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Adsorption and Movement of Carbofuran in Two Soils of Rajasthan: A Verification of Co-Solvent Theory and a Comparison of Batch Equilibrium and Soil Thin Layer Chromatography Techniques Results

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Annotation: The adsorption and movement of carbofuran in two different types of uncontaminated soils in methanol water mixtures at different volume fractions (f_s =0. 25. 0. 50, 0. 75 and 1. 0) has been studied by batch equilibrium and soil thin -layer chromatography (Soil TLC) techniques, respectively. The measured equilibrium adsorption isotherms for both soils studied were S-shaped for methanol /water mixtures at all f_s values. All isotherms were in close agreement with the Freundlich equation. Higher adsorption and a lower movement of carbofuran was observed on loam soil than sandy loam soil at all f_s values for methanol /water systems, and was anticipated by the Freundlich constants, K_m, and the R_f values. The K_m and R_f values also confirmed that the adsorption of carbofran decreased while it's movement increased with increasing f_s values. The values of the Freundlich constant K_m were used to evaluate the co-solvent theory for describing the adsorption of carbofuran in methanol -water mixtures. For each soil, the values of the adsorption coefficient K_m decreased in a linear logarithmic fashion as f_s increased, the slope of the log K_m versus f_s plots being essentially the same for both the soils studied. Thus, the co-solvent effects on the adsorption could be expressed by a single parameter (σ_s) which combines the characteristics of the solvent (methanol) and the adsorbate (carbofuran). The aqueous phase partition coefficient K_w (mol^{-1}) normalised on f_{oc} for carbofuran was evaluated by extrapolating $f_s = 0$. The affinity of carbofuran towards the organic carbon and clay content of the soils was evaluated by calculating the $K_{oc}$and K_{cc} values. The data obtained indicated that, although the affinity of carbofuran was better correlated with the organic matter content. The contribution of the clay content of soils towards carbofuran adsorption can not be ignored. The negative magnitude of the Gibb's free energy (ΔG°) indicated the spontaneity of the adsorption of Carbofuran onto soils. The leaching index (LEACH) and Groundwater Ubiquity Score (GUS) indexes were also calculated for predicting leaching potential for carbofuran instudied soils indicated it's high potential to leach into ground water.

Keywords: Carbofuran, Adsorption, Movement, Co-solvent theory, Freundlich constant (K_{m}), Aqueous phase partition coefficient (K_{ow}), Leaching Index (LEACH), Groundwater Ubiquity Score (GUS) index, Gibb's free energy (ΔG°), Soil TLC.

1. INTRODUCTION

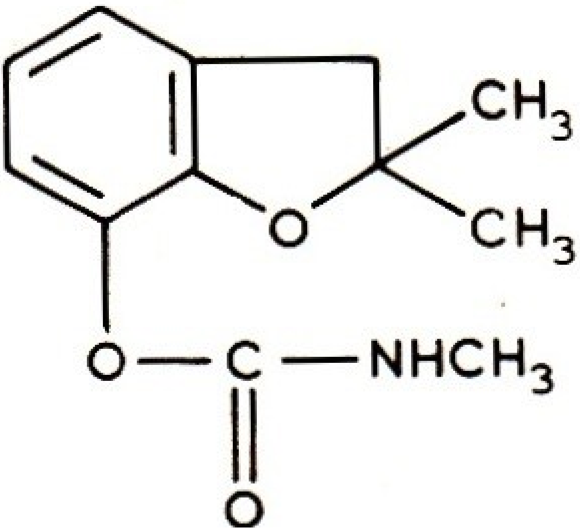
Pesticides are chemicals widely used in modern agriculture since a long time for controlling, preventing, destroying or repeling any pest, viz insects, pathogens, weeds, etc [1]. These chemicals represent different classes of compounds and can be classified according to their purpose of usage. For example, insecticides for control of insect pests, herbicides for control of weeds, fungicides for control of fungi, etc.

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 interactly with the colloidal fractions of soil - the organic matter fraction and clays.

Soils all over the world are exposed directly or indirectly to chemicals and it is a major issue to be able to assess how the chemicals will be distributed and degraded in the soil environment. Adsorption, an important process which determines the risk of chemicals to pollute the environment, is defined as the ability of soils to retain the chemicals so that they do not runoff or leach which may lead to pollution of surface and groundwater [4]. Adsorption is a process in which the pesticide forms chemical bonds with colloidal materials, such as soil organic matter and clay particles. Adsorption is an extremely important process affecting the fate of pesticides[5, 6]. Apart from the organic matter and clay contents, the adsorption process is influenced by size, shape, configuration, molecular structure, chemical functions, solubility, polarity, environmental temperature and the acid-base nature of the pesticide molecule itself [7-9]. Therefore, adsorption is the key in controlling pesticide advective-dispersive, transport, degradation and bioaccumulation [10]. 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 [11-16]. The adsorption and movement of pesticides in soils, which are essential, play a vital role in determining their efficacy for crop protection and their potential for environmental contamination [17, 18]. Frequent detection of pesticides in surface and groundwater [19-24] has increased the interest of both Soil and environmental Scientists towards the study of the adsorption and movement of pesticides in soils, as a means of overcoming the problem arising from the presence of pesticides in surface and groundwater. The literature associated with these aspects has been reviewed by several researchers [25-29]. Carbofuran is a non-ionic broad spectrum systemic acaricide, insecticide and nematicide included in the general group of carbamate derivative pesticides [30-33].

It is widely used in agriculture [34]. for long time to control of soil dwelling and foliar feeding insects including wireworms, white grubs, weevils, stem borers, aphids and several other insects [35-37]. In India, carbofuran is used extensively to control rice pests in paddy fields as well as pests in vegetable and fruit holdings. As a result of its widespread use, air, food, surface water and underground water could become contaminated with carbofuran residue and its metabolites[38-41] and this could affect human health. Carbofuran is highly toxic to animals and humans both by oral and inhalation routes and therefore, may pose a serious threat to those in contact with it in manufacturing and formulating plants as well as in crop fields [42, 43]. Due to its acute toxicity, the fate of its residue in terms of both adsorption and mobility is of great concern, especially since carbofuran has been reported to be more persistent than other carbamate or organophosphorus insecticides [44]. Carbofuran is moderately mobile in soil and of moderate water solubility which strongly influences their environmental fate including leaching potential [45-47]. The maximum concentration of carbofuran admitted by World Health Organization (WHO) in drinking water is 3µg / L [48]According to the United States Environmental Protection Agency (US EPA), has set the maximum acceptable carbofuran concentration in drinking water as 40 µg / L [49]. 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 [31]. Due to its acute toxicity, the fate of its residue in terms of both adsorption and mobility is of great concern. It's structure can be represent as :



Several workers [50-62] have studied the effect of different factors, such as organic matter, exchangeable cations, temperature, cationic, anionic and non-ionic surfactants on adsorption and movement of carbofuran in soils. However, on waste disposal and land treatment sites, it is likely that the soil solution will consist of a mixture of water and various miscible organic solvents. Only a few experimental studies to date have focused on the adsorption of pesticides from non-aqueous. solvents and solvent mixtures [63-70]. Hower, no information of this type on the adsorption and movement of carbofuran is available in literature on Rajasthan origin soils. With this in mind, it is necessary to characterise the adsorption and movement of Carbofuran not only from aqueous solutions but also from aqueous organic mixed solvents and methanol is one such organic solvent having high industrial use and high frequency of disposal at landfills.

Hence, an attempt has been made in the present study to examine the effect of water-miscible organic solvents (methanol) on the adsorption and movement of carbofuran in two different types soils of Rajasthan and to verify the co-solvent theory proposed by Rao et al. [71]. Methanol was selected because of it is completely soluble in water, a proton donor[72]and expected to be found in most waste streams from industrial wastes.

The main objectives of this investigation were to examin the effects of a miscible organic co-solvent (methanol) adsorption and movement of Carbofuran in soils and to verify the co-solvent theory from the Freundlich partition coefficient, K_m values. These studies will help in understanding the behavior of Carbofuran in the presence of methanol and prove useful in assessing near-source carbofuran transport / movement in soils in the event of spillage or discharge of organic wastes containing water-soluble solvents. The another purpose of this study was also to understand the basic chemistry of carbofuran interaction and leaching potential in soils by calculating the free energy change ($\Delta G°$), leaching index (LEACH index) and Ground water Ubiquity Score(GUS index). values from the organic carbon -based partition coefficient ($K_{oc.}$) Values.

1.1. CO-SOLVENT THEORY

The cosolvent theory was proposed by Rao et. al. [71] 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 many workers [73-78]. This theory is expressed by the equation:

$$\log [K_m / K_w] = - \alpha \sigma_s f_s \text{ -----(1)}$$

where $f_{s,}$ is the volume fraction of co-solvent and K is the equilibrium adsorption constant (ml g^{-1}) with the superscript m and w designating values for K in mixed solvent and water, respectively. The term σ_s reflects represents the index of the solubilizing power of the co-solvent and α is an empirical constant which accounts for water - co-solvent or co-solvent -adsorbent interaction.

The value of σ_s in equation(1) is referred to as the co-solvency power and can be equated to the hypothetical liquid-liquid partition coefficient [79]. Thus, the value $\sigma_{s.}$ may be evaluated approximately as:

$\sigma_s = \log (S_a / S_w)$ ——---(2)

where, S_a (μg ml^{-1}) and $S_{w,}$

(μg ml^1) are the solubilities of the hydrophobic organic compounds in neat co- solvent and in water, respectively. The value of $\sigma_{s,}$ has been shown [80] to be strongly correlated with solute properties, such as octanol-water partition coeffi- cients, molecular surface area, and solvent properties such as dielectric constant, interfacial tension and bulk surface tension.

1.2. IMPORTANCE OF THE THEORY

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 adsorption constants for adsorption from aqueous solution by plotting a graph between K_m versus f_s and extrapolating to $f_s = 0$.

In the latter respect, the theory is particularly important since it is very difficult to determine the adsorption constants of highly hydrophobic compounds from water.

2. MATERIALS AND METHODS

2.1. Chemicals and *Reagents*

Pesticide chosen for this investigation was carbofuran (Furadan 3G)having molecular weight 221. 30, melting pointis 150. 0 to 152. 2°C, Vapour pressure 2. 7 Mpa and aqueous 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 of concentration 400 μg ml^{-1} was prepared by dissolving the requisite amount of carbofuran in methanol.

2.2. Collection of Soil Samples

In present investigation the two representative soils used were randomly collected from the topsoil (0-30 cm depth) from cultivated agricultural fields (at 12 points within each location) having no previous history of pesticide application from the Kundera and Banasthali villages of Sawaimadhopur and Tonk districts of Rajasthan, India. Prior to the analyses, the soil samples were air-dried, crushed gently and sieved through a sieve with a mesh size of 2mm and stored in plastic bags at room temperature before use. The physico-chemical properties of the studied soils were determined by using standard methods of soil analysis. The mechanical composition of soils was estimated by the International pipette method [81]. The pH values of the 1:2. 5 soil/water suspension were determined by method proposed by Jackson [82]. The organic carbon and organic matter content of soils were determined by Walkley and Black [83] and Cation -exchange capacity and calcium carbonate contents of soil samples were estimated by the methods [81, 84]. The results are summarized 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 ($cmolp^{+}kg^{-1}$)	18. 50	8. 80
8-Surface Area (m^2/g)	130. 50	80. 50

2.3. Batch Equilibrium 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 triplicate and each isotherm determination consisted of 31flasks 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 3 hours in an incubator at 25 ± 1°C and for 24h. After equilibration, the soil suspensions were then centrifuged at 10, 000 rpm for 15 minutes using a Beckman Model L3-50 Ultracentrifuge, the supernatant being collected and estimated spectrophotometrically at 490 nm using the method proposed by Mithyantha and Perur [85] in which 5 ml of supernatant was mixed with 5 ml of 0. 2% sulphanilic 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 µg/ml. All experiments were performed at a constant temperature of 25°C. This method has a detection limit of 1 $\mu g ml^{-1}$. The concentration of the Carbofuran in the supernatant ($C_{e\,;}$ $\mu g\ ml^{-1}$)was measured, and the amount of carbofuran adsorbed on the soils (x/m, $\mu g\ g^{-1}$) was calculated from the concentration difference between the initial and equilibrium concentrations of cabofuran in solution according to the following expression:

$$x / m = (C_o - C_e) V / W \text{ - ——-(3)}$$

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

2.4. Movement by Soil Thin Layer Chromatography (soil TLC)

The movement of carbofuran in the soils was studied using the soil TLC technique [29] and latter used by Singh et al. [86]. Soil TLC plates of 0. 5 mm thickness were prepared by spreading a soil/water slurry having a soil/water ratio of 1:2 onto 20 x 20 cm^2 clean glass plates with the help of a TLC spreader The plates were dried at room temperature and then activated by heating at 100-105°C for 1/2 h, deactivated and stored in a desiccating chamber. Two lines were scribed on each plate at distances of 3 cm and 13 cm above the base to maintain a standard development distance of

10 cm on the plates. A 10 μL volume of carbofuran solution of 1000 μg/ml concentration in methanol was applied as a spot onto the TLC plates with the help of the lambda pipette held 3 cm above the bottom of the plates. A 2 cm wide strip of paper towel moistened with the eluents (water and methanol) was wrapped around the bottom of the plates to prevent disintegration of the soil layer when it came into contact with the eluents. The carbofuran -spotted plates were eluted in distilled water and co-solvent (methanol) solutions of different volume fraction (fs = 0. 25, 0. 50, 0. 75, 1. 00), positioning the plates at an angle of 45° in the glass tank. After the eluent had migrated to a distance 10 cm from the base line, the plates were taken out and dried at room temperature. The movement of carbofuran was detected by spraying the developed plates with a 5% methanolic KOH solution followed by a 0. 1 % p- nitrobenzene diazonium tetrafluoroborate solution. The development of violet coloured spots indicated the presence of carbofuran. The movement of carbofuran was expressed in terms of the frontal R_f values and measured using the relationship[29] :

Frontal R_f=Distance moved by spot / Distance moved by developer – - - (4)

$R_f = 1/10 [R_T + R_L / 2]$------(5)

Where R_T and R_L are the tailing and lateral fronts, respectively.

R_B = Distance moved by bottom of spot /Distance moved by developer —-----------(6)

and $R_m = \log (1/R_f - 1)$ —---(7)

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

The standard Gibb's free energy (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 [87]. The physical adsorption was mainly involved below the threshold. The ΔG° for the adsorption of carbofuran was calculated by substituting the K_{oc} values obtained from equation (12) into the equation proposed by Kim and Feagley [88] and later used by several workers [46, 89, 90].

$\Delta G° = -RT \ln K_{oc}$ —-------(8)

where ΔG° is the Gibbs' free energy change (k j mol^{-1}), R is the universal gas constant (8. 314 j / mol^{-1} K^{-1}) and T is the absolute temperature(K). K_{oc} (adimensional) is the normalizes organic carbon partition coefficient.

2.6. Evaluation of Leachability indexes for Carbofuran :

The pesticide leachability (or mobility) in the soil profile and the risk of groundwater contamination can be calculated by using the two indexes, leaching index (LEACH) and groundwater Ubiquity Score (GUS).

2.6.1. Leaching Index (LEACH) for Carbofuran :

Leaching index (LEACH) for carbofuran was calculated using the equation proposed by Laskowski et al. [91] and later used by Singh and Srivastava [46].

LEACH index = $(S_w \times t_{1/2}) / (V_P \times K_{oc})$ ---(9)

where S_w 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), V_P is the vapour pressure of carbofuran at 25°C (8. 3 $\times 10^{-6}$ mmHg) and K_{oc} (adimensional) is the organic carbon partition coefficient. The LEACH index is based on the assumption that mobility in soil is inversely proportional to the rate of decomposition in soil, and that movement by leaching through the soil is directly proportional to the quantity of chemical in the water of the air /water /soil system. The leaching index has no trigger value : the lower the LEACH value the lower the risk of contamination.

2.6.2. Evaluation of Groundwater Ubiquity Score (GUS) index :

The GUS index assesses the leachability of pesticides and possibility of finding these chemicals in groundwater. The groundwater Ubiquity Score (GUS) index is calculated by the equation proposed by Gustafson 1989 [92]

$GUS_{index} = \log_{10} (t_{1/2\text{-soil}}) \times [4 - \log_{10} (K_{oc.})]$ —-(10)

This index is based on two parameters : mobility in soil, given by the organic carbon partition coefficient (K_{oc}, adimensional) and soil persistence quantified by the soil degradation half-life of pesticide assuming first-order kinetics expressed in days ($t_{1/2\text{-soil}}$) and K_{oc} is the Freundlich distribution coefficient normalized to organic carbon content of the soil. The index allows pesticides to be split according to trigger values, as explained in the discussion.

3. RESULTS AND DISCUSSION

3.1. Adsorption Isotherms of carbofuran on soils:

Adsorption isotherms (Figs 1 and 2) were drawn between the amount of carbofuran adsorbed

($\mu g\ g^{-1}$) of soil and the amount of carbofuran in solution at equilibrium ($\mu g\ ml^{-1}$) in methanol-water mixtures of different f_s values.

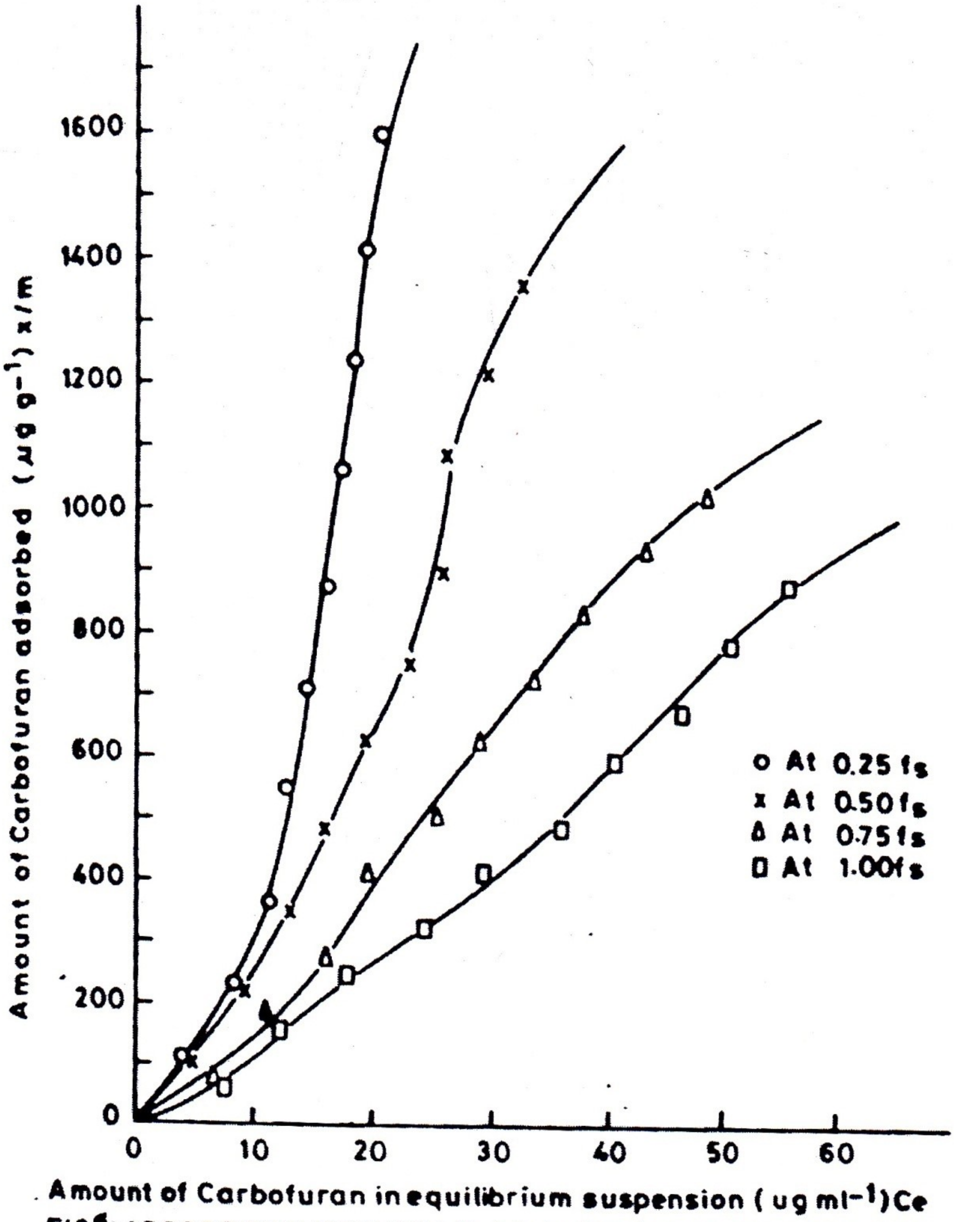


FIG1-ADSORPTION ISOTHERMS OF CARBOFURAN ON LOAM SOIL

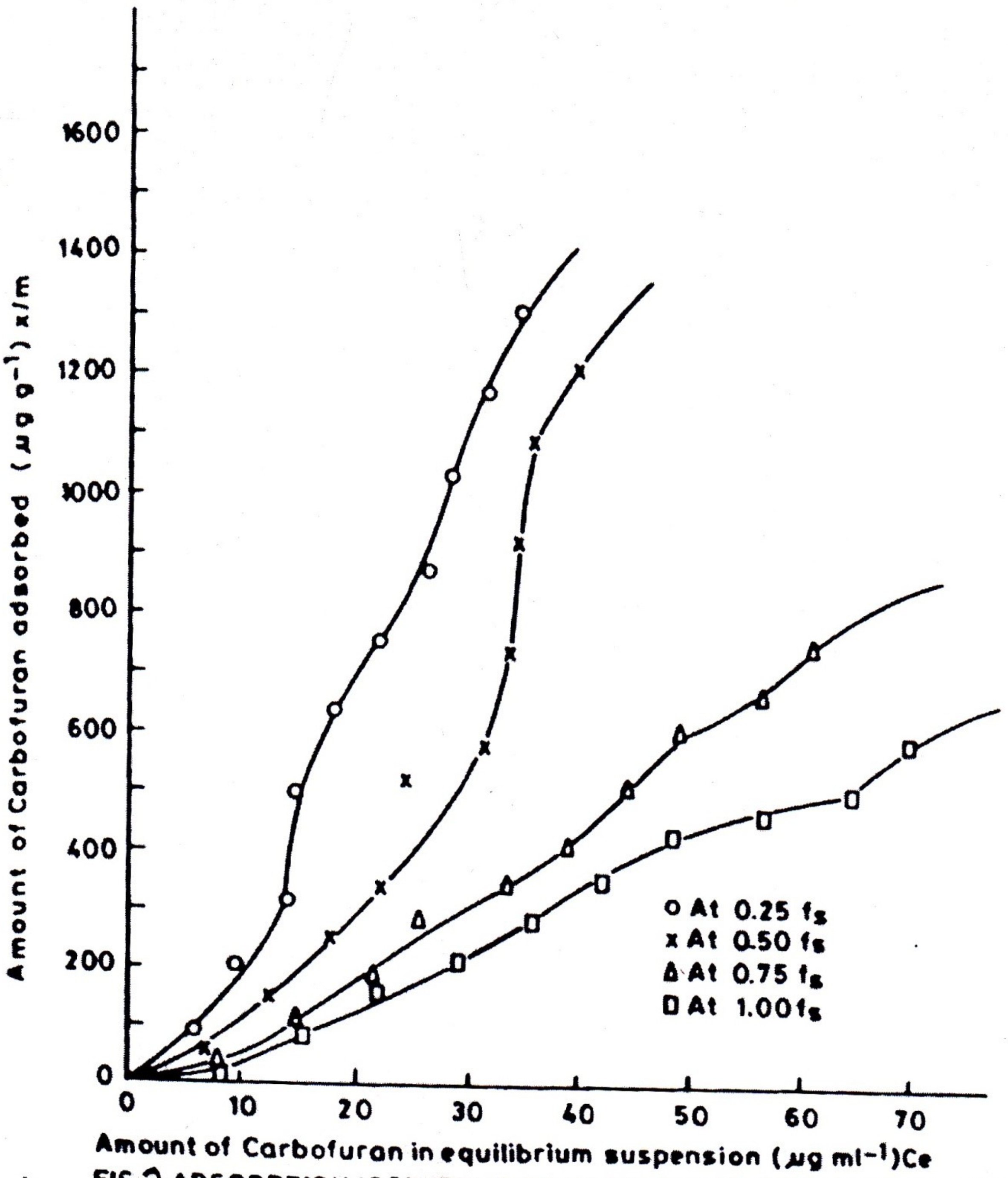


FIG. 2: ADSORPTION ISOTHERMS OF CARBOFURAN ON SANDY LOAM SOIL

These isotherms show that the adsorption of carbofuran was higher on loam soil than on sandy loam soil at all f_s values and adsorption decreased with increase in f_s value. The higher adsorption on loam soil than on sandy loam soil may be due to the greater amount of organic matter, clay, calcium carbonate content and higher surface area, cation exchange capacity (CEC) and lower pH in loam soil than sandy loam soil. 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.

The multiple-point adsorption Isotherms were used to determine the Freundlich adsorption coefficient (K_m) which is widely used to measure the adsorption of chemicals on certain adsorbent [93]. The adsorption isotherms thus obtained at all f_s values yielded S-shaped curves as described by Giles et al [94] which suggests multilayer adsorption and vertical orientation of adsorbed pesticide molecules at the adsorbent surface, with the availability of new sites to the solvent as adsorption occurs. It also indicates that the solvent and solute compete with each other for adsorption sites on the soil colloidal surface. The upward nature of the curves shows that, after complete adsorption on the adsorbent surface, adsorbate molecules attract each other and become associated to a considerable extent.

3.2. Mathematical Modeling of Adsorption Isotherms :

From the batch studies performed, Isotherms of an adsorption process was constructed using the Freundlich model. It describe the distribution of adsorbate molecules between the liquid and the solid phase [95] showing the amount of pesticide adsorbed per unit weight of the soil(x/m) and the pesticide concentration in the solution at equilibrium (C_e). The adsorption curves and values of important variables of the linearized forms of Isotherms equations for the studied pesticide (carbofuran) in soil samples were also determined.

3.4. Freundlich Model:

The Freundlich isotherm is an empirical model describing multilayer adsorption with non-uniform distribution of adsorption enthalpy and affinities onto the heterogeneous adsorbent surface without lateral interaction [96, 97]. The energetically favored binding sites are theorized to be occupied first and the binding strength decreases sequentially with increased coverage of the sites. The model can be described by the following equation:

$x /m = K_m C_e^{1/n}$ —(11)

where x/m is the amount of adsorbate (Carbofuran) at equilibrium ($\mu g\ g^{-1}$) ; C_e is the equilibrium concentration of the adsorbate ($\mu g\ ml^{-1}$) and K_m, is the Freundlich affinity coefficient or Freundlich solid -wster distribution coefficient ($\mu g^{1-n}\ ml^n\ g^{-1}$) and 1/n is the exponential coefficient (constant) associated with the energy distribution of the adsorption site, also being a measure of favorability of adsorption (for the values of 1/n between 0 and 1)[98]. These two empirical adsorption constants are dependent on the nature of adsorbate, adsorbent and co-solvent of the system. The adsorption data for carbofuran in both soils were calculated using the linearized Freundlich equation[99, 100] over the entire range of all the concentrations studied at all f_s values.

$\log x/m = \log K_m + \log C_e^{1/n}$------(12)

A linear relation is obtained when log (x/m) is plotted against log $C_e$for each sample under the present investigation, where values of K_m and 1/n (Table 2) were obtained from the intercept and slope, respectively of a straight line [101]. The magnitude of K_m expresses the relative adsorption for the adsorbate[102] for systems having comparable 1/n values and extent or degree of adsorption[103]. The values of 1/n provide an idea of the intensity of adsorption and reflects the degree to which adsorption is a function of concentration [4, 103, 104,] which varies in a regular manner with the nature of the adsorbate[105] for a given adsorbent. For 1/n >1, pesticide adsorption increase without limit, for 1/n <1 the sorption approaches a limit. For 1/n =1, the adsorption of chemicals would be is linearly proportional to the equilibrium and the distribution coefficient (K_d) would be appropriate to use [106]. The sequence of K_m values for carbofuran adsorption on soils follows the order loam>sandy loam soil. This order of K_m values confirms the above order of adsorption at all f values. The higher values of K_m at lower f_s in both soils also confirm that adsorption decreases with increase in fs value. The results are in accordance with theoretical approach proposed by Rao et al [71] who quantified the adsorption and transport of hydrophobic organic chemicals from aqueous and aqueous-organic mixtures. They found that adsorption coefficients from aqueous-organic binary solvent mixtures decreased exponentially as the fraction of organic solvent increased. The values of 1/n<1 (Table 2) for methanol-water mixtures indicate the degree of non- linearity between solution equilibrium concentration and adsorption. The variable slopes of adsorption isotherms obtained for different pesticide-soil systems studied reveal that pesticide adsorption on soil is a complex phenomenon involving different types of adsorption sites with different surface energies[107]. All regression lines generated had a coefficient of determination (r^2) of at least 0. 99 (Table 2), which indicates an excellent fit of the data to the Freundlich equation. It was in agreement findings by several researchers for the adsorption of non-ionic pesticides from soils [108-110].

Table 2. Freundlich Constants (K_m, 1/n), Leaching Index (LEACH), GUS index 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							
f_s	1. 00	0. 75	0. 50	0. 25	1. 00	0. 75	0. 50	0. 25
K_m	3. 16	4. 00	5. 30	6. 60	5. 62	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	1. 00	0. 94	0. 97	0. 99	1. 00	1. 00	0. 98	0. 94
K_{cc}	33. 26	42. 11	55. 79	69. 47	32. 11	40. 17	53. 66	66. 91
K_{oc}	1580. 00	2000. 00	2650. 00	3300. 00	1652. 94	2067. 65	2761. 76	3444. 12
K_{om}	902. 86	1142. 86	1514. 29	1885. 71	952. 54	1191. 53	1591. 53	1984. 75
LEACH index	2. 55 $\times10^6$	2. 04$\times10^6$	1. 53 $\times10^6$	1. 22 $\times10^6$	2. 67 $\times10^6$	2. 61 $\times10^6$	1. 59 $\times10^6$	1. 28 $\times10^6$
GUS index	1. 36	1. 19	0. 99	0. 82	1. 33	1. 16	0. 95	0. 78
ΔG°(kj mol^{-1})	-18. 36	-18. 90	-19. 90	-20. 16	-18. 26	-18. 83	-19. 52	-20. 07

3.5. Evaluation of Organic carbon partition coefficient (K_{oc}), organic matter partition coefficient (K_{om})and Clay content partition coefficient (K_{cc}):

The affinity of carbofuran adsorption towards organic carbon, organic matter and clay contents (K_{om}, K_{oc} and K_{cc}) of the soils was evaluated based on the obtained Freundlich distribution coefficient, K_m parameters for carbofuran by the equations proposed by many workers [111-114] and later used by Singh [115, 116].

$K_{oc.}$ = (K_m × 100) / % OC ---(13)

K_{om} =(K_m ×100) / %OM —--(14)

K_{cc} = (K_m × 100) / % Clay Content (CC)—-(15)

Where OC is soil organic carbon content, OM is soil organic matter content and CC is the clay content of soil [117]. The results obtained are summarized 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, organic matter and clay content of the soils may be compared through the use of the K_{oc}, K_{om} and K_{cc} values. In the present study, loam soil had higherK_{oc} and 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 [118] 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 since K_{oc} and K_{om} values were higher than K_{cc} values. The results are in accordance with the work of Walker and Crawford [119] and Stevenson [120] who reported that, up to an organic matter content of ca. 6%, both organic and mineral surfaces are involved in adsorption.

Stevention [120] 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.

3.6. Movement of carbofuran on soils

The results of the effect of co-solvent (methanol) on the movement of carbofuran in soils at different volume fractions of (0. 0, 0. 25, 0. 50, 0. 75 and 1. 00) of methanol water mixtures are summarised in

Table 3 and expressed in terms of frontal R_f, R_f, R_B and R_m values. Increasing the concentration of methanol in the mobile phase, resulted the higher values of frontal R_f, R_f, R_B and decrease in R_m values which showed increase in the movement of carbofuran in both the soil (Table 3). As the volume fraction of methanol increases in the mobile phase, continually became better solvent for carbofuran and hence a strong solute-solvent interaction occurred resulting decreasing adsorption of carbofuran. The soil TLC experiments here illustrated the role of carbofuran-methanol interaction indicating the degree of adsorption of carbofuran. The results are in accordance with the work of Hassett et al. [121] who used soil TLC and studied the influence of increasing ethanol content on the movement of a-naphthol in aqueous systems. They reported that as the percentage of ethanol increases the movement increases which indicated the decrease in adsorption of the organic compounds. Similar results were reported by several workers[29, 122-126] while studing the role of solute-solvent interaction in hydrophobic adsorption illustrated by soil TLC technique. The theoretical approach proposed by Rao et al. [71] and later Singh and Singh [63] also show that an increase in organic cosolvent fraction resulted exponential decrease in adsorption coefficients due to increase hydrophobic organic compounds solubility. The movement of carbofuran increases with increase in volume fraction (f_s) of methanol. The R_f values (Table 3) obtained are inversely proportional to the K_m values (Table 2).

Table 3. Effect Of Different Volume Fractions of Co-solvent (Methanol)On The Movement Of Carbofuran In Soils

Properties	Volume fraction of methanol(f_s)				
	0. 00	**0. 25**	**0. 50**	**0. 75**	**1. 00**
	Sandy loam soil				
Frontal R_f	0. 85	0. 92	0. 95	1. 00	1. 00
R_f	0. 43	0. 60	0. 73	0. 76	0. 82
R_B	0. 00	0. 28	0. 56	0. 45	0. 64
R_m	0. 12	0. 09	0. 50	0. 43.	0. 66
	Loam soil				
Frontal R_f	0. 70	0. 85	0. 90	0. 95	0. 95
R_f	0. 35	0. 55	0. 64	0. 71	0. 80
R_B	0. 00	0. 25	0. 38	0. 47	0. 60
R_m	0. 27	0. 09	0. 21	0. 39	0. 60

3.7. Verification of co-solvent Theory:

The co-solvent Theory equation (1) can be verified from the Freundlich adsorption constant K_m values obtained at different f_s values (Table 2). The dependence of K^m at different f_s values for carbofuran adsorption by soils from methanol-water mixtures is shown in Fig 3, and it is consistent with the expectation based on eqation (1).

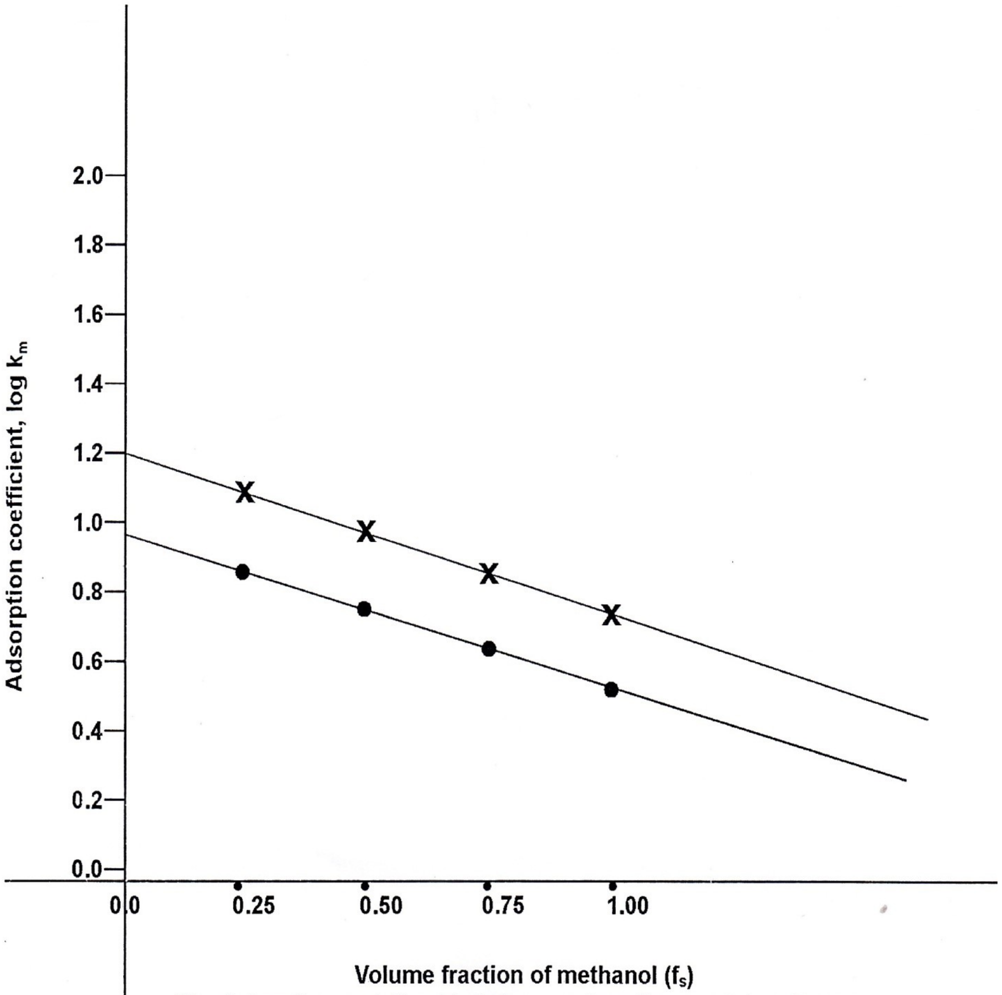


Fig. 3. Log-linear relationship between adsorption coefficient (K_m) and volume fraction (f_s) of carbofuran from methanol-water mixtures by (x) loam soil and (●) sandy loam soil.

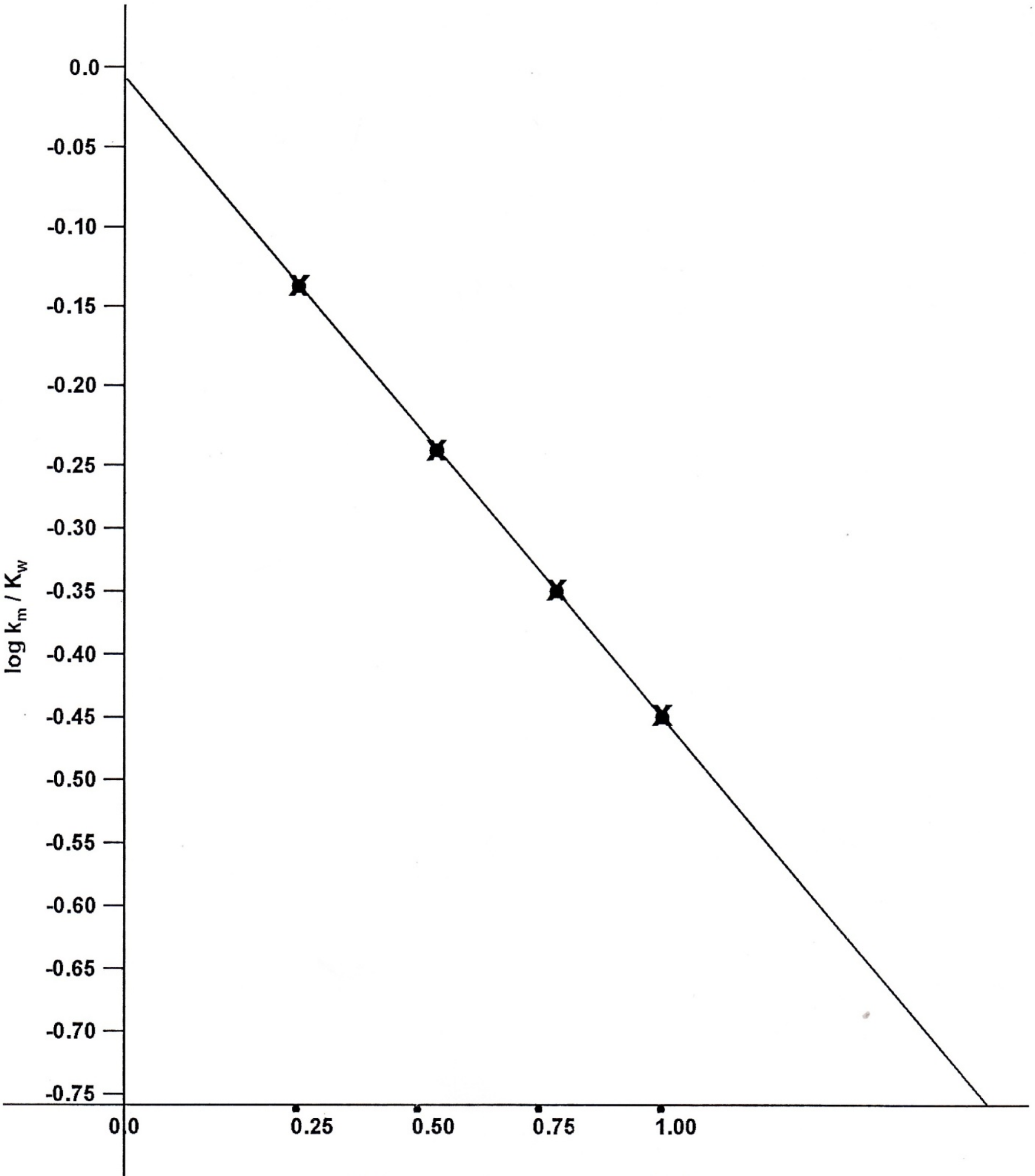
Such an inverse relationship between log K_m and f_s is the direct consequence of an exponential increase in solute solubility with increasing inco-solvent content [71, 73] and suggests that solvophobic interactions are dominant for carbofuran adsorption from aqueous and mixed solvents. The aqueous phase adsorption constant (K_w) for soils can be determined from Fig 3, by extrapolating to $f_s = 0$, and the values obtained are summarized in Table 4.

Table 4. Summary of The Adsorption Isotherms data used to evaluate the Co-solvent Theory on the basis of Freundlich constant

(K_m)

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_m	3. 16 4. 00 5. 30 6. 60	5. 62 7. 03 9. 39 11. 71
log K_m	0. 50 0. 60 0. 72 0. 82	0. 72 0. 85 0. 97 1. 07
K_w	8. 91 8. 91 8. 91 8. 91	15. 85 15. 85 15. 85 15. 85
K_m / K_w	0. 36 0. 45 0. 60 0. 74	0. 36 0. 44 0. 59 p. 74
log K_m / K_w	-0. 45 -0. 35 -0. 23 -0. 13	-0. 45 -0. 35 -0. 35 -0. 13

The values of the relative constants K_m / K_w were determined by dividing K_m values by K_w, and a graph was plotted between log (K_m / K_w) and f_s (Fig 4).



Volume fraction of methanol (f_s)

Fig. 4. Relative adsorption coefficient (K_m/K_w) as a fraction of volume fraction of methanol (f_s) for adsorption of carbofuran from methanol-water mixtures by (x) loam soil and (●) sandy loam soil.

It is evident from eqn (1) that the relative adsorption coefficients of the carbofuran-soil combination can be described by a single line (Fig 4) and the value of the slope ($\alpha\sigma_s = 0.44$) estimated from this plot of methanol-water system is dependent on the carbofuran and methanol properties and not on soil properties. Thus, the value of the slope $\alpha\sigma_s$ for carbofuran estimated from the data for different soils is expected to be the same and this justifies the assumption of the model being valid. The σ_s value estimated from equation (2), by using the solubilities of carbofuran in water and in methanol, is found to be 2. 23. The α value was calculated by dividing $\alpha\sigma_s$ by σ_s. The α value is found to be 0. 20 and appears to be solute-independent. Values of $\alpha < 1$ imply that methanol-soil interactions result in the effect of methanol on adsorption being somewhat smaller than that on solubility. Even larger discrepan- cies ($\alpha = 1$) between solubility and adsorption beha- viour in presence of organic co-solvents were reported by Fu and Luthy [77, 78]. It is very difficult to determine the adsorption of carbofuran from aqueous solutions because of its low solubility, so the adsorption from mixed solvents as determined in this study and extrapolating to $f_s = 0$ was used to estimate the adsorption constant (K_w) in the queous phase. The lends support to our suggestions that for pesticides having low aqueous solubility, K_m should be first determined in mixed solvent and then the aqueous phase adsorption constant K_w can be determined.

3.8. The standard Gibb's Free Energy Change (ΔG°):

Based on the constants obtained from the Freundlich approximation of the experimental data, a thermodynamic parameter determining the spontaneity of the adsorbate -adsorbent interactions, namely the standard Gibb's free energy (ΔG°). 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 - 18. 26 to - 20. 16 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 ΔG° value indicates that the carbofuran adsorption process is thermodynamically favorable and can conduct spontaneously[127]. The greater the absolute magnitude of the ΔG° value, the higher is the extent to which the adsorption reaction may take place [54]. Smaller ΔG° values also suggests that carbofuran adsorption by soils is often promoted by weak physical forces [128]. 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 [129]. Similar results were reported by Ahmad et al. [89] and Rajasekharam and Ramesh [90].

3.9. Leaching Index (LEACH)

for Carbofuran :

The results obtained are tabulated in Table 2. It will be seen from leaching index data recorded that higher LEACH index values were obtained in loam soil than sandy loam soil at all f_s values.. This leaching index order is directly proportional to the $K_{m.}$ The larger LEACH index 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 [46]. and Singh [130].

3.10. Groundwater Ubiquity Score (GUS) index :

The application of the GUS index splits the studied pesticide into three groups : " leachers ", "non-leachers ", and borderline compounds ", based on sorption and persistence properties in soil. The GUS values were calculated for carbofuran at all f_s values are tabulated in Table 2.

The pesticides with GUS index values higher than 2. 8, are characterize "leachers " with a high risk for contamination, borderline pesticides with GUS index values between 1. 8 and 2. 8 and "non-leachers ", pesticides with GUS index values lower than 1. 8 [131]. The GUS index values of the present study (Table 2) indicates that at f_s 0. 25 and 0. 50 in both the soils, the GUS index values for carbofuran are less than 1. 8, comes in non-leacher category according Papa et al. [131]. But when the f_s value is increased the GUS index value is also increased in both the soils and comes in transitional category. The higher values of GUS index values are found in sandy loam soil than loam soil indicates higher movement / leaching and lower adsorption of Carbofuran in sandy loam soil than loam soil. Similar results were reported by many researchers [90, 132].

4. CONCLUSIONS

The adsorption of carbofuran by two different uncontaminated soils at four f_s values (0. 25, 0. 50, 0. 75 and 1. 00) from water-methanol mixtures has been investigated by using a batch-shake technique. Higher adsorption of carbofuran was obtained in loam soil than in sandy loam soil, and decreased with increasing fs values in both soils. The data presented here have clearly demonstrated the validity of the co- solvent theory for predicting the adsorption of carbofuran from binary solvent mixtures. From the adsorption data, Freundlich constants K_m was evaluated. Freundlich constant K_m values were also used to evaluate the co-solvent theory for each soil, the adsorption coefficient K_m values decreasing log-linearly as f_s increased and the slopes of log K_m versus f_s plots being essentially the same for both soils. Thus, the co- solvent effects on adsorption could be specified by a single paramater (σ_s) that combined the characteristic of solvent (methanol) and the adsorbate (carbofuran). For an adsorbate with low aqueous solubility, the adsorption data from the mixed solvent was extrapolated to f_s =0 to estimate the aqueous phase adsorption constant K_w value. The data presented suggested that methanol-soil interaction may not increase the accessibility of carbofuran to soil organic matter to the same extent as reported for less. hydrophobic organic solvents. The significant smaller and negative values of ΔG°further confirmed that Carbofuran adsorption by soils is an exothermic spontaneous process and is promoted by weak physical forces. The calculated LEACH and GUS index values from adsorption data for carbofuran in both the soils indicate that Carbofuran is less adsorbed in sandy loam soil thal loam soil and it's potential to leach to shallow aquifers and ground water is greater in sandy loam soil.

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