DIFFERENTIAL PULSE ADSORPTIVE STRIPPING VOLTAMMETRIC DETERMINATION OF DIMETHOATE PESTICIDE IN AGRICULTURAL RUN-OFF AND GROUND WATER SAMPLES

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Abstract: A selective and sensitive differential pulse adsorptive stripping voltammetric method was developed for the determination of dimethoate using Hanging mercury drop electrode (HMDE) in BR buffer pH range of 2.0 to 6.0. The peak observed for the dimethoate are attributed to the reduction of carbonyl group (>C=O) and showed to be pH 4.0. The optical parameters such as effect of pH, accumulation potential, accumulation time and scan rate were studied. The relationship between peak current and dimethoate concentration was linear within the concentration range of 0.012 to 20.0 μg mL^{-1}. The standard deviation and relative standard deviation were found to be ±0.05 and 1.22% respectively. The method is simple, sensitive and free of interferences and diverse ions. The method has been satisfactorily applied to the determination of dimethoate in agriculture run-off and ground water samples.

Keywords: Dimethoate, pesticide, water samples and HMDE.

Introduction: Pesticides are substances used for preventing, destroying, repelling or mitigating any pest. The agriculture sector dominates the economic scenario in India. The use of pesticides benefits in increasing agricultural production but the repeated and indiscriminated usage of certain pesticides have led to their accumulation in plants, animals, soils and sediments, thus effecting widespread contamination of the environment [1-2]. Afterward, the pesticide molecules may undergo different pathways in the environment, depending on the types of interaction with the soil components.[3] In soils rich in organic matter or/and clay, pesticide molecules may become immobilised by strong absorption [4] that facilitates their degradation by sunlight, microorganisms or chemical reactions. In these cases, the degradation products may be toxic or not. In mineral soils, where the interaction is commonly very weak, they may be leached by rain or irrigation waters reaching rivers, dams or under-ground waters. Under such circumstances, the risk of contamination of potable sources is quite serious.

Dimethoate[O,O-dimethyl-S-(N-methyl carbomoylmethyl)-phosphorodithioa -te] is a systematic organo phosphorous insecticide (Fig. 1), widely applied on crops, trees and ornamental plants to control house flies around livestock pens, processing plants and human dwellings, grasshoppers on livestock forage and in extensive application the pesticide finds its way into the surface water bodies through agricultural runoff and into human being through food grains. Due to the continuous increase in the application of such pesticide, the necessity of water analysis is always growing.The traditional techniques such as spectrophotometry [5], HPLC [6-7], GC [8], mass spectrometry [9] electrochemical techniques [10-12] which is one of the most adequate due to the very low value obtainable for the detection limit. However, the above techniques very expensive and demanding well-equipped laboratory installations and a well-trained analysis team. On the other hand, electroanalytical procedures can overcome many of such difficulties by analyzing environmental samples without extractions and purification steps, thus shortening and undervaluing the pesticide analysis.

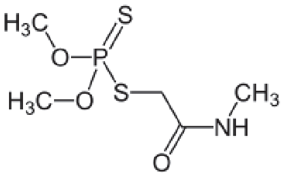


Fig.1. Chemical structure of dimethoate

The aim of this work is to study the electrochemical behaviours of the dimethoate by differential pulse absorptive stripping voltammetry onto HMDE and to establish the initial steps in the development of an electroanalytical procedure to analyses dimethoate in agricultural run-off and ground water samples.

Experimental:

Instrumentation and reagents: The electrochemical measurements were carried out with Metrohm 757 VA Computrace. Three electrode system consisting of HMDE as working electrode, Ag/AgCl (salt KCl) was used as a reference electrode and a platinum wire as an auxiliary electrode which displays negative potential range. Elico Li-129 model glass-calomel combined electrode was employed for measuring pH values. All reagents used were of analytical reagent grade. Briton-Robinson (BR) buffer was purchased from Sigma Aldrich. The analytical technical grade pesticide standard of dimethoate was of 99.4% purity supplied from Riedel-de Haen. A stock solution of Dimethoate (1000 μg mL^{-1}) was prepared in acetone. Working solutions of dimethoate were prepared daily by diluting the stock solution within the concentration range of 0.012 to 20 μg mL^{-1}.

Results and discussion:

Cyclic voltammetric study of dimethoate: An aliquot of standard solution of dimethoate of concentration 10.0 μg mL^{-1} was taken in the cell at pH 4.0. The potential of working electrode was cycled between −0.8 to −1.0 vs. Ag/AgCl at a scan rate of 100 mV/s. A single well defined peak was obtained at -0.925 for dimethoate due to the $2e^-$ reduction of the carbonyl group. In the reverse scan, no anodic peak was observed. Hence the reaction is irreversible. The cyclic voltammograms of the dimethoate of concentration 10.0 μg mL^{-1} were registered under similar conditions. Fig.2.shows the cyclic voltammetric behaviour of dimethoate.

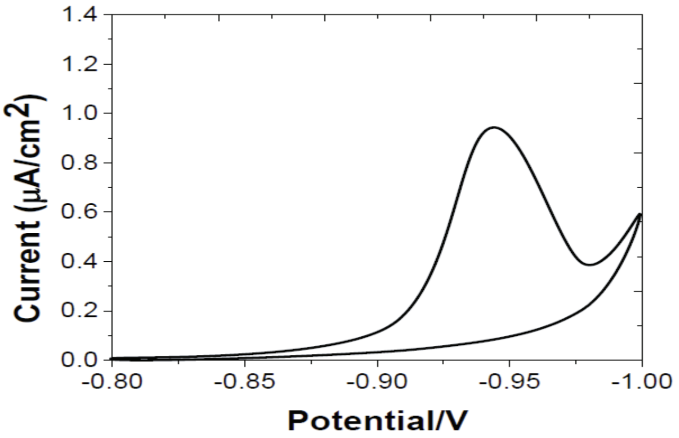


Fig. 2. Cyclicvoltammogram of dimethoate of concentration 10.0 μg mL^{-1} using HMDE in BR buffer of pH 4.0.

Voltammetric determination of dimethoate at HMDE

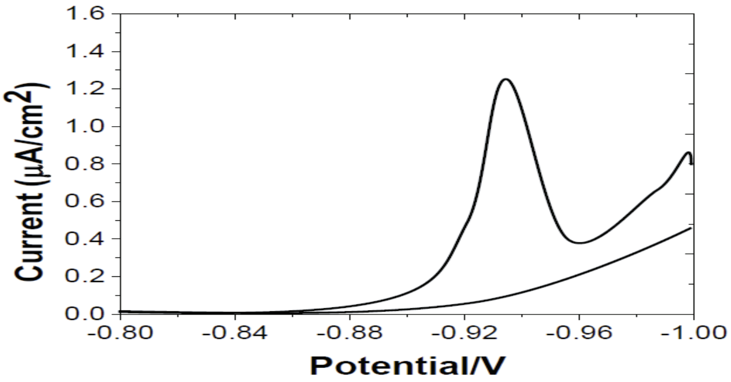


Fig. 3. Differential pulse adsorptive stripping voltammograms of dimethoate of concentration 10.0 μg mL^{-1} atHMDE in B-R buffer of pH 4.0.

A stock solution of dimethoate of concentration 0.1 M was prepared by dissolving an appropriate amount of dimethoate in methanol. A working standard of concentration 10.0 μg mL^{-1} was prepared from the stock solution 1.0 mL of standard solution and 9.0 mL of BR buffer of pH 4.0 was placed in the electrolytic cell and purged with nitrogen gas for 15 minutes. The electrode potential was scanned from -0.8 to -1.0 V vs. Ag/AgCl. Dimethoate exhibited maximum peak current at −0.925 V in B-R buffer of pH 4.0. The differential pulse adsorptive stripping voltammogram of the blank was also recorded under similar conditions (Fig. 3).

An increase in pH shifts the peak potential to negative value indicating the involvement of protons in the reduction reaction. Over the pH range 2.0- 6.0, the maximum peak signal was obtained at 4.0. The optimum accumulation time and accumulation potentials were obtained as 60 sec. and -0.6V vs. Ag/AgCl respectively. The influence of scan rate on the peak signal was studied over the range 20 -200 mV/s. The i_p vs. $v^{1/2}$ plot gives a straight line with equation $I_p(\mu A) = 0.0956\ v^{1/2}$ (mV/s) - 0.1853 with $R^2 = 0.997$. Hence the reduction reaction is diffusion-controlled.

Effect of Ph: The influence of pH on the peak current was studied for 10.0 μg mL^{-1} of dimethoate between pH 2.0 to 6.0. The peak current increases with pH initially and reaches a maximum value at pH 4.0 and then decreases as shown in (Fig.4). The increase in pH shifted the peak potentials to more negative values suggesting proton participation in the reduction process.

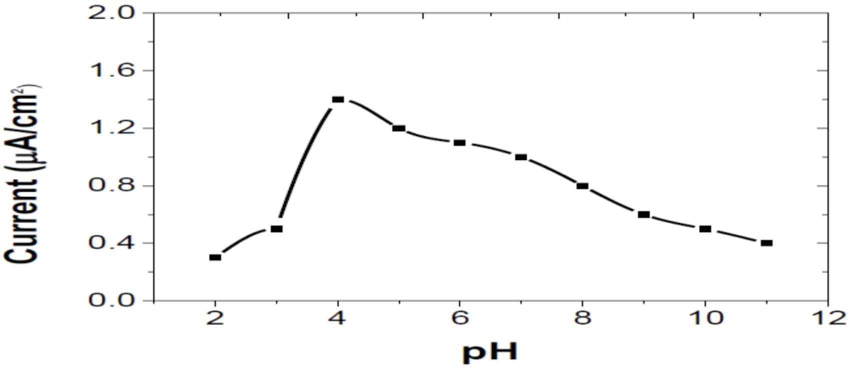


Fig. 4. Effect of pH on the peak current of dimethoate of concentration 10.0 μg mL^{-1}at HMDE in B-R buffer

Effect of accumulation potential and accumulation time

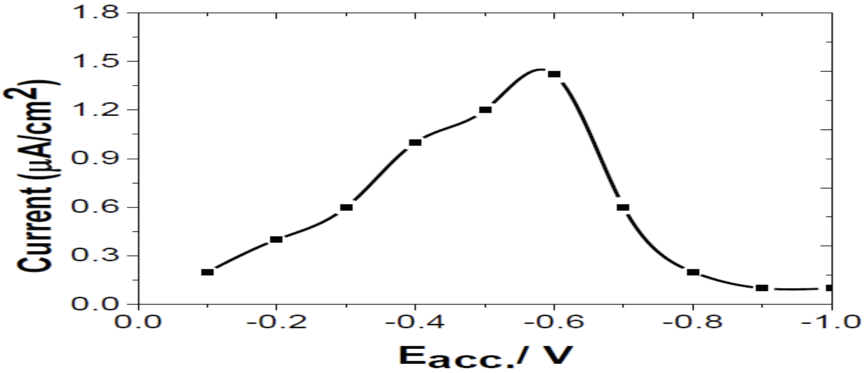


Fig. 5. Effect of accumulation potential on peak current of 10.0 μg mL^{-1} dimethoate at HMDE at pH 4.0.

The effect of accumulation potential on the peak signal was investigated at working electrode for 10.0 μg mL^{-1} of dimethoate. It was found that ip value reaches maximum value at -0.6 V vs. Ag/AgCl and the maximum peak current at 0.6 μA (Fig. 5) was due to the increased rate of accumulation, owing to the favorable orientation of molecules by the applied electric field at the electrode-solution interface. The variation of peak current with accumulation time was studied for a concentration of 10.0 μg mL^{-1} dimethoate solution. As the pre-concentration time increased, the peak current also increases slowly and reaches a maximum value at 60 sec. (Fig. 6).With further increase in accumulation time, no effect on the peak signal was observed indicating that the electrode surface was saturated with the analyte molecules.

Determination of dimethoate in water samples: The determination of dimethoate in water samples from agriculture run-off and ground water samples from YSR district, India. Before analysis, the water samples were centrifuged at 4000 rpm to remove the solid impurity and the pH was adjusted to 4.0 with the addition of BR buffer. The obtained water samples without addition of dimethoate did not shows the signals of analytes, and consequently, the determination of the dimethoate concentration was performed using the standard addition method. The results of different concentrations detected by differential pulse adsorptive stripping voltammetric method was listed in Table 1. It is found that the results obtained by differential pulse adsorptive stripping voltammetric method was in good agreement with the actual addition with the recovery from 98.00% to 99.40%, indicating potential for practical dimethoate detection. These results indicate that the proposed method is reliable and it has potential for practical application.

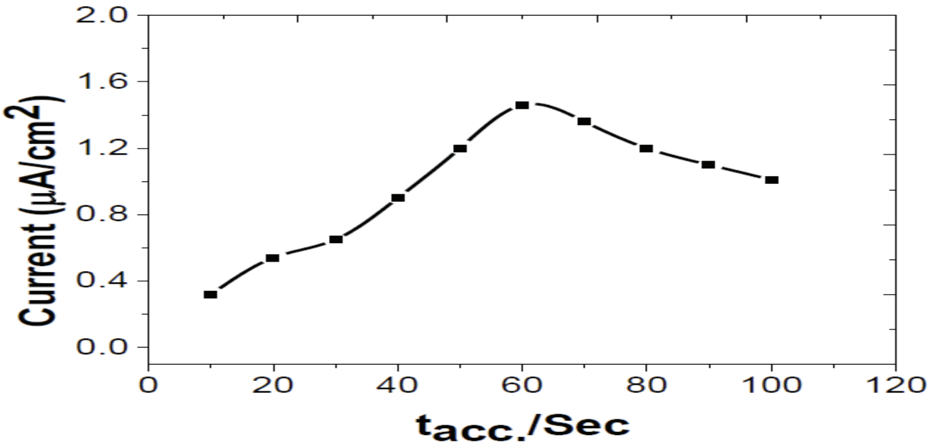
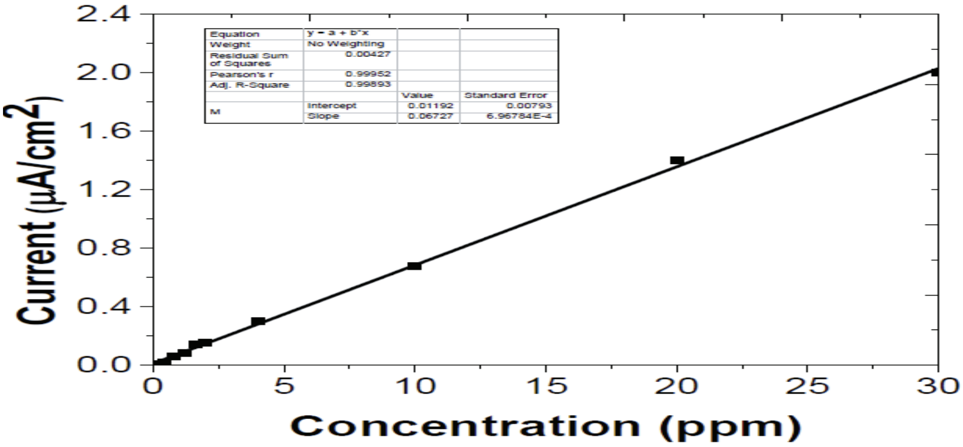


Fig.6. Effect of accumulation time on peak current of dimethoate of concentration 10.0 μg mL^{-1} at HMDE at pH 4.0.

Calibration plot: A calibration plot was obtained between peak signal and the concentration of dimethoate over the range 0.012 to 20.0 μg mL^{-1}. The peak current increases linearly with the concentration of dimethoate. The linear regression equation was given by Ip(μA) = 0.011C (ng/mL) + 0.06 with $R^2 = 0.999$ (Fig.7.). The limits of detection and limits of quantitation were calculated as 0.84 μg mL^{-1} and 0.65 μg mL^{-1} respectively.

The developed procedure was applied in agricultural run-off and ground water samples for the determination of dimethoate of concentration 10.0 μg mL^{-1} in spiked water samples. Five replicate determinations were carried out in each case using the voltammetric method. The mean recoveries (%R) from 98.00% to 99.40% and relative standard deviation (% RSD) 0.07 respectively.



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	0.00427		
Pearson's r	0.99952		
Adj. R-Square	0.99893		
		Value	Standard Error
M	Intercept	0.01192	0.00793
	Slope	0.06727	6.96784E-4

Fig. 7. Calibration plot of dimethoate

Table 1. Determination of dimethoate in water samples by differential pulse adsorptive stripping voltammetry

Samples	**Added** (μg mL^{-1})	**Found** (μg mL^{-1})^{a,b}	**Recovery** (%)	**S.D**
Agriculture runoff	5.0	4.90	98.00	0.12
	10.0	9.82	98.20	0.06
Ground water	5.0	4.96	99.20	0.08
	10.0	9.94	99.40	0.02

^{a,}Collected from YSR (Dist), ^{b}(n=5)

Conclusion: This study confirmed the applicability for the direct differential pulse adsorptive stripping voltammetric determination of the insecticide dimethoate. Differential pulse adsorptive stripping voltammetric in BR buffer solution of pH 4.0 was found to be suitable for the determination of dimethoate with a linear response in the concentration range of 0.12 to 20.0 μg mL^{-1}. The developed procedure was successfully applied for the determination of dimethoate in agricultural run-off and ground water samples. The recovery result shows that differential pulse adsorptive stripping voltammetric is a simple, reliable and inexpensive method for the determination of dimethoate in water samples.

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