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ELECTROCHEMICAL BEHAVIOUR AND ANALYSISOF PYRIFENOX

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ABSTRACT: Electrochemical reduction behaviour of Pyrifenox has been studied using d.c. polarography, cyclic voltammetry, a.c. polarography and differential pulse polarography in Britton-Robinson buffer ranging from pH 2.0 to 12.0. Pyrifenox is found to be reduced in a single reduction process and is attributed to the facile four electron reduction of azomethine group (>C=N-). Quantitative determination is carried out in the concentration range 1.0×10^{-5} M to 2.2×10^{-8} M. Kinetic parameters such as diffusion co-efficient (D) and forward rate constant ($K^{o}_{f,h}$) values are evaluated and reduction mechanism is proposed. The result indicates that the process of the compound is irreversible and diffusion controlled. A simple and rapid differential pulse polarographic method has been developed for the determination of Pyrifenox in an agricultural formulations and environmental samples employing both calibration and standard addition methods.

Key words: Pyrifenox, Reduction behaviour, Mechanism, Analysis, Formulations, Environmental samples.

INTRODUCTION

Pyrifenox [2', 4'-dichloro-2(3-pyridyl) acetophenone O-methyloxime] (Figure.1) is an azomethine group containing pesticide and is extensively used to controlling pests of commercial crops in agriculture.

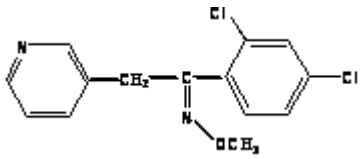

Figure 1. Structure of Pyrifenox

Many researchers [1-7] have studied the polarographic behaviour of some azomethine group containing pesticides and drugs in solution of varying pH at the dropping mercury electrode. Malcolm et al [8] determined azomethine pesticides in grain formulations. Many papers have been published dealing with the estimation of azomethine group containing pesticides using thin layer chromatography [9] and high performance liquid chromatography [10]. Lawrence et al [11] determined formetanate in fruits and vegetables by reverse phase liquid chromatography.

In the present work the emphasis has been on electrochemical study of Pyrifenox pesticide to get more information on the reduction mechanism of the compound and the electrode kinetics concerned, employing advanced electrochemical techniques such as d.c.polarography, cyclic voltammetry, a.c. polarography, differential pulse polarography, millicoulometry and control potential electrolysis. A rapid, simple and sensitive differential pulse polarography method has been applied to determine the Pyrifenox pesticide in an agricultural formulations and environmental samples.

MATERIAL AND METHODS

D.C. polarographic measurements were carried out by using model 364 polarographic analyzer coupled with a BD8 Kipp and Zonen recorder. A Metrohm unit: E 506 polarecord coupled with E 612 VA-scanner, E 648 VA-combistand, E 608 VA-controller, and a digital electronics 2000 X-Y/t recorder were used for cyclic voltammetric, a.c. polarographic and differential pulse polarographic measurements. A three-electrode combination was used with the dropping mercury electrode (DME) as working electrode in d.c.polarography, a.c.polarogroahy and differential pulse polarography, and with a hanging mercury drop electrode (HMDE) in cyclic voltammetry. Saturated calomel electrode (SCE) was used as the reference electrode in d.c. polarography and Silver electrode (Ag/AgCl (s), Cl^-) was used as reference electrode for cyclic voltammetry, a.c. polarography and differential pulse polarography. Platinum electrode was used as counter electrode for all the techniques. A modified cell with mercury pool cathode, SCE, platinum wire gauze electrode, and spot galvanometer, was used for controlled potential electrolysis. All the measurements were performed at 25±0.2 ^{0}C.

Pyrifenox was obtained from Rhone-Poulenc (India) Ltd., mumbai. The purity of the sample was tested by melting point determination and TLC analysis. Britton-Robinson buffers of pH 2.0 to 12.0 were prepared by using 0.2 M boric acid, 0.05 M citric acid, and 0.1 M trisodium orthophosphate. All the chemicals used were of pure analar grade. Stock solution of Pyrifenox was prepared by dissolving the required amount in double distilled water and making up to volume with the supporting electrolyte to obtain the desired concentration. Before running the voltammograms the test solution was purged with purified nitrogen for 10 min. A 0.02% aqueous solution of Triton X-100 was used to eliminate the polarographic maxima.

A standard stock solution (1×10^{-3} M) of the compound was prepared by the dissolution of the appropriate amount of the Pyrifenox pesticide in double distilled water. A 10 ml of the solution (9 ml of the supporting electrolyte + 1 ml of unknown concentration of the depolarizer) is transferred into a polarographic cell and polarogram is recorded after complete deaeration for 15 min. After obtaining the polarogram, small increments (0.2 ml) of the standard solution of electroactive species is added to the cell, deaerated for 1 min. and the polarogram is again recorded under similar conditions. In the same manner, 10 polarograms are recorded for 10 standard additions. The amount of unknown species is calculated by using relevant equation. In the present study the best conditions are obtained at pH 2.0 with a drop time 2 sec, a pulse amplitude 50 mV and applied potentials of -0.85 V for Pyrifenox. The relative standard deviations and correlation coefficients are found to be 1.10% and 0.962.

RESULTS AND DISCUSSION

Characterization of wave/peak

The electrochemical behaviour of pyrifenox has been studied over the pH range 2.0 to 12.0. In acidic solutions (pH $\leq$ 6), pyrifenox is found to be reduced in a single reduction process (figures 2 to 5). No wave/peak is observed in neutral and alkaline media. The single wave/peak is attributed to the facile four electron reduction of azomethine group that gets converted to the corresponding amino group.

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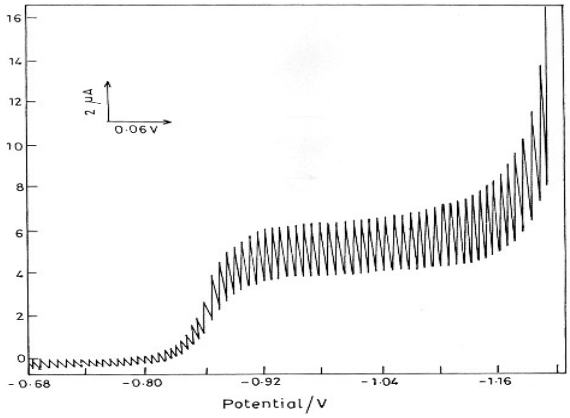


Figure 2. Typical d.c. polarogram of pyrifenox in pH 2.0, Concerntaion: 0.5 mM, Drop time: 3 sec

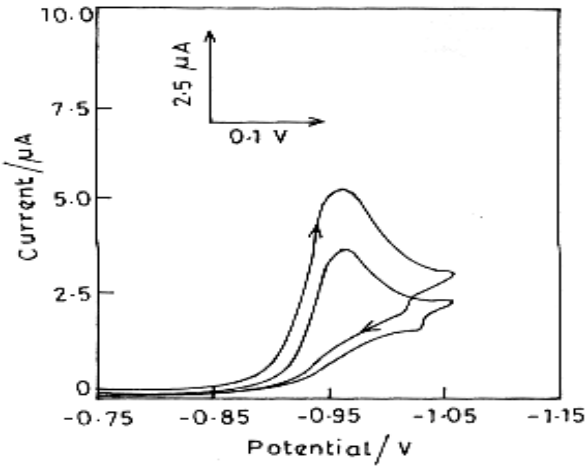


Figure 3. Typical cyclic voltammogram of pyrifenox in pH 4.0, Concerntaion: 0.5 mM, Scan rate: 40 mV/sec

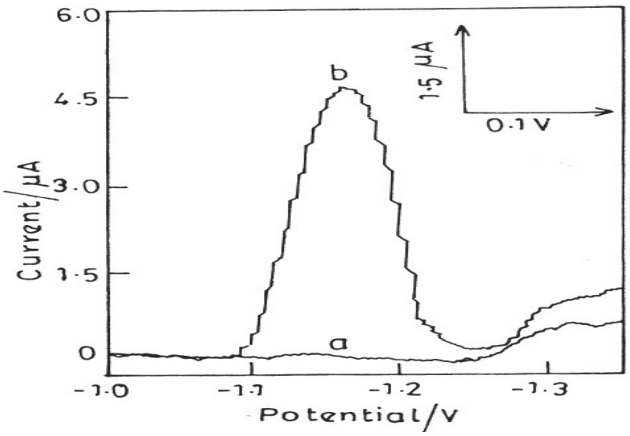


Figure 4. Typical a.c. polarogram of pyrifenox in pH 6.0, Concerntaion: 0.5 mM, Drop time: 3 sec (a. base line, b. a.c.peak)

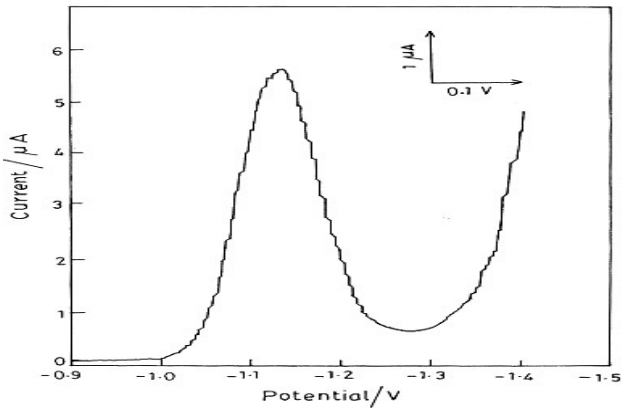


Figure 5. Typical differential pulse polarogram of pyrifenox in pH 6.0 concerntaion: 0.5 mM, Drop time: 2 sec, Pilse amplitude 50 mV

Nature of the electrode process

The plots of i_d vs $h^{1/2}$ (Figure.6), i_p vs $v^{1/2}$ (Figure.7) and i_m vs $t^{2/3}$ (Figure.8) are observed to be linear and passing through origin in each of the supporting electrolytes employed, indicating adsorption free and diffusion controlled nature of the electrode process for pyrifenox. In a.c.polarographic measurements, the base current is not seen to depress before and after the a.c.peak also confirming the adsorption free nature of the process. The experimental constancy of $i_p/Cv^{1/2}$ with scan rate has shown the electrode process to the free from any kinetic complications.

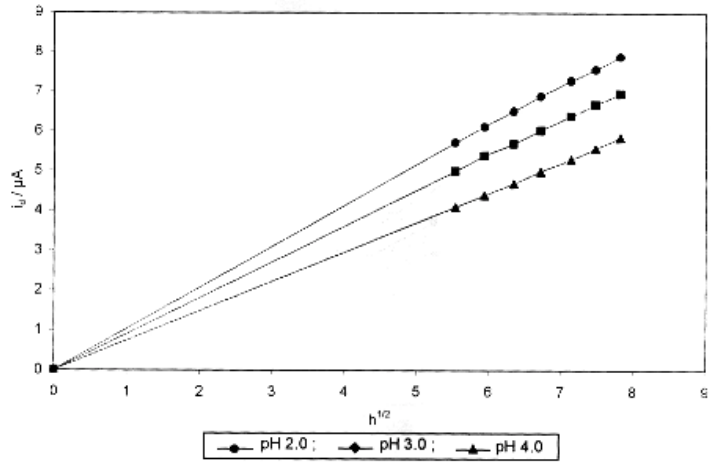


Figure 6. plots of pyrifenox i_d vs $h^{1/2}$ Concerntaion: 0.5 mM

The reduction process is found to be irreversible for pyrifenox as evidenced from the disobedience of Tomes' criterion, log-plot analysis and dependence of $E_{1/2}$ with the concentration of electroactive species in d.c.polarography, the absence of anodic peak in the reverse direction and the variation of peak potential with scan rate in cyclic voltammetry. The marginal variation of peak potential (E_m) with concentration and non-linearity in the pots of i_m vs.$1-\sigma/1+\sigma$ in differential pulse polarography also confirm the irreversible nature of the electrode process. The $E_{1/2}$ and E_p values of the Pyrifenox is found to be pH dependent and shift towards more negative values with increase in pH of the buffer systems indication the proton involvement in the electrode process.

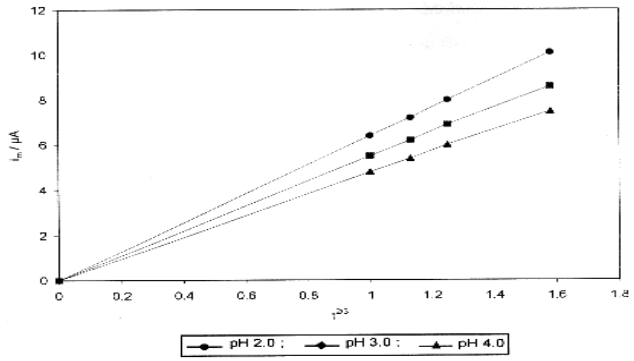


Figure 7. plots of pyrifenox i_p vs $v^{1/2}$ Concerntaion: 0.5 mM

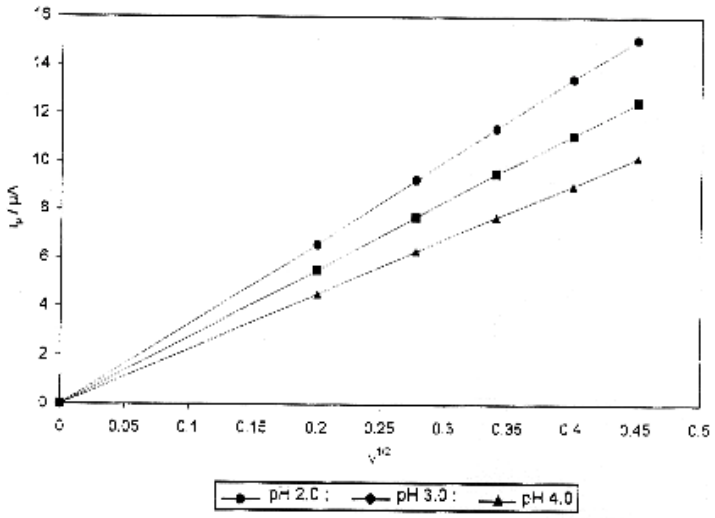


Figure 8. plots of pyrifenox i_m vs $t^{2/3}$ Concerntaion: 0.5 mM

Identification of the product

The electrochemical technique, millicoulometry has been employed in the present investigation to evaluate the number of electrons involved in the reduction process. From the comparison of wave heights observed, the number of electrons involved in the reduction process of the pyrifenox is determined as four in pH 2.0.

The final products of the reduction of pyrifenox in pH 4.0 are identified by analysing the 2×10^{-3}M solutions of electroactive species subjected to controlled potential electrolysis. Electrolysis is carried out at potentials of -1.00 V for the respective compounds by using mercury pool electrode. During the electrolysis, the solutions are stirred and purged with oxygen free nitrogen. After the electrolysis, the solution is extracted three times with 20 ml of acetone.

The combined extracts are dried over anhydrous sodium sulphate and the solvent is removed by evaporation. The reduction products are confirmed as corresponding amines by IR spectral studies. The characteristic peaks for amine group are shown in Figure.9 (N-H stretch: 3351 cm^{-1}, 3275 cm^{-1} and N-H bend: 1650 cm^{-1}).

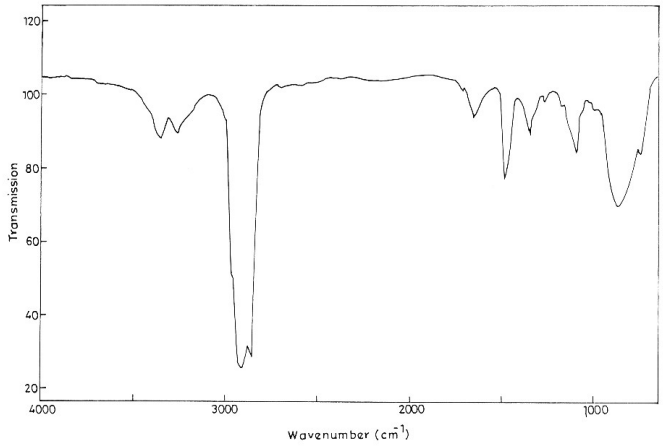


Figure.9. I.R. Spectrum of the reduction product of pyrifenox

Kinetic data

The various kinetic parameters of the electrode process such as transfer coefficients, diffusion coefficients and rate constants, calculated for pyrifenox compound from different techniques, are reported in Tables-1 to 4. The adsorption free nature of the electrode process is clearly evident from the nearly equal diffusion coefficient values obtained from all the techniques. The slight decrease in diffusion coefficient values with increase in pH may be due to less availability of protons.

Table 1: Typical d.c. polarograpahic data of pyrifenox Concentration: 0.5mM, Drop time: 3 sec.

pH of the supporting electrolyte	$-E_{1/2}$/V	i_d/µA	αn_a	$D\times10^6$/cm^2 s^{-1}	$K^0_{f,h}$/cm s^{-1}
2.0	0.86	5.7	0.93	2.50	1.65×10^{-10}
4.0	0.97	5.1	0.89	2.09	3.13×10^{-9}
6.0	1.11	4.9	0.81	1.97	5.13×10^{-12}

The heterogeneous forward rate constant values ($k^0_{f,h}$) of pyrifenox under investigation are seen to decrease gradually with increase in pH of the supporting electrolyte. This may account for shift of reduction potentials towards more negative values with increase in pH.

Table 2: Typical Cyclic voltammetry data of pyrifenox Concentration: 0.5mM, Scan rate: 40mV/sec.

pH of the supporting electrolyte	$-E_p$/V	i_p/µA	αn_a	$D\times10^6$/cm^2 s^{-1}	$K^0_{f,h}$/cm s^{-1}
2.0	0.85	5.8	0.83	2.44	1.69×10^{-7}
4.0	0.96	5.2	0.88	2.14	3.09×10^{-10}
6.0	1.13	4.8	0.79	1.75	5.07×10^{-12}

Table 3: Typical a.c. polarograpahic data of pyrifenox Concentration: 0.5mM, Drop time: 3 sec.

pH of the supporting electrolyte	$-E_s$/V	i_s/µA	αn_a	$D\times10^6$/cm^2 s^{-1}	K_s/cm s^{-1}
2.0	0.84	5.3	0.47	2.61	3.40×10^{-6}
4.0	0.96	4.9	0.42	2.02	5.31×10^{-8}
6.0	1.15	4.6	0.39	1.82	1.36×10^{-11}

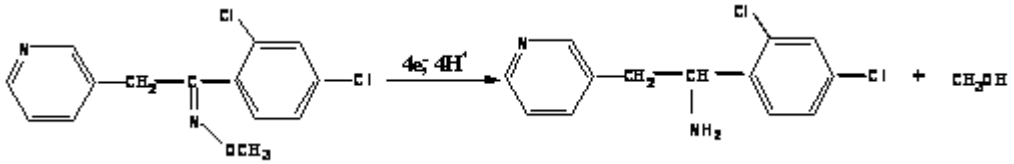
Table 4: Typical differential pulse polarograpahic data of pyrifenox Concentration: 0.5mM, Drop time: 2 sec, pulse amplitude: 50 mV

pH of the supporting electrolyte	$-E_m$/V	i_m/µA	αn_a	$D\times10^6$/cm^2 s^{-1}	$K^0_{f,h}$/cm s^{-1}
2.0	0.85	6.5	0.73	2.88	5.10×10^{-8}
4.0	0.91	6.1	0.88	2.13	3.10×10^{-10}
6.0	1.14	5.7	0.72	1.93	4.73×10^{-12}

This trend is particularly evident when the proton transfer is involved in the electrode process. Possibly an increase in pH increases the dissociation constant of the protonated species and these factors affect the protonation rate. Consequently, the reduction potentials are shifted to more negative values. The a.c. polarographic rate constant values (k_s) are found to the different from the values obtained from other techniques since the former values relate to standard potentials.

Electrode mechanism

On the basis of results obtained form different techniques as well as from literature, [12, 13] the following mechanism can be proposed for all the three compounds (scheme 1).



Scheme 1: Electrode mechanism of pyrifenox

Analysis

In the present investigation, differential pulse polarography has been employed for the quantitative estimation of pyrifenox compound using the currents obtained for azomethine group reduction employing both calibration and standard addition methods. The polarographic peak obtained in pH 2.0 is well resolved and can be utilised for the analysis experiments. The technique is used to determine pyrifenox over the concentration range 1.0×10^{-5} M to 2.2×10^{-8}. The calibration plots based on the peak heights are found to be 2×10^{-8} M for pyrifenox, which are calculated from the expression dl=3Sd/m, where Sd is standard deviation, dl is detection limit and m is slope of the plot.

Standard stock solution (1×10^{-3} M) of the compounds is prepared by the dissolution of the appropriate amount of the compound in double distilled water. A 10 ml of the solution (9 ml of the supporting electrolyte +1 ml of unknown concentration of the depolarizer) is transferred into a polarographic cell and polarogram is recorded after complete deaeration for 15 minutes. After obtaining the polarogram, small increments (0.2 ml) of the standard solution of electroactive species is added to the cell, deaerated for one minute and the polarogram is again recorded under similar conditions. In the same manner, 10 polarograms are recorded for 10 standard additons .The amount of unknown species is calculated by using relevant equation. In the present study the best conditions are obtained at pH 2.0 with a drop time 2 sec, a pulse amplitude 50 mv and applied potentials of -0.85 V for pyrifenox. The relative standard deviations and correlation coefficients are found to be 1.56% and 0.942 for pyrifenox.

The developed analytical procedure has been applied for the estimation of the compounds in agricultural formulations, grains, soil and water samples. The required quantity of pyrifenox formulation (Dorado) corresponding to a stock solution of 1×10^{-3} M are accurately measured and transferred in to a 100 ml calibrated flask containing acetone. A solution of 1×10^{-5} M is prepared by dilution this stock solution with a buffer. The above described procedure is applied for the determination of the compound in their formulation. The assay result for the formulation is given in Table.5.

Table.5: Determination of pyrifenox in agricultural formulations
Pulse amplitude: 50 mV, Drop time: 2 s

Name of Compound	Labelled amount (mg)	Average amount found* (mg)±SD	Average recovery (%)
Dorado	5.0	4.95 ±0.01	99.00
	10.0	9.91 ±0.02	99.10
	15.0	14.94±0.02	99.60

Collected soil sample is air dried, allowed to pass through 2.8 mm sieved and homogenized in a ball mill. Aliquots (25 g) of grains and soil samples are taken into a 250 ml Erlenmeyer flask and spiked with 10 ml of different concentrations of the pesticide stock solutions and kept in contact for 4 hours. After this period the pyrifenox is extracted with acetone for 15 min. in successive extractions. After the evaporation of the solvent, the residue is dissolved in ethanol and added to the cell containing buffer solution. The recoveries obtained from the spiked soil and grain samples are shown in table.6.

Table 6: Recoveries of pyrifenox added to grains and soils, Pulse amplitude: 50mV, Drop time: 2 sec.

Amount added (mg)	Average amount found* (mg) ± SD		Average recovery (%)	
	Rice	Soil	Rice	Soil
10.0	9.83±0.030	9.84±0.041	98.40	98.40
20.0	19.83±0.023	19.88±0.021	99.15	99.40

*Each value is an average of four determinations

A 1000 ml of well and tap water samples are collected and spiked with different concentrations of the compounds .All the spiked samples are thoroughly shaken for few minutes. Then the solutions are passed through a Sep-Pak C_{18} cartridge previously activated with 10 ml of acetone and 5 ml of deionised water. Elutions are carried out with 10 ml of ethanol and filtered through anhydrous sodium surfate. The organic phase is evaporated to dryness and residues are dissolved in ethanol and added to the cell containing buffer. The recoveries are presented in table 7.

Table 7: Recoveries of pyrifenox added to spiked water samples Pulse amplitude: 50mV, Drop time: 2 sec.

Sample type	Amount added (mg)	Average amount found* (mg)±SD	Average recovery (%)
Tap water	2.0	1.94±0.032	97.00
	4.0	3.92±0.020	98.00
	6.0	5.91±0.026	98.50
Well water	2.0	1.93±0.030	96.50
	4.0	3.91±0.026	97.75
	6.0	5.95±0.031	98.00

*Each value is an average of four determinations

CONCLUSION

The work describes the voltammetric behaviour of pyrifenox based on the reduction of azomethine group at dropping mercury electrode and hanging mercury drop electrode. The recovery result shows that differential pulse polarography is a simple, reliable and inexpensive method for the determination of pyrifenox in formulations. The main advantage of the proposed method over the other ones is that the excipietns do not interfere and a separation procedure is not necessary.

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