



ASSESSMENT OF THERMODYNAMIC BEHAVIOUR OF INSECTICIDES IN INDIAN SOILS BY DIFFERENTIAL PULSE POLAROGRAPHY

Lalasaheb Kashid*¹, Nilkanth Shinde²

¹Department of Chemistry, Vidya Pratishthan's, Arts, Science and Commerce College, Baramati, Pune, Maharashtra, India

²Department of Chemistry, Nowrosjee Wadia College, Pune, Maharashtra, India

*Corresponding author: lmkashid@gmail.com

ABSTRACT

The differential pulse polarographic method was developed and validated for the investigation of electrochemical and thermodynamic properties of imidacloprid in soil. In DPP method, electrochemical reduction behavior of imidacloprid was studied in Britton-Robinson buffer (pH 3.0-10) as a supporting electrolyte. The range of linearity ($R^2 = 0.996$) of imidacloprid was found to be from $1.0 \mu\text{g mL}^{-1}$ to $12.0 \mu\text{g mL}^{-1}$, the limit of detection (LOD) is $0.6552 \mu\text{g mL}^{-1}$ and the limit of quantification (LOQ) is $2.184 \mu\text{g mL}^{-1}$. The validated differential pulse polarography method was successfully applied for the study of thermodynamic parameters. It was observed from Freundlich parameters that the value of K_f for selected insecticide is normalized with % organic matter in four soils. The value of $1/n$ for all soils is less than one which indicates a greater affinity of adsorption of insecticides on soils in the order of $\text{KS}_1 > \text{KS}_2 > \text{KS}_3 > \text{KS}_4$. The proposed method is accurate, precise, fast and economical.

Keywords: Differential Pulse Polarography, Imidacloprid, Insecticide, Validation, Soil.

1. INTRODUCTION

The use of pesticides in the agricultural and non-agricultural sector has led to several environmental problems. The issues related to them have not yet attracted the attention of the scientific community. The pesticides imidacloprid [1-(6-chloro-3-pyridyl-methyl)-N-nitro-imidazolidin-2-ylideneamine] has been increasingly used in India [1] and belongs to the fastest growing group of insecticides introduced to the market, referred to as neonicotinoids [2]. It is used as a seed, soil, crop and structural treatment.

Pesticide adsorption processes are very important for determining the fate and distribution of pesticides in the soil/water environment because they determine the number of pesticides that can reach the target organism and the amount that can be volatilized, degraded or leached. The sorption is affected by the physical and chemical properties of pesticides and soils [3]; it also appears that sorption may be affected by contact time in the soil. Soil-pesticide interactions have been examined extensively elsewhere [4].

Pesticide soil adsorption coefficient K_d , soil organic carbon adsorption coefficient K_{oc} , free energy ΔG and retardation factor R_f are the basic parameters used by

pesticide scientists and regulatory agencies around the world to describe the environmental fate and behavior of pesticides. They are a measure of the adsorption strength of pesticides on the surface of the soil and other adsorbents, and therefore also a measure of their mobility in the soil.

Various analytical methods have been developed for the detection and quantification of the pesticides, such as the High Performance Liquid Chromatography (HPLC) [5, 6], Gas Chromatography (GC) [7-10], Enzyme Linked Immunosorbent Assay (ELISA) [11-13], Differential Pulse Polarography (DPP) [14, 15] and Radioimmunoassay (RIA) [16] but all these methods have disadvantages except DPP such as long analysis time, consume a lot of reagents and expensive. Because of this, it was proposed to develop a cost effective electroanalytical differential pulse polarographic method for the determination and decontamination of imidacloprid in the soil environment.

This study aims to evaluate the adsorption characteristics of imidacloprid in four soil series through DPP on the surface soil layer. To better understand the factors affecting adsorption, the adsorption behavior of pesticides is related to the selected pesticides and soil

properties. The thermodynamic parameters of the interaction of imidacloprid in the soil were also evaluated.

2. EXPERIMENTAL

2.1. Material and Methods

2.1.1. Soil Characterization

Four soil samples were collected from the study area of Baramati tahsil, Pune district of Maharashtra state, India. From a climatological point of view, it is located in the rain shadow area of the Western Ghats. From a geomorphologically point of view, it is located in the Karha and Nira basins in the central part of the Bhima Basin. The latitude of the Tahsil is between 18 2 44 N and 18 23 19 N, and the longitude is between 74 13 8 E

and 74 42 47 E. Table 1 lists the soil sampling locations. All the soil was air-dried and sieved through a 2 mm sieve. Various physical and chemical properties of soil samples were analyzed, which are considered to be important for the adsorption and migration of pesticides. These included pH, soil texture, organic C, cation exchange capacity (CEC), bulk density, particle density and porosity. The international pipette method [17] was used to estimate the % clay, silt, and sand. The pH of the soils was determined on a 1:2.5 soil-water suspension using a glass electrode and organic matters present in the soil were determined by the Walkley-Black method. The CEC was determined by the ammonium acetate method [18]. All these soil properties are given in Table 2.

Table 1: List of soil sampling station (location in lat. long; deg min s)

Location	Likely source	Sample identity	BD*
18 06 44.0 N; 74 39 27 E	Agricultural	KS ₁	1.426
18 03 55.0 N; 74 29 23 E	Agricultural	KS ₂	1.4030
18 11 43.0 N; 74 37 14 E	Agricultural	KS ₃	1.3647
18 16 36.0 N; 74 31 24 E	Agricultural	KS ₄	1.3488

BD*- bulk density in (gm cm⁻³)

Table 2: Selected Physico-Chemical Properties of Soil Samples

Soil	%sand	% silt	%clay	Texture	% OM ¹	CEC ²	Porosity ³	pH
KS ₁	29.21	18.23	52.56	Clay	2.3230	57.24	0.4087	8.3
KS ₂	64.46	13.50	22.04	Clay loam	1.8207	65.23	0.3968	8.1
KS ₃	67.83	13.42	18.75	Sandy loam	0.8251	52.23	0.3283	7.9
KS ₄	64.58	16.42	19.00	Sandy clay loam	0.4035	48.26	0.4000	7.8

% organic matter¹, cation exchange capacity² meq/100 g of soil, Porosity³=PD-BD/PD, PD=Particle density, BD= bulk density

2.1.2. Chemicals

Analytical reagent grade chemicals were used for the preparation of solutions in doubly distilled water. The purity of reference standard imidacloprid was 99.9%. Solutions were prepared in Britton-Robinson 0.04 M buffer solutions.

2.1.3. Equipment Used

Polarographic analyzer model CL-362 supplied by Elico Ltd, Hyderabad with PC through its RS 232C interface with the help of ELICO's windows based software, was used for polarographic measurements. Dropping mercury as the working electrode, saturated calomel as reference and platinum wire as auxiliary was used as electrodes. The pH measurements were carried out with the help of an Elico pH meter. UV-VIS spectrophotometer, PerkinElmer Lambda 25 was used for measurement of absorbance of imidacloprid in BRB solution.

2.1.4. Method Development

A DPP method was performed in a polarographic cell with three electrodes system. 10.0 ml aliquot of BRB solution as a supporting electrolyte was placed in a polarographic cell containing required imidacloprid concentration using a micropipette. Before analysis, the solution was degassed by bubbling pure nitrogen into the cell for 7 minutes. After recording a blank, a small amount of imidacloprid insecticide standard solution was added to the cells and degassed for 2 minutes, and the polarogram was recorded again under similar conditions.

2.2. Method Validation

The instrumental and experimental parameters were optimized to obtain the best characteristics of imidacloprid in terms of peak current at peak potential. DPP methods can be used for investigating the electrochemical properties and the quantitative analysis

of pesticide at the dropping mercury electrode. This method can be used for the analysis of pesticides in soil samples.

2.3. Adsorption Experiments

The thermodynamic adsorption study of insecticides was done by using a batch equilibration method. Air-dried soil (2.0 g) was placed in a flask containing 20.0 mL of insecticide solution with a range of initial concentrations (0.01 mg mL^{-1} to 0.18 mg mL^{-1}) C_0 , to give a 1:10 soil-to-solution ratio. The pesticide working solution was obtained by diluting the stock solution with 0.01 M CaCl_2 . The flask was sealed and stirred on a reciprocating shaker at 25°C for 24 hours. After equilibration, the suspension was centrifuged at 1500 rpm for 15 minutes, and the aqueous solution was extracted with dichloromethane. The extracts were dried and reconstituted to 0.04 M BRB buffer. These samples were analyzed by DPP using optimized parameters.

3. RESULTS AND DISCUSSION

3.1. DPP Behavior of Imidacloprid Insecticide

In DME, the reduction behavior of pesticides was studied using DPP in BR buffer at different pH of 1-10. It was observed that imidacloprid obtained a clear DPP reaction at pH 8.0 (fig. 1). At this pH, I_p is found to be proportional to the concentration of the pesticide in the solution. At pH 8.0 partial reduction of imidacloprid takes place and the NO_2 group gets reduced to the NH_2 group [19, 20].

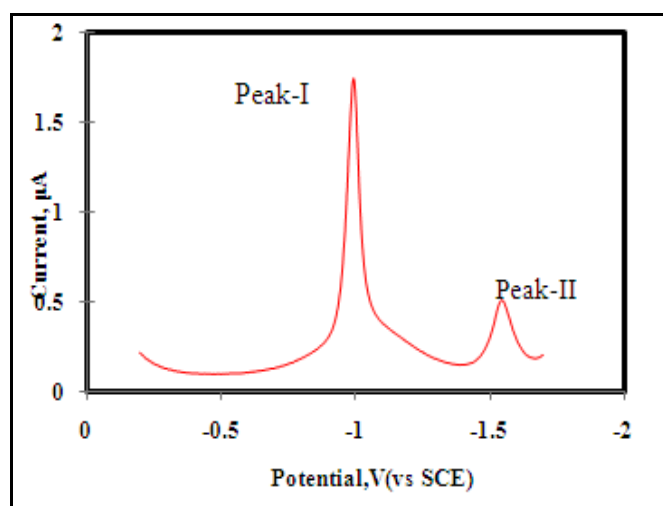


Fig. 1: DPP behavior of imidacloprid in BRB at pH 8.0

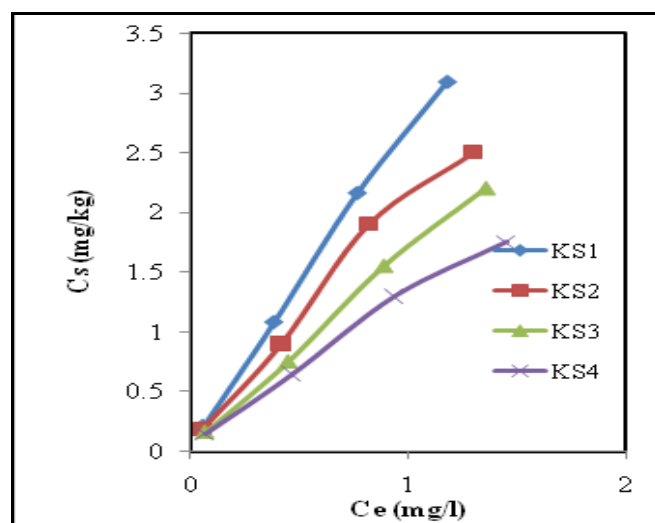


Fig. 2: Adsorption isotherm of insecticide in four soils

3.2. Quantitative Determination of Imidacloprid Insecticide by DPP

A DPP study was carried out using optimum analytical parameters at peak potential (E_p) -0.974 V , to observe a relationship between I_p and concentration of insecticide, a calibration curve and polarogram was prepared by a series of standard solution of imidacloprid. The range of linearity was found to be from $1.0 \mu\text{g mL}^{-1}$ to $12.0 \mu\text{g mL}^{-1}$ with limit of detection of (LOD) $0.6552 \mu\text{g mL}^{-1}$ and limit of quantification (LOQ) was $2.184 \mu\text{g mL}^{-1}$. The R^2 value was 0.996. The actual amount of imidacloprid found in the cell were calculated using the obtained regression equation ($I_p (\mu\text{A}) = 415.5C \pm 0.513$). The recoveries obtained were $97.29 \pm 0.79 \%$, $97.26 \pm 0.40 \%$ and $99.47 \pm 0.40 \%$ respectively.

3.3. Thermodynamic adsorption study of Imidacloprid by DPP

The effects of soil properties on the adsorption of pesticides were examined on four soils (fig. 2). From these results, simple correlation and multiple regression analyses were carried out to develop simple models for the prediction of imidacloprid sorption based on soil properties. The DPP polarogram was used to determine the equilibrium concentration of imidacloprid. The amount of insecticide in four different soils samples adsorbed after equilibration was calculated by using a regression equation. The adsorption isotherms tested for soils were found to confirm the Freundlich relationship.

$C_s = K_f C_e^{1/n}$ [1]
 Where C_s is the amount of insecticide adsorbed on soil (mg/kg), C_e is the equilibrium concentration of

insecticide in solution (mgL^{-1}). Agreement to the Freundlich equation existed for all soils with correlation $R^2 > 0.98$ (Fig. 3 and 4).

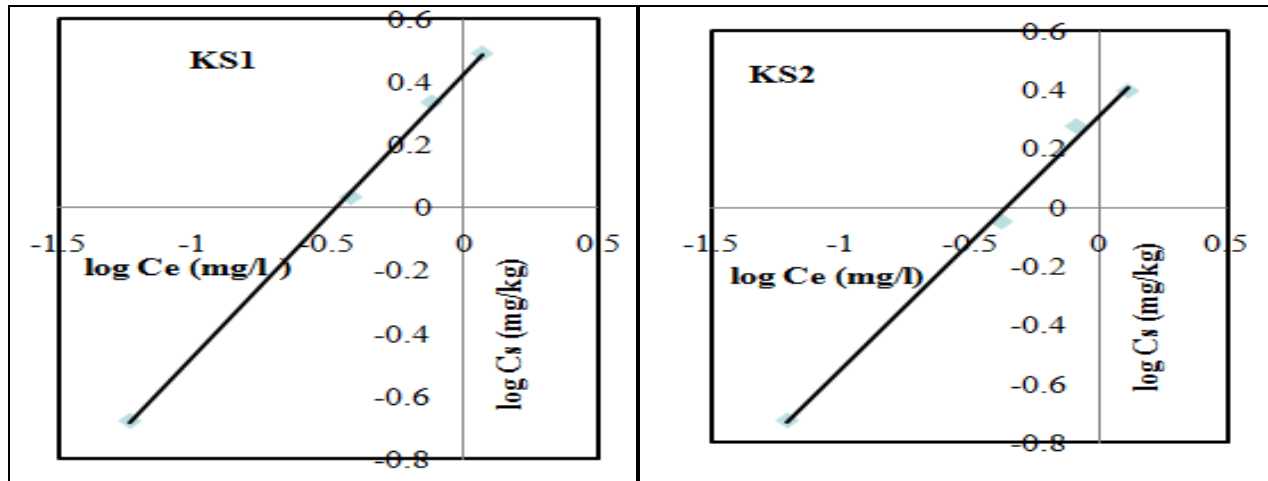


Fig. 3: Freundlich adsorption isotherm of imidacloprid insecticide on KS_1 and KS_2 soil

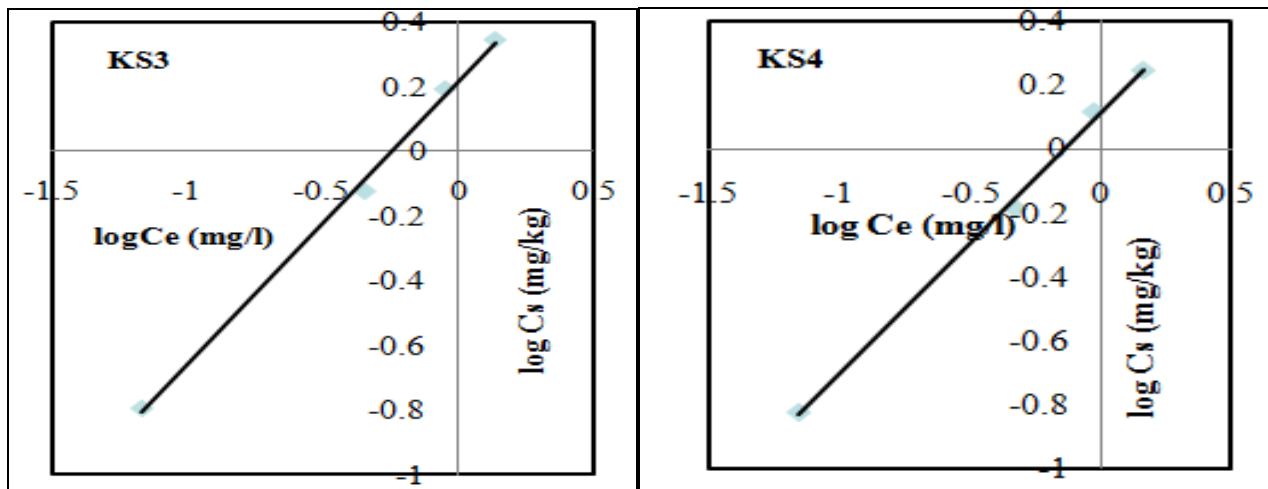


Fig. 4: Freundlich adsorption isotherm of imidacloprid insecticide on KS_3 and KS_4 soil

The calculated value of K_f for imidacloprid is ranged from 1.294 to 2.650. The value of K_f indicates strong initial adsorption and $1/n$, reciprocal of the slope of isotherms are listed in table 3. The value of $1/n$ for all soils is less than one, indicates a greater affinity of adsorption of imidacloprid on the soil. The adsorption of imidacloprid per grams of the soil was found to be in the order of $KS_1 > KS_2 > KS_3 > KS_4$ soil. This relation consists of organic matter of different soil. The K_f values of insecticide also normalized to organic carbon content of the soil. In this study, the K_{oc} value of imidacloprid would be 220 to 457 classified as moderately mobile in soil KS_1 , KS_2 , KS_3 and KS_4 soils. When imidacloprid is

attached to soil it is not as easily released as it was originally captured [21-23]. The adsorption free energy of imidacloprid on the soil is given by the following formula:

$\Delta G = - RT \ln K_{oc}$ [2]

Where ΔG is the free energy change (J); soil organic carbon sorption coefficient K_{oc} , R is the universal gas constant, 8.314 J/K mol and T is the absolute temperature (K). The heat of sorption of insecticide released between 10.75 and 13.366 kJ mol⁻¹. The negative value of the free energy change indicates that the reaction is spontaneous and has a high affinity for imidacloprid. It was also observed that the retardation

factor goes on decreasing for all soil with better correlation with organic carbon for KS₁, KS₂, KS₃ and KS₄ soils than other soil properties. The correlation coefficient of soil parameter and pesticide parameters of neonicotinoid insecticide in four soil samples are shown in table 4. They are a measure of the strength of sorption of insecticide to soil and other geosorbent surfaces and thus a measure of mobility in the soil. The soil properties % OC, % clay, % silt, % sand, CEC and pH correlated with an environmental parameter of selected insecticide in four soil samples, it was observed

that sorption coefficient K_d of imidacloprid, is strongly correlated with % OC of four selected soils.

It is also believed that soil CEC has the greatest impact on the adsorption mechanism of the soil to chemicals [24]. The trend we observed is that K_d decreases, and K_f conforms to the CEC sequence of different soils (except KS₂ clay soil). Among all other variables, CEC has the highest correlation coefficient with K_f and K_d. This is because CEC reflects the OM and clay content in the soil.

Table 3: Thermodynamic parameters of imidacloprid on different soils

Soil Samples	K _f	1/n	R ²	K _d	R _f	K _{oc} Lkg ⁻¹	ΔG kJ mol ⁻¹
KS ₁	2.650	0.865	0.999	2.96	11.32	220.0	-13.36
KS ₂	2.094	0.861	0.996	2.36	9.344	223.6	-13.40
KS ₃	1.644	0.877	0.997	1.84	8.648	385.3	-14.75
KS ₄	1.294	0.817	0.997	1.52	6.125	457.7	-16.06

Table 4: Correlation coefficient of soil and pesticides environmental parameters of imidacloprid insecticide

Parameters	K _f	K _d	K _{oc}	R _f	ΔG
% OC	0.9793	0.9794	-0.8317	0.9456	0.8202
% Clay	0.8702	0.8772	-0.6367	0.7981	0.5986
% Silt	0.3974	0.4196	-0.1055	0.2436	0.0070
% Sand	0.8313	-0.8404	-0.5844	-0.7469	-0.5376
CEC	0.7382	0.7357	-0.9370	0.7178	0.9286
pH	0.9978	0.9994	-0.9329	0.9494	0.9107

4. CONCLUSION

The proposed differential pulse polarographic method was applied for electro-analytical behavior and thermodynamic study of imidacloprid insecticides in soil offers sensitive, trace level determination of insecticide, providing adequate reproducibility and recovery. The method gives more efficiency, a reduced amount of chemicals, and more sensitivity in comparison to other reported methods. The method is simple, enables faster determinations and also permits the detection of the target molecule in the presence of many inorganic salts and other pesticides.

5. ACKNOWLEDGEMENT

The author would like to thanks Principal, Vidya Pratishthan's, Arts, Science and Commerce College for giving all possible analytical facilities to carry out the research work.

Conflict of Interest

None declared

6. REFERENCES

- Elbert A, Nauen R, Leicht W. Imidacloprid: A Novel Chloronicotinyl Insecticide: Biological Activity and Agricultural Importance, Springer, Berlin, Heidelberg, 1998.
- Tomizawa M, Yamamoto I. *J. Pesticide Sci.*, 1993; **18**:91-98.
- Koskinen WC, Harper SS. The retention process: Pesticides in the soil environment: processes, impacts and modeling, 1990; **2**:51-77.
- Rao PSC, Davidson JM. Retention and transformation of selected pesticides and phosphorus in soil-water systems: A critical review. U.S. Environ. Prot. Agency, 1982.
- Da Rocha CG, Ramos França FH, Lima Cardoso CA. *A.J. Chemistry*, 2012; **3**:242-249.
- Garrido FA, Egea Gonzalez FJ, Martinez Vidal JL, Parrilla Vazquez P, Mateu Sanchez SM. *J. Chromatography A.*, 2000; **869**:497-504.
- Blasco C, Fernandez M, Pico Y, Font G, Manes J. *Anal. Chim. Acta.*, 2002; **461**:109-116.

8. MacDonald L, Meyer TR. *J. Agric. Food Chem.*, 1998; **46(8)**:3133-3138.
9. Vilchez JL, El-Khattabi R, Fernfindez J, Gonzfilez-Casado A. *J. Chromatogr., A*, 1996; **746**:289-294.
10. Aguera A, Almansa E, Malato S, Maldonado MI, Fernandez-Alba AR. *Analisis*, 1998; **26**:245-250.
11. Ramesh A, Thirugnanam PE, Balakrishna-murthy P. *Indian Journal of Biotechnology*, 2007; **6**:365-371.
12. Watanabe E, Eun H, Baba K, Arao T, Ishii Y, Endo S, Ueji M. *J. Agric. Food Chem.*, 2004; **52(10)**:2756-2762.
13. Kima H, Shelver LW, Li QX. *Analytica Chimica Acta*, 2004, **509**:111-118.
14. Kashid LM, Pawar NJ. *International Journal of Scientific and Research Publications*, 2015; **5(1)**: 1-6.
15. Kashid LM, Satpute SS, Jagtap DK. *Journal of Chemistry and Chemical Sciences*, 2018; **8(3)**:458-466.
16. Won-Bo Shim, Yakovleva ME, Yeol Kim K, Bo-Ram Nam, Vylegzhanina ES, Alexander AK et al. *J. Agric. Food Chem.*, 2009; **57(3)**:791-796.
17. Black CA. *Methods of soil analysis. Am. Soc. Agron, Inc., Medison*, 1965; Wisc: 1572.
18. Blakemore LC, Searle PL, Daly BK. *Methods for Chemical Analysis of Soils*. 1987; New Zealand Soil Bureau Scientific Report.
19. Navalon A, El-Khattabi R, Gonzalez-Casado A, Vilchez JL. *Microchim Acta.*, 1999; **130**:261-265.
20. Kotoucek M, Opravilova M. *Anal Chim Acta.*, 1996; **329**:73-81.
21. Cox L, Koskinen WC, Yen PY. *J. Agric. Food Chem.*, 1997; **45**:1468-1472.
22. Cox L, Koskinen WC, Yen PY. *J. Environ. Sci. Health B.*, 1998; **33**:123-134.
23. Cox L, Koskinen WC, Celis R, Yen PY, Hermosin MC, Cornejo J. *Soil Sci. Soc. Am. J*, 1998; **62**:911-915.
24. Mallawatantri AP, McConkey BG, Mulla DJ. *J. Environ. Qual.*, 1996; **25**:227-235.