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Influence of Organic Co-solvent (Methanol) on Adsorption of Carbofuran in Two Divergent Textured Soils of Rajasthan : A verification of Co-solvent Theory

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ABSTRACT: The batch equilibrium technique was used to investigate the effect of different volume fractions ($f_s=0.25, 0.50, 0.75$, and 1.0) of organic co-solvent (methanol) on the adsorption of carbofuran on two divergent textured soils of Rajasthan (loam and sandy loam). The measured equilibrium adsorption isotherms for both the soils investigated were S-shaped for co-solvent /water mixtures at all f_s values. All isotherms being well fitted by the Freundlich equation. The higher adsorption of carbofuran was observed on loam soil than sandy loam soil at all f_s values and as anticipated from the values of the Freundlich constants, K_F , and the partition coefficient, K_D . The order of the calculated values of K_F and K_D showed that adsorption of carbofuran in both soils decreased with increase in f_s values. The higher K_F and K_D values at lower f_s confirm that carbofuran adsorption decreased with increase in ' f_s ' values. The decreased in adsorption of carbofuran in methanol -water mixture meant a greater potential of ground water contamination through leaching from potential sites.

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_c . The leaching index and Gibbs free energy (ΔG°) were evaluated from K_{oc} values of adsorption data at all f_s values. The negative magnitude of the Gibbs free energy (ΔG°) indicated the spontaneity on the adsorption onto soils studied.

The leaching index (LI) of carbofuran calculated for the soils studied indicated its high potential to leach into shallow aquifers and ground water. The adsorption data have been used to evaluate the co-solvent theory for describing adsorption of carbofuran in methanol-water mixtures. The aqueous phase partition coefficient K_{Dw} (mol g^{-1}) normalised with respect to $f_{oc} = 0$ and the aqueous phase adsorption constant K_w for carbofuran were evaluated by extrapolating to $f_s = 0$

KEYWORDS: Carbofuran, Adsorption, distribution coefficient, partition coefficient, co-solvent theory, Leaching Index, Gibbs free energy (ΔG°), Freundlich equation.

I. INTRODUCTION

The use of synthetic organic pesticides has considerably magnified in last few decades in intensive agricultural [1] for controlling insects pests and harmful phytopathogens (2). Their indiscriminate and heavy use in modern agriculture is not only beneficial, but may also have negative consequences on the environment and human health [3]. For this reason, understanding and studying the behaviour of these chemicals in different environmental compartments are of paramount importance to evaluate the impact of these pollutants on the environment. The soil plays an important role in the fate and behaviour of pesticides in the environment. It is a major sink of pesticides, whether the compounds are directly (e.g., by incorporation) or indirectly (e.g., aerial spraying) applied. 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. A fraction of pesticide that enters the soil is lost by leaching, photodecomposition, plant uptake, surface runoff and volatilisation. These processes combined may under certain conditions, contribute appreciably to the total loss of a pesticide. In the majority of cases, however, the bulk of

applied pesticide adsorbed by inorganic and organic soil constituents, chemically transformed and microbially degraded or metabolized. These processes of dissipation are more or less interdependent.

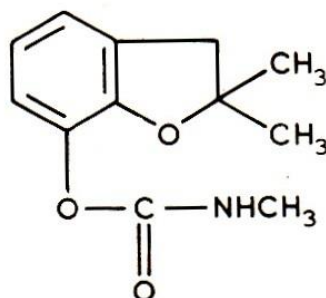
Consequently, the fate and behaviour of these organic contaminants in soils has been the subject of intensive research, with particular interest directed on the adsorption and movement of pesticides in the soil.

Adsorption is one of the major processes affecting the interactions between pesticides and the solid phase in the soil environment. It 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.

Adsorption 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. The adsorption 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 [5]. The transport of an organic chemical is also significantly affected by chemical sorption onto soil. As the adsorption process is of profound importance for environmental fate. It has been investigated intensively over the last several years mostly in the soils by various researchers [4, 6-8]. The literature associated with this adsorption of pesticides in soils has been reviewed earlier by many workers [9-12].

It has been reported by several researchers [13-19] that chlorinated hydrocarbons, organophosphates and carbamate pesticides are found in surface and ground water samples as pollutants. This has also contributed to the need for experimental studies of pesticide adsorption in soils, so as to overcome the problems arising from the presence of pesticides in surface and ground water.

Carbamate pesticides are used increasingly in agriculture as a replacement for environmentally more persistent organochlorine pesticides. Carbofuran (2,3-Dihydro-2,2-dimethyl-7-benzofuranyl-N-methyl carbamate) is a systemic, non-ionic, broad-spectrum and second largest selling anticholinesterase carbamate which has been used widely as an insecticide, nematocide and acaricide in agricultural practice throughout the world 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 nematocide. It is toxic, carcinogenic, recalcitrant, 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]. According to the United States Environmental Protection Agency (US EPA), has set the maximum acceptable carbofuran concentration in drinking water as $40\mu\text{g} / \text{L}$ [23]. Like that of any other soil-applied pesticide, its effectiveness depends upon the soil properties, the environmental conditions and its ability to reach the target organisms in an adequate concentration for a certain period of time. Carbofuran losses in runoff occur largely in water and comprise up to 1.9% of the application [24]. Therefore, the removal of carbofuran from soil and water is necessary. Its structure can be represented as:



A lot of research work has been undertaken on the adsorption of carbofuran in soils, clays, activated carbon, flyash, synthetic inorganic ion-exchangers with aqueous solutions [25-36]. However, under waste disposal and land treatment sites, it is likely that the solution will consist of a mixture of water and various miscible organic solvents. This is what happens under waste disposal sites where residues of pesticides and cosolvents may be encountered. The presence of co-solvents may increase or decrease the adsorption of pesticides in soils [37-41]. But information on this

type of study is not available in literature with regard to adsorption of carbofuran in divergent textured soils of Rajasthan. Keeping this in mind, an interest has developed in the study of the adsorption of carbofuran from aqueous-organic mixed solvent. In the present study methanol was used as co-solvent because it is completely soluble in water, a proton donor [42] and expected to be found in most waste streams from industrial wastes. The main objectives of this investigation were to examine the effects of a miscible organic co-solvent (methanol) on the adsorption of carbofuran in soils and to verify the co-solvent theory from the partition coefficient K_D values. These studies will help in understanding the behaviour of carbofuran in the presence of methanol and may prove useful in accessing near-source carbofuran movement / transport in soil in the event of a spillage or discharge of organic wastes containing water-soluble solvents.

II. CO-SOLVENT THEORY

The cosolvent theory was proposed by Rao et.al. [37] to describe the adsorption of hydrophobic organic compounds to soils. The theory has been applied to the adsorption of several organic compounds having moderate and intermediate hydrophobicity by Nkedi-Kizza et al. [38], Walters and Gulseppl-Elle [39]; and Fu and Luthy [43, 44]. This theory is expressed by the equation:

$$\log [K_{mi} / K_{wi}] = - \alpha \sigma_s \text{-----}(1)$$

where f_s , is the volume fraction of co-solvents and K_{mi} and K_{wi} are the mole-based partition coefficients (mol g^{-1}) for water-cosolvent (methanol) mixtures and cosolvent free water, respectively. The term σ_s reflects the solute-liquid interactions and represented by the slope of the log-linear relationship between mole fraction solubility and f_s , and α is related to solute-soil and solvent-soil interactions via liquid and organic carbon phase activity coefficients [37, 43,44].

Statistical average of the volume based adsorption partition coefficients K_D (ml g^{-1}) was determined by the equation as :

$$K_D = \Sigma (x / m \cdot C_e) / \Sigma (C_e)^2 \text{---} (2)$$

The mole-based equilibrium adsorption partition coefficient (K_{mi}) values were determined by the equation:

$$K_{mi} = K_{di} / V_i \text{-----}(3)$$

Where V_i is the molar volume of the liquid phase (ml mol^{-1}).

This theory is important for two reasons:

1-The theory enables prediction of adsorption of organic solute from a specified mixture of water and miscible organic solvents. This has implication for understanding the fate and transport of organic contaminants in real world, complex wastes streams such as industrial waste and land fill leachates.

2 -The theory can be utilized to estimate the partition coefficient for adsorption from aqueous solution by plotting a graph between K_{di} versus f_s extrapolating to $f_s = 0$.

This theory is particularly important because it is very difficult to determine the adsorption partition coefficient of highly hydrophobic compounds from water.

III. EXPERIMENTAL

3.1. Reagents :

Carbofuran (Furadan 3G)

having molecular weight 221.30 , melting point is 150.0 to 152.2°C , Vapour pressure 2.7 Mpa and water solubility 700 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 (3G) of the concentration (1000 $\mu\text{g ml}^{-1}$) was prepared by dissolving 0.1 g active ingredient in 100 ml of methanol. A 100 ml of this solution was diluted to 250 ml in methanol giving a 400 $\mu\text{g ml}^{-1}$ carbofuran concentration.

3.2. Collection of Soil Samples

In present investigation the soils used were collected from the surface horizon (0-30 cm depth) from cultivated agricultural fields having no previous history of pesticide application from the Kundera village near Ranthambhour National Park in Sawaimadhopur district and the village Banasthali in Tonk district (Rajasthan) in India. The soil samples were air-dried ,ground to pass through a 2mm sieve and stored in plastic bags at room temperature before use. The physico-chemical properties of the soils were determined by using standard methods of soil analysis and results obtained are summarised in Table 1.

Table 1. Physico-chemical Properties of Soils Studied

Soil Properties	Loam Soil (Kundera)	Sandy loam Soil (Banasthali)
1-Mechanical composition		
Sand (%)	48.0	65.0
Silt (%)	34.5	25.50
Clay (%)	17.5	9.50
Texture	loam	Sandy loam
2-EC(dsm^{-1}) (1:2 soil-water ratio)	0.35	0.38
3-pH (1:2 soil -water ratio)	7.6	7.9
4- CaCO_3 (%)	8.5	5.50
5-Organic carbon (%)	0.34	0.20
6-Organic matter (%)	0.59	0.35
CEC ($\text{cmolp}^+\text{kg}^{-1}$)	18.50	8.80
8-Surface Area (m^2/g)	130.50	80.50

3.3 Adsorption Studies :

The adsorption of carbofuran on two soils of Rajasthan having divergent texture (loam and sandy loam) was carried out by using the batch equilibrium technique .In the present study four different fixed volume fractions (f_s , 0.25,

0.50, 0.75, 1.0) of methanol / water mixtures were utilized by taking ten concentrations of carbofuran (200, 400, 600, 800, 1000, 1200, 1400, 1600, 1800, 2000 μg) solutions in different flasks. The experiments were conducted in duplicate and each isotherm determination consisted of twenty one flasks for each of the ten carbofuran doses and one blank flask containing soil and no carbofuran. The total volume of each flask was made 20 ml by adding requisite volume of methanol and water to get the desired f_s , values. To these solutions 1 g of each soil was added and the suspensions shaken for three hours in an incubator at $20 \pm 1^\circ\text{C}$ and left standing overnight. The suspensions were then centrifuged at 10000 rpm for ten minutes using a Beckman Model L3-50 Ultracentrifuge, the supernatant being collected and estimated spectrophotometrically [45] at 490 nm and the amount adsorbed was calculated. All experiments were performed at a constant temperature of 20°C .

This method has a detection limit of 1 $\mu\text{g}/\text{ml}$.

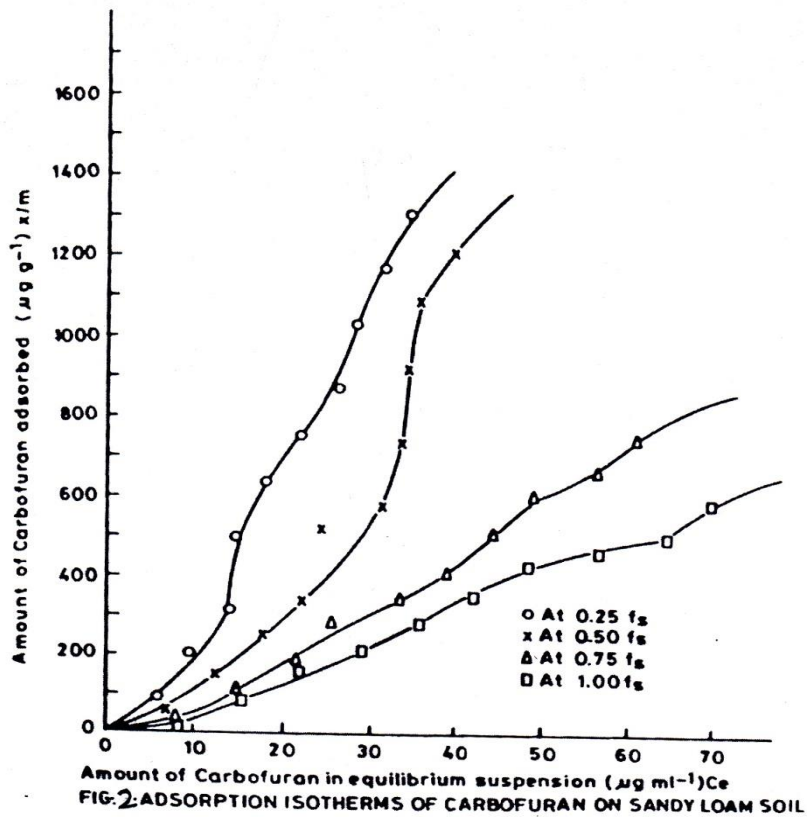
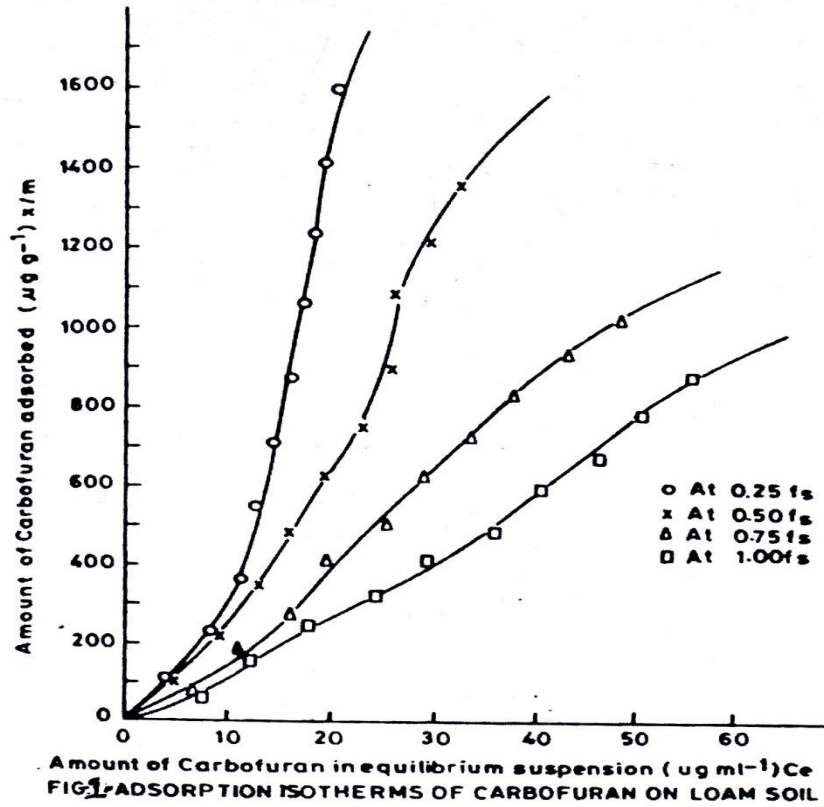
The amount of carbofuran adsorbed was calculated as the difference between the initial and equilibrium concentrations in solution according to the following expression:

$$x / m = (C_o - C_e) V / W \text{ ----(4)}$$

where x / m is the surface concentration of carbofuran in the soil ($\mu\text{g g}^{-1}$). C_o is the initial concentration of carbofuran in solution ($\mu\text{g ml}^{-1}$). C_e is the equilibrium concentration of carbofuran in solution ($\mu\text{g ml}^{-1}$). V is the volume of the solution and W is the weight of soil employed.

IV. RESULTS AND DISCUSSION

Adsorption isotherms (Figs 1& 2) have been constructed between the amount of carbofuran adsorbed ($\mu\text{g g}^{-1}$ soil) and the amount of carbofuran in suspension at equilibrium in $\mu\text{g ml}^{-1}$. These isotherms show that the adsorption of carbofuran was higher on loam soil than sandy loam soil at all the f_s values studied. The higher adsorption of carbofuran on loam soil may be due to the greater amount of organic matter content, clay content, CaCO_3 content and higher surface area, CEC and lower pH in loam soil than sandy loam soil. These isotherms also show that adsorption of carbofuran decreased with increasing f_s values. The lower adsorption of carbofuran at higher f_s values was brought about by the increased solubility of carbofuran due to the presence of methanol in the aqueous phase (21, 22). All isotherms are S-shaped [46] indicating an enhanced adsorption of carbofuran at higher concentration. The S-shaped isotherm also suggests that the adsorption of carbofuran was readily achieved possibly due to marked localization of attractive forces to the carbonyl group ($>\text{C}=\text{O}$) of carbofuran leading to action with sites on the surface of the soils,





4.1.Evaluation of Adsorption Constants (K_F and $1/n$) :

All the isotherms were in close agreement with Freundlich equation :

$$x/m = K_F C_e^{1/n} \quad (5)$$

where x/m is the amount of carbofuran adsorbed ($\mu\text{g g}^{-1}$), C_e , is the concentration of carbofuran at equilibrium ($\mu\text{g ml}^{-1}$) and K_F and $1/n$ are two empirical adsorption constants. In all the cases the coefficients of determination (r^2) values were greater than 0.93. The values of K and $1/n$ for carbofuran-soil combinations were estimated by linear regression of log transformed data and values are tabulated in Table 2. K_F is a measure of strength of adsorption, while $1/n$ indicates the degree of linearity between solution equilibrium concentration and adsorption. On comparing the values of K_F for soils, it is clear that the higher values of K_F for loam soil than sandy loam soil confirm the above order of adsorption. The higher values of K_F at lower f_s , also confirm that adsorption decreases with increase in f_s values. The results are in accordance with the theoretical approach proposed by Rao et al. [37]. Results mentioned in Table 2 indicates that the value of adsorption intensity ($1/n$), which reflects the degree of nonlinearity of the adsorption, were greater than unity indicating S-type isotherms (Figs 1& 2) as described by Giles et al. [46]. It indicates that new sites become available to the solvent for sites as the adsorption occurs, and there is competition of solvent for soils on the adsorbing surface. Similar results were also reported by Moreal and Van Bladel [47,38]. The S-shaped isotherms also suggest that adsorption of carbofuran was easier probably due to marked localization of forces of attraction over the carbonyl group ($>C=O$) of the carbofuran leading to interaction with soil sites. The lower adsorption at higher f_s values can also be explained as methanol is a compound having two different moieties: one is hydrocarbonaceous (hydrophobic), the other is polar. Carbofuran may interact with methanol by H-bonding between alcoholic group (OH) and the electron donating carbonyl ($>C=O$) group of carbofuran. This mechanism of interaction could explain the reduction of adsorption of carbofuran from methanol-water mixtures.

Table 2.Freundlich Constants ($K_F,1/n$), Partition Coefficient (K_D), Leaching Index (LI) , and Gibb's free energy (ΔG°) for Carbofuran Adsorption onto Soils at Different Volume Fractions (f_s) of Co-solvent (Methanol).

Parameters	Volume fraction of methanol (f_s)							
	Sandy loam Soil.				Loam Soil			
	1.00	0.75	0.50	0.25	1.00	0.75	0.50	0.25
K_D	8.49	11.57	24.84	35.84	15.17	21.59	37.89	61.82
K_F	2.70	4.00	5.30	6.60	4.69	7.03	9.39	11.71
$1/n$	1.25	1.30	1.25	1.53	1.36	1.36	1.45	1.58
r^2	0.9965	0.9398	0.9674	0.9862	0.9951	0.9961	0.9792	0.9407
K_c	89.37	121.79	261.47	377.26	86.69	123.37	216.51	353.26
K_{oc}	4245.00	5785.00	12420.00	17920.00	4461.76	6350.00	11144.12	18182.35
K_{om}	2425.72	3305.71	7097.14	10240.00	2571.19	3659.32	6422.03	10477.97
LI	0.99×10^6	0.73×10^6	0.34×10^6	0.24×10^6	0.95×10^6	0.66×10^6	0.38×10^6	0.23×10^6
ΔG° (kj mol ⁻¹)	-20.68	-21.45	-23.33	-24.25	-20.81	-21.67	-23.06	-24.28



4.2.Verification of the Co-solvent Theory with Respect to K_D

Selected properties of water/methanol mixtures, such as the volume fraction of methanol (f_s), the mass fraction of methanol (f_m) and the mole-fraction of methanol (f_{mol}), were evaluated by using the following equations (6),(7)and (8) respectively .

$$f_s = V_m / (V_m + V_w) \quad \text{---(6)}$$

$$f_m = [1 + (P_w / P_m) (1 - f_s) / f_s]^{-1} \quad \text{---(7)}$$

$$f_{mol} = [1 + (P_w + M_m / P_m M_w) (1 - f_s) / f_s]^{-1} \quad \text{---(8)}$$

where, V_m , V_w , are the volumes, P_m , P_w , the densities and M_m , M_w , the molecular weights of methanol (m) and water (w) respectively. Liquid densities, P_{mix} ($g\ ml^{-1}$), are based on f_m , and data for 20°C were taken from Table 3-III Perry and Chilton [49]. The molar volume, V ($ml\ mol^{-1}$), was as evaluated from the equation.

$$V = (1 / P_{mix}) [(M_m f_{mol} + M_w (1 - f_{mol}))] \quad \text{---(9)}$$

The values are summarised in Table 3.

Table 3.Selected Properties of Methanol -Water Mixtures .

Properties	Volume fraction of methanol (f_s)				
	1.00 f_s	0.75 f_s	0.50 f_s	0.25 f_s	0.00 f_s
Volume fraction of methanol(f_s)					
Mass fraction of methanol (f_m)	1.00	0.75	0.50	0.25	0.00
Mole fraction of methanol (f_{mol})	1.00	0.704	0.442	0.209	0.00
Liquid density $P_{mix}(g\ ml^{-1})$					
Molar volume , $V(ml\ mol^{-1})$	1.00	0.573	0.309	0.130	0.00
	0.792	0.872	0.927	0.965	0.998
	40.40	29.80	24.10	20.50	18.00

Adsorption isotherm data (K_D , K_m , K_{moc} and $\log K_{moc}$) used to evaluate the co-solvent theory are summarized in Table 4. The K_m values were determined by dividing the K_D , values by the molar volume of liquid phase molar volume $V(ml\ mol^{-1})$. The K_m values were normalized relative to the organic carbon fraction (f_{oc}) of the respective soils to yield the K_{moc} values.



Table 4 .Data Summary of The Adsorption Isotherm Used to Evaluate the Co-solvent Theory

Parameters	Volume fraction of methanol(f _s)							
	1.00	0.75	0.50	0.25	1.00	0.75	0.50	0.25
	Sandy loam soil				Loam soil			
K _D (ml g ⁻¹)	8.49	11.57	24.80	35.84	15.17	21.59	37.89	61.82
n	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
K _m (mol g ⁻¹)	0.21	0.39	1.03	1.75	0.38	0.7245	1.57	3.02
K _{moc}	103.50	191.28	507.73	861.23	108.84	210.00	455.71	874.09
log K _{moc}	2.11	2.28	2.71	2.94	2.04	2.32	2.66	2.94

Linear regression of the combined log K_{moc} data for the soils led to the following relationships :

$$\log K_{moc} = -1.28 f_s + 3.3 \dots(10)$$

On plotting log K_{moc} verses f_s (Fig.3), the values of log K_{moc} being well described by a single straight line over the entire range studied. These data show that the cosolvent theory is applicable to the adsorption of carbofuran as has been observed for the adsorption of other solutes on soils from water-methanol mixtures [38,43,44]. The data for all the soils studied fitted a single line when normalised on as would be expected according to the co-solvent theory [37].

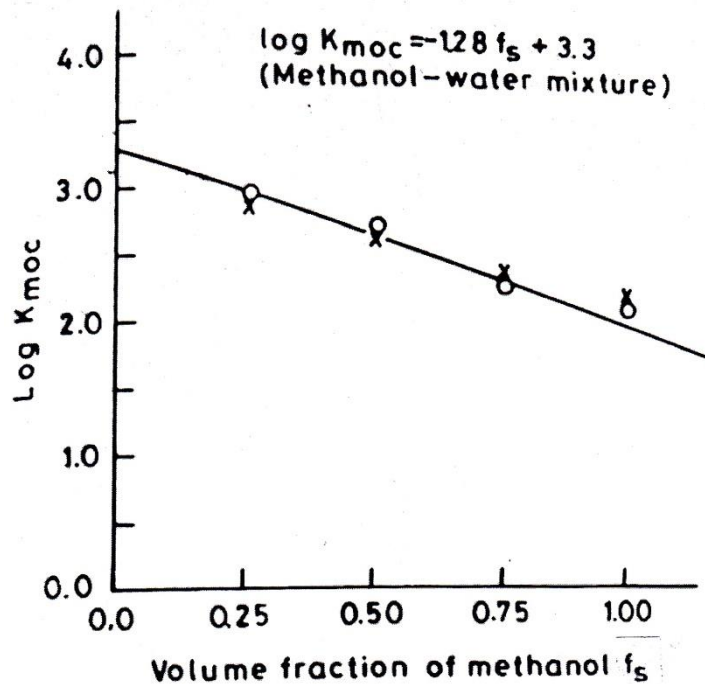


FIG.3- LOG-LINEAR PLOTS OF ADSORPTION PARTITION COEFFICIENT LOG K_{moc} Vs. f_s .

4.3. Extrapolated Estimate of Aqueous Phase Partition Coefficient K_{dw} :

The intercept value of 3.3 in equation (10) is equal to the logarithm of the aqueous phase partition coefficient K_{dw} (mol g^{-1}) for carbofuran. This value can be correspondingly converted to conventional dimensionless units by adding $\log V$ for water ($\log V = 1.26$) to it. The value of the aqueous phase partition coefficient for the adsorption of carbofuran on to soils was thus determined as 4.56 ml g^{-1} .

The value of the slope -1.28 for methanol /water mixture depicted in Fig.3 corresponds to the term $-\alpha\sigma_s$, of equation (1), i.e the slope reflect the combined effects of both α and σ_s . The term σ_s represents the effect of methanol on the solubility of carbofuran. The values of σ_s corresponds the slope of the log-linear relationship between the mole fraction solubility and volume fraction of methanol (f_s) which was calculated as proposed by Fu and Luthy [43, 44] using the solubilities of carbofuran in methanol-free water and in methanol of $7.0 \times 10^5 \mu\text{g l}^{-1}$ and $1.187 \times 10^8 \mu\text{g l}^{-1}$, respectively. The value comes out to be 2.8. The apparent value of α ($= 0.46$) was evaluated by dividing $\alpha\sigma_s$ by α_s .

The low values of α suggests that methanol-soil interaction may have been responsible for the more effective adsorption at high f_s values. The presence of methanol may expand the organic matrix of the soil resulting in an increase in accessibility of carbofuran to the soil organic matter. The manner in which this phenomenon impacts on the adsorption of carbofuran on to soils in the presence of methanol as a co-solvent is an issue for further study.

4.4.Evaluation of K_{om} , K_{oc} and K_c :

The affinity of carbofuran adsorption towards organic matter, K_{om} , and clay content, K_c of the soils was evaluated by the equations proposed by many workers (50 -52) and later used by Singh, D (53-55).

$$K_{oc} = (K_D \times 100) / \% \text{ soil organic carbon} \text{ ----(11)}$$

$$K_{om} = (K_D \times 100) / \% \text{ soil organic matter content} \text{ ---(12)}$$

$$K_c = (K_D \times 100) / \% \text{ soil clay content} \text{ ---(13)}$$

The values so obtained are summarised in Table 2. These parameters could provide an assessment of the environmental fate of organic chemicals and also an indication of the extent to which chemical partitioning occur between the solid and solution phases in the soils and suggest whether the chemical is likely to leach through the soil or be rendered immobile. The affinity of carbofuran towards the organic matter and clay content of the soils may be compared through the use of the K_{om} and K_c values. In the present study, loam soil had higher K_{om} values than sandy loam soil at all f_s values which is the common case of high organic matter content (Table 1). Hamaker and Thompson (56) suggested that this tendency was due to the significant contribution made by mineral phases towards adsorption. The present study shows that carbofuran adsorption correlated better with the organic matter content of the soils rather than with the clay content.

4.5. Evaluation of Leaching Index (LI) for Carbofuran :

Leaching index (LI) for carbofuran was calculated using the equation proposed by Laskowski et al. [57] and later used by Singh and Srivastava [27].

$$LI = (S \times t_{1/2}) / (V_P \times K_{oc}) \text{ ---(14)}$$

where S is the water solubility of carbofuran at 25°C (700 mg L⁻¹), $t_{1/2}$ is the half-life of carbofuran in soil (50 days) and V_P is the vapour pressure of carbofuran at 25°C (8.3 × 10⁻⁶ mmHg). The results obtained are tabulated in Table 2. It will be seen from leaching index data recorded that higher LI values were obtained in loam soil than sandy loam soil at all f_s values. This leaching index order is directly proportional to the K_F and K_D . The larger LI value in loam soil may be attributed to its greater adsorption capacity. In other words, greater environmental concern relates to the leaching of carbofuran from sandy loam soil of Banasthali relative to loam soil of Kundera. Similar results were reported by Singh and Srivastava [27].

4.6. Evaluation of the Gibb's Free Energy Change (ΔG°):

The ΔG° can be used to judge the adsorption reaction.

To identify the physical and chemical mechanism of adsorption, Gibb's free energy change (ΔG°) of 40 kJ mol⁻¹ is considered as a threshold [58]. The physical adsorption was mainly involved below the threshold.

The free energy change (ΔG°) for the adsorption of carbofuran was calculated by substituting the K_{oc} values obtained from equation (11) into the equation proposed by Kim and Feagley [59] and later used by several workers [27, 60, 61].

$$\Delta G^\circ = -RT \ln K_{oc} \text{ -----(15)}$$

where ΔG° is the Gibbs' free energy change (kJmol⁻¹), R is the universal gas constant (8.314 kJ / (kmol)) and T is the absolute temperature (273+25= 298 K). The results obtained for both the soils at all f_s values are summarised in Table 2. The ΔG° values for both the soils at all f_s values ranged from -20.68 to -24.28 kJ mol⁻¹. All ΔG° values in both soils were less than threshold value 40 kJ mol⁻¹. It suggests that the adsorption was mainly physical process. The negative values of ΔG° indicates that the adsorption of carbofuran on to the soils was a spontaneous nature [62]. Smaller ΔG° values also suggests that carbofuran adsorption by soils is often promoted by weak physical forces [63]. The attractive forces in physical adsorption involve surface energies that are often less than a few kJ mol⁻¹, suggesting a diffusion-controlled mechanism for the adsorption of pesticides [64]. Similar results were reported by Ahmad et al. [60] and Rajasekharam and Ramesh [61].

V. CONCLUSIONS

The adsorption of carbofuran in soils from methanol /water mixtures containing different volume fractions (f_s) have been studied by batch shaking techniques. The results of this study indicate that higher adsorption of carbofuran was obtained in soil containing higher amount of organic matter and clay content, with the affinity of carbofuran being better correlated with organic matter content of the soils than with their clay content. The data presented here clearly demonstrate the validity of the co-solvent theory [37] for predicting the adsorption of hydrophobic organic compounds from binary solvent mixtures. Extrapolation of the adsorption data from co-solvent / water systems to $f_s=0$ allowed the aqueous-phase distribution coefficient, K_{dw} to be estimated. This supports our suggestion that partition coefficients should be determined in mixed solvents for hydrophobic pesticides, thereby allowing the corresponding aqueous-phase partition coefficients, K_{dw} , to be determined. The negative magnitude of the Gibbs free energy (ΔG°) indicated the spontaneity on the adsorption onto soils studied.

The leaching index (LI) of carbofuran calculated for the soils studied indicated it's high potential to leach into shallow aquifers and ground water

REFERENCES

1. Yadav, I.C., Devi, N.L., Syed, J.H., Cheng, Z., Li, J and Zhang, G., Soil Environ. Toxicol. Chem., 511: 123-137 (2015).
2. Ozkara, A., Akyil, D and Konuk, M., Pesticides, Environmental pollution and health. Environmental Health Risk - Hazardous Factors to Living Species. IntechOpen., (2016)
3. Qing Li, Q., Loganath, A., Seng Chong, Y., Tan, J and Philip Obbard, J., J. Toxicol. Environ. Health A., 69 (21) :1987-1005 (2006).
4. Koskinen, W.C and Harper, S.S (1990). The retention Process :mechanism, In 'Pesticides in the Soil Environment :Processes, Impacts and Modeling' (Ed.H.H.Cheng)pp 51-78.(Soil Science Society of Amer:Madison, WI.).
5. Stevenson F.J (1994). Organic matter reactions involving pesticides in soil. In 'Humus chemistry :genesis, composition, reaction :2nd end, pp .453-471 (John Wiley and Sons Inc.;New York.
6. Helling, C.S, Kearney, P.C and Alexandar, M., Advance in Agronomy., 23:147-239(1971).
7. Khan, S.U. Occurrence and persistence of pesticide residues in soil. In: pesticides in soil environment. Amsterdam :Elsevier, 240(1980).
8. Carringer, R.D., Weber, J.B and Monaco, T.J., J. Agric. Food Chem. 23:568-573(1975).
9. Bailey, G.W and White, J.L, Residue. Rev. 32., 29-92 (1970).
10. Cheng, H.H., Phytochem. Ecol. 9:209(1989)
11. Wauchope, R.D., Yeh, S., Linders, J., Kloskowski, R., Tanaka, K., Rubin, B., Katayama, A., Kordel, W., Grestl, Z., Lane, M and Unsworth, J.B., Pest. Manag. Sci. 58: 419(2002).
12. Lunagariya, D.D, Patel, K.G, Singh, S, Parekh, V and Ahlawat, T.R, Inter. Res. J. Pure & Applied Chem. 21 (24) :35-41 (2020).
13. Peoples, S.A.: Maddy, K.T.; Cusick, W.; Jackson, T.: Cooper, C. and Fredrickson, S.A. (1980). A study of samples of well water collected from selected areas in California to determine the presence of DBCP and certain other pesticides residue. Bull. Environ. Contam. Toxicol. 24: 611-618.
14. Rothschild, E.R.; Manser, R.J. and Anderson, M.P. (1982). Investigation of aldicarb ground water in selected areas of the control sand plain of Wisconsin. Ground Water. 20: 437-440.
15. Weaver, D.J; Zalkin, R.J.S.F. and Oshima, R.J. (1983). Pesticide movement to ground water I. Survey of ground water basins for EDB, DBCP, Simazine and Carbofuran. State of California, Department of Agriculture, p. 67.
16. Cohen, S.Z.; Creeger, S.M., Carsel, R.F. and Enfield, C.G. (1984). Treatment and disposal of pesticide wastes. Amer. Chem. Soc. Symp. Ser.
17. Spalding, R.F.; Junk, G.A. and Richard J.J. (1980). Areal, vertical and temporal differences in ground water chemistry II. Organic constituents. Pest. Monitor. 14: 70-73.
18. Hallberg, G.R. (1989). Pesticide pollution of ground in humid United States. Agric Ecosyst. Environ. 26: 299-367.

19. Leistra, M. and Boesten J.J.T.I. (1989). Pesticide contamination of ground water in Western Europe. *Agric. Ecosyst. Environ.* 26:369-389
20. Remya, N and Lin, J.-C, *Sep. Purif. Technol.* 76 :244-252 (2011) .
21. Lu, L.-A, Ma, Y.-S, Kumar, M and Lin, J G, *Chem. Eng. J.* 166 :150- 156 (2011).
22. World Health Organization (WHO) , WHO guide lines for drinking -water quality ,World Health Organization (WHO) ,Geneva ,2004.
23. United States Environ .Protection Agency (USEPA) , *Drinking Water Quality Standards* ,1996.
24. Caro, J.H., Taylor, A.W and Freeman, H.P., *Environ. Contem. Toxicol.*, 3:437(1975).
25. Singh, R.P, *Pestic. Res. J.* 8 (2) : 139-145 (1996).
26. Singh, D, *Pest. Manag. Sci.* 56 : 195-201 (2000).
27. Singh, R P and Srivastava, Garima ., *Adsorption Sci & Technol.* ,27(2):(2009).
28. Gnanavelrajah, N and Kandasamy, T, *Amer. Eurasian J. Agric. & Environ. Sci.*, 12: 1475-1478 (2012).
29. Khairatul, A.M, Ngan, C.K and Ismail, B.S, *J. Trop. Agric and fd Sc.* 41 :127-136(2013).
30. Rama Krishna, K and Philip, L., *J. Hazardous Materials.*, 160:559-567(2018).
31. Tanya, C, Britt, M, I, Marivil and Andrew, C, *Environ. Sci. & Pollution. Res. Inter.*, 26: p.986(2019).
32. Salman, J.M., Njoku, V O and Hameed, B.H., *Chemical. Engi. J.*, 173:361-368(2011).
33. Titus, Y.M., Victor, O., Thompson, N.E., Modes, S., Joseph, N.O., Kagbu, J.A and Enmanuel, G C., 4(7):2370-2373 (2013).
34. Felsot, A and Wilson, J. *Bull. Environ. Contam. Toxicol.* 24, 778-782 (1980)
35. Varshney, K.G., Singh, R.P and Rani, S., *Ecotoxicol. Environ. Saf.* 11:179-183(1986).
36. Makhoukhi, F.EI., Dahchour, A, Rabet, M.EI.M., Belguiti, M.A.EI and Hajaji, S.EL., *Der Pharma. Chemica.* ,8(13):180-189(2016).
37. Rao, P.S.C.; Hornsby, A.G.; Kilcrease, D.P. and Nkedi-Kizza, P. (1985). Sorption and transport of hydrophobic organic chemicals in aqueous and mixed solvent systems. Model development and preliminary evaluation. *J. Environ. Qual.* 14:376-383.
38. Nedi-Kizza, P., Rao, P.S.C. and Hornsby, A.G., *Environ. Sci. Technol.* 19: 975-979 (1985).
39. Walters, R.W. and Gulsepple-Elle, A., *Environ. Sci. Technol.* 22: 819-825(1988).
40. Miller, N.A.; Wolf, D.C and Scott, H.D. , *Water Air. Pollut.* 39: 101-112(1988).147
41. Arienzo, M.; Sanchez-Camazano, M.; Crisanto Herrero. T and Sanchez-Martin, M.J., *Chemosphere.* 27: 1409-1417(1993).
42. Synder, LR (1978). *Separation and purification perry E.S.W. eisserger. A., Eds. Wiley-Interscience, New York, pp. 25-75.*
43. Fu, J. and Luthy, R.G. , *J. Environ. Engg.* 112: 328-345 (1986a).
45. Fu, J. and Luthy, R.G., *J. Environ. Engg.* 112: 346-366(1986b).
45. Mithyantha, M.S and Perur, N.S. , *Curr. Sci.* 43: 578-583 (1974).
46. Giles, C.H., MacEwan, T.H. Nakhwa, S.N., and Smith, D.J. *Chem. Soc.* 3973 -3993 (1960).
47. Moreale, A. and Van Bladel, R. ., *Soil Sci.*, 127: 1(1979).
48. Singh, R.P and Singh, D., *Adsorption Sci & Technol.*, 15(2): 135-145(1996).
49. Perry, R.H. and Chilton, C.H. (1973). *Chemical Engineers Hand Book* ,5th Eds, McGraw-Hill :New York.
50. Grestl, Z., *Pestic. Sci.* 15:9-17(1984).
51. Singh, D., *Inter. J. Trend. Scient. Res & Devel. (IJTSRD)*., 4(6):1435-1443(2019).
52. Singh, D., *Inter. J. Tren. Sci. Res & Dev (IJTSRD)*., 4(3):1210-1216(2019).
53. Singh, R.P and Singh, D., *Ecotoxicol. Environmental Chem.*, 57:171-185(1996).
54. Singh, R.P and Singh, D., *J. Indian Soc. Soil Sci.*, 46(2):217-223(1998).
55. Singh, R.P and Singh, D ., *Pestic Res. J.*, 8(1): 61-70(1996).
56. Hamakar, J.W and Thompson, J.M (1972) .*Adsorption. In Organic Chemicals in the Soil Environment (C.A.I. Goring and J.W. Hamakar, Eds.)* , Vol. I., 49-143, Dekker New York.
57. Laskowski, D.A., Goring, C.A.I., McCall, P.J and Swann, R.L. (1982) .*Terrestrial environment In Environmental risk analysis for chemicals (ed R.A. Conway)* , pp.198-340. New York: Van Nostrand Reinhold.
58. Carter, M.C., Kilduff, J.E. and Weber, W.J. , *Environ Sci & Technol.*, 29:1773-1780(1995).



59. Kim, J.H and Feagley, S.E.J., Environ. Sci. Health B., 33:55(1998).
60. Ahmad, K.S., Rashid, N and Azhar, S., Eurasian J Soil Sci, 5(1), 1-12(2016).
61. Rajasekharam, C and Ramesh, A., Res. and Rev: J. Ecol and Environ. Sci (RRJEES), 2(1), 40-46(2014).
62. Kumari, K and Singh, R.P., Pestic. Res. J., 4: 43(1992).
63. Weber, J B., Pestic. Sci., 39:31(1993).
64. Khan, S.U., Can. J. Soil. Sci., 53:429(1973).



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