



PULSE POLAROGRAPHIC INVESTIGATIONS OF ADSORPTION STUDY AND LEACHING OF CARBARYL ON FIVE SOILS TO EVALUATE GROUNDWATER CONTAMINATION

Devender Kumar Sharma¹, Tilak Dharmani² and Nisha Sharma³

^{1,2}Department of Chemistry, Himachal Pradesh University, Shimla -171005, India

³Department of Chemistry, Rajiv Gandhi Govt. Degree College, Chaura Maidan Shimla, Himachal Pradesh-171004 India

Abstract

Pesticide adsorption by the soil is a naturally occurring phenomenon and affects ground and surface water contamination through leaching. The pesticide leaching is evaluated in terms of groundwater ubiquity score (GUS). A pulse polarographic investigation on the adsorption of carbaryl on five soils has been carried out by a batch equilibrium technique to evaluate its leaching potential an index to evaluate surface and ground water contamination. The proposed pulse polarographic investigation is based on the appearance of an analytically useful diffusion-controlled peak at -110 mV upon hydrolysis and subsequent reaction of insecticide with carbon disulphide and copper(II) perchlorate. Carbaryl in the range 0.27 to 4.02 $\mu\text{g mL}^{-1}$ can be assayed with a correlation coefficient of 0.989. The GUS for carbaryl with all five soils with different characteristics has been found in the range 1.81-2.17 which classify it as a transition insecticide thus has a potential to contaminate surface and ground water.

Keywords- Carbaryl, Pulse polarography, Soil-adsorption study, Environmental toxicity, Leaching/GUS.

I. INTRODUCTION

The pesticide leaching is an important process with regard to contamination risk of aquatic environment and is strongly influenced by the interaction of a pesticide with soil. Pesticide adsorption by soil is a naturally occurring phenomenon which affect processes like toxicity, mobility, persistence and volatilization of a pesticide and which in turn affect the ground and surface water contamination. The frequent detection of pesticides including carbaryl in surface and ground water has led to some experimental studies on their adsorption on soils for evaluation of their leaching potential [1,2]. The present study dealing with the adsorption of carbaryl on five soils with different characteristics is also a useful contribution in this direction. To accomplish above objectives various analytical methods viz. chromatography [3-5], spectrophotometry [6,7], fluorimetry [8,9], immunoassay [10], enzymatic [11], have been developed and standardised.

But comparatively less work has been done in investigating polarographic methods in this regard. The latter are now finding greater use in pesticide analysis because determination can be done even at trace level without any interference from inert carriers commonly present in their formulations.

We have found pulse polarography a reliable and sensitive technique for the analysis of pesticides [12,13]. The advantage of this technique have now been extended to the analysis of carbaryl and its subsequent application to study its adsorption behaviour on five soils with different soil characteristics for evaluation of the environmental toxicity of the insecticide. The method has also been validated for the analysis of carbaryl in its commercial formulation and its recovery from grain and water samples.

II. EXPERIMENTAL

2.1 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 working electrode, saturated calomel electrode (SCE) as reference electrode, and platinum as an auxiliary electrode. Domestic microwave oven, (Samsung electronics, New Delhi, India) was used to carry out hydrolysis. Genei (TM) shaking incubator, Bangalore, India was used in soil adsorption study.

2.2 Reagents and samples

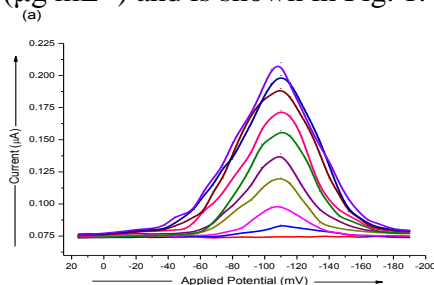
Acetonitrile (Merck Schuchardt OHG, Germany) was kept over phosphorus pentoxide (5 g L^{-1}) and distilled twice. The analytical standard of carbaryl (supplied by the courtesy of Environmental Protection Agency EPA, NC, USA) was used and its stock solution ($10^{-4} \text{ mol L}^{-1}$) was prepared in acetonitrile. The purity was checked by reported method [14]. Sodium perchlorate (Merck Schuchardt OHG, Germany) solution ($10^{-1} \text{ mol L}^{-1}$ in acetonitrile) was prepared by dissolving 12.24 g of pure compound in 1 L of acetonitrile. and used as supporting electrolyte. Copper(II) perchlorate solution in acetonitrile ($2 \times 10^{-3} \text{ mol L}^{-1}$) was prepared and standardized as described earlier [15]. Triton-X-100 (Merck Schuchardt OHG, Germany), 0.002% in acetonitrile was used as suppressor. Sodium bicarbonate (Merck, LR), 2% solution was prepared in distilled water. Methyl isobutyl ketone (MIBK, Merck, AR) was used as supplied. Carbon disulphide (Merck, AR), 1% solution in acetonitrile was used.

2.3 Sample collection and Preparation

The soils 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 [16,17] at the University of Horticulture and Forestry, Solan, Himachal Pradesh, India.

2.4 Preparation of calibration graph for carbaryl insecticide (as dithiocarbamate)

Aliquots (0.1-2.0 mL) of stock solution ($10^{-4} \text{ mol L}^{-1}$ in acetonitrile) of carbaryl were taken in 25 mL-measuring flasks and volume made to 2 mL with acetonitrile. Each solution was mixed with 2% aqueous solution of sodium bicarbonate (0.5 mL), carbon disulphide (0.5 mL ~ 1% in acetonitrile), 0.5 mL of water and kept in microwave oven for 40 sec. Each solution was mixed with copper(II) perchlorate (1mL, 0.002M in acetonitrile) and then extracted with 3 mL MIBK containing 2-3 crystals of sodium perchlorate. The MIBK extract was mixed with Triton-X -100 (2 mL, 0.002 % in acetonitrile) and final volume made to 15 mL with sodium perchlorate (0.1 mol L^{-1} in acetonitrile). Nitrogen gas was bubbled through the solution for 5 min. The differential pulse polarogram of each solution was recorded at room temperature (24 ± 1) °C with following instrumental parameters : initial potential = 100 mV; drop time = 1 sec; pulse amplitude = 50 mV and scan rate = 6 mV/sec. Calibration graph was constructed by plotting peak current (μA) (corresponding to -110 mV peak) versus concentration of carbaryl ($\mu\text{g mL}^{-1}$) and is shown in Fig. 1.



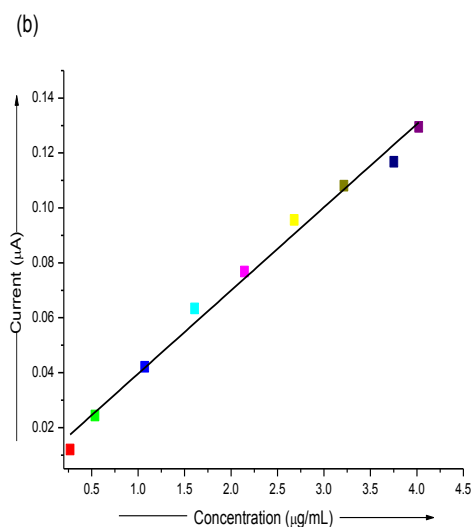


Figure 1. Relationship between peak current and concentration (calibration graph) for carbaryl: Differential pulse polarographic procedure

2.5 Formulation analysis

A wettable powder (WP) formulation, “Sevin” containing 50% active ingredient (carbaryl) procured from an authorized pesticide dealer was used. A single large sample of formulation equivalent to 10.05 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 (0.1–0.4 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.

2.6 Determination of carbaryl in grains (wheat and rice) and water samples

Carbaryl standard solution was prepared by dissolving 10 mg Carbaryl in 50mL acetonitrile; 10mL of this solution was diluted to 100mL with acetonitrile for a final concentration of 20 µg mL⁻¹ Carbaryl. Aliquots (0.25–1.0 mL) of the standard solution of Carbaryl 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 2.0 mL 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 (0.25–1.0 mL) of standard solution having a concentration of 20 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.

2.7 Soil adsorption study

Adsorption isotherms of carbaryl on five Indian soils of different soil characteristics (Table 3) were obtained by the batch equilibration technique using 50 mL conical flask. Triplicate soil samples (2 g) were equilibrated with carbaryl solution in the concentration range from 10.05-60.3 µg mL⁻¹ on shaker (150 rpm) at two temperatures 20 °C and 30 °C for 6 hr equilibrium time (estimated time required for equilibrium to be reached between carbaryl adsorbed and in solution). After equilibration, the suspensions were centrifuged and the equilibrium concentrations (C_e) were determined in supernatants by the polarographic procedure described above. Adsorption isotherms were evaluated by using Freundlich's adsorption equation which is written as

$$X = K_f C_e^{nf} \quad (1)$$

Where X is the amount of pesticide adsorbed mg/Kg of the adsorbent; C_e is the equilibrium solution concentration (mgL^{-1}); K_f and n_f are adsorption coefficients that characterize the adsorption capacity of 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

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

Another parameters for the adsorption process viz. distribution coefficient or soil-adsorption coefficient (K_d), soil organic carbon partition coefficient (K_{oc}) and Groundwater Ubiquity Score (GUS) have been calculated by using equations 3-5 respectively [18-20].

$$K_d = X/C_e \quad (3)$$

$$K_{oc} = K_d \times (100/\% \text{OC}) \quad (4)$$

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

Where $t_{1/2}$ = 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[20]. The thermodynamic parameters viz. Gibb's free energy (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) have also been calculated by using equations 6-8 respectively [21].

$$\Delta G^\circ = -RT \ln K_d \quad (6)$$

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

$$\Delta S^\circ = ((\Delta H^\circ - \Delta G^\circ)/T) \quad (8)$$

Where R = gas constant, T = absolute temperature. All these parameters for the adsorption of carbaryl on five Indian soils with different soil characteristics were calculated and the results are shown in Tables 4 and 5.

III. RESULTS AND DISCUSSION

3.1 Standardization of reaction conditions

The proposed polarographic method is based on microwave assisted alkaline hydrolysis of carbaryl to methylamine which in the presence of carbon disulphide and copper(II) perchlorate is quantitatively transformed to copper(III) methyl dithiocarbamate and latter gives a diffusion-controlled peak at -110 mV vs SCE. The optimum time required for complete hydrolysis (in microwave) of carbaryl to methylamine (dithiocarbamate) was obtained by varying the time of hydrolysis from 10-80 sec. It has been observed that maximum current intensity was obtained corresponding to 40 sec hydrolysis time (Fig.2).

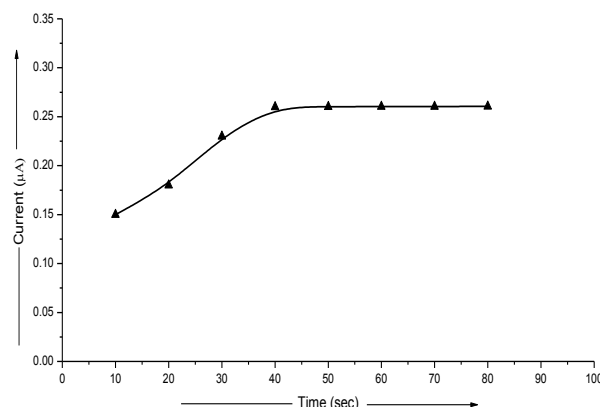
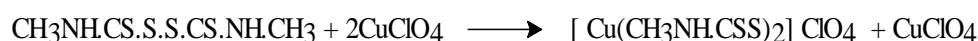
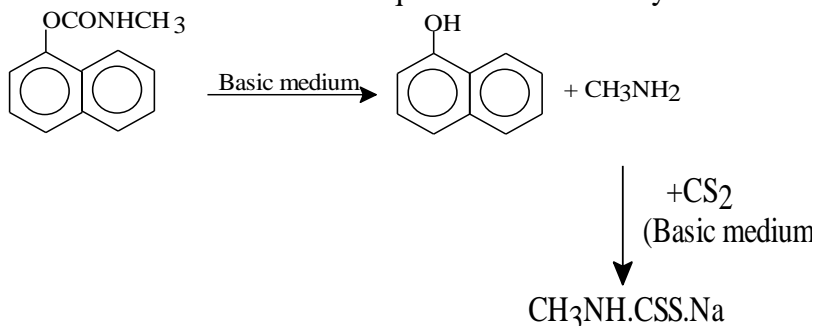


Figure 2. Effect of reaction time on hydrolysis of carbaryl in microwave

Methyl isobutyl ketone (MIBK) is an extracting solvent of choice because it is safe in comparison of commonly used toxic extracting solvents and extract the copper(II)-methyl dithiocarbamate complex quantitatively.

3.2 Proposed mechanism for the polarographic method

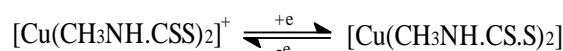
Microwave assisted alkaline hydrolysis of carbaryl in basic medium forms corresponding methylamine [22] which reacts with an excess of carbon disulphide to form methylthiocarbamate. The latter reacts with copper(II) perchlorate to form copper(III)-methylthiocarbamate (I) **Scheme (1)** showing analytical useful well defined diffusion controlled peak at -110 mV vs SCE. The electrode process is diffusion controlled which is evident from the linear relationship obtained between diffusion current and square root of mercury column height (h).



(I)

Scheme (1)

The reaction taking place at the dropping mercury electrode is supposed to involve the reduction of copper(III) dithiocarbamate to copper(II) dithiocarbamate with one electron change **Scheme (2)**.



Scheme (2)

The formation of copper(III) methylthiocarbamate complex of type (I) through reaction of dithiocarbamate with copper(II) perchlorate to form copper(III)-methylthiocarbamate has been thoroughly established in our laboratory[23,24].The role of perchlorate anion (a bulky anion) in stabilizing the higher oxidation states of metals especially copper(III) methylthiocarbamate complexes is also quite well known[25].

Under the optimized experimental conditions, the proposed method obeys the linear relationship between the concentration of carbaryl and peak current intensity in the range 0.27-4.02 $\mu\text{g mL}^{-1}$. The linear regression equation has the value of slop and intercept as (0.0303 and 0.00934) respectively with correlation coefficient 0.989. The method is accurate and precise with a maximum relative standard deviation of 1.1 %. The method has been applied for the determination of carbaryl in commercial formulations, grains and spiked water samples. The recoveries from commercial formulations were in the ranges 93.6-97.2% of the nominal content with RSDs in the range 0.4-1.4% (Table 1). The recoveries of the insecticide from grains and spiked water samples were good, ranging from 86.7-94.1%, with RSDs ranging from 0.6-1.2% (Table 2).

Table 1. Assay of a commercial formulation of carbaryl containing 50% active ingredient (Sevin)

Amount taken, μg	Recovery, % ^a	
	Present method	Comparison method ^b
4.02	94.4±0.6	92.8±0.4
8.04	93.6±1.4	90.4±0.8
12.06	97.2±0.8	93.6±0.6
16.08	95.4±0.4	91.8±1.2

^a Values are mean of five determinations with standard deviation (\pm), ^b Comparison method ¹⁴

Table 2. Recovery of carbaryl from fortified grains (Wheat and Rice) and water samples

^a Values are mean of five determinations with standard deviation (\pm), ^b Comparison method ¹⁴

Active ingredient added, μg	Recovery of active ingredient ^a , %					
	Present method			Comparison method ^b		
	Wheat	Rice	Water	Wheat	Rice	Water
5.0	89.7 \pm 0.9	86.7 \pm 0.6	91.3 \pm 0.7	87.6 \pm 1.0	84.4 \pm 0.7	89.4 \pm 1.2
10.0	90.2 \pm 0.7	89.4 \pm 0.9	90.7 \pm 0.8	86.2 \pm 0.7	87.2 \pm 0.9	88.5 \pm 0.6
15.0	92.3 \pm 0.6	94.0 \pm 0.8	94.1 \pm 1.2	90.2 \pm 1.4	91.3 \pm 0.8	92.2 \pm 1.0
20.0	92.9 \pm 0.8	93.4 \pm 1.2	93.7 \pm 1.0	91.4 \pm 1.2	90.7 \pm 1.0	91.7 \pm 0.8

The environmental fate of carbaryl like any other insecticide is strongly influenced by its interaction with soil through sorption which is a naturally occurring process. The toxicity of carbaryl is dependent mainly on its concentration in soil solution phase i.e. unadsorbed fraction of the insecticide and also its adsorption by soil which in turn is dependent on soil characteristics such as organic carbon content, clay content, temperature, pH and cation exchange capacity of soil. In view of this the method has been applied to study adsorption of carbaryl on five soils of different characteristics to evaluate its leaching potential and the extent to surface and ground water contamination. The various characteristics of five soils are given in Table 3 and soil adsorption study has been made by using batch-equilibrium technique at two temperatures viz. 20°C and 30°C by Freundlich's adsorption equation.

Table 3. Characteristics of the different Indian soils used in the adsorption study of carbaryl

Soil Sample	pH	Clay, %	Organic carbon, %	Cation Exchange Capacity, meq/100g
I	7.2	32.6	0.8	13.1
II	7.6	18.2	0.9	12.9
III	6.5	20.0	1.5	11.0
IV	6.8	23.4	1.6	12.8
V	7.6	14.1	0.7	11.6

The adsorption isotherms have been classified as S-type of Gile's classification (Table 4) according to the initial slope of the curve. S-type of isotherms represents a system where solid surface has high affinity for the solvent than for solutes [26] (e.g. water competes strongly with solute for adsorption sites). Freundlich's adsorption coefficients K_f and n_f were calculated from the plot of $\log X$ versus $\log C_e$ (Fig.3) from Freundlich's adsorption equation and the results are presented in Table 4.

Table 4. Adsorption parameters for the adsorption of carbaryl on five Indian soils at 20 \pm 1°C and 30 \pm 1°C

Soil Sample	K_f	n_f	K_d	K_{oc}	GUS	Adsorption isotherm
20 °C						
I	2.41	1.80	4.27	533.20	1.85	S-type
II	2.74	1.13	4.18	463.51	1.93	S-type
III	3.42	1.15	5.39	359.38	2.09	S-type
IV	3.53	1.16	5.56	347.57	2.12	S-type
V	3.37	1.04	3.98	569.13	1.81	S-type
30 °C						
I	3.73	1.01	3.89	486.06	1.90	S-type
II	3.53	1.01	3.77	418.73	2.00	S-type
III	1.92	1.32	5.03	335.11	2.14	S-type
IV	3.05	1.18	5.12	320.09	2.17	S-type
V	1.47	1.29	3.68	525.86	1.81	S-type

The adsorption coefficient K_f represents the amount of pesticide adsorbed at an equilibrium concentration of 1 mgL^{-1} and n_f represents the variation in adsorption with varying concentration of

pesticide [27]. The observed values of n_f were more than 1, in all five soils types with each insecticide, indicating that with an increase in the concentration of each insecticide, the percentage adsorption of each insecticide by the soil decreased. This might be due to the fact that at higher concentration there may be difficult to access the adsorption sites.

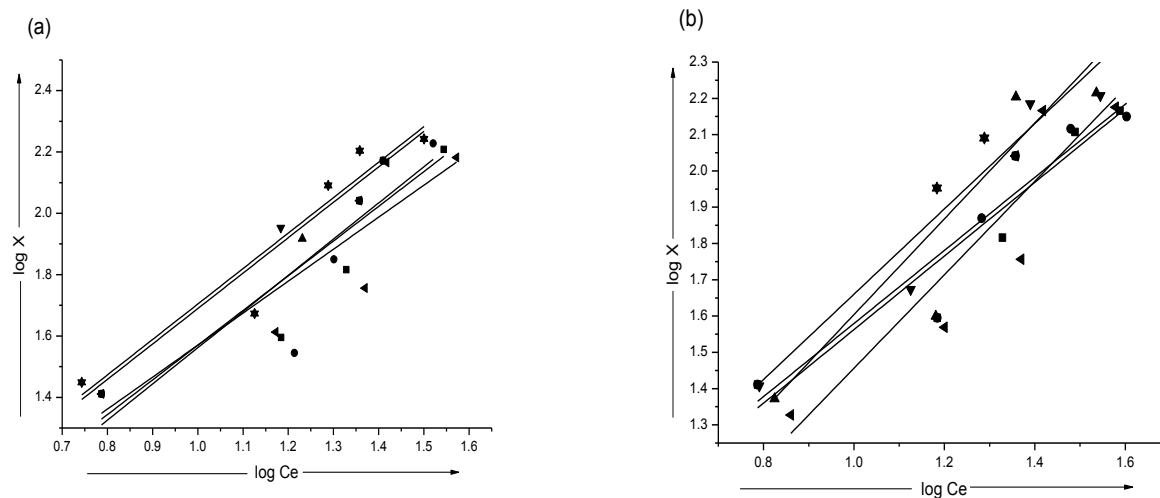


Figure 3. Plot of $\log X$ versus $\log C_e$ for the evaluation of Freundlich's adsorption coefficients K_f and n_f at 20 ± 1 °C (a) and at 30 ± 1 °C (b)

Other parameters such as soil adsorption coefficients (K_d), soil organic carbon partition coefficient (K_{oc}), Gibb's free energy for adsorption process (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) for the adsorption of above insecticides were also calculated and are presented in Tables 4 and 5.

Table 5. Thermodynamic parameters for the adsorption of carbaryl on five Indian soils

Soil samples	$\Delta G^\circ / \text{KJ mol}^{-1}$		$\Delta H^\circ / \text{KJ mol}^{-1}$	$\Delta S^\circ / \text{KJ K}^{-1} \text{mol}^{-1}$
	20°C	30°C	25°C	25°C
I	-3.49	-3.42	-6.88	-0.011
II	-3.53	-3.34	-7.62	-0.014
III	-4.10	-4.07	-5.10	-0.0034
IV	-4.18	-4.12	-6.09	-0.0065
V	-3.37	-3.28	-5.78	-0.0082

K_d for a pesticide is soil-specific and vary with soil texture and its organic matter content, but the soil organic carbon partition coefficient (K_{oc}) is less soil specific [28] and is calculated by normalizing adsorption coefficient (K_d) with the organic carbon (OC) content of the soil. The values of K_d represents the extent of adsorption and in general higher the K_d value, greater is pesticide adsorption [29]. Among the five soils used, adsorption was maximum in soil IV, followed by soil III, soil I, soil II and soil V. The higher adsorption in soil IV and III can be explained on the basis of higher organic content of these soils (Table 3). The values of K_{oc} for carbaryl on five soils types at 20 °C and 30 °C decreased with increased fraction of organic carbon content indicating that adsorption is not only influenced by OC content of soil alone but also governed by some other factors. The value of CEC is directly proportional to hydrophobic nature of adsorbent i.e. greater the value of CEC of soil, the surface will be more hydrophobic (low water solubility) thus has higher adsorption affinity for soils with higher CEC [30].

The K_d values for carbaryl at two temperatures viz. 20 °C and 30 °C were 3.98-5.56 and 3.68-5.12. The adsorption of carbaryl in five soils has been found maximum at 20 °C than at 30 °C. This may be due to the fact that at high temperature adsorption decreases due to the weakening of binding

forces between pesticide and soil particles. Similar results have also been reported in literature in the adsorption study of other pesticides [31].

The thermodynamic parameters for the adsorption of carbaryl insecticide on five soils were also evaluated and are presented in Table 5. The ΔG° values for adsorption of carbaryl were negative at both temperatures. The magnitude of ΔG° also showed that the interactions of pesticides with the soil were thermodynamically spontaneous process and adsorption occurred through a bonding mechanism. At constant temperature, the higher the value of ΔG° the slower is the rate of adsorption. The results obtained in the present study indicate an increase in the values of ΔG° with temperature. Variation of ΔG° with temperature may be due to the increase in the degree of freedom of adsorbed molecules, which enhances the desorption rather than adsorption at higher temperatures [32-34]. The enthalpy change ΔH° calculated for carbaryl were in the range (-5.10 to -7.62). The negative values of ΔH° indicated that the interaction of pesticides with the soil is an energetically favourable exothermic process. The ΔH° values explain the binding strength of pesticides to the soil; the lower negative value of ΔH° indicates stronger binding. This indicates that the interactions between the pesticide and the studied soil samples were stronger at lower temperature [32-34]. The entropy change ΔS° calculated for carbaryl were negative indicated that the adsorption involves stabilization, association, fixation or immobilization of the pesticide molecules as a result of which adsorption decreased the degree of freedom, causing negative entropy effect and increasing the order of the system [32-34]. To evaluate the leaching potential of carbaryl, groundwater ubiquity score (GUS) was calculated from the measured organic carbon distribution coefficients and average half life time [20]. The groundwater ubiquity score (GUS) values for carbaryl were (1.81-2.17) classify carbaryl as transitional insecticide and has a potential to contaminate groundwater [35]. The toxicity due to carbaryl can be reduced by adjusting the application dose according to soil properties and soils amended with farmyard manure and compost. The latter application will also improve the soil fertility and health by serving as source of soil nutrients. The environmental contamination and health hazards derived from the use of carbaryl can also be reduced by using its controlled release formulations.

IV. CONCLUSION

The proposed pulse polarographic method for the analysis of carbaryl is remarkably simple and sensitive with quantification limit of 0.27 to 4.02 $\mu\text{g mL}^{-1}$ with correlation coefficient 0.989 without any interferences from inert carriers commonly present in its formulations. Pesticides are major source of pollution. Following applications, these chemicals enter soil and then to aquatic environment through leaching resulting into surface and ground water contamination. The risk of leaching for carbaryl has been evaluated using the proposed method based on its adsorption on five soils of different characteristics at two different temperatures viz. 20 °C and 30 °C. From the adsorption study it is concluded that overall observed Koc values (320-569) suggesting moderate adsorption of carbaryl on all soil types (Koc in the range 300-1000 corresponds to moderate adsorption [36]). Carbaryl is adsorbed maximally in case of soil IV, followed by soil III, soil I, soil II and soil V in terms of K_d and Koc values.

The leaching potential in terms of GUS in the range 1.81-2.17 classify it as transition pesticide of Gustafson's classification [37] thereby it poses potential risk to aquatic environment. Hence it should be used judiciously to prevent ground water contamination.

BIBLIOGRAPHY

- [1] Mondal, N.K.; Chatteraj, S.; Sadhukhan, B. and Das, B., 2013. Evaluation of carbaryl sorption in alluvial soil. *Songklanakarin J. Sci. Technol.*, **35**(6): 727-738.
- [2] El Ouardi, M.; Alahiane, S.; Qourzal, S.; Abamrane, A.; Assabbane, A. and Douch, J. 2013. Removal of Carbaryl Pesticide from Aqueous Solution by Adsorption on Local Clay in Agadir. *American J. Anal. Chem.*, **4**: 72-79.
- [3] Faraji, M.; Noormohammadi, F.; Jafarnejad, S. and Moradi, M. 2017. Supramolecular-based solvent microextraction of carbaryl in water samples followed by high performance liquid chromatography determination. *Int. J. Environ. Anal. Chem.*, **97**(8): 730-742.

- [4] Roudani, A.; Mamouni, R.; Saffaj, N.; Lanknifli, A.; Gharby, S.; El Baraka, N.; Bakka, A. and Faouzi, A. 2017. Method validation in the determination of Carbaryl pesticide in water samples using sonication and liquid chromatography–tandem mass spectrometry. *J.Mat. and Environ. Sci.*, **8(7)**: 2409-2420.
- [5] Shen, F.; Wang, L.H.; Zhou, Q.; Huang, X.; Zhang, J.; Zhu, P.; Dai, X. and Xu, Y. 2017. Simultaneous Determination of Aniline, Benzidine, Microcystins, and Carbaryl in Water Using Ultra-Performance Liquid Chromatography–Electrospray Ionization Tandem Mass Spectrometry. *Water Air Soil Pollut.*, **228**: 69-78.
- [6] Mukdasai, S.; Thomas, C. and Srijaranai, S. 2013. Enhancement of sensitivity for the spectrophotometric determination of carbaryl using dispersive liquid microextraction combined with dispersive μ -solid phase extraction. *Anal Methods.*, **5**: 789-796.
- [7] Murthy, P. K.; Sulochana, M. and Naidu, N. V. 2012. A novel spectrophotometric method for the determination of Carbaryl in Environmental samples. *Der Pharma Sinicia.*, **3**: 224-228.
- [8] Xu, J.C.; Rong, X.S.; Tian, T. and Qiu, F.X. 2014. Fluorescent Sensor and Application in Determination of Carbaryl Residues. *Adv. Mat. Res.*, **955-959**: 1220-1223.
- [9] Koc, F.; Yigit, Y.; Das, Y. K.; Gurel, Y. and Yarali, C. 2008. Determination of Aldicarb, Propoxur, Carbofuran, Carbaryl and Methiocarb Residues in Honey by HPLC with Post-column Derivatization and Fluorescence Detection after Elution from a Florisil Column. *J. Food Drug Anal.*, **16(3)**: 39-45.
- [10] Dong, T.; Sun, J.; Liu, B.; Zhang, Y.; Song, Y. and Wang, S. 2010. Development of a sensitivity improved immunoassay for the determination of carbaryl in food samples. *J. Sci. Food Agric.*, **90(7)**: 1106-1112.
- [11] Ni, Y.; Cao, D. and Kokot, S. 2007. Simultaneous enzymatic kinetic determination of pesticides, carbaryl and phoxim, with the aid of chemometrics. *Anal. Chim. Acta.*, **588(1)**: 131-139.
- [12] Kashid, L. M. and Pawar, N. J. 2015. Voltammetric behaviour of imidacloprid and its electrochemical mineralization assessment by differential pulse polarography. *Int. J. Sci. Res. Pub.*, **5**: 1-7.
- [13] Aydin, Z.Y. and Yilmaz, U.T. (2016). The Determination of Ammeline by Differential Pulse Polarography /Application to Milk. *Gazi Univ. J. Sci.*, **29(3)**: 549-558.
- [14] Stansbury, Jr H. A, Miskus R and Zweig G, 1964. *Analytical Methods for Pesticides, Plant Growth Regulators, Food Additives*, (Academic Press, New York) p. 437.
- [15] Verma, B. C. and Kumar, S. 1977. Non-aqueous redox determination of ascorbic acid with copper(II). *Talanta*, **24**: 694–695.
- [16] Jackson, M L, 1967. *Soil Chemical Analysis*, (Prentice-Hall Publisher, New Delhi, India) p. 57, 205.
- [17] Walkey, A. and Black, I. A. 1934. An examination of the Degtjareff method for determining soil organic matter and a proposed modification of the chromic acid titration method. *Soil Sci.*, **37**: 29-38.
- [18] Vischetti, C.; Marucchini, C.; Leita, L.; Cantone, P.; Danuso, F. and Giovanardi, R. 2002. Behaviour of two sunflower herbicides (metobromuron, acetonifin) in soil. *Eur. J. Agron.*, **16**: 231-238.
- [19] Raturi, S.; Islam, K. R.; Carroll, M. J. and Hill, R. L. 2005. Carbaryl, 2,4-D and triclopyr adsorption in thatch-soil ecosystems. *J. Environ. Sci. Health Part B*, **40**: 697-710.
- [20] Papa, E.; Castiglioni, S.; Gramatica, P.; Nikolayenko, V.; Kayumov, O. and Calamari, D. 2004. Screening the leaching tendency of pesticides applied in the Amu Darya basin (Uzbekistan). *Water Res.*, **38**, 3485-3494.
- [21] Bhardwaj, D.; Sharma, P. and Tomar, R. 2007. Restriction of pesticidal movement in contaminated soil and water. *Ind. J. Chem.*, **46A**, 1796-1800.
- [22] Robert, T R and Hutson, D H, 1999. *Metabolic Pathways of Agrochemicals Part 2, Fungicides and Insecticides*, (Royal Society of Chemistry, UK) p. 16.
- [23] Sharma, D.K.; Gupta, A.; Kumar, S. and Verma, B. C. 2007. Voltammetric studies of Cu(II) Dithiocarbamate reactions and a differential pulse polarographic method for the determination of dithiocarbamates. *J. Ind. Chem. Soc.*, **84(1)**: 20-24.
- [24] Sharma, D K.; Chauhan, C.; Gupta, A. and Sharma, N. 2007. A pulse polarographic method for the determination of primary and secondary amines and its application to the analysis of organic isocyanates. *J. Ind. Chem. Soc.*, **84(11)**: 1145-1147.
- [25] Golding, R M.; Harris, C M, Jessop, K J and Tennant, W C, 1972. Oxidation of dithiocarbamate metal complexes. *Aus. J. Chem.* **25(12)**: 2567-2576.
- [26] Oliveira, M F.; Johnston, C T.; Premachandra, G S.; Teppen, B J.; Li H.; Laird, D A.; Zhu, D. and Boyd, S. A. 2005. Spectroscopic Study of Carbaryl Sorption on Smectite from Aqueous Suspension. *Environ. Sci. Technol.*, **39(23)**: 9123-9129.
- [27] Jaya, M.; Singh, S B. ; Kulshrestha, G. and Arya, S. 2009. Adsorption behaviour of alachlor on soil, FYM and charcoal. *Pest. Res. J.*, **21(1)**: 101-104.
- [28] Chen, J P.; Pehkonen, S.O. and Lau, C.C. 2004. Phorate and terbufos adsorption on to four tropical soils. *Col Surf A*, **240**: 55-61.
- [29] Kumar, M. and Philip, L. 2006. Adsorption and desorption characteristics of hydrophobic pesticide endosulfan in four Indian soils. *Chemosphere*, **62**: 1064-1077.
- [30] Pal, O.R. and Vanjara, A.K. 2001. Removal of malathion and butachlor from aqueous solution by clays and organoclays. *Sep Puri Technol.*, **24**: 167-172.
- [31] Farahani, G.H.N. 2007. Adsorption and desorption of carbofuran in Malaysian soils. *Adv Environ. Biol.*, **1(1)**: 20-26.
- [32] Almalike, L.B.; Al-Najar, A.A. and Kadhim, Z.N. 2015. Chemical Kinetic and Thermodynamic of Adsorption-

desorption of cypermethrin in soil of South Iraq. *Int. J. Adv. Res. Technol.*, **4(9)**: 17-25.

- [33] Shariff, R. M. 2011. Thermodynamic Adsorption-desorption of Metolachlor and 2,4-D on Agricultural Soils. *Int. J. Chem.*, **3(4)**: 134-146.
- [34] Shariff, R. M. and Shareef, K.M. 2011. Thermodynamic Adsorption of Herbicides on Eight Agricultural Soils. *Int. J. Sci. Eng. Res.*, **2(6)**: 1-8.
- [35] Hiller, E.; Khun, M.; Zemanova, L.; Jurkovic, L. and Barta, M. 2006. Laboratory study of retention and release of weak acid herbicide MCPA by soils and sediments and leaching potential of MCPA. *Plant Soil Environ.*, **52(12)**: 550-558.
- [36] Kenaga, E.E. 1980. Predicted bioconcentration factors and soil sorption coefficients of pesticides and other chemicals. *Ecotoxicol. Environ. Safety*, **4(1)**: 26-38.
- [37] Gustafson, D. I. 1989. Groundwater ubiquity score: a simple method for assessing pesticide leachability. *Environ. Toxicol. Chem.*, **8**: 339–357.