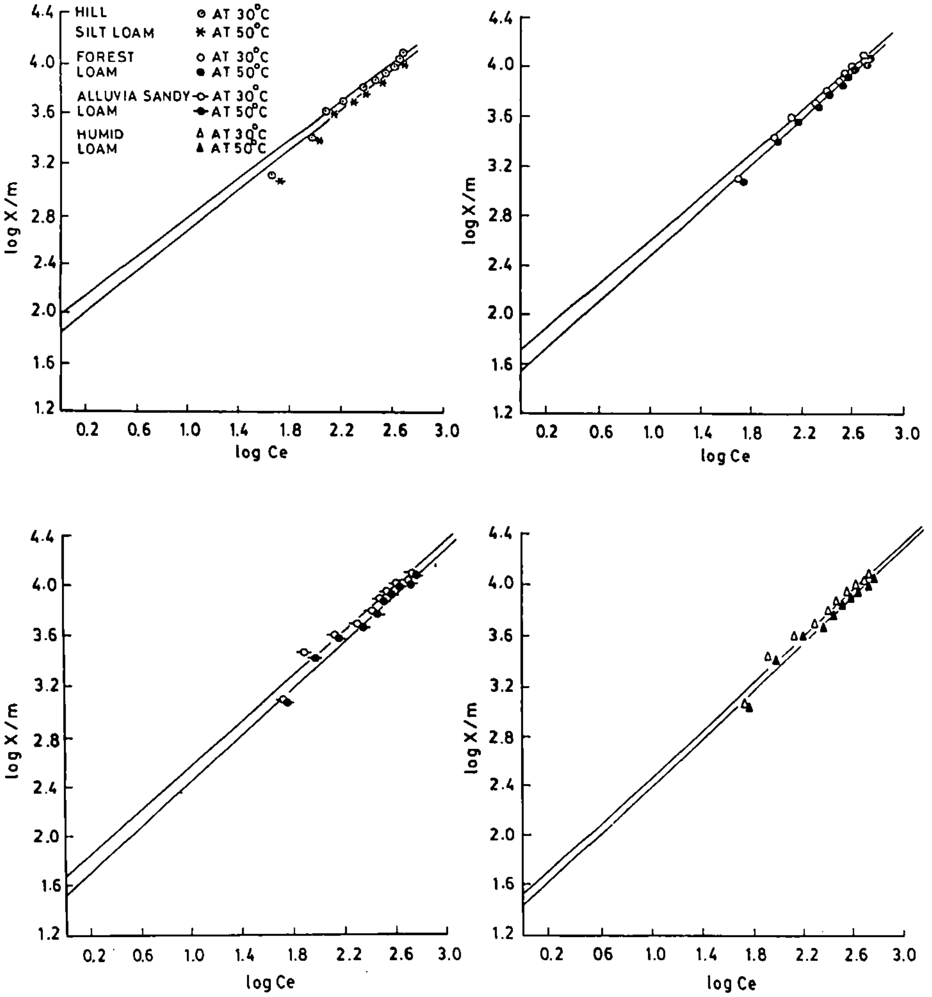


Figure 4 Freundlich isotherms of cypermethrin sorption on soils at 30°C and 50°C.

matter content level below 2% the sorption was significant on clay surfaces or on inorganic surfaces.

Two important conclusions can be made based on the data presented in Table 2. First the fact that the Freundlich equation describes cypermethrin sorption isotherms over a wide concentration range suggests that sorption sites were not saturated at any concentration considered in this study. The amount of cypermethrin sorbed by the soil continued to increase with each increase in solution concentration[30]. Second assumption was cypermethrin sorption isotherms measured were nonlinear, i.e. 1/n less than 1 (Table 2). Linear sorption isotherms have generally accepted for low pesticide concentrations[31–34].

Table 3 Values of various thermodynamic parameters for the sorption of cypermethrin on soils.

Thermodynamic parameters	*Hill soil*		*Forest soil*		*Alluvial soil*		*Humid soil*	
	30°C	50°C	30°C	50°C	30°C	50°C	30°C	50°C
K_o	1.32×10^6	1.088×10^6	9.845×10^5	7.294×10^5	8.061×10^5	5.403×10^5	4.424×10^5	2.683×10^5
ΔG° $KJ.mol^{-1}$	-35.374	-37.174	-34.621	-36.104	-34.120	-35.302	-32.614	-33.430
ΔH° $KJ.mol^{-1}$	-8.103		-12.155		-16.207		-20.258	
ΔS° KJ.degree mol^{-1}	0.0900		0.0741		0.0591		0.04078	

The higher statistical average of K_d-values (Table 2) obtained for hill silt loam soil followed by forest loam, alluvial sandy loam and humid loam soils confirms the above order of sorption.

The results of thermodynamic parameters obtained at 30°C than 50°C for soils are summarized in Table 3. The higher values of thermodynamic equilibrium constant K_c at 30°C than at 50°C for all the soil-cypermethrin interaction, indicating the higher preference of cypermethrin for soils at lower temperature. However, these values were higher for hill silt loam soil followed by forest loam, alluvial sandy loam and humid loam soils at both the temperatures again confirms the above order of cypermethrin sorption. The negative values of standard free energy changes (∠G°), indicated that the reactions were spontaneous with high affinity for cypermethrin. Negative values of standard enthalpy (∠H°) changes indicated that cypermethrin interaction with soils are exothermic and a decrease in temperature favours the reaction products which are energetically stable with a high binding of cypermethrin to soil sites. The positive values of standard entropy changes (∠S°) recorded in the present investigation indicate the stability of soil cypermethrin complex in the system. A single large molecule of cypermethrin may replace a number of water molecules thus there is a large gain in entropy due to freedom in the restriction of the water molecule. It is evident that higher sorption of cypermethrin on hill silt loam soil and forest loam soil resulted in a large increase in entropy change in comparison to other soils. These soils have higher colloidal matrix and possess a thick envelope of water molecules around the surface. When sorption of cypermethrin takes place a substantial quantity of water molecules which are expected to be rendered free might have caused large increase in the entropy of cypermethrin sorption on hill silt loam soil. The change in entropy of the system may also be interpreted by giving an indication of steric factors involved in the formation of activated complex during sorption. The steric factor accounts for the fraction of collision having proper orientation and configuration to allow reaction to occur. The lower is the value of ∠S°, the lower is the steric factor. Relatively higher value of ∠S° in hill silt loam soil suggest greater interaction of cypermethrin with the soil in comparison to those in other soils.

Acknowledgements

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