Electrochemical Evaluation of the Environmental Stability of Thiamethoxam Insecticide in Soil Matrices

Lalasaheb.Kashid

Department of Chemistry, Vidya Pratishthan's, Arts, Science and Commerce College, Baramati, Pune-413133, Maharashtra, India

Abstract— The differential pulse polarography (DPP) method was developed and validated to investigate the electrochemical and thermodynamic properties of thiamethoxam in soil. This validated technique was successfully employed to assess the thermodynamic parameters of thiamethoxam adsorption behavior. The adsorption of thiamethoxam in four different soils followed the Freundlich isotherm, with 1/n values less than one, indicating favorable sorption conditions. Sorption strength was higher in soils with greater organic carbon content, with the order of sorption strength being S1 > S2 > S3 > S4. The Koc values indicated that thiamethoxam was more mobile in soils with lower organic matter content. In sandy soils (S3 and S4), the pesticide's leaching potential was enhanced due to the coarser texture and lower sorption capacity. Sorption coefficients Kd and Kf showed strong positive correlations with both organic carbon content and cation exchange capacity (CEC), reflecting the combined influence of organic matter and clay content on sorption behavior. These results highlight that the mobility and retention of neonicotinoids in soils are significantly influenced by soil properties, providing valuable insights for the development of effective environmental management strategies for pesticide use.

Index Terms- Differential Pulse Polarography, thiamethoxam, Insecticide, Soil, adsorption

I. INTRODUCTION

Neonicotinoids, a widely used class of insecticides, have gained attention due to their persistence and mobility environmental matrices in [1]. Thiamethoxam, a second-generation neonicotinoid, is frequently detected in various environmental compartments, including soils, water, and food products [2]. Its potential to leach into groundwater has been reported under conditions of heavy rainfall [3]. Sorption and desorption behavior in soil significantly influence its environmental fate and bioavailability [4]. Adsorption studies indicate that thiamethoxam exhibits variable affinity depending on

soil type and organic matter content [5]. The degradation pathways of neonicotinoids, including photolysis and microbial degradation, have also been identified as major transformation mechanisms [6]. Analytical techniques such as ELISA and HPLC have been employed to detect thiamethoxam residues in various samples including water [7], fruit juices [8], and honey [9]. ELISA methods have demonstrated detection limits as low as 16 pg/mL in some matrices [10], while HPLC remains the standard for residue quantification in environmental samples [11]. However, limited studies have explored the electrochemical behavior of thiamethoxam in soil systems [12]. The electrochemical approach provides a sensitive and environmentally relevant alternative for evaluating pesticide-soil interactions [13]. This study aims to investigate the sorptive behavior and environmental stability of thiamethoxam in diverse soil matrices using electroanalytical techniques [14]. Understanding these interactions is essential for predicting its transport, persistence, and potential ecological risks [15]. However, limited studies have explored the electrochemical behavior of thiamethoxam in soil systems. The electrochemical approach provides a sensitive and environmentally relevant alternative for evaluating pesticide-soil interactions. This study aims to investigate the sorptive behavior and environmental stability of thiamethoxam in diverse soil matrices using electroanalytical techniques. Understanding these interactions is essential for predicting its transport, persistence, and potential ecological risks.



Fig-1: Chemical structures of the Thiamethoxam insecticides belonging to the group of neonicotinoids

II.MATERIALS AND METHODS

A. Equipment Used

Polarographic measurements were carried out using a CL-362 polarographic analyzer (Elico Ltd., Hyderabad) connected to a PC via RS-232C and operated with Elico's Windows-based software. The setup included a dropping mercury working electrode, a saturated calomel reference electrode, and a platinum auxiliary electrode. pH was measured using an Elico pH meter. Absorbance was measured using a PerkinElmer Lambda 25 UV-VIS spectrophotometer.

B. Chemicals

All chemicals used were of analytical reagent grade, and solutions were prepared using doubly distilled water. The reference standard of thiamethoxam (99.9% purity) was used, and all working solutions were prepared in 0.04 M Britton-Robinson buffer.

C. Soil Sampling and Analysis

Four agricultural soil samples from Baramati tahsil, Pune district (rain shadow region of the Western Ghats) were collected from 0–20 cm depth after removing surface debris. The samples were homogenized, air-dried, ground, sieved (2 mm), and stored. Standard procedures were used to analyze key physico-chemical properties influencing pesticide sorption and mobility (Table-1).

Table -1: Selected physico-chemical properties of soil samples

| Soil Sample | Texture | % OM ¹ | CEC ² | Porosity ³ | BD ⁴ | pН |
|-----------------------|--------------------|-------------------|------------------|-----------------------|-----------------|------|
| S_1 | Clay | 2.3229 | 57.25 | 0.4088 | 1.4250 | 8.2 |
| S ₂ | Clay loam | 1.8210 | 65.24 | 0.3967 | 1.4032 | 8.01 |
| S_3 | Sandy loam | 0.8255 | 52.28 | 0.3285 | 1.3641 | 8.0 |
| S_4 | Sandy clay loam | 0.4034 | 48.24 | 0.4003 | 1.3485 | 7.7 |

% organic matter¹, cation exchange capacity² meq/100 g of soil, Porosity³=PD-BD/PD, PD=Particle density, BD^4 = bulk density

III. METHOD DEVELOPMENT

The sorption of thiamethoxam was studied using the batch equilibration method. Air-dried soil (2.0 g) was mixed with 20.0 mL of insecticide solution (0.01–0.18 mg/mL), prepared in 0.01 M CaCl₂ to maintain ionic

strength and aid soil particle flocculation, ensuring a 1:10 soil-to-solution ratio. The sealed flasks were shaken for 24 hours at 25 °C. After equilibration, the suspensions were centrifuged at 1500 rpm for 15 minutes, and the supernatants were extracted with methylene chloride. Extracts were dried and reconstituted in 0.04 M Britton-Robinson buffer (BRB) for electroanalytical analysis. The amount of thiamethoxam sorbed was determined by calculating the difference between initial and equilibrium concentrations. Equilibration time was validated through preliminary kinetic studies using triplicate samples. A validated Differential Pulse Polarography (DPP) method was employed for the quantification of thiamethoxam in soil samples.

IV. RESULT AND DISCUSSIONS

A. DPP Behavior of Thiamethoxam Insecticide

The electrochemical of reduction behavior thiamethoxam was investigated using Differential Pulse Polarography (DPP) at a Dropping Mercury Electrode (DME) in Britton-Robinson (BR) buffer over a pH range of 1.0 to 10.0. Among the tested pH values, the most defined and intense polarographic peak current (Ip was observed at pH 7.0 (Fig. 1), indicating optimal electrochemical activity under neutral conditions. At this pH, the peak current showed a linear relationship with thiamethoxam concentration, suggesting that the electrochemical reduction is diffusion-controlled and suitable for quantitative analysis. The reduction mechanism is attributed to the partial reduction of the nitro group (-NO₂) present on the thiamethoxam molecule, which is known to undergo a two-electron, two-proton process to form an amino group (-NH₂) under mildly acidic to neutral conditions [16,17].



Fig.-2: DPP Reduction Behavior of Thiamethoxam in BR Buffer at pH 7.0:

B. Quantitative determination of thiamethoxam

Quantitative of determination thiamethoxam insecticide was carried out using Differential Pulse Polarography (DPP) at an optimal peak potential of -0.974 V. A calibration curve was constructed using standard solutions of thiamethoxam in the concentration range of 1.0 to 16.0 μ g mL⁻¹ (3.4×10⁻⁷ to 5.4×10^{-6} M), showing excellent linearity with a regression equation of Ip = 187.7C + 0.428 and a correlation coefficient (R²) of 0.997. The method exhibited high sensitivity, with a limit of detection (LOD) of 0.035 μ g mL⁻¹ (1.19×10⁻⁷ M) and a limit of quantification (LOQ) of 0.116 μ g mL⁻¹ (3.97×10⁻⁷ M). Recovery studies demonstrated good accuracy and precision, with recoveries of $99.46 \pm 1.78\%$ (RSD: $99.64 \pm 0.89\%$ 1.79%), (RSD: 0.89%), and $99.39 \pm 0.58\%$ (RSD: 0.59%). These results confirm that the developed DPP method is reliable and suitable for the quantitative analysis of thiamethoxam in soil and environmental matrices.

C. Thermodynamic adsorption study of thiamethoxam by DPP

The equilibrium sorption isotherms of neonicotinoid insecticides, thiamethoxam, and were studied in four different soil types using the batch equilibration method, and the equilibrium concentrations were analyzed by Differential Pulse Polarography (DPP) as shown in fig. 3. The amount of pesticide sorbed was determined by calculating the difference between the initial concentration (Ci) and the equilibrium concentration (Ce) of the pesticide in solution, assuming that the loss in solution represented adsorption to the soil. The amount adsorbed (Cs, in mg/kg) was calculated using the formula

$$C_s = rac{(C_i - C_e) imes V}{M_s}$$

Where V is the solution volume and Ms is the soil mass.

The resulting adsorption data conformed well to the Freundlich isotherm model with correlation coefficients (R^2) exceeding 0.98, indicating a strong fit across all soils.

$$C_s = K_f C_e^{1/n}$$

The Freundlich constants (Kf) for thiamethoxam from 0.586 to 1.303, with 1/n values below 1, indicating

favorable and nonlinear sorption behavior. The order of insecticide sorption across soil types was found to be S1 > S2 > S3 > S4, corresponding to their organic matter content as in in fig. 4 to 7.



Fig-5: Freundlich adsorption isotherm of thiamethoxam insecticide on S₂ soil



Fig-7: Freundlich adsorption isotherm of thiamethoxam insecticide on S_4 soil

Sorption strength was evaluated using the organic carbon normalized sorption coefficient (Koc), calculated as

$$K_{oc} = \left(rac{K_d}{\% ext{OC}}
ight) imes 100$$

Thiamethoxam showed Koc values between 118.7 and 217.8, indicating moderate to high mobility in soils. Lower Koc values in KS1 and KS2 soils suggest higher mobility due to high water solubility and weaker sorption. Despite this, thiamethoxam may undergo irreversible sorption via binding to organic matter and entrapment in micropores. In S3 and S4 soils (sandy loam and sandy clay loam), Koc values were also below 500, confirming moderate mobility. Sorption behavior strongly correlates with soil organic carbon content; higher OC increases sorption strength. In sandy soils, pesticide dispersion increases with

coarser texture, enhancing leaching potential. Such mobility makes pesticides more prone to environmental transport, especially during heavy irrigation or rainfall. The strong influence of organic carbon highlights its role in insecticide retention.

In environmental engineering, understanding the spontaneity of pesticide sorption onto soils is critical for assessing environmental fate and transport. The thermodynamic parameter Gibbs free energy change

Table 2: Thermodynamic parameters ofthiamethoxam on different soils

| Soil Sample | Kf | 1/n | R ² | Kđ | Rf | Koc Lkg ⁻¹ | ∆G kJ mol ⁻¹ |
|-----------------------|-------|-------|----------------|------|-------|--------------------------|----------------------------|
| \mathbf{S}_1 | 1.303 | 0.849 | 0.990 | 1.60 | 6.582 | 118.7 | -11.83 |
| S ₂ | 1.161 | 0.894 | 0.998 | 1.32 | 5.667 | 125.3 | -11.97 |
| S ₃ | 0.941 | 0.871 | 0.997 | 1.04 | 5.323 | 217.8 | -13.34 |
| S_4 | 0.586 | 0.834 | 0.999 | 0.66 | 3.225 | 198.6 | -13.99 |

 (ΔG) is a key indicator of whether the sorption process occurs spontaneously. It is calculated using the equation:

$\Delta G = - RT \ln Koc$

Where ΔG is the free energy change (J); soil organic carbon sorption coefficient Koc, 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.

In this study, the ΔG values for the sorption of neonicotinoids such as imidacloprid, thiamethoxam, and acetamiprid onto soils ranged from -10.75 to -13.366 kJ mol⁻¹, as shown in Table 5.5. These negative values confirm that the sorption process is thermodynamically favorable and spontaneous, with a strong affinity between the pesticide molecules and soil organic matter. Additionally, the movement of pesticides through soil can be evaluated using the **retardation factor (Rf)**, which estimates how much slower a pesticide travels compared to the groundwater flow. It is calculated by the equation:

$$Rf = 1 + rac{Kd \cdot
ho_b}{\eta}$$

Where *Kd* is the linear sorption coefficient (mL/g), ρb is the bulk density of soil (g/cm³), and η is the porosity of the soil. Typically, ρb and η do not vary significantly across soils, so *Rf* is primarily influenced by *Kd*. The calculated *Rf* values for imidacloprid,

thiamethoxam, and acetamiprid showed a decreasing trend across soil samples S1 to S4, which correlated well with decreasing organic carbon content. Soils with higher organic carbon (e.g., S1 and S2) exhibited higher Rf values, indicating greater pesticide retention and reduced mobility as shown in table 2. This highlights the critical role of soil organic matter in governing both the sorption intensity and transport potential of neonicotinoids in different agricultural soils.

D. Statistical correlation of soil characteristics with sorption and mobility indicators of thiamethoxam.

The correlation of soil properties with pesticide environmental parameters namely Kd, Koc, Rf, and $\Delta \mathbf{G}$ is essential for understanding the fate and mobility of neonicotinoid insecticides in the environment. Analysis of four different soil samples for thiamethoxam, revealed that % organic carbon (%OC) showed the strongest positive correlation with sorption coefficients, indicating higher pesticide retention in organic-rich soils. Similarly, cation exchange capacity (CEC) also significantly influenced Kd and Kf values, highlighting its role in insecticide soil interactions, likely due to its association with both clay and organic matter. Soil pH was another influential factor, showing high positive correlation, especially with thiamethoxam, suggesting pHdependent sorption behavior. In contrast, % sand negatively correlated with sorption parameters, pointing to increased pesticide mobility in sandy soils. These findings align with previous studies [18-[19] and emphasize the importance of CEC and %OC in determining pesticide behavior in different soil types

Table 3: Correlation coefficient of soil parameter andInsecticideenvironmentalparametersofthiamethoxam insecticide.

| Parameters | K _f | K _d | K _{oc} | R _f | ΔG |
|------------|----------------|----------------|-----------------|----------------|---------|
| %OC | 0.8930 | 0.9417 | -0.7848 | 0.8755 | 0.8542 |
| %Clay | 0.7006 | 0.7837 | -0.6820 | 0.6851 | 0.6670 |
| % Silt | 0.1117 | 0.2361 | -0.3537 | 0.0764 | 0.1376 |
| % Sand | -0.6425 | -0.7330 | 0.6570 | -0.6240 | -0.6157 |
| CEC | 0.8439 | 0.8000 | -0.8315 | 0.7527 | -0.6157 |
| pH | 0.9431 | 0.9754 | -0.9800 | 0.8939 | 0.9469 |

V.CONCLUSION

The adsorption of thiamethoxam on four different soils followed the Freundlich isotherm, with 1/n values less than one, indicating favorable sorption behavior. Sorption strength was greater in soils with higher organic carbon content, following the order S1 > S2 >S3 > S4. The Koc values indicated that thiamethoxam was more mobile in soils with lower organic matter. In sandy soils (S3 and S4), the leaching potential of the pesticide was higher due to coarser texture and reduced sorption capacity. The sorption coefficients Kd and Kf exhibited strong positive correlations with organic carbon content and cation exchange capacity (CEC), the latter reflecting the combined influence of organic matter and clay content. These findings highlight that the mobility and retention of neonicotinoids in soils are strongly influenced by soil properties and can support the development of effective environmental management strategies for pesticide application

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