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Electrochemical Behavior and Analysis of Cyphenothrin in Formulations and Grain Samples

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ABSTRACT
A sensitive method for the determination of pyrethorid cyphenothrin by differential pulse adsorptive stripping voltammetry at a hanging mercury drop electrode (HMDE)(pH6.0) was described. The cyclic voltagramms demonstrate the adsorption of these compounds at the mercury electrode. A symmetric study of the various operational parameters that affect the stripping response was carried out by the differential pulse voltammetry. With an accumulation potential of -0.6V and 60 s an accumulation time, the limit of detection was $2.45x10^{-8}$ mol/L to $1.5x10^{-8}$ mol/L, the relative standard deviation (n=10) correlation coefficient values 0.995, 1.1% respectively. Finally the proposed method was applied for determination of the cyphenothrin in storage bags of wheat and rice under FCI's storage system.

Key Words: *cyphenothrin, voltammetry, mercury electrode, grain samples*

1. INTRODUCTION

Cyphenothrin [(RS) α-cyano-3-phenoxy-benzyl (1 RS, 3RS) 2,2-dimethyl-3-(2-methylprop-1-eneyl)cyclopropane carboxylate)]is member of pyrethroid family of chemicals. Cyphenothrin is one of the most stable pyrethroid insecticides and also the most persistent in the field. Cyphenothrin is abroad-spectrum insecticide used for the control of insect disease vectors and widely used in agriculture to control insect pests.

Cyphenothrin was used mainly on vegetables fruits, cereals and grains. Several papers have been described the development of analytical procedure for determination of pyrethroids in different matrices. Alfen sodimuceio [1,2] developed a procedure for detecting pyrethroid residue in vegetables and milk by gas chromatography electron-capture detection. Effect of pyrethroids on pentobarbital-induced sleeping time in relation to the chemical structure was studied in mice by Ryozo et al.[3]. Margao Oortgiesen et al.[4] studied effect of pyrethroids on neurotransmitter-operated ion channels in cultured mouse neuroblastoma cell. Nishimura et al.[5] studied the effect of a range of pyrethroids on-end plate potentials and muscle action potentials in the pectoralis nerve-muscle of the clawed frog. A new rapid and selective electron ionization gas chromatography-mass spectrometry method in selective ion mode (SIM) was developed for the determination of 13 pyrethroid insecticide molecules in whole blood [6]. Ramesh et al.[7] determined residue of different synthetic pyrethroid insecticides in whole blood and serum by using negative ion chemical ionization-gas chromatography, mass spectrometry.

Several chromatographic methods have been reported for the determination of cyphenothrin in agricultural soil, milk, indoor air, water, environmental matrices, and biological samples [8-13]. Electrochemical reduction of pyrethroid insecticides based on esters of α-cyano-3-phenoxybenzylalchol at glassy carbon and mercury electrodes in acetronitrile has been studied by Darren et al.[14]. Electrochemical investigations of pyrethroid insecticides in nonaqueous solvents and environmental samples were reported by Coomber et al. and Oudou et al. [15,16]. Analysis of pyrethroid compounds is mainly performed by chromatographic methods. Since such analytical processes require many steps, they are not only labor-intensive but also time-consuming. Therefore, development of a sensitive, convenient, and economical method is required for the analysis of pyrethroid residues in a large number of food samples. The aim of the present work is to develop a sensitive electro analytical procedure applied for the determination of cyphenothrin in agricultural formulations, vegetables, and in storage bags of wheat and rice under Food Corporation of India's storage system.

2. EXPERIMENTAL

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Voltammetric measurements were carried out using Metrohm E-506 (Herisau, Switzerland) Polarecord in combination with Metrohm 663 VA stand with 612 VA scanners. A three-electrode system , and a platinum wire as the auxiliary electrode were used. pH measurements were carried out using digital pH meter (Hanna Instruments, Italy).

Reagents: Cyphenothrin (purity 98%) was supplied by "Reidel de Haen, Seelze", Germany. These samples are used directly without any further purification. The purity of the sample was tested by determining their melting points and thin layer chromatographic experiments.

2.1. Preparation of Standard Solution of Cyphenothrin

Stock solution (1.0×10^{-3} mol l^{-1}) was prepared by dissolving cyphenothrin in methanol (Sigma-Aldrich, supplied by SD Fine Chemicals, India). All dilute solutions were freshly prepared daily from the stock solution.

Buffer Solutions

Universal buffers of pH range from 2.0 to 12.0 were prepared using 0.2 mol. l^{-1} boric acid, 0.05 mol l^{-1} citric acid (Sigma-Aldrich, supplied by SD Fine Chemicals) and 0.1mol.l^{-1} trisodium orthophosphate (Sigma-Aldrich) used as a supporting electrolyte. All the chemicals used were of analytical grade.

3. RESULTS AND DISCUSSION

3.1. Cyclic voltammetric characteristics

The effect of pH on the voltammograms is investigated by recording the current voltage curves for non-aqueous solutions of cyphenothrin at a concentration of 0.7 mM in universal buffer system over the pH range of 2.0 to 12.0. Irrespective of the pH of the buffer system used, cyphenothrin exhibits a single, well-defined two-electron peak in all the techniques which is attributed to the reduction of >C=C< group to the corresponding saturated product (Figure1). The peak current (ip) is dependent on scan rate (v) and pH of the supporting electrolyte. The peak potentials are found to be varied towards the more negative side with increase in pH. The determination of number of electrons (n) involved during the electrode process, in cyphenothrin, has been carried out by millicoulometry. According to this technique, 'n' is found to be two for cyphenothrin in acidic as well as neutral and basic media. In the present investigation, controlled potential electrolysis is employed to get the reduction product. Controlled potential electrolysis has been carried out in a modified cell with a three-electrode system.

consisting of hanging mercury drop electrode(HMDE) as working electrode, a saturated calomel electrode as the reference.

Electrolysis of the electro active substance has been carried out at −0.82 V vs SCE, and the product formed after the controlled potential electrolysis is identified and confirmed as the saturated product of the corresponding electro active species by IR spectral data (absence of C=C stretch at 1640–1680 cm^{-1}, C–H stretch 2960 cm^{-1}, C–H bend 1465 cm^{-1}).

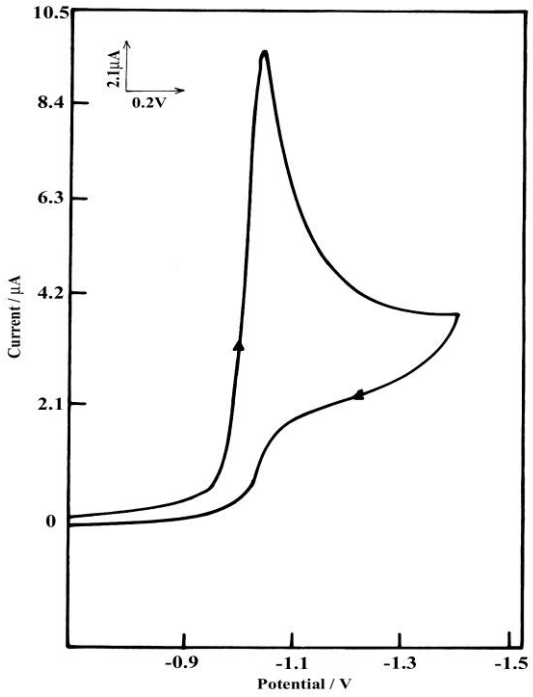

Figure 1. Typical cyclic voltammogram of cyphenothrin at HMDE with accumulation time of 60 s; accumulation potential, −0.8 V; rest time, 10 s; stirring rate, 2,000 rpm; scan rate, 40 mV s^{-1}; pulse amplitude, 25 mV; concentration, 1×10^{-5} mol l^{-1}; pH 6.0.

3.2. Electrode mechanism

With the above mentioned conclusions, the electrochemical reduction mechanism of cyphenothrin can be proposed as follows:

3.3. Differential pulse-adsorptive stripping voltammetric studies

By using differential pulse adsorptive stripping voltammetry (DP-AdSV), cyphenothrin yields a single well-defined peak at HMDE Fig. 3. This peak was followed by establishing the optimum experimental conditions to carry out DP-AdSV. From the present experimental results, we proposed

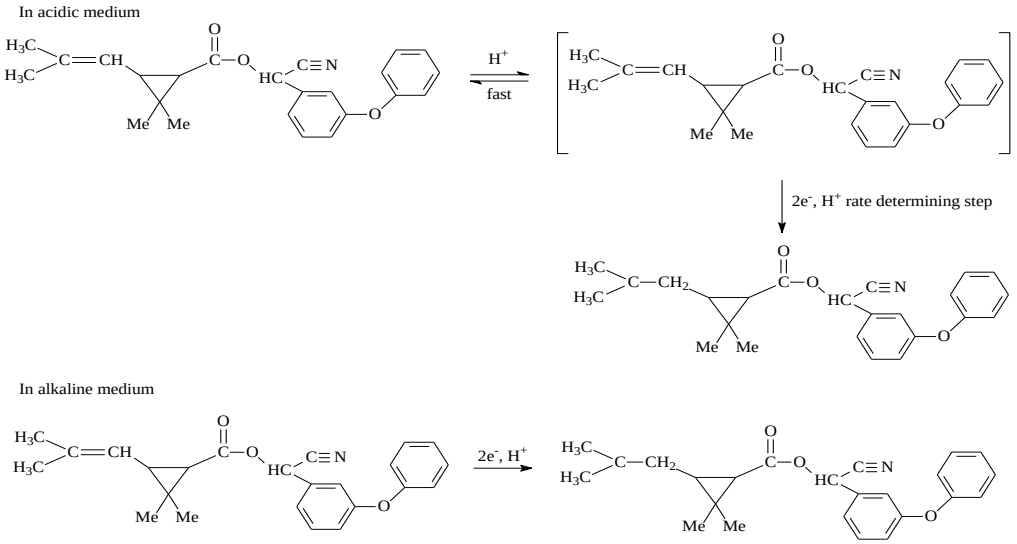

Figure. 2 Reduction mechanisms of cyphenothrin in acidic/alkaline mediums

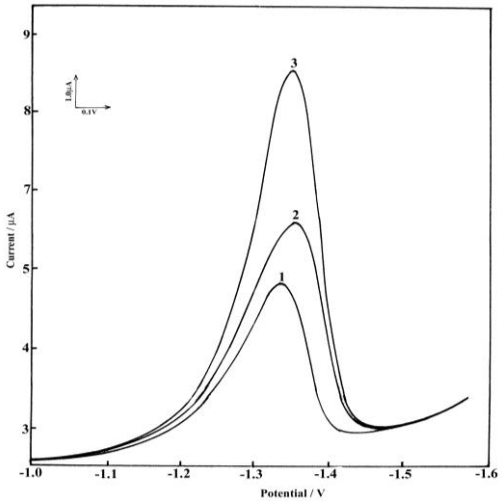

Figure 3. Typical differential pulse adsorptive stripping voltammograms of cyphenothrin at HMDE (6.0): (a) accumulation time: 60 sec., at HMDE, accumulation potential:-0.8V; rest time: 10 sec., stripping rate: 2000 rpm, (3) concentration : 1 x 10^{-5} M

reduction mechanisms of cyphenothrin in acidic and alkaline mediums (figure. 2).

3.4. Effect of pH

The influence of pH on the adsorptive stripping voltammetric response for 1x10^{-7} mol l^{-1} cyphenothrin was examined in universal buffer of pH 2.0 to 12.0 after pre-concentration of the cyphenothrin onto the HMDE for 60 sec. A single irreversible peak was generated in solutions of pH 6.0. It can be observed from Fig.VI.13 when that the pH was increased above 6.0, it shifts to more negative potentials.

3.5.Effect of accumulation potential and time

The effect of accumulation potential on the DP-AdSV current of the peak of cyphenothrin has been investigated after pre-concentration of the pesticides onto the HMDE for 60 sec. over the potential range 0.0 to -1.4V. A much more peak developed peak current was achieved at potential range -0.8V (figure.5). Therefore, a pre-concentration potential of -0.8V was chosen over the rest of the study.

The effect of accumulation time period on the DP-AdSV current of the peak for 1.0 x 10^{-5} mol l^{-1} cyphenothrin in universal buffer pH 6.0 was also investigated. As shown in Fig. 6. accumulation time period of 45-95 sec. at -0.8 V generated a much more peak current.

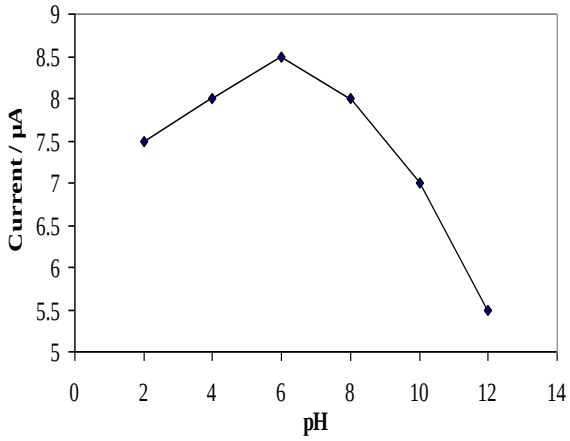

Figure. 4. Effect of pH on cyphenothrin solution at HMDE; accumulation time: 60 sec.; accumulation potential: -0.8V; rest time: 10 sec., stirring rate: 2000 rpm; scan rate: 40 mVs^{-1}; pulse amplitude: 25 mV.

3.6. Effect of scan rate

The scan rate has varied from 20 to 60 mVs^{-1}. The peak current has increased with an increase in the scan rate to 40 mVs^{-1}, after that the peak current

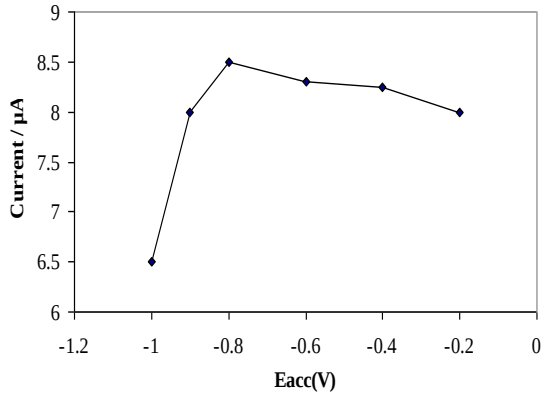

Figure 5. Effect of accumulation potential on cyphenothrin solution at HMDE; accumulation time: 60 sec.; accumulation potential: -0.8V; rest time: 10 sec., stirring rate: 2000 rpm; scan rate: 40 mVs^{-1}; pulse amplitude: 25 mV

has decreased. Therefore 40 mVs^{-1} could be selected for further studies.

The influence of several instrumental parameters known to affect the differential pulse adsorptive stripping current response at the HMDE such as mercury drop size, stripping rate, pulse amplitude, rest period and purge time were optimized. For this study, each variable was changed while the others were kept constant. The working conditions decided upon were medium drop size, 2000 rpm, 25 mV, 10 sec. and 10 min. respectively. The stripping current was not modified when varying the rest period, since it was found that 10 sec. was sufficient to allow for the formation of uniform concentration of the analyte in the mercury drop.
Other experimental parameters such as temperature were optimized. The stripping peak currents were not modified when the temperature varied between 20 and 50°C. The value chosen was 25°C, because it was room temperature.

The optimal values of these parameters were chosen from the study of variation of the peak current (i_p) of 0.5 mM cyphenothrin with universal buffer of pH 6.0. The peak current of cyphenothrin was found to increase linearly, an increase with scan increment.

3.7. Quantitative determination of cyphenothrin in various samples

The DP-AdSV peak obtained for the reduction >C = C< group in cyphenothrin at pH 6.0 is well resolved and is highly reproducible, and it is, therefore, chosen for the analysis of cyphenothrin in agricultural formulations, vegetables and food grain samples.

3.8. Recommended analytical procedure

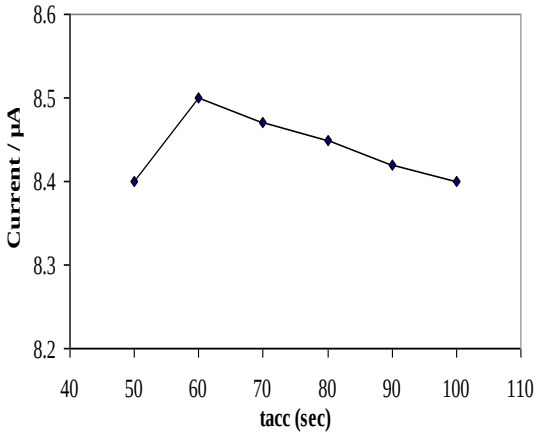

Fig ure 6. Effect of accumulation time on the DP-AdSV response at HMDE; accumulation potential: -0.8V; rest time: 10 sec., stirring rate: 2000 rpm; scan rate: 40mVs^{1}; pulse amplitude: 25 mV

A stock solution is prepared by dissolution of the appropriate amount of the electro active species in methanol. One ml of standard solution is transferred into a voltammetric cell and diluted with 9 ml supporting electrolyte and deoxygenated with N_2 gas for 10 min. After the voltammogram is recorded, small increments (0.2 ml) of standard solution are added and then voltammograms are recorded after each addition under similar conditions. In the present study, the best precision is obtained at pH 6.0 with a drop time of 2 sec., pulse amplitude of 50 mV and an applied potential of -0.8 V. Under these conditions the current is linear function with the concentration of electro active species in the range of 2 x 10^{-9}M to 2 x 10^{-5}M. The lower detection limit 1.9 x 10^{-10}M was obtained with correlation coefficient and relative standard deviation of 0.995, 1.1% respectively.

3.9. Quantitative determination of cyhenothrin in formulations and vegetables

The developed procedure has been applied for the estimation of these pesticide formulations. The required quantity of formulation (Pestanel, Gokilaht) corresponding to 1.0 x 10^{-3}M stock solution is accurately measured and transferred into a 50 ml volumetric flask containing 50 ml of methanol. A solution of approximately 1x10^{-7}mol l^{-1} is prepared by diluting this stock solution with the universal buffer. Assay results for cyphenothrin in formulations at pH 6.0 are given in Table 1.

Table 1. Determination of cyphenothrin in formulation.

Compound	Labelled amount (mg)	Amount found (mg)	Recovery (%)	Standard deviation
Gokilant®	4.0	3.95	98.75	0.009
	8.0	7.95	99.38	0.014
	10.0	9.91	99.10	0.015
Pestanal®	4.0	3.94	98.50	0.021
	8.0	7.93	97.88	0.010
	10.0	9.96	99.60	0.009

Table 2. Recoveries of cyphenothrin added to cabbage and tomato.

Name of the formulation	Labeled amount (mg)	Amount found		Recovery (%)		Standard deviation	
		Cabbage	Tomato	Cabbage	Tomato	Cabbage	Tomato
Gokilaht	2.0	1.96	1.94	98.00	97.00	0.014	0.009
	6.0	5.94	5.97	99.00	99.50	0.021	0.014
	10.0	9.81	9.84	98.10	98.40	0.016	0.030
Pestanal	15.0	14.89	14.83	99.26	98.86	0.025	0.027
	20.0	19.87	19.82	99.35	99.10	0.017	0.010

Table 3. Persistence of residues of Cyphenothrin on wheat and rice penetrated during spraying on jute bags.

Sample	Period after Treatment	1.0 g				1.5 g			
		R_1	R_2	R_3	Mean	R_1	R_2	R_3	Mean
Wheat	1h	1.66	0.92	0.40	0.99	1.91	0.98	1.44	1.44
	15 days	0.44	0.59	0.54	0.52	0.98	0.76	0.50	0.75
Rice	1h	1.58	0.84	0.51	0.97	1.76	0.83	1.33	1.30
	15 days	0.55	0.44	0.31	0.43	0.96	0.78	0.50	0.74

Further the method is selective for the determination of cyphenothrin in vegetables such as cabbage and tomato which have been chosen for the analysis of cyphenothrin. Known amounts of cyphenothrin (Pestanel, Gokilant) are sprayed on cabbage and tomato crops and left for 1-2 hrs. The extracts are prepared by the treatment of crushed samples with 100 ml of acetone. Then the extracts are allowed to dry. The residue of cyphenothrin is dissolved in methanol and transferred into a 50 ml volumetric flask. Then the voltammograms are recorded in the same manner as described earlier. The results obtained using the AdSV method shown in Table 2. Recovery of cyphenothrin ranging from 97.00% to 99.50% is found, which indicates the high accuracy and reproducibility of the proposed adsorptive stripping voltammetric method.

3.10.Quantitative determination of cyphenothrin in real samples

The utility of the described method has also been tested for analysis of cyphenothrin in wheat and rice under FCI's storage system. Wheat and rice stocks of usual dimension and capacity are selected in Food Corporation of India godowns at Hyderabad. Small jute bags of 4 kg capacity are chosen for these studies. The jute bags are filled with wheat and rice and properly stitched. The dosages used are 1.0 and 1.5 gm^{-2} of active ingredient (a.i.) of cyphenothrin. Required quantity of cyphenothrin is dissolved in 50 ml of methanol and sprayed on the jute bags with the help of small hand sprayer.

The samples of wheat and rice are ground to a powder in an electrically operated grinder. The samples are extracted with acetone and the extract is filtered through a Buchner funnel. Then the extract is allowed to dry. The residue of cyphenothrin is dissolved in methanol and transferred to a 50 ml volumetric flask. The residue of cyphenothrin in wheat and rice in jute bags is estimated by DP-AdSV and the results are presented in Table.3.

It is clear from the data that the residue of cyphenothrin on wheat was 0.98 and 1.39 ppm and on the rice 0.99 and 1.47 ppm just after spraying of cyphenothrin 1.0 and 1.5 gm^{-2} a.i., respectively. The residue of cyphenothrin on wheat in samples collected 15 days after the spraying were 0.44 and

0.80 ppm. Similarly on the rice they were 0.54 and 0.77 ppm. These results suggest that even after 15 days of application of cyphenothrin fell within the detection limit. Hence in the light of above data, the use of cyphenothrin at dosages of 1.0 and 1.5 gm^{-2} a.i. treatment for the control of storage pests is without any health hazard whatsoever to the consumers.

The proposed method is free from interference due to ingredients present in cyphenothrin and also other constituents present in vegetable and storage bags of wheat and rice. The proposed method is simple, inexpensive, rapid, reliable, and sensitive and which does not involve any elaborate clean-up procedures compared to other methods.

4. CONCLUSION

This study showed the efficacy of a hanging mercury drop electrode for the analysis of cyphenothrin in vegetable, wheat, and rice samples by cyclic voltammetry and DP-AdSV voltammetry with sensitivities in the order of 10^{-9} M, respectively. Cyphenothrin could be determined with negligible interferences. With the help of cyclic voltammetry, we proposed reduction mechanisms in both acidic and alkaline mediums. Cyclic voltammetric experiments have shown that the electrode system is diffusion-controlled. The proposed procedure is convenient to apply for the determination of cyphenothrin in food samples and also pyrethroid class compounds.

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***Biographical Sketch**

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