# Differential Pulse Polarographic Determination of Carbofuran in Environmental Samples

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## Abstract

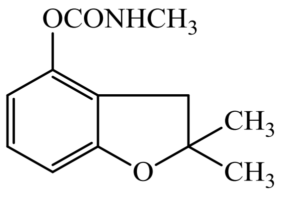
*In the view of the potential hazards associated with the widespread use of carbofuran insecticide, a remarkably new simple and sensitive differential pulse polarographic (DPP) method has been developed for determination in environmental samples viz. soil, water and foodstuffs for its safer and effective use. The proposed method is based on the microwave assisted alkaline hydrolysis of the insecticide to methylamine which is measured pulse polarographically as its copper methyldithiocarbamate complex through reaction with carbon disulphide and copper (I) perchlorate in acetonitrile is yielding analytically useful diffusion controlled peak at -105mV (vs SCE). The linear relationship of peak current with the concentration of the insecticide forms the basis of its quantification. The insecticide can be determined in the linearity range from 0.22 to 6.63 μg mL$^{-1}$ with a correlation coefficient of 0.99. The method has been applied to the analysis of carbofuran in its commercial formulation and its recovery from vegetable and water samples for monitoring health hazards.*

*Recoveries of the insecticide from grains and spiked water samples were good, ranging from 85.3-96.4% with RSDs ranging from 0.7-1.2%. The method has also been validated for investigating the sorption of carbofuran on four soils with different characteristics to evaluate its leaching behaviour which is a measure of ground and surface water contamination. The leaching potential of the insecticide in terms of groundwater ubiquity score (GUS) has values in the range 2.22-2.38 classifying it as transition leacher, hence it has potential to contaminate groundwater.*

**Keywords**: Carbofuran, Differential pulse polarography, Environmental toxicity, Soil-adsorption study, Leaching potential, GUS.

## Introduction

N-methyl carbamate follows organophosphorus compounds amongst most widely used insecticides worldwide. Carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranyl-N-methyl carbamate (I) is an effective contact and systemic broad spectrum carbamate insecticide, nematicide and acaricide based on N-methyl carbamate class.[1-3] It is used for the control of insects on fruits, vegetables, grains and crops. It is also used for protection of sorghum seed, sugarbeet seed and seedling from insect pests in soil. Carbofuran is highly toxic to mammals, acute oral $LD_{50}$ value for rats is 8-11 mg/kg.[4,5]



I

The toxicity of carbofuran includes inhibitory effects on cholinesterase enzyme and irreversible neuromuscular disturbance on inhalation.[2] The environmental pollution caused by the extensive use of this indispensable chemical is of major concern because of its high toxicity and consequently poses a serious risk to both the environment and the human and consequently offers detrimental effects to both human life and environment.[6] Pesticides pollute soil and water both by direct application to crops and through their residues.[7,8] They enter the soil in different ways e.g. by rinsing deposits from crops by rain or irrigation water and by incorporation in crop residues. In the soil, the pesticides get fractionated between solution phase (in free form) and solid phase (in bound form through adsorption on clay and organic fractions).[9]

Adsorption of pesticides affects their bioactivity, mobility, persistence, toxicity, volatilization, and bioaccumulation and influences their final fate in the soil.[10] All such processes determine the extent of contamination of surface and ground water. The frequent detection of carbofuran insecticide in the environmental samples viz foodstuffs and water[11,12] has led to a number of experimental studies on its residual and sorption studies on soils.[13-15]

Various analytical methods viz. fluorescence, voltammetric, enzymatic, immunosensor, chromatographic, capillary zone electrophoresis and spectrophotometric methods have been reported in literature.[16-23] However, most of these methods require expensive instrumentation and highly trained personnel on one hand and round the clock power supply on the other hand and also long analysis time.

Nowadays, polarographic methods are finding greater use in pesticides analysis because the determination can be done even at larger dilution and with smaller volumes of solution without any interference from inert carrier commonly present in formulated products.

In the context of accuracy and trace determination, the polarographic methods with differential pulse mode (DPP) find wide acceptance. In the present work, a differential pulse polarographic method has been developed to the analysis of carbofuran and subsequently adapted to the analysis of this insecticide in environmental samples viz. soil, water and foodstuffs for safer and effective use, its commercial formulation and its recovery from grain and water samples.

The method has also been validated to study the sorption of this insecticide on four soils with different characteristics at two temperatures viz. 20ºC and 30ºC and in its commercial formulations. The latter aspect is essential not only to ensure the quality of the marketed samples of the insecticide but also to get reliable residue/sorption data. The sorption and thermodynamic parameters for the sorption of the insecticide have also been calculated to study the risk of the contamination of water by the carbofuran.

## Material and Methods

**Apparatus:** All polarographic measurements were made with an Elico (Hyderabad, India) polarographic analyzer (model CL-90). The electrode system consisted of dropping mercury electrode (DME) as a working electrode, saturated calomel electrode (SCE) as a reference electrode and platinum as an auxiliary electrode. Domestic microwave oven (Samsung electronics, New Delhi, India) was used to carry out hydrolysis. Genei shaking incubator (Bangalore, India) has been used in soil adsorption study.

**Reagents and Samples**: Acetonitrile (Merck Schuchardt OHG, Germany) was kept over phosphorus pentoxide (5 g $L^{-1}$) and distilled twice. The analytical standard of carbofuran (supplied by Rallis India Ltd., Mumbai) was used and its stock solution ($2\times10^{-4}$ mol $L^{-1}$) was prepared in acetonitrile. The purity was checked by reported method.[23]

Sodium perchlorate (Merck Schuchardt OHG, Germany) solution ($10^{-1}$ mol$L^{-1}$ in acetonitrile) was prepared by dissolving 12.24 g of pure compound in 1 L of acetonitrile and used as supporting electrolyte. Potassium hydroxide (Merck, Mumbai, India, LR, $10^{-1}$ mol $L^{-1}$ in water), acetic acid (Ranbaxy, SAS Nagar, Punjab, India, LR, $10^{-1}$ mol $L^{-1}$ in water) were prepared in distilled water. Methyl isobutyl ketone (MIBK, Merck, Mumbai, India, AR) was used as received.

Perchloric acid (Merck, Mumbai, India, AR, 1% in water) and sodium bicarbonate (Merck, Mumbai, India, LR), 2% solution were prepared in distilled water. Copper(I) perchlorate solution in acetonitrile ($2\times10^{-3}$ mol $L^{-1}$) was prepared and standardized as described earlier.[24]

Triton-X-100 (Merck Schuchardt OHG, Germany), 0.002% in acetonitrile was used as suppressor. Carbon disulphide (Merck, AR) and methyl isobutyl ketone (MIBK, Merck, AR) were used as supplied.

**Sample collection and Preparation:** The soil samples used in the sorption study were collected with hand trowel at the depth of 0.5 cm from selected regions of Solan District of Himachal Pradesh, India. The soil samples were air dried and passed through 2 mm sieve to remove stones and large particles and kept in glass bottles prior to experiment. The soil characteristic viz. pH, organic carbon (%), clay (%) and Cation Exchange Capacity (CEC) were determined by reported methods[25,26] at the University of Horticulture and Forestry, Solan, Himachal Pradesh, India.

**Preparation of calibration graph:** Aliquots (0.1 to 3.0 mL) of the stock solution ($2\times10^{-4}$mol $L^{-1}$) of carbofuran in acetonitrile were taken in 10 mL measuring flasks and volume made to 3.0 mL with acetonitrile. Each solution was mixed with aqueous potassium hydroxide (1 mL, $10^{-1}$ mol $L^{-1}$) and kept in microwave oven for 60 sec. The resulting solution is neutralized by adding 0.5 mL of 1% perchloric acid and made slightly basic with 1 mL of 2% sodium bicarbonate. Each solution was mixed with one drop of carbon disulphide (~100 μL) and well shaken. Then 1 mL of copper(I) perchlorate ($2\times10^{-3}$ mol $L^{-1}$ in acetonitrile) was added and the light yellow coloured complex formed was extracted in methyl isobutyl ketone (3mL).

The yellow MIBK extract was dried with ~2 g of sodium sulphate and transferred in polarographic cell, mixed with Triton-X-100 (2 mL, 0.002% in acetonitrile), and final volume was made to 20 mL with sodium perchlorate ($10^{-1}$mol $L^{-1}$ in acetonitrile). Nitrogen gas was bubbled through each solution for 5 min. The differential pulse polarogram of each solution was recorded at room temperature (25 ± 1)°C with the following instrumental parameters: initial potential = 200 mV, drop time = 1 sec, pulse amplitude = 50 mV, and scan rate = 6 $mVs^{-1}$. A calibration graph was constructed by plotting peak current (μA) (corresponding to −105 mV peak) vs concentration of carbofuran (μg $mL^{-1}$) as shown in fig. 1.

**Formulation analysis:** A granule formulation "Furadan" containing 3% active ingredient (carbofuran) procured from an authorized pesticide dealer was used. A single large sample of formulation equivalent to 11.05 mg active ingredient was taken with 10 mL acetonitrile, and filtered. The residue was washed 2–3 times with acetonitrile. The filtrate and washings were diluted to a known volume (25 mL) with acetonitrile. 2.5 mL of this solution was further diluted to 25 mL with acetonitrile. Suitable aliquots (0.25–1.0 mL) of the above solution were taken and processed for analysis as described above for the pure compound. Assay results are given in table 1.

**Determination of carbofuran in grains (maize and wheat) and water samples:** Carbofuran standard solution was prepared by dissolving 11 mg carbofuran in 50mL acetonitrile, 10mL of this solution was diluted to 100mL with acetonitrile for a final concentration of 22 μg $mL^{-1}$ carbofuran. Aliquots (1.0–2.5 mL) of the standard solution of carbofuran were added to 5 g portions of grains (maize and rice). The sample were mixed thoroughly and extracted 5 times, each time using 5mL chloroform. The combined extracts were shaken for 5 min and filtered. The filtrate was heated on the water bath at 40°C and the solvent was evaporated off. The residue was dissolved in 3.0mL acetonitrile and placed in polarographic cell and processed for analysis as described above for the pure compound. Assay results are presented in table 2.

The proposed method has also been applied to the determination of insecticide in spiked water samples. Aliquots (1.0–2.5 mL) of standard solution having a concentration of 22 µg $mL^{-1}$ were added to 25mL water samples and were mixed thoroughly. The samples were extracted with chloroform and processed for analysis in the same manner as described above. The results are presented in table 2.

**Soil adsorption study:** Carbofuran adsorption isotherms on four Indian soils of different soil characteristics (Table 3) were obtained by the batch equilibration technique using 50 mL conical flask.

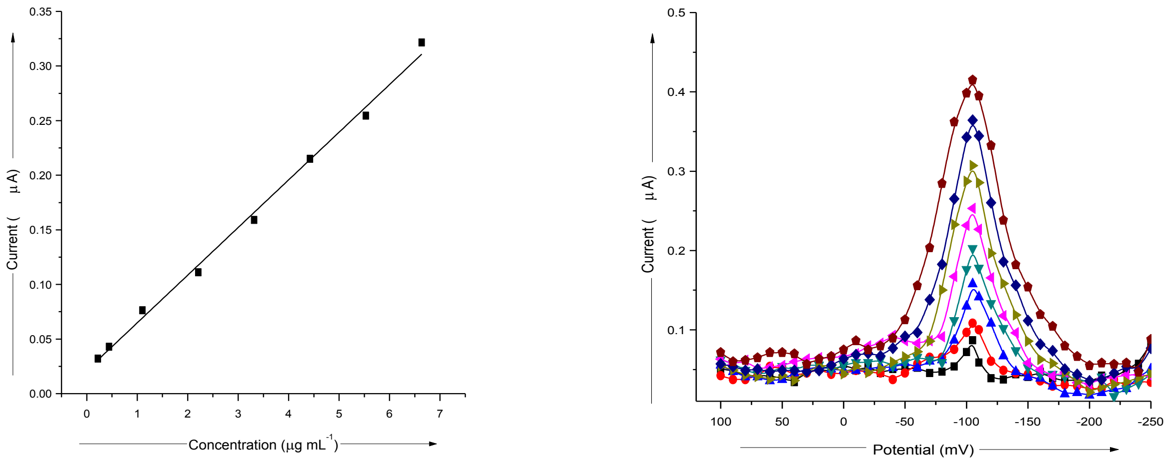


**Figure 1: Relationship between current and concentration (calibration graph) for carbofuran**

### Table 1
### Assay of a commercial formulation of carbofuran containing 3% active ingredient (Furadan).

| Amount taken (µg) | Recovery (%)[a] | |
|---|---|---|
| | Present method | Comparison method[b] |
| 0.55 | 94.1±0.8 | 93.7±1.0 |
| 1.10 | 96.6±0.6 | 94.9±0.8 |
| 1.65 | 97.3±0.9 | 95.1±0.7 |
| 2.20 | 95.9±0.7 | 94.5±0.8 |

[a]Values are mean of five determinations with standard deviation (±).
[b]Reference method. [23]

### Table 2
### Recovery of carbofuran from fortified grains (Maize and Wheat) and water samples.

| Active ingredient added, µg | Recovery of active ingredient [a], % | | | | | |
|---|---|---|---|---|---|---|
| | Present method | | | Comparison method[b] | | |
| | Maize | Wheat | Water | Maize | Wheat | Water |
| 1.10 | 87.4 ± 0.7 | 85.3 ± 0.8 | 90.6 ±1.0 | 85.8±0.8 | 87.0±0.9 | 87.2±0.8 |
| 1.65 | 86.3± 0.8 | 87.9 ± 0.7 | 92.4 ± 0.9 | 84.6±1.0 | 85.4±0.8 | 90.6±0.9 |
| 2.20 | 90.7 ±0.8 | 93.6 ± 0.9 | 93.7 ± 0.7 | 89.6±0.9 | 90.2±0.9 | 90.8±0.8 |
| 2.75 | 92.2 ± 0.9 | 93.9 ±1.2 | 96.4 ± 0.8 | 90.5±1.2 | 92.4±0.7 | 93.4±1.0 |

[a]Values are mean of five determinations with standard deviation (±)
[b]Comparison method of analysis.[23]

Triplicate soil samples (2 g) were equilibrated with carbofuran solutions in the concentration range from 17.7 to 88.5 µg $mL^{-1}$ on shaker at 150 rpm at two temperatures 20 °C and 30 °C for 6 hr equilibrium time (estimated time required for equilibrium to be reached between pesticide adsorbed and in solution). After equilibration, the suspensions were centrifuged and the equilibrium concentrations (Ce) were determined in supernatants by the proposed method described above. Adsorption isotherms were evaluated by using Freundlich's adsorption equation:

$$X = K_f C_e^{n_f} \qquad (1)$$

where X is the amount of pesticide adsorbed mg $kg^{-1}$of the adsorbent, Ce is the equilibrium concentration in solution (mg $L^{-1}$), and $K_f$ and $n_f$ are adsorption coefficients that characterize the adsorption capacity of the adsorbent. The adsorption coefficients $K_f$ and $n_f$ are calculated from the least square methods applied to the linear form of the Freundlich's adsorption equation.

$$\log X = \log K_f + n_f \log C_e \qquad (2)$$

Other adsorption parameters for adsorption process, namely, soil-adsorption coefficient ($K_d$), soil organic carbon partition coefficient ($K_{oc}$), Gibb's free energy ($\Delta G^o$) and groundwater ubiquity score (GUS) have been calculated by using the following equations.[27-29]

$$K_d = \frac{X}{C_e} \qquad (3)$$

$$K_{oc} = K_d \times \left(\frac{100}{\%O.C.}\right) \qquad (4)$$

$$GUS = \log t_{1/2}\left[4 - \log(K_{oc})\right] \qquad (5)$$

where R = gas constant, T = absolute temperature, $t_{1/2}$ = pesticide persistence (half-life), OC = organic carbon content of soil. GUS score is used to study the leaching behaviour of pesticides and these can be classified as leacher in which GUS values are higher than 2.8, transition with GUS values between 1.8 and 2.8 and non-leacher pesticides with GUS values lower than 1.8.[29]

The thermodynamic parameters viz. Gibb's free energy ($\Delta G^o$), enthalpy change ($\Delta H^o$) and entropy change ($\Delta S^o$) have also been calculated by using equations 6-8 respectively.[30]

$$\Delta G^o = -RT \ln K_d \qquad (6)$$

$$\ln\{(K_d)_2/(K_d)_1\} = \Delta H^o/R\ \{(T_2-T_1)/\ T_1T_2\} \qquad (7)$$

$$\Delta S^o = ((\Delta H^o - \Delta G^o)/\ T \qquad (8)$$

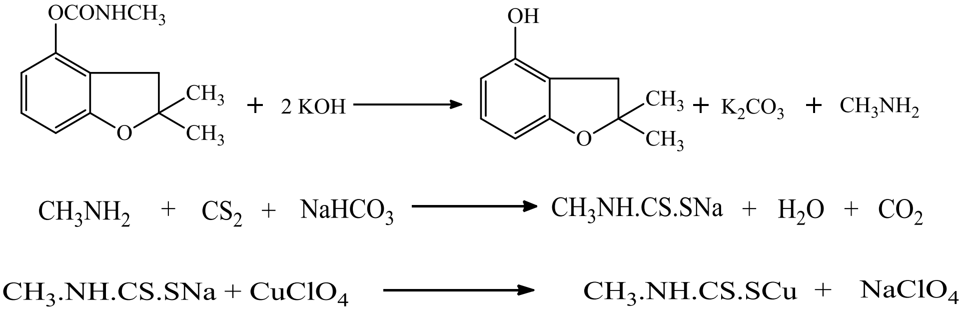
All these parameters for the adsorption of carbofuran on four Indian soils with different characteristics were calculated.

## Results and Discussion

**Standardization of reaction conditions:** The proposed polarographic method is based on microwave assisted alkaline hydrolysis of carbofuran to methylamine (as dithiocarbamate). The effect of time of microwave assisted hydrolysis was studied and best results have been obtained corresponding to 60 sec showing maximum current intensity. Methyl isobutyl ketone (MIBK) is an extracting solvent of choice because it is safe in comparison of commonly used toxic extracting solvents and extracting the copper(I)-methyl dithiocarbamate complex quantitatively from aqueous solution.

**Proposed mechanism for the polarographic method:** Differential pulse polarography is well known for its sensitivity and selectivity and has emerged as a reliable and sensitive tool for trace analysis. In a significant effort in this context, we have been able to develop a remarkably sensitive method for the determination of carbofuran as copper(I) methyl dithiocarbamate in acetonitrile formed by the microwave assisted alkaline hydrolysis of carbofuran and complexation of resulting methyl amine with copper(I) perchlorate in the presence of carbon disulphide scheme 1.

Acetonitrile has been a solvent of choice in the present study because of its convenient liquid range, ready availability, wide electrochemical range, moderate dielectric constant (facilitating the solubility of this compound), low toxicity and resistant to oxidation or reduction. Further, copper(I) perchlorate in acetonitrile shows excellent solution stability.[24, 31]



$$CH_3NH_2 + CS_2 + NaHCO_3 \longrightarrow CH_3NH.CS.SNa + H_2O + CO_2$$

$$CH_3.NH.CS.SNa + CuClO_4 \longrightarrow CH_3.NH.CS.SCu + NaClO_4$$

**Scheme 1:** Proposed mechanism for the polarographic method

Using sodium perchlorate as supporting electrolyte in acetonitrile, a linear base line having a plateau parallel to the potential axis was obtained over a wide range of potential.

The copper(I) methyldithiocarbamate complex in the presence of sodium perchlorate as an electrolyte and Triton-X 100 as suppressor yielded well-defined, diffusion-controlled peak at −105 mV against SCE electrode. It is evident from the linear relationship obtained between diffusion current and square root of mercury column height (h) that the electrode process is diffusion controlled. The peak at -105 mV can be considered due to the formation and reduction of copper(III) dithiocarbamate complex formed from copper(I)-carbofuran (as methyldithiocarbamate derivative). The formation of these copper(III) complexes has thoroughly been established in our laboratory.[32,33]

In the present case, a peak at -105 mV can be explained on the basis of a well-known observation that in view of the susceptibility of dithiocarbamates to air oxidation,[34] dithiocarbamate samples always contain traces of corresponding thiuram disulphides as an impurity/contaminant. The later initiates the reaction and thus helps it to proceed to completion, of course, through the formation of copper(III) dithiocarbamate complex with one electron change.

$$CH_3NH.CS.SCu + CH_3NH.CS.S.S.CS.NHCH_3 \longrightarrow [Cu(CH_3NH.CS.S)_2]^+ + CH_3NH.CSS^-$$

$$[Cu(CH_3NH.CSS)_2]^+ \underset{-e}{\overset{+e}{\rightleftharpoons}} [Cu(CH_3NH.CS.S)_2]$$

That copper(I)-dithiocarbamate complexes exist in equilibrium with copper(III) dithiocarbamate complex, is also well known.[35,36] The role of perchlorate anion (a bulky anion) in stabilizing the higher oxidation states of metals especially copper(III) methyldithiocarbamate complexes is also quite well known.[35]

The reaction taking place at the mercury electrode is supposed to involve the reduction of copper(III) methyl dithiocarbamate complex undergoing one electron change. The same is established by making use of the equation of polarographic waves.[37].

$$E = E_{1/2} + \frac{0.0591}{n}\left\{\frac{\log(i_d - i)}{i}\right\}$$

It is followed from the above equation that the plot of {log (id-i)/ i} against the corresponding potential (E ), a straight line should be obtained with a slope of 0.0591/ n for a reversible reaction and value of n i.e. number of electrons taking part in the reversible reaction can be determined. In the present case a straight line with slope 0.071 is obtained indicating number of electron involved to be 0.83 (=1).

The remarkable sensitivity of the new peak coupled with the excellent linear relationship obtained between current intensity of the peak and concentration of carbofuran in the range 0.22 to 6.63 µg mL$^{-1}$ with a correlation coefficient of 0.99 has been made the basis of this method. The proposed method shows good precision and accuracy with maximum relative standard deviation (RSD) of 1.0%. The method has successfully been applied to the analysis of a commercial formulation of carbofuran for its active ingredient content for the purpose of quality control with recoveries in the range of 94.1–97.3% of the nominal content with RSDs in the range of 0.6–0.9% (Table 1).

The results have, however, been compared with an independent method.[23] The method has been applied with success to the determination of this insecticide in residues on environmental samples for the purpose of monitoring pollution and health hazards. Recoveries of the insecticide from fortified grain (Maize and rice) and water samples were good ranging from 85.3% to 96.4% with RSDs ranging from 0.7–1.2% (Table 2) showing good precision and accuracy of the method.

**Soil Adsorption Study:** The proposed method has been successfully applied to study the adsorption of carbofuran on four soils of different soil characteristics for predicting its movement in soil and aquifer to determine extent of groundwater contamination. Soil characteristics viz**.** organic matter content, clay content and cation exchange capacity (CEC) affect the magnitude of pesticide adsorption. In the present case, the adsorption isotherms of carbofuran insecticide on four Indian soils of different characteristics (Table 3) have been evaluated by Freundlich's adsorption equation.

According to the initial portion of the curve, these isotherms have been classified as S-type of Gile's classification.[38]. S-types of isotherms represent a system where solid surface has high affinity for the solvent than for solutes.[39] The Freundlich's adsorption coefficients $K_f$ and $n_f$ were calculated from the plot of log X versus log Ce (Figure. 2) and results are shown in table 4.

The adsorption coefficient $K_f$ represents the amount of pesticide adsorbed at an equilibrium concentration of 1 mg L$^{-1}$ and another coefficient $n_f$ represents the variation in adsorption with varying concentrations of pesticide.[40] The Freundlich constant $n_f$ is a measure of the deviation from linearity of the adsorption.The observed value of $n_f$ was more than 1 in all the four cases and indicates that there is competition between pesticide and water molecules for the adsorption sites on surface of the adsorbents.[41] This might be due to the reason that at higher concentration, there is an increased difficulty to access the adsorption site.

The adsorption of pesticide on soil depends on its different soil characteristics. The organic matter content and the clay of soils play a very important role in the sorption of pesticides on to the soil. It is found that the amount of pesticides adsorbed by soils increases as the total soil organic carbon content and clay content increase.[42]

**Table 3**
**Characteristics of the different Indian soils used in the adsorption study of carbofuran**

| Soil Sample | pH | Clay (%) | Organic carbon (%) | Cation Exchange Capacity (meq/100g) |
|---|---|---|---|---|
| I | 7.44 | 32.6 | 0.6 | 13.1 |
| II | 7.48 | 10.2 | 0.8 | 12.8 |
| III | 7.38 | 9.3 | 0.7 | 12.2 |
| IV | 7.41 | 18.2 | 1.0 | 12.9 |

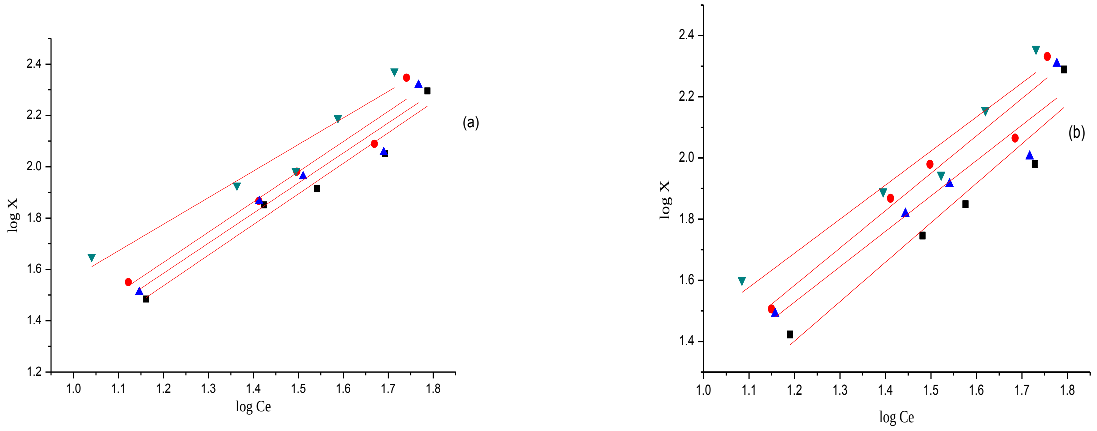


**Figure 2: Plot of log X versus log Ce for the evaluation of Freundlich's sorption coefficients $K_f$ and $n_f$ for four soils (a) at 20 °C (b) at 30 °C**

**Table 4**
**Adsorption parameters for the adsorption of carbofuran insecticide on four Indian soils at 20 °C and 30 °C temperature**

| Soil Sample | $K_f$ | $n_f$ | $K_d$ | $K_{oc}$ | GUS | Adsorption isotherm |
|---|---|---|---|---|---|---|
| **20 °C** | | | | | | |
| I | 1.27 | 1.19 | 2.53 | 421.41 | 2.22 | S-type |
| II | 1.64 | 1.18 | 3.05 | 380. 81 | 2.29 | S-type |
| III | 1.51 | 1.17 | 2.77 | 396.03 | 2.26 | S-type |
| IV | 3.42 | 1.03 | 3.87 | 387.26 | 2.28 | S-type |
| | | | **30 °C** | | | |
| I | 1.40 | 1.29 | 2.07 | 344.69 | 2.36 | S-type |
| II | 1.31 | 1.22 | 2.86 | 358.02 | 2.33 | S-type |
| III | 1.38 | 1.16 | 2.44 | 349.16 | 2.35 | S-type |
| IV | 2.25 | 1.11 | 3.34 | 334.27 | 2.38 | S-type |

**Table 5**
**Thermodynamic parameters for the adsorption of carbofuran on four Indian soils**

| Soil samples | $\Delta G^o$ (kJ mol$^{-1}$) | | $\Delta H^o$ (kJ mol$^{-1}$) | $\Delta S^o$ (kJ K$^{-1}$ mol$^{-1}$) |
|---|---|---|---|---|
| | 20 °C | 30 °C | 25 °C | 25 °C |
| I | -2.26 | -1.83 | -14.81 | -0.043 |
| II | -2.71 | -2.65 | -4.75 | -0.007 |
| III | -2.48 | -2.25 | -9.36 | -0.023 |
| IV | -3.30 | -3.04 | -10.87 | -0.026 |

This is because the particles of organic matter or clay provide soils with an increased number of adsorptive sites onto which pesticides molecules can bind. Another soil parameter is cation exchange capacity (CEC) which is directly proportional to hydrophobic nature of adsorbent i.e. greater the value of CEC of soil, its surface will be more hydrophobic. The organic pesticides are more hydrophobic (low water solubility), thus have higher adsorption affinity for the soils with higher CEC.[43] High adsorption of carbofuran in soil IV could be explained by high percentage of organic carbon content. The value of $K_d$ represents the extent of adsorption and in general higher is the $K_d$ value, the greater is the pesticide adsorption.[40]

Hence, carbofuran is adsorbed maximally in the case of soil IV. Of the four soils of different characteristics studied, the decreasing sorption order is: Soil IV > Soil II > Soil III > Soil I. Though $K_d$ for a pesticide is soil-specific and its value varies with soil texture and organic matter content, the soil organic carbon partition coefficient (Koc) is less soil specific[44] and has been calculated by normalizing adsorption coefficient ($K_d$) with the organic carbon (OC) content of the soil and gives more accurate results with regards to mobility of a pesticide in any kind of soil. The results of adsorption of carbofuran on four Indian soils at 20 $^oC$ and 30 $^oC$ temperatures are shown in table 4.

The thermodynamic parameters for the adsorption of carbofuran on four soils have also been evaluated and are presented in table 5. The negative value of $\Delta G^o$ and $\Delta H^o$ in all the soil types studied suggests the energetically favourable adsorption process.[45,46] The magnitude of $\Delta G^o$ also showed that the interactions of pesticides with the soil were thermodynamically spontaneous process. The negative values of $\Delta H^o$ indicated that the interaction of pesticides with the soil is an energetically favourable exothermic process. From the negative value of $\Delta H^o$ it can be inferred that the value of soil adsorption coefficients decreased with rise in temperature. This is due to the effect of temperature on the weak binding between carbofuran and soil particles. The negative value of $\Delta S^o$ is due to decrease in randomness with adsorption.[45,46]

Groundwater Ubiquity Score (GUS) is the most commonly used model which relates pesticide persistence (half life) and adsorption in soil (Koc). The leaching potential of insecticides in terms of GUS index was determined by using experimentally observed Koc value for each soil sample and literature reported half life of carbofuran. The GUS for carbofuran was from 2.22 to 2.38 classifying it as a transient pesticide, therefore it possesses a real hazard to groundwater contamination at greater extent. However, toxicity due to excessive use of this insecticide can be minimized by adjusting the application doses according to soil properties.

## Conclusion

The proposed method used to accomplish this study is simple, rapid, reliable and does not involve elaborate clean up procedures required with other methods. The observed GUS value of this insecticide which is less than 2.8 for all soils used, classifies it as a transition leacher pesticide in terms of leaching behaviour, thereby it poses potential risk to the aquatic environment. Hence, this insecticide should be used judiciously to prevent surface and groundwater contamination.

The mobility of the insecticide into ground water can be reduced by adding organic amendments such as farmyard manure and compost with higher organic content which will increase its adsorption and reduce the mobility of the insecticide.

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