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Adsorption of Endosulfan in Two distinct Soils of Rajasthan :Evaluation of Thermodynamic Parameters , Adsorbability Index (AI) , the First-order Molecular Connectivity Index (1X) and Leachability indexes for Endosulfan

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ABSTRACT: The adsorption thermodynamics of endosulfan onto two divergent textured (Black clay loam and Red loam) soils of Rajasthan from methanol/water mixtures ($f_s = 0.1$) have been investigated at 25°C and 50°C via adsorption isotherms, the Freundlich equation, distribution coefficient measurements and thermodynamic parameters. The measured equilibrium adsorption isotherms were S-shaped for both two soils at both temperatures. The adsorption of endosulfan onto both the soils increased with increasing temperature. The highest adsorption was obtained at both temperatures in black clay loam soil than red loam soil, as anticipated from the values of the Freundlich constant K_F , and the distribution coefficient K_D . The affinity of endosulfan towards the organic carbon, organic matter and clay content of the soils was evaluated from calculations of the values of K_{oc} , K_{om} and K_{cc} . The predicted values of $\log K_{ow}$ were also evaluated by using the aqueous solubility, the 1-octanol/water partition coefficient (K_{ow}), the adsorbability index (AI) and the first-order molecular connectivity index (1X) of endosulfan. Use of the AI and indices of endosulfan gave predicted $\log K_{ow}$ values close to those observed experimentally.

The leaching index (LEACH) of the adsorption of endosulfan calculated for the soils studied indicated it's high potential to leach into shallow aquifers and ground water. The mobility residues of endosulfan in soil was calculated using GUS equation. The GUS (Ground water Ubiquity Score) values were found to less than - in both the soils studied.

The thermodynamic equilibrium constant (K_o), the standard free energy (ΔG°), the standard enthalpy change (ΔH°) and the standard entropy change (ΔS°) were all calculated in order to predict the nature of the adsorption process.

KEYWORDS: Endosulfan ,Adsorption ,Thermodynamic parameters (K_o , ΔG° , ΔH° and ΔS°), Distribution coefficient (K_D), Freundlich constant (K_F) ,Adsorbability index (AI), First -order molecular connectivity index ($^1\chi$). Leaching Index(LEACH) and GUS index .

I. INTRODUCTION

The use of synthetic organic pesticides is one of the most important factors behind the increase in agricultural productivity in 20th century. Their excessive and indiscriminate use in agricultural and public health sectors for controlling insects, pests and vector-borne diseases is a matter of serious environmental concern because these chemicals are recognized as a source of potential adverse impact. Many pesticides are mobile in soil and readily migrate into ground water and contaminate [1].

Soil is ultimate sink for bulk of pesticides used in agriculture or public health programme. Some pesticides are directly applied into soil to control soil borne pests and pathogens or for their systematic action to control phytophagous pests. Even when applied on crop, most part of applied pesticides finds its way into soil by various routes, irrespective of the method and target of application. According to some estimates, as much as 50 per cent of the foliar applied pesticide falls on the soil depending on the plant canopy, wind speed, formulation and dust particle/ droplet size [2,3]. Indirectly pesticides reach the soil when moved plant foliage is ploughed into the soil or when pesticide-treated seeds are In some instances, pesticide reach the soil by missing the targets, by runoff from the treated plants or by spillage during the

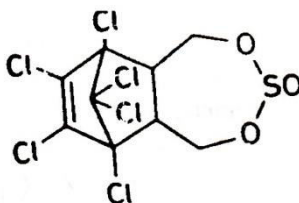
application. A pesticide on reaching soil surface is acted upon by a number of processes - physical, chemical and biological. On reaching the soil surface, pesticides tend to interact with the colloidal fractions of soil - the organic matter fraction and clays. The behaviour of pesticides is also directly related to the nature and properties of a soil and its constituents [4] which vary tremendously in their composition, physical structure and chemical environment.

Adsorption is the attraction and repulsion phenomenon at soil surface and exerts the most profound influence of the several processes operating to determine the fate and behaviour of pesticides in soil, it has been investigated intensively over the last several decades mostly in the soils

[4, 6-10]. It governs the relative availability of a pesticide, its volatilisation, physical distribution, breakdown, biological activity and even its susceptibility to microbial metabolism [11-16] . It depends upon the nature and properties of the pesticide such as acidity (pka), basicity (pkb), solubility, shape and configuration, charge distribution, polarity of molecule, molecular size and polarizability and its concentration in the solvent. The literature on this aspect has been reviewed by several researchers [17-20].

Endosulfan is a broad -spectrum and high -effective organochlorine pesticide, and has been used extensively throughout the world for the control of numerous insects and mites for fruit, vegetables, tea, cotton, maize, soybean and many cereal crops since 1950s [21,22]. Its technical preparation consists of two stereoisomers, α and β -endosulfan in an approximate ratio of 70:30 [23,24]. It is extremely toxic to fish and aquatic invertebrates, and is a priority pollutant for international environmental agencies [25]. The solubility of endosulfan in water is low, but it persists in soil and water environment for 3–6 months or more [26-28]. Endosulfan contamination is frequently found in the environment even at considerable distances from the point of its original applications [29,30]. It has also been detected in the atmosphere, soils, sediments, estuaries, surface and rainwaters, and food stuffs [31-37].

As endosulfan is found in groundwaters, it is apparent that there is significant mobility of these chemicals through the soil [38-42]. Due to its high toxicity, bioaccumulation, long residual period in soil, and long -distance transportation, Endosulfan was listed in persistent organic pollutant (POPs) [43]. Endosulfan in soil mainly originates from agricultural application [44] and atmospheric deposition near the pesticide plant [45]. Pesticide migration from soil to plant and water body is dependent on its residue in soil to a great extent, which is directly related to its adsorption and desorption abilities [46]. On the other hand, endosulfan is a hydrophobic organic contaminant (HOC), and is easy to be adsorbed by soil colloids, which may reduce microbial degradation efficiency [47]. Therefore, the knowledge of the adsorption characteristics of endosulfan in soil is necessary for understanding its environmental behaviors and developing remediation technology. Recently several researchers [48-53] have studied the adsorption and movement of endosulfan with water-miscible organic solvents, surfactants and aqueous solutions in soil. However, the effect of temperature on endosulfan adsorption has not been available in literature. Hence, an attempt has been made in the present study to investigate the adsorption of endosulfan in two texturally different soils of Rajasthan at two different temperatures, viz., 25°C and 50°C. Various Thermodynamic parameters such as Thermodynamic equilibrium constant (K_o), standard free energy change (ΔG°), standard enthalpy change (ΔH°), and standard entropy change (ΔS°) have also been calculated in order to predict the nature of the adsorption. Endosulfan represents the following structure.





II.II.EXPERIMENTAL

Materials and Methods :

The two soils of different agro-climatic zones of Rajasthan were used in the present study . The soils were collected from the cultivated field at a depth 0-30 cm with no background of pesticide application , Black Clay loam soil from Indergarh village of Bundi district and Red loam soil from Haldi Ghati area of Udaipur districts of Rajasthan . The Soil samples were air-dried ,ground to pass through a 2mm sieve and stored in plastic bags at room temperature. The physicochemical properties of both the soils were determined by the standard methods and resulted values are summarized in Table 1.

Table-1 Physico-chemical Parameters of Soils Studied

Soil Properties	Black clay loam soil	Red Loam Soil
1-Mechanical composition		
Sand (%)	39.90	43.10
Silt (%)	29.60	44.90
Clay (%)	30.50	12.00
Texture	Clay loam	Loam
2-EC(dsm ⁻¹)	1.50	0.35
3-pH	8.1	7.4
4-CaCO ₃	6.50	3.4
5-Organic carbon (%)	0.52	0.20
6-Organic matter (%)	0.90	0.35
CEC (cmolp ⁺ kg ⁻¹)	25.50	10.80
8-Surface Area (m ² /g)	225.50	150.50

Endosulfan (water solubility S_w, 0.325 mg L⁻¹ , log K_{ow} = 3.60 ,vapoure pressure(mmHg) at 25°C=1.73×10⁻⁷ ,Half-life =50 days) was obtained from Indo Gulf Fertilizers & Chemicals Corporation Ltd., Sultanpur (U.P.), India. All other chemicals and reagents were of A.R. grade as obtained from Merck and CDH Chemicals Ltd. Stock solutions of endosulfan of concentration 1000 µg/ml was prepared by dissolving the requisite amount of endosulfan in methanol.

Adsorption studies:

Adsorption experiments were carried out by using the batch equilibrium technique. Suitable aliquots (1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0 and 10.0 ml) of endosulfan solution of concentration 1000 µg/ml were introduced into different 100 ml glass stoppered conical flasks . Each experiment was conducted in triplicate and each isotherm determination involved 31 flasks for each of 10 endosulfan doses and one blank containing soil without endosulfan . The volume of

each flask was made up to 20 ml with requisite volume of methanol and distilled water at a fixed volume fraction ($f_s = 0.1$). To these solutions 1 g of each soil was added and resulting suspensions shaken in a temperature -controlled shaker for 3 hours at $25^\circ\text{C} \pm 1^\circ\text{C}$ for the first set of the experiment and at $50^\circ\text{C} \pm 1^\circ\text{C}$ for the second set. In each case, the suspensions were stored overnight before subsequent study.. Preliminary experiments revealed a contact time of 24 h as sufficient for equilibrium to be attained in both systems. Subsequently, the suspensions were centrifuged at 15 000 rpm for 10 min using a Beckman model 13-50 ultracentrifuge. The amount of endosulfan in the supernatants was estimated spectrophotometrically [54]. This method has a detection limit of 1 $\mu\text{g}/\text{ml}$. The amount of endosulfan adsorbed was calculated as the difference between the initial and equilibrium concentrations in solution according to the following expression:

$$x/m = [C_0 - C_e] V / W \quad \text{---(1)}$$

where x/m is the surface concentration of endosulfan in the soil ($\mu\text{g}/\text{g}$). C_0 , is the initial concentration of endosulfan in solution ($\mu\text{g}/\text{ml}$), C_e , is the equilibrium concentration of endosulfan in solution, V is the volume of the solution and W is the weight of soil employed.

Evaluation of the Adsorbability Index (AI) and the First-order molecular Connectivity Index (1X) of endosulfan :

The adsorbability index (AI) proposed by Abe et al [55] is an empirical molecular descriptor derived from a group contribution method based on molecular refractivity for predicting the adsorption of 157 compounds onto activated carbon. This index was also applied to predict the soil sorption coefficient of the same 157 compounds [56].

The adsorbability index (AI) of endosulfan was evaluated from equation (2) by inserting the values of A and I derived from the work of Abe et al [55] as tabulated in Table 2 :

$$AI = \Sigma A + \Sigma I \quad \text{..(2)}$$

where A and I are the factors for respective increase and decrease in the adsorbability of the atom or functional group in the molecule from aqueous solution onto the various soils studied, the AI value for endosulfan being equal to 5.47.

The first-order molecular connectivity index (1X) for endosulfan was evaluated by substituting the above value of AI into the following equation proposed by Okouchi and Saegusa [56] :

$$^1X = 1.16 AI - 0.68 \quad (3)$$

from which a corresponding value of 5.67 was obtained.

Table.2. Values of A and I According to Abe et al.(1986)

	A			I
C	0.26	aliphatic		
	0.12	-OH	(alcohols)	-0.53
N	0.26	-O-	(ethers)	-0.36
O	0.17	-CHO	(aldehydes)	-0.25
S	0.54	N	(amines)	-0.58



Cl	0.59	-COOR	(esters)	-0.28
Br	0.86	>C=O	(ketones)	-0.30
NO ₂	0.21	-COOH	(fatty acids)	
-C=C-	0.19	aromatics		
iso	-0.12	-OH, -O-, N-, COOR, >C=O, - COOH		0
tert	-0.32	α-amino acids		
cyclo	-0.28			-1.55

Evaluation of Leaching Indexes :

The two traditional indexes, the leaching index (LEACH) [9] and groundwater Ubiquity Score (GUS) indexes [57] were applied to calculate leachability of pesticides .

LEACH index for Endosulfan :

The leaching index (LEACH) assesses the potential degree of groundwater and river water contamination. It is calculated using the equation proposed by Laskowski et al [9] and later used by Papa et al. [58].

$$LEACH\ index = (S_w \times t_{1/2}) / (V_p \times K_{oc}) \quad \text{---(4)}$$

where S_w is the water solubility (0.325 mg L⁻¹), $t_{1/2}$ is the degradation half-life in soil (50 days), V_p is the vapour pressure (1.73×10⁻⁷ mmHg) and K_{oc} (adimensional Table 3) is the organic carbon partition coefficient .Leaching Index has no trigger value : the lower the LEACH value, the lower the risk of contamination .Results obtained are summarised in Table.

Evaluation of Groundwater Ubiquity Score (GUS) Index for Endosulfan :

The GUS index assesses the leachability of pesticides and the possibility of finding these compounds in groundwater. It is calculated by the equation proposed by Gustafson [57] :

$$GUS = \log_{10}(t_{1/2-soil}) \times [4 - \log_{10}(K_{oc})] \quad (5)$$

Where $t_{1/2-soil}$ is the soil degradation half-life assuming first-order kinetics. This index is based on two parameters : mobility in soil given by the organic carbon partition coefficient (K_{oc} , adimensional), and the soil persistence, quantified by the disappearance half-life in the soil, defined in field conditions and expressed in days ($t_{1/2}$). The results obtained are summarised in Table.3

Evaluation of Various Thermodynamic Parameters :

The thermodynamic equilibrium constant K_o , for the adsorption was calculated by the equation proposed by Biggar and Cheung [59] and later used by Singh [60]

$$K_o = (C_s / C_e) \cdot (y_s / y_e) \quad (6)$$

Where, C_s ($\mu\text{g} / \text{g}$) is the amount of endosulfan adsorbed per gram of the solvent in contact with soil and C_e , the concentration of endosulfan in equilibrium suspension in $\mu\text{g} / \text{ml}$. y_s and y_e are the activity coefficients of the adsorbed solute and solute in equilibrium suspension, respectively and assumed to be unity [61] in dilute range of the studies.

The values of C_s , were calculated by using the equation on proposed by Fu et., [62].

$$C_s = (p/M)A / \{S / N.(x/m)\} \quad (7)$$

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

The cross-sectional area (A) of the solvent molecule is estimated by using the following equation [63].

$$A = 1.091 \times 10^{-16} [M \times 10^{24} / (Np)]^{2/3} \quad \text{---(8)}$$

As the concentration of solute in the solution approached zero, the activity coefficient, y approached unity. Equation (7) may be written as

$$\lim_{C_s \rightarrow 0} C_s / C_e = K_o \quad \text{---(9)}$$

$C_s \rightarrow 0$

The values of K_o were obtained by plotting on (C_s / C_e) versus C_s and extrapolating to zero C_s .

Thermodynamic parameters such as standard free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) changes for adsorption of endosulfan are evaluated from the equations proposed by Glasstone [64] and later used by Singh [65].

$$\Delta G^\circ = -RT \ln K_o. \quad (10)$$

Where R = universal gas constant ($R = 8.314 \text{ kJ} / \text{mol}$), T was the temperature in degree Kelvin.

The standard enthalpy change (ΔH°) was calculated from the Van't Hoff isochore.

$$\ln [K_o(T_2) / K_o(T_1)] = - \Delta H^\circ / R [1 / T_2 - 1 / T_1] \quad \text{---(11)}$$

And the standard entropy change, ΔH° , was calculated by the equation.

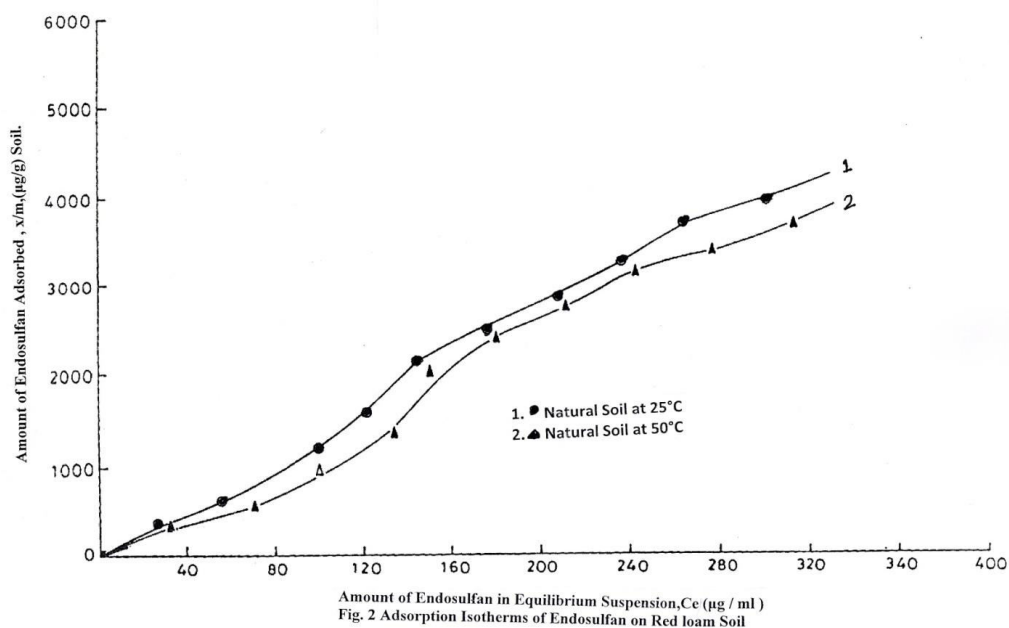
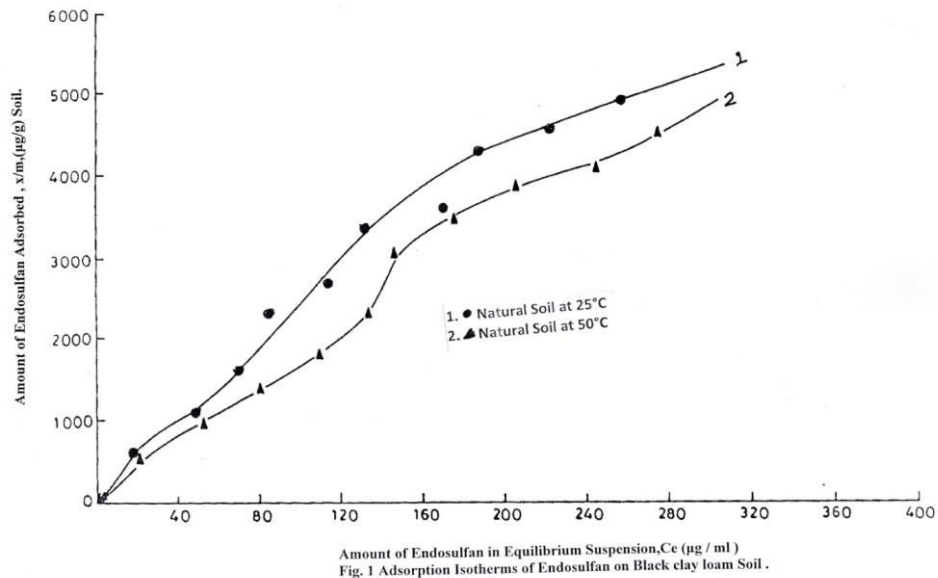
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (12)$$

III.RESULTS AND DISCUSSION

It is evident from the data listed in Table 1 that the two soils of Rajasthan differed widely in their physicochemical parameters. The higher values of organic matter content, clay content, calcium carbonate content, cation exchange capacity (CEC), electrical conductivity (EC) were obtained in black clay loam soil than Red loam soil. The pH value was in reverse order.

Adsorption Isotherms :

Adsorption isotherms of endosulfan onto the two soils at 25°C and 50°C are depicted in Figs. 1 & 2, respectively which shows plots of the amount of endosulfan adsorbed per unit mass of solid adsorbent (x / m , $\mu\text{g} / \text{g}$) versus the equilibrium concentration (C_e , $\mu\text{g} / \text{ml}$). The isotherms (Figs. 1 & 2) are similar to 'S' shaped as defined by Giles et al. [66] and suggest that the adsorption of endosulfan enhanced at higher concentrations. The S-shaped isotherms also suggest that adsorption of endosulfan was easier probably due to the marked localization of the forces of attraction over the $>S = O$ group of endosulfan leading to interaction with soil sites.



Adsorption Freundlich Equation :

Adsorption of endosulfan was greater at 25°C than 50°C for both the soils investigated. The adsorption isotherms for both the soils at 25°C and 50°C could be fitted by the empirical Freundlich equation [67] .

$$\log (x/m) = \log K_F + 1/n (\log C_e) \text{ ---(13)}$$

where x/m is the surface concentration of the adsorbate per unit amount of adsorbent ($\mu\text{g/g}$), C_e is the adsorbate equilibrium solution concentration ($\mu\text{g/ml}$). K_F , and $1/n$ are Freundlich constants associated with the affinity of the adsorbate for the adsorbent and degree of curvature of the isotherms, respectively. Values of K_F and $1/n$ were obtained



from the intercept and slope ,respectively of a straight line [68] .The dimensions of K_F , are $(\mu\text{g}^{(1-n)} \text{ml}^n) \text{g}^{-1}$ whereas $1/n$ is dimensionless. In general,all the regression lines generated by using the Freundlich relationship had a coefficient of determination (r^2) were greater than 0.982 at both the temperatures (25°C and at 50°C) and indicated an excellent fit of the adsorption data by the above equation (Table3).It was in agreement findings by several workers for the adsorption of non-ionic pesticides from soils [69-71] .The values of K_F , and $1/n$ for endosulfan / soil combinations were estimated from the linear regression of the logarithmically transformed data and values so obtained are summarized in Table 3.

Table 3.Adsorption Data for Endosulfan at 25°C and 50°C in Two Soils Studied

Soils	K_F	$1/n$	K_D	r^2	K_{oc}	K_{cc}	K_{om}	$\log K_{om}$	LEAC H index	GUS index
Clay loam										
At 25°C	50.52	0.846	21.38	0.984	9715.38	165.64	5613.33	3.75	0.97×10^4	0.022
At 50°C	39.80	0.966	15.36	0.983	7653.85	130.49	4422.22	3.65	-	-
Loam										
At 25°C	19.20	0.984	14.58	0.958	9600.00	160.00	5485.71	3.74	0.98×10^4	0.030
At 50°C	15.30	1.030	9.60	0.988	7650.00	127.50	4371.43	3.64	-	-

Adsorption Constants :

The magnitude of K_F , expresses the relative adsorption capacity for the adsorbate [72] for a system having comparable $1/n$ values and extent or degree of adsorption [74]. The sequence of K_F , for adsorption of endosulfan onto the soils studied confirms the above order of adsorption. The value of $1/n$ provides an idea of the intensity of adsorption which varies with the nature of the adsorbate for given adsorbent ; $1/n$ values also indicates the degree of non-linearity($1/n < 1$) between the solution equilibrium concentration and adsorption.The variable slopes of adsorption isotherms obtained for different pesticide-soil systems studied reveal the pesticide adsorption on soil is a complex phenomenon involving different types of adsorption sites with different surface energies [74].

Comparing the values of K_F and $1/n$ for both the soils ,it is clear that endosulfan adsorbed to a greater extent on Black clay loam soil than Red loam soil (Figs.1&2) .The higher values of K_F and lower values of $1/n$ at 25°C again confirms the higher adsorption of endosulfan at lower temperature[75] .

Determination of distribution coefficient (K_D):

Since the values of $1/n$ departed from unity , it was considered appropriate to use the distribution coefficient , K_D , as a measure of the soil adsorption capacity[76,4] ,since this may also be related to adsorption under equilibrium conditions [77].The statistical average of all K_d values for each soil at 25°C and 50°C evaluated from the relationship :

$$K_D = \frac{\sum (x / m \cdot C_e)}{\sum (C_e)^2} \quad (14)$$

where Σ for the summation of values.The K_D values thus obtained are also given in Table 3.The sequence of K_D values again confirms the above order of adsorption.

Determination of Organic Carbon Partition Coefficient (K_{oc}), Organic Matter Partition Coefficient (K_{om}) and Clay content partition Coefficient (K_{cc}):

From the Freundlich constant, K_F values, the adsorptive capacity of organic carbon, organic matter and clay content for soils was evaluated by calculating the values of K_{oc} , K_{om} and K_{cc} using the relationships [78-81]. These are the important parameters that play a significant role in environmental fate assessment of organic chemicals. The results so obtained also being tabulated in Table 3. It will be noted from this table that the red loam soil possessed higher K_{oc} and K_{om} values than black clay loam soil, which is common for the case of low organic matter soils. This is probably due to the clay content of the

Soils being responsible for a significant proportion of the adsorption [82]. The present study shows that both the organic carbon and clay contents of the soils were responsible for endosulfan adsorption, with this being better correlated with the organic carbon content rather than the clay content since the K_{oc} values were higher than the K_{cc} values. The results are in accordance with the work of Walker and Crawford [84] and Stevenson [84] who reported that, up to an organic matter content of ca. 6%, both organic and mineral surfaces are involved in adsorption. Stevenson [85] pointed out that the amount of organic matter required to coat the clay would depend on the soil type and the kind and amount of clay present in soils

$$K_{oc} = (K_F \times 100) / \% \text{ OC} \quad \text{---(15)}$$

$$K_{om} = (K_F \times 100) / \% \text{ OM} \quad \text{---(16)}$$

$$K_{cc} = (K_F \times 100) / \% \text{ Clay content} \quad \text{--- (17)}$$

Modelling of Adsorption Behaviour of Soils :

Besides the data obtained from experimental determinations, several researchers as listed below have evaluated the predicted $\log K_{om}$ values under standard conditions using the following equations 18 to 24.

$$\log K_{oc} = 3.64 - 0.55 \log S \quad [\text{Kenaga and Goring 1978 (85)}] \quad \text{---(18)}$$

$$\log K_{oc} = 0.937 \log K_{ow} - 0.006$$

[Brown and Flag 1981(86)] ----(19)

$$\log K_{om} = \log K_{ow} - 0.317 \quad [\text{Hassett et al. 1980, (87)}] \quad \text{---(20)}$$

$$\log K_{om} = 0.544 \log K_{ow} + 1.377$$

[Layman 1990 (88)] ----(21)

$$\log K_{om} = 0.53 \cdot^1X + 0.54 \quad [\text{Sabijic 1987 (89)}] \quad \text{----(22)}$$

$$\log K_{om} = 0.53 \cdot^1X + 0.62 \quad [\text{Meylan et al. 1992 (90)}] \quad \text{---(23)}$$

$$\log K_{om} = 0.64 \text{ AI} + 0.16 \quad [\text{Okouchi and Saegusa 1989(56)}] \quad \text{----(24)}$$

where S represent the water solubility expressed in ug/ml, K_{ow} is the 1-octanol/water partition coefficient, AI is the adsorbability index and 1X is the first-order molecular connectivity index for the different organic compounds studied. The predicted $\log K_{oc}$ values obtained from equations (18) and (19) were also evaluated in terms of $\log K_{om}$ and the corresponding values obtained are summarized in Table 4.



Table 4. Comparison of the Predicted values of log K_{om} obtained from equations (18) to (24) with average of the Experimental observed values of log K_{om} for the adsorption of endosulfan onto soils studied.

Average experimental value of log K _{om}	Predicted value of log K _{om}	Δ ^a	% Error ^b
3.70	3.67	0.03	0.81
	3.08	0.62	16.75
	3.23	0.47	12.70
	3.30	0.40	10.81
	3.55	0.15	4.05
	3.62	0.08	2.16
	3.66	0.04	1.08

^aΔ = Experimental value of log K_{om} – Predicted value of log K_{om}

^b% Error = [1 - (Predicted value of log K_{om}) / (experimental value of log K_{om}) × 100]

The predicted log K_{om} values for endosulfan were evaluated by substituting the appropriate values of the above coefficients for endosulfan in equations (18) to (24), with the corresponding data again being listed in Table 4 . It will be seen from Table 4 that the predicted log K_{om} values obtained from the aqueous solubility and 1-octanol/water partition coefficient (K_{ow}) of endosulfan were in erroneous compared to the average value obtained experimentally. However, when the adsorbability index (AI) and the first-order molecular connectivity index (¹X) were taken into consideration, the predicted K_{om} values were very close to those observed experimentally. Hence, the two latter parameters are better able to predict the adsorption behaviour of endosulfan than aqueous solubility or the I-octanol /water partition coefficient (K_{ow}). Since the value of the adsorbability index (AI) and first -order molecular connectivity Index (¹X) are quantified by the shape and size of endosulfan .Hence it may be stated that structure of endosulfan has a dominant effect on the soil sorption process.

Groundwater Ubiquity Score (GUS) :

The application of the GUS index splits the studied pesticides into three groups : "leachers" , "non-leachers " ,and "borderline", compounds based on adsorption and persistence properties in soils . From the half -life of endosulfan (50days) and calculated K_{oc} values (Table 3) ,the GUS values were calculate and given in Table3.

The index allows pesticide to be split according to trigger values . According to this index , a chemical would be classified as "leacher" if GUS values > 2.8, with a high risk for contamination , "non-leacher" with GUS values. < 1.8 and "borderline " compounds with GUS values between 1.8 and 2.8 [57] . The GUS values calculated for each soil are in the range 0.022 to 0.030 .The value indicates the leaching potential of the endosulfan residue was found to non-leachable through the soil .Similar results were reported by many workers[91-92].

Leaching (LEACH) index :

The results of leaching index (LEACH) obtained are summarised in Table 3.It will be seen from the leaching index data recorded that higher LEACH values were obtained for Black clay loam soil than Red loam .This LEACH order is



directly proportional to the values of K_F and K_D values. The larger LEACH values for clay loam soil may be attributed to its greater adsorption capacity. In other words, greater environmental concerns relate to the leaching of endosulfan from red loam soil relative to black clay loam soil. Similar results were reported by Singh and Srivastava [93, 57].

Effect of Temperature on Soil Adsorption of Endosulfan :

When the effect of temperature on the adsorption of endosulfan on soils was compared, the isotherms obtained (Figs. 1 and 2) clearly indicate that endosulfan adsorption was higher in Black clay loam soil than Red loam soil and adsorption of endosulfan decreased with an increase in temperature, as expected from the exothermic nature of the physical adsorption [83] or could be interpreted to increase in the aqueous solubility of the pesticide [94]. The lower adsorption also at higher temperature is partly due to a weakening of the attractive forces between endosulfan and the soil sites and partly due to the enhancement of the thermal energy of the adsorbate, thereby making the attractive forces between endosulfan and the soil sites sufficient to retain the endosulfan. However, the nature of the reaction is unaffected in soils. This is further confirmed by the values of K_F , and K_D , (Table 3). An increase in the temperature might be expected to have a greater potential impact because such an increase could lead to a loss of water from preferential adsorption sites thereby making these sites available to pesticides. Hence, the decrease in adsorption observed in the present case was probably due to a weakening in the van der Waals forces of attraction between endosulfan and the soils [95].

Thermodynamic Parameters :

The values of the thermodynamic parameters such as the thermodynamic equilibrium constant, K_0 , the standard free energy, enthalpy and entropy changes (ΔG° , ΔH° and ΔS°) obtained at 25°C and 50°C are listed in Table 5.

Table .5. The values of thermodynamic parameters associated with adsorption of Endosulfan at 25°C and 50°C on the soils studied.

Soil	Temperature (°C)	K_0	ΔG° kJ mol ⁻¹	ΔH° kJ mol ⁻¹	ΔS° kJ mol ⁻¹ degree ⁻¹
Clay loam	25	7.05×10^6	-39.07		0.2039
	50	3.58×10^6	-40.52	21.69	0.2088
Loam	25	6.57×10^7	-44.60		0.2262
	50	3.17×10^7	-46.38	22.82	0.2142

The higher values of the thermodynamic equilibrium constant, K_0 , at lower temperatures for all the soil-endosulfan interactions indicate the higher preference for soils at lower temperature. The negative values of the standard free energy (ΔG°) show that the reaction is spontaneous with high affinity for endosulfan at both the temperatures. The higher values of ΔG° at 50°C than those at 25°C might be due to the existence of weak attractive forces at higher temperature. This suggests a high persistence and resistance to degradation of endosulfan in soils and also confirms the nature of the isotherms obtained at different temperatures (Figs. 1 and 2). The positive values of the standard enthalpy changes (ΔH°) indicate that the process is endothermic in nature.

The positive values of the standard entropy changes, ΔS° , obtained in the present investigation indicate the stability of the soil-endosulfan complexes formed in the system. In other systems involving smaller molecules, it is possible that the adsorption of the large Endosulfan molecule would lead to the displacement of these molecules from the exchange complex and their subsequent desorption. The net result would then be an overall increase in entropy for the total system [96] rather than a decrease in the degree of randomness due to immobilization of the endosulfan molecule [59].

IV. CONCLUSIONS

The adsorption of endosulfan onto two texturally different soils of Rajasthan (black clay loam and red loam) at two different temperatures, viz., 25°C and 50°C, was studied using batch equilibrium techniques. The higher adsorption of endosulfan was obtained in clay loam soil than Red loam soil at both the temperatures. The values of the Freundlich constant, K_F , and the distribution coefficient, K_D , were calculated from the adsorption data obtained at two temperatures. The results obtained showed that the adsorption of endosulfan was greater at 25°C than 50°C. From the values of K_{oc} and K_c , it was concluded that other soil components in addition to organic matter contributed to the adsorption of endosulfan onto the soils studied. The negative values of ΔG° and the positive values of ΔH° obtained for the adsorption of endosulfan onto both soils indicate that the adsorption process was spontaneous and endothermic. In summary, the present study has shown that a high organic matter content in soils and an elevated temperature both contribute to higher levels of endosulfan adsorption. Thus, whenever this combination of factors exists, the probability of residual toxicity occurs.

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