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Adsorption of Carbofuran in Two different Soils of Rajasthan :Evaluation of Thermodynamic Parameters ,Adsorbability Index (AI) , the First-order Molecular Connectivity Index ($^1\chi$) and Leachability indexes for Carbofuran

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ABSTRACT: The adsorption thermodynamics of Carbofuran on to two divergent textured (loam and loamy sand) soils of Rajasthan from methanol / water mixtures at $f_s = 0.25$ have been investigated at 25°C and 45°C temperatures. The adsorption isotherms, Freundlich constant, distribution coefficient and thermodynamic parameters measured. The measured equilibrium adsorption isotherms were S-shaped for both the soils at 25°C and 45°C temperatures. The adsorption of carbofuran on both the soils decreased with increasing temperature. The higher adsorption was observed on loam soil than loamy sand soil at both the temperatures, as anticipated from the values of the Freundlich constant, K_F , and the distribution coefficient, K_D . The affinity of carbofuran 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 $\log K_{OM}$ 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 ($^1\chi$) of carbofuran. Use of the AI and $^1\chi$ indices of carbofuran gave predicted $\log K_{OM}$ values close to those observed experimentally. The leaching index (LEACH) of the adsorption of carbofuran calculated for the soils studied indicated it's high potential to leach into shallow aquifers and ground water. The mobility residues of carbofuran in soil was calculated using GUS index (Ground water Ubiquity Score) equation. The GUS index values were found to less than 1.8 (non-leacher category) in both the soils studied.

The thermodynamic equilibrium constant (K_0), the standard free energy change (ΔG°), the standard enthalpy change (ΔH°) and the standard entropy change (ΔS°) were calculated in order to predict the nature of the adsorption process.

KEYWORDS : Carbofuran , Adsorption , Thermodynamic parameters (K_0 , ΔG° , ΔH° and ΔS°), Distribution coefficient (K_D), Freundlich constants (K_F), Adsorbability index (AI), First -order molecular connectivity index ($^1\chi$), Leaching index (LEACH), GUS index.

I. INTRODUCTION

The use of organic pesticides (including herbicides, fungicides, and insecticides) in agricultural and horticultural practices has increased dramatically in recent decades throughout the world, with a corresponding increase in concern with respect to the potential of residues from these non-point sources to leach and contaminate the groundwater [1-3]. So soil and groundwater pollution has become a major issue in agriculture during the past several years because the

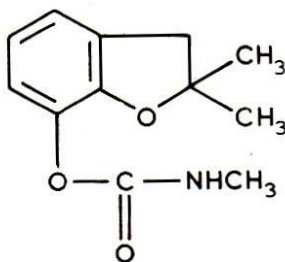


increased use of these agron-chemicals has led to a greater emphasis on serious environmental contamination. In these circumstances, the ability to predict the fate of such chemicals released into the environment is an essential prerequisite to their efficient and safe management as well as to the establishment of realistic regulatory controls. The soil plays an important role in the fate of pesticides in the environment. These contaminants (pesticides) enter the soil mainly by deliberate application, by spillage and leakage, and by atmospheric deposition. As a result, the soil is a sink for pesticides. While these chemicals may be lost from the soil, significant concentrations may be retained within soils. Consequently, the fate and behaviour of organic pesticides in soil has been subject of intensive research. The fate and behaviour of a pesticide in soil is governed by a variety of physical, chemical and biological processes, which are often complex and dynamic. These include adsorption, volatilisation, chemical and biological degradation, plant uptake, surface runoff, and leaching. Several books and review articles have been written on fate and behaviour of pesticides in soil and water environment [4-14]. Adsorption is one of the major processes affecting the interactions between pesticides and the solid phase in the soil environment. It is the attraction and repulsion phenomenon at the surface and exerts more pronounced influence amongst the several processes operating to determine the fate and behaviour of pesticides in soil.

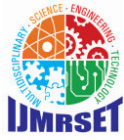
It depends upon the nature and properties of the pesticide such as acidity (pK_a), basicity (pK_b), solubility, shape and configuration, charge distribution, polarity of molecule, molecular size, and polarizability and its concentration in the solvent. Adsorption also plays an important role in regulating the rates and magnitudes of other processes that govern the fate and transport of organic contaminants in soils, sediments, and aquifers. The sorption process may cause a decrease in the biological activity of a pesticide and its rate of biological degradation, or enhance non-biological degradation due to catalysing hydrolysis.

The literature associated with this aspect has been reviewed earlier by many workers [15-18].

Carbofuran (2,3-Dihydro-2,2-dimethyl-7-benzofuranyl-N-methyl carbamate) is a systemic non-ionic broad spectrum carbamate insecticide/nematicide which has been used widely in agriculture [19] for long time to control of many fruit and vegetables crops [20]. It has been noted that soil-dwelling pests especially nematode problem in soil have been causing problems for vegetable growers and farmers therefore, increasingly applied carbofuran to soil as a nematicide. It is soluble in water and highly mobile in soil, thereby having high potential for ground water contamination [21]. The maximum concentration of carbofuran admitted by World Health Organization (WHO) in drinking water is $3 \mu\text{g}/\text{L}$ [22] while according to the USEPA, the maximum acceptable carbofuran concentration in drinking water is $40 \mu\text{g}/\text{L}$ [23]. Therefore, the removal of carbofuran from soil and water is necessary. Its structure can be represented as:



A considerable amount of research work has been undertaken on adsorption behaviour of carbofuran in soils, clays, activated carbon, flyash and synthetic inorganic ion-exchangers [24-38]. However, information related to the effects of temperature on adsorption behaviour of carbofuran on Rajasthan origin soils is not available in literature. Hence, an attempt has been made in present investigation to study the effect of temperature on adsorption of carbofuran on two distinct soils of Rajasthan. From the adsorption data various parameters such as thermodynamic parameters (K_o , ΔG° , ΔH° and ΔS°), Distribution coefficient (K_D), Freundlich constants (K_F , $1/n$), Coefficient of determination (r^2), Adsorbability index (AI), First-order molecular connectivity index (χ^1), Leaching index (LEACH), GUS index, organic carbon partition coefficient, Organic matter Partition Coefficient and clay content partition coefficient were evaluated. These parameters were very useful in predicting the basic chemistry and the leachability potential of carbofuran in soils.



II. EXPERIMENTAL

Materials and Methods

The soils used in the present study were collected from surface horizon(0-30cm.) by taking samples from various representative sites of agricultural cultivated fields from village Kharva in Ajmer and from the village Kundera in Sawaimadhopur districts of Rajasthan, India. The collected soil samples were air-dried, ground to pass through a 2-mm sieve and stored in plastic bags in room temperature.

The physicochemical properties of both the soils were determined by the standard techniques. The mechanical composition of soils was estimated by the International pipette method [39]. The pH values of the 1:2.5 soil/water suspension were determined by method proposed by Jackson [40]. The organic carbon and organic matter content of soils were determined by Walkley and Black [41] and Cation -exchange capacity and calcium carbonate contents of soil samples were estimated by the methods [42,39]. The results are summarized in Table 1.

Table1. Physico-chemical Parameters of Two Different Soils Studied

Soil Properties	loam Soil of Kundera	Loamy sand of Kharva
1-Mechanical composition		
Sand (%)	48	71.50
Silt (%)	34.50	20.20
Clay (%)	17.50	8.30
Texture	loam	Loamy sand
2-EC(dsm^{-1})	0.35	2.90
3-pH	7.6	8.7
4- CaCO_3	8.5	0.35
5-Organic carbon (%)	0.34	0.25
6-Organic matter (%)	0.59	0.43
CEC ($\text{cmolp}^+\text{kg}^{-1}$)	18.50	11.50
8-Surface Area (m^2/g)	130.50	125.50

Carbofuran (aqueous solubility 320 mg / L ; $\log K_{ow} = 2.315$) was obtained from Pesticide India (Udaipur, Rajasthan). All other chemicals and reagents were of (BDH) AR grade.

A stock solution of carbofuran(500 $\mu\text{g}/\text{ml}$) was prepared by dissolving the requisite amount of carbofuran in methanol.

Adsorption Studies:

The adsorption studies of carbofuran onto the two natural soils of divergent texture at 25°C and 45°C was carried out using the batch technique. The studies were performed at a fixed 0.25 f_s (where f_s is the volume fraction of methanol). Suitable aliquots (0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, and 5.0 ml) of carbofuran solution (500 $\mu\text{g}/\text{ml}$) were taken in different 50 ml glass stoppered conical flasks .The final suspension of each flasks were made up to 20 ml



by adding requisite volume of methanol and distilled water to get the desired f_s (0.25) volume. To these solutions 1 g of each soil was added and the resulting soil suspensions shaken in a temperature-controlled shaker for 3 h at $25 \pm 1^\circ\text{C}$ for the first set of experiment and at $45 \pm 1^\circ\text{C}$ for 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. All the experiments reported herein were conducted in triplicate. After storage as mentioned above, the suspensions were centrifuged at 15000 rpm for 10 min using a Beckman model L3-50 ultracentrifuge. The amount of carbofuran in the supernatants was estimated spectrophotometrically using the method proposed by Mithyantha and Perur [43] in which 5 ml of supernatant was mixed with 5 ml of 0.2% sulphanic acid and 5 ml of 0.3% sodium nitrite solutions and allowed to stand for 30 min. Then 10 ml of 4 M sodium hydroxide was added and the volume made up to 50 ml with distilled water. After 1 h, an orange-yellow colour developed and was measured at 490 nm using a Bausch and Lomb Spectronic 20 instrument. This method has a detection limit of $1 \mu\text{g/ml}$. To study the effect of temperatures, suspensions prepared as above were shaken at 45°C using natural soils as adsorbents.

The amount of carbofuran adsorbed was calculated as the difference between the initial and equilibrium concentrations in solution according to the following expression:

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

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

Evaluation of the adsorbability index (AI) and the molecular connectivity Index (1X)

The adsorbability index (AI) proposed by Abe et al [44] 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 [45].

The adsorbability index (AI) of carbofuran was evaluated from equation (2) by inserting the values of A and I derived from the work of Abe et al [44] 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 carbofuran being equal to 4.74.

The first-order molecular connectivity index (1X) for carbofuran was evaluated by substituting the above value of AI into the following equation proposed by Okouchi & Saegusa [45] :

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

from which a corresponding value of 4.8184 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

Calculation of Leaching Indexes :

The two traditional indexes, the leaching index (LEACH) [46] groundwater Ubiquity Score (GUS) indexes later used by papa et al. [47] were applied to calculate leachability of pesticides .

LEACH index for Carbofuran :

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 [46] and later used by Papa et al. [47].

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

where S_w is the water solubility of carbofuran (320 mg L⁻¹), t_{1/2} is the degradation half-life of carbofuran in soil (50 days), V_p is the vapour pressure of carbofuran (8.3 × 10⁻⁶ 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 .

Evaluation of Groundwater Ubiquity Score (GUS) Index for Carbofuran : The GUS index was used for determining the leachability of pesticides and the possibility of finding pesticides in groundwater. It is calculated by the equation proposed by Gustafson [48]:



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

Where $t_{1/2\text{-soil}}$ 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 index allows pesticides to be split according to Tigger values, as explained in the discussion.

Table 3. Adsorption Data for Carbofuran at 25°C and 45°C in Two Different 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
Loam										
At 25°C	51.30	0.826	29.05	0.998	8544.12	157.24	4923.72	3.69	0.23×10^6	0.12
At 45°C	35.46	0.872	22.85	0.997	6720.59	130.57	3872.88	3.59	-	-
Loamy sand										
At 25°C	25.14	0.888	17.20	0.996	5058.82	207.22	4000.00	3.60	0.38×10^6	0.51
At 45°C	19.94	0.899	13.00	0.998	3823.53	156.63	3023.26	4.48	-	-

Evaluation of thermodynamic parameters :

The thermodynamic equilibrium constant K_o , for the adsorption was calculated by the equation proposed by Biggar and Cheung [49] and later used by many workers [50,51].

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

Where, C_s ($\mu\text{g/g}$) is the amount of carbofuran adsorbed per gram of the solvent in contact with soil and C_e , the concentration of carbofuran in equilibrium suspension in $\mu\text{g/ml}$. y_s and y_e are the activity coefficients of the adsorbed solute and solute in equilibrium suspension, respectively and assumed to be unity [52] in dilute range of the studies.

The values of C_s , were calculated by using the equation on proposed by Fu et. [53].

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

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 carbofuran adsorbed as expressed in $\mu\text{g/g}$.

The cross-sectional area (A) of the solvent molecule is estimated by using the following equation [54].

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



As the concentration of solute in the solution approached zero, the activity coefficient, γ approached unity. Equation (6) 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 carbofuran are evaluated from the equations proposed by Glasstone[55] and later used by Singh [56].

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

Where R = universal gas constant ($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) 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, ΔS° , was calculated by the equation.

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

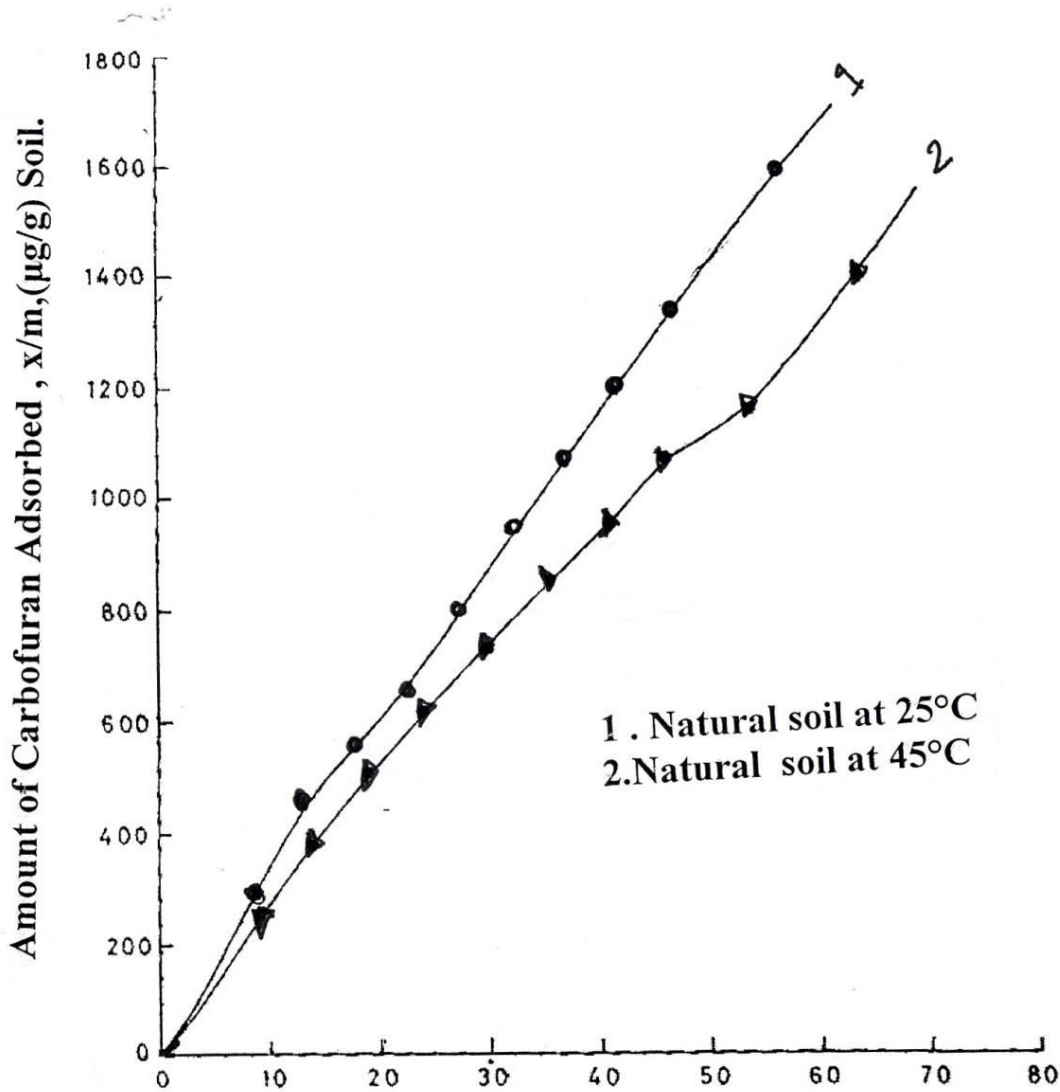
III. RESULTS AND DISCUSSION

It is evident from the data listed in Table 1 that both the soils used in the present study were differed widely in their physico-chemical parameters. The higher values of organic matter content, clay content, calcium carbonate content (CaCO_3), cation exchange capacity (CEC) and surface area were obtained in loam soil than loamy sand soil. The pH and EC values were in reverse order.

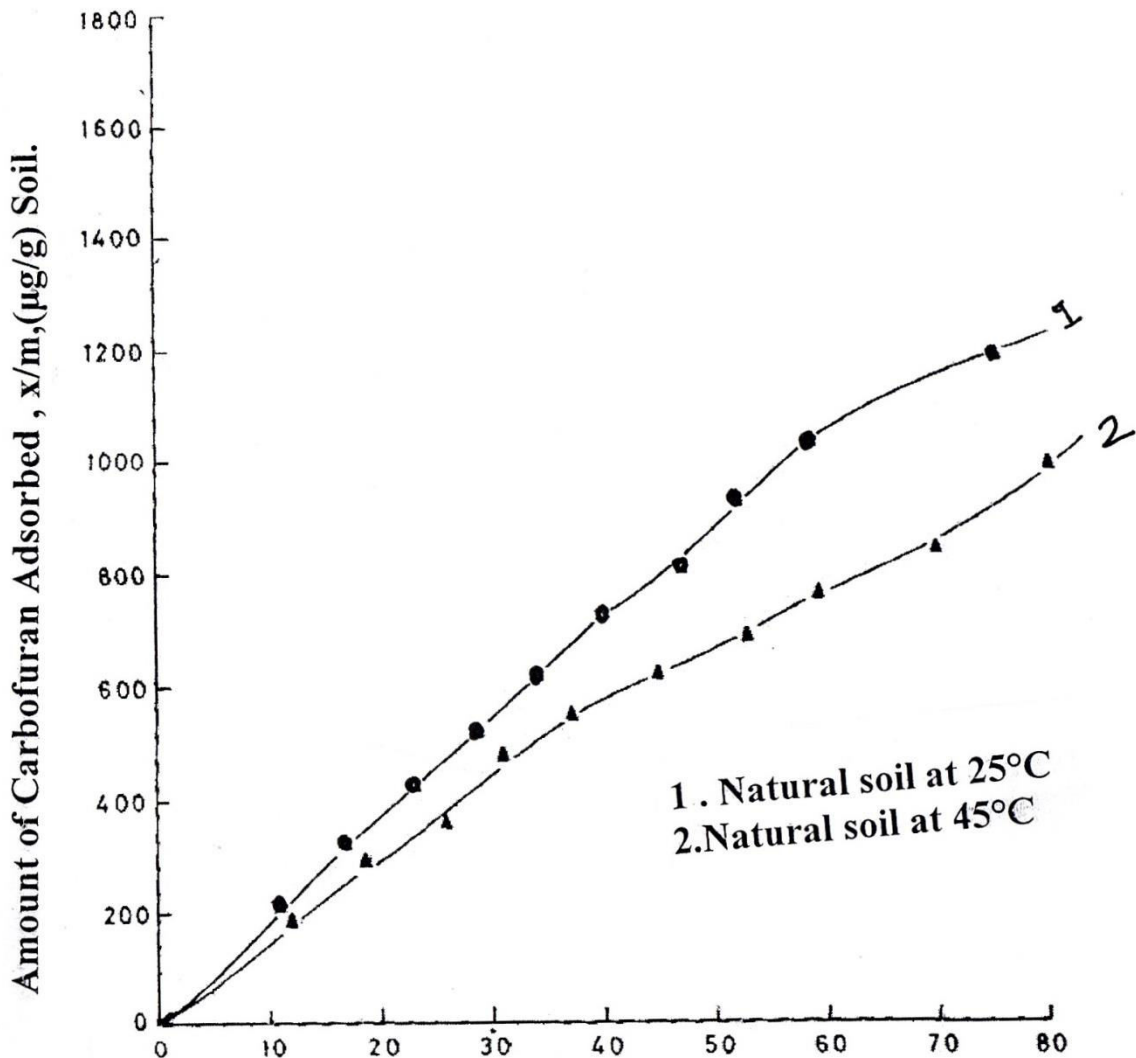
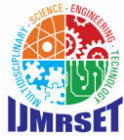
Adsorption Isotherms :

Adsorption isotherms linking the amount of carbofuran adsorbed ($\mu\text{g/g}$) on soil and the amount of carbofuran in equilibrium suspension ($\mu\text{g/ml}$) were plotted and are depicted in Figs.1 & 2. The isotherms for both the soils at 25°C and 45°C temperatures are S-shaped

[57]. The adsorption isotherms clearly indicate that carbofuran adsorption was higher on loam soil than loamy sand soil. The higher adsorption of carbofuran on loam soil may be due to the greater amount of organic matter content, clay content, CEC and Surface area in loam soil and other variations in the soil properties. The S-shaped adsorption isotherms for both the soils at both temperatures also suggest that the adsorption was probably due to the marked localization of the attractive force on the $>\text{C}=\text{O}$ group of carbofuran leading to interaction with soil sites.



Amount of Carbofuran in Equilibrium Suspension, C_e ($\mu\text{g} / \text{ml}$)
Fig. 1 Adsorption Isotherms of Carbofuran on loam Soil at 25°C and 45°C Temperatures.



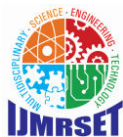
Amount of Carbofuran in Equilibrium Suspension, C_e ($\mu\text{g} / \text{ml}$)
 Fig. 2 Adsorption Isotherms of Carbofuran on loamy sand Soil at 25°C and 45°C Temperatures.

Determination of Freundlich Constants (K_F and $1/n$):

The adsorption behaviour of carbofuran in both the soils at 25°C and 45°C was fitted to the Freundlich adsorption equation :

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

Where , K_F and $1/n$ are two empirical adsorption constants associated with the affinity of the adsorbate for adsorbent and the degree of curvature of the isotherms. The Freundlich constant K_F has the dimension $(\mu\text{g}^{(1-n)} \text{ml}^n) / \text{g}$ and it is a measure of the degree or strength of adsorption .While $1/n$ is dimension less and it provides an idea of intensity of



adsorption which varies with the nature of the adsorbate for a given adsorbent ; $1/n$ also indicates the degree of non-linearity ($1/n < 1$) between solution equilibrium concentration and adsorption . The variable slopes of adsorption isotherms obtained at two temperatures studied reveal the pesticide adsorption on soil is a complex phenomenon involving different types of adsorption sites with different surface energies [58] . In general the values of the coefficient of determination , r^2 (Table 3) at least 0.99 ,which indicates an excellent fit of the data to the Freundlich equation.

The values of K_F and $1/n$ for soil / carbofuran combinations were estimated by linear regression of the logarithmically - transformed data with the resulted values so obtained being presented in Table 3. The magnitude of K_F expresses the relative adsorption capacity for the adsorbate [59] for a system having comparable $1/n$ values or degree of adsorption[60] .

Comparing the values of K_F and $1/n$ for soils , it is clear that carbofuran adsorbed to a greater extent on loam soil than loamy sand 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 carbofuran at lower temperature in both the soils.

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 , since this may also be related to adsorption under equilibrium conditions[61] . The statistical average of all K_D values for both the soils at 25°C and 45°C were 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 ,from which it is seen that the sequence of K_D values also confirms the above order of adsorption.

Calculations of Organic Carbon partition Coefficient (K_{OC}), Organic matter Partition Coefficient (K_{OM}) and Clay Content Partition Coefficient (K_{CC}) :

The normalised adsorption coefficients relative to organic carbon(K_{OC}) ,organic matter(K_{OM}) and clay content(K_{CC}) were evaluated by using the equations proposed by many workers [62-66] . The results obtained are summarised in Table 3.

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

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

$$K_{CC} = (K_D \times 100) / \% \text{ clay content} \quad (17)$$

These are the important parameters that play a significant role in environmental fate assessment of organic chemicals .They provide an indication of the extent to which a chemical partitioning occurs between the solid and solution phases in soil, and suggests whether the chemical is likely to leach through soil or be rendered immobile.

In the present study ,the high K_{OC} and K_{OM} values obtained at both temperatures lead to the conclusion that organic matter is the main parameter governing the adsorption of carbofuran. However ,the variability in K_{OC} and K_{OM} values among both the soils at both temperatures also show that adsorption was not governed exclusively by the organic matter content of the soils and the other components may also contribute to the adsorption process [67].

The results are in accordance with the work of Walker and Crawford [68] and Stevenson [69] who reported that, up to an organic matter content of 6%, both organic and mineral surfaces are involved in adsorption. Stevenson [69] 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.



Modeling of Adsorption Behaviour in Soils :

In addition to experimental determinations, several researchers (as listed below) have evaluated the predicted log K_{OM} values using the following equations 18 to 24.

$$\log K_{OC} = 3.64 - 0.55 \log S \text{ [Kenaga and Goring 1978 (70)] } \text{---(18)}$$

$$\log K_{OC} = 0.937 \log K_{OW} - 0.006$$

[Brown and Flag 1981 (71)----(19)

$$\log K_{OM} = \log K_{OW} - 0.317 \text{ [Hassett et al.1980,1981 (72,73)] } \text{---(20)}$$

$$\log K_{OM} = 0.544 \log K_{OW} + 1.377$$

[Layman 1990 (74)] ---(21)

$$\log K_{OM} = 0.53 \cdot {}^1X + 0.54 \text{ [Sabijic 1987 (75)] } \text{---(22)}$$

$$\log K_{OM} = 0.53 \cdot {}^1X + 0.62 \text{ [Meylan et al. 1992 (76)] } \text{---(23)}$$

$$\log K_{OM} = 0.64AI + 0.16 \text{ [Okouchi and Saegusa 1989 (45)] } \text{----(24)}$$

where S and WS represent the solubility in water expressed in $\mu\text{g} / \text{ml}$ and mg / L . respectively, 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 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)-(24) with average of the Experimental observed values of log K_{OM} for the adsorption of carbofuran onto soils studied.

Average experimental value of log K_{OM}	Predicted value of log K_{OM}	Δ^a	% Error ^b
3.59	2.02	1.57	43.73
	2.32	1.27	35.38
	1.92	1.67	46.52
	1.76	1.83	50.97
	2.40	1.19	33.16
	3.09	0.50	13.93
	3.17	0.42	2.20
	3.19	0.40	1.12

^a Δ = experimental value of log K_{OM} – Predicted value of log K_{OM}



$$b\% \text{Error} = [1 - (\text{Predicted value of } \log K_{OM}) / (\text{experimental value of } \log K_{OM}) \times 100]$$

The predicted $\log K_{OM}$ values for carbofuran were evaluated by substituting the appropriate values of the above coefficients for carbofuran in equations (18) to (24), with the corresponding data again being listed in Table 4. It will be seen from the Table 4 that the predicted $\log K_{OM}$ values obtained from the aqueous solubility and 1-octanol/water partition coefficient (K_{OW}) of carbofuran were in error 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 provides a better prediction of the adsorption behaviour of carbofuran than aqueous solubility and the value of 1-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 carbofuran molecule mm .Hence it may be stated that structure of carbofuran has a dominant effect on the soil sorption process.

Leaching Indexes:

The results of LEACH index and GUS index values in both the natural soils at 25°C obtained are summarised in Table 3.

It will be seen from the leaching index data (Table 3) recorded that higher LEACH index values were obtained for loam soil than loamy sand .This LEACH index value order is directly proportional to the K_F and K_D values. The larger LEACH index values for loam soil may be attributed to its greater adsorption capacity .In orther words ,greater environmental concerns relate to the leaching of carbofuran from loamy sand soil relative to loam soil. Similar results were reported by Singh and Srivastava [77].

From the half -life ($t_{1/2\text{-soil}}$) of carbofuran found in literature (50 days) and calculated K_{OC} values (Table 3) , the GUS index values calculated for both the soils are in the range 0.12 to 51 .These values comes in the category less than 1.8 (non-leacher category) according to Papa et al [47].These values indicates that the leaching potential of the carbofuran residue was found to non- leachable through the soils studied .Similar results were reported by many workers [78,79].

Effect of Temperature on Adsorption:

When the effect of temperature on the adsorption of carbofuran on soils is compared, it is clear from the isotherms (Figs. 1 & 2.) that carbofuran adsorption decreases with increase in temperature, as expected from the exothermic nature of the adsorption phenomenon. The lower adsorption at higher temperature is partly due to the weakening of attractive forces between carbofuran and soil sites and partly due to enhancement of thermal energies of the adsorbate, thus making the attractive forces between carbofuran and soil sites sufficient to retain carbofuran. However, the nature of the reaction remains the same in both the soils. This found further confirmation from the K_F and K_D values (Table 3). Increase in temperature provides greater potential impact because the elevation in temperature causes loss of water from preferential adsorption sites thereby making these sites available to the pesticide. So here decrease in adsorption was probably due to weakening of van der Waal's forces of attraction between carbofuran and soils (80).

Thermodynamic Parameters:

The results of thermodynamic parameters such as thermodynamic equilibrium constant K_o , the changes in standard free energy ,enthalpy and entropy (ΔG° , ΔH° and ΔS°) for carbofuran adsorption on both the soils obtained at 25 °C and 45°C are tabulated in Table 5 .



Table 5. The values of thermodynamic parameters associated with adsorption of carbofuran at 25°C and 45°C on the soils studied.

Soil	Temperature (°C)	$10^4 \times K_o$	$\Delta G^\circ \text{kJ mol}^{-1}$	$\Delta H^\circ \text{kJ mol}^{-1}$	$\Delta S^\circ \text{kJ mol}^{-1} \text{degree}^{-1}$
Clay loam	25	487.69	-38.15	-15.76	0.0751
	45	326.98	-39.66	-15.76	0.0751
Loamy sand	25	361.88	-37.41	-11.88	0.0857
	45	267.69	-39.13	-11.88	0.0857

The higher values of thermodynamic equilibrium constant K_o at 25°C than 45°C for all soil / carbofuran interactions indicates the higher preference of carbofuran for soils at lower temperature. However, these values were higher at both the temperatures in loam soil than loamy sand soil, which again confirms the above order of carbofuran adsorption.

The negative values of standard free energy change, ΔG° indicated that the reactions were spontaneous with high affinity for carbofuran. The increased negativity of ΔG° at 45°C relative to that at 25°C (Table 5) reflects the high affinity of carbofuran towards the various soils at higher temperatures. The negative values of standard enthalpy change, ΔH° indicated that carbofuran interaction with soils are exothermic and decrease in temperature favoured the reaction products which are energetically stable with the high binding of carbofuran to soil sites. The positive values of standard entropy change, ΔS° obtained in the present study indicate the stability of soil-carbofuran complex formed in the system. In other system involving smaller molecules, it is possible that the adsorption of the large carbofuran molecule would lead to the displacement of these molecules from the exchange complex and their subsequent desorption. The net results would then be an overall increase in entropy for the total system [81] rather than a decrease in the degree of randomness due to immobilisation of the carbofuran molecule [49].

IV. CONCLUSIONS

The adsorption of carbofuran onto two texturally different Rajasthan soils at two different temperatures viz. 25°C and 45°C, was studied using batch equilibrium techniques. The values of Freundlich constant, K_F , and the distribution coefficient, K_D , were calculated from the adsorption data obtained at both temperatures. The results obtained showed that the adsorption of carbofuran was greater at 25°C relative to the at 45°C. From the values of K_{OC} and K_{CC} , it was concluded that other soil components in addition to organic matter contributed to the adsorption of carbofuran onto the soils studied. The negative values of ΔG° and the negative values of ΔH° obtained for the adsorption of carbofuran onto both the soils indicate that the adsorption process was spontaneous and exothermic. 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 carbofuran adsorption. Thus, whenever this combination of factors exists, the probability of residual toxic occurs. Leachability of carbofuran was calculated in both the natural soils by using LEACH index and GUS index equations.

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