Voltammetric Behaviour and Analysis of Fluchloralin

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Abstract: The electrochemical reduction behavior of fluchloralin has been studied by D.C.polarography, differential pulse polarography, millicoulometry and controlled potential electrolysis in the universal buffers ranging from 2.0 to 12.0. Kinetic parameters were evaluated and a reduction mechanism was proposed. A simple and rapid differential pulse polarographic method has been developed for the determination of fluchloralin in formulations, grains, soils and spiked water samples. The lower detection limit was found to be 1.5×10^{-8} M. Both the standard addition and calibration methods were used for the analytical measurements.

Keywords*: Fluchloralin, Voltammetric behaviour, Analysis, Formulations, Environmental samples.

Introduction

Nitro group containing pesticides are extensively used in agriculture throughout the world. Fluchloralin is one of the dinitroaniline pesticide families and is an economically important class of agricultural compound used to prevent the growth of grasses and weeds in cultivated crops. Mostly chromatograhic methods are reported for the analysis of dinitroaniline herbicides[1-5]. Among the suitable analytical methods, voltammetric methods play an important role because of its rapidity and selectivity in the analysis of pesticide residues such as several workers[6-11] has studied. The polarographic behaviour of nitro group containing compounds in solutions of varying pH at dropping mercury electrode. Very little attention has been paid to the electrochemical study of this compound. This work elucidates the electrochemical behaviour of fluchloralin by D.C.polarography, cyclic volatmmetry, A.C.polarography and differential pulse polarography (DPP). DPP method has been used for the determination of fluchloralin in various environmental matrices.

Experimental

Model 364 polarogrphic analyser supplied from PRC coupled with BD 8 Kipp and Zonen x-t recorder was used for D.C.polarographic measurements. Other techniques were carried out using 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. All electrochemical cell designed with three-electrode design at 25 ± 0.1 ^{0}C. The dropping mercury electrode (area: 0.0223 cm^2, flow rate of Hg:2.73 mg/sec and mercury column height:35 cm) and hanging mercury drop electrode (with an area of 0.0328 cm^2) were used as working electrodes. Reference electrodes employed were Ag/AgCl (s), Cl$^-$ electrode for cyclic voltammetry, A.C.polarography and differential pulse polarography and saturated calomel electrode (SCE) for D.C.polarography. Platinum electrode was used as counter electrode for all the techniques to complete electrolytic current. A modified cell with mercury pool cathode, SCE, platinum wire gauze electrode and spot galvanometer was used for controlled potential electrolysis.

Pure fluchloralin was obtained from Ciba-Geigy Pvt. Ltd., Mumbai and was used without further purification. Universal 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 fluchloralin was prepared by dissolving the required amount in ethanol and making up to volume with the supporting electrolyte to obtain the desired concentration. The test solution was purged with purified nitrogen for 10 min before the voltammograms were run. A 0.02% aqueous solution of Triton x-100 was used to eliminate the polarographic maxima.

Results and Discussion

Fluchloralin was found to exhibit a single well defined wave/peak in the entire pH range 2.0 to 12.0 in all the techniques. This single wave/peak was attributed to the simultaneous reduction of two nitro groups in the eight electron process to the corresponding hydroxylamine groups. Typical voltammograms are shown in Figures 1 - 4.
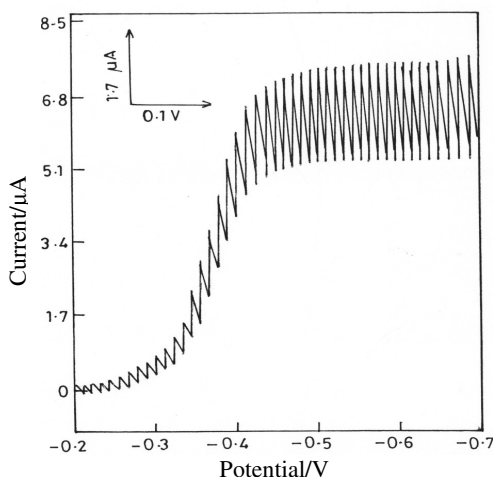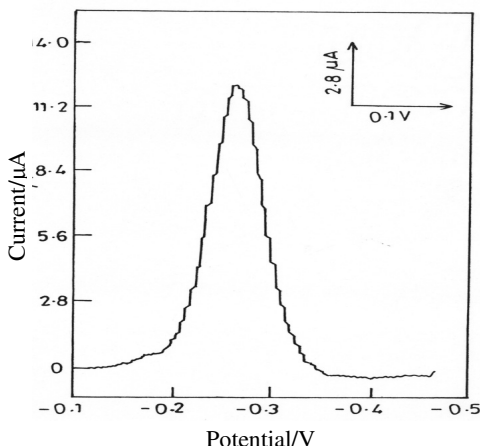

Figure 1. Typical D.C. polarogram of fluchloralin in pH 8.0, Con:0.5 mM Drop time:3s
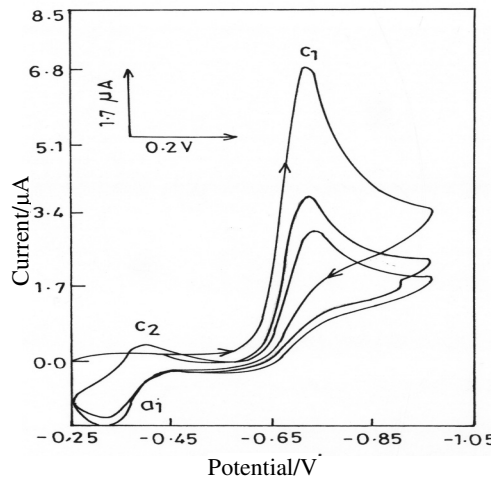
Figure 2. Typical cyclic voltammogram of fluchloralin in pH 4.0, Con: 0.5 mM Scan rate: 40 mVs^{-1}
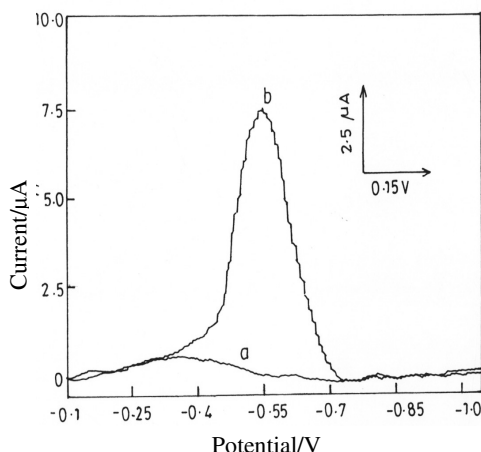
Figure 3. Typical A.C. polarogram of fluchloralin in pH 6.0, Con:0.5 mM Drop time: 2s **a**: base line, **b**: A.C.peak.

Figure 4. Typical differential pulse polarogram fluchloralin in pH 4.0, Con: 0.5 Scan rate: 40 mVs^{-1}

In cyclic voltammetric experiments, a small anodic peak (a_1) has been observed in the reverse scan at higher pH values (pH≥10) for fluchloralin (Figure 2). It is likely that a nitroso compound is formed, whose function at the electrode surface may be responsible for the anodic peak. In the second scan, another small cathodic peak (c_2) at more positive potentials than c_1 is noticed. The anodic peak (a_1) may be due to the oxidation of hydroxylamine formed at c_1 to nitroso derivative and the cathodic peak (c_2) may be attributed to the reduction of the nitroso derivative to the hydroxylamine again.

## Nature of the electrode process

The nature of the wave/peak is found to be diffusion controlled and adsorption free in the buffer systems taken, as shown by the linear plot of i_d *vs.* $h^{1/2}$ (Figure 5), i_p *vs.* $v^{1/2}$ (Figure 6) and i_m *vs.* $t^{2/3}$ (Figure 7) which is found to pass through origin. The irreversibility of the electrode process is confirmed by the log-plot analysis of the wave. The slope of E_{dc} *vs.* {log(i/id-i)-0.506 log t} plot exceeds appreciably 54.2/n mV. The variation of peak potential with scan rate also indicates the irreversible nature of the electrode process. Further, $E_{1/2}$, E_p and E_m values were observed to have shifted towards more negative values with increasing concentration of the depolarizer. The $E_{1/2}$ and E_p values of fluchloralin were found to be dependent on pH of the buffer solutions, indicating proton involvement in the electrode process. The number of protons involved in the rate determining step is found to be two as evidenced from the linear plots of $E_{1/2}$ *vs.* pH (Figure 8).

Identification of the product

Millicoulometry was employed to find out the number of electrons involved in the electrode process. It is found to be eight (for each nitro group four electrons) for the reduction of two nitro groups in fluchloralin at acidic (pH 2.0) and basic (pH 12.0) medium. Controlled potential electrolysis (CPE) has been carried out in a modified cell with mercury pool cathode, saturated calomel electrode and platinum wire as anode. This experiment was carried out in pH 4.0 at applied potentials of -0.24V for fluchloralin. After electrolysis, the reduced products are extracted with ether.
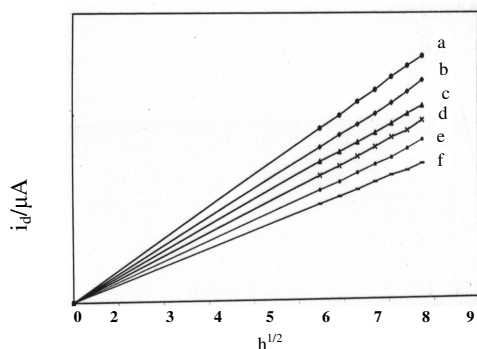
a=pH 2.0; b=pH 4.0; c=pH 6.0; d=pH 8.0; e=pH 10.0; f=pH 12.0

Figure 5. i_d *vs* $h^{1/2}$ plots of fluchloralin Con.0 0.5 mM
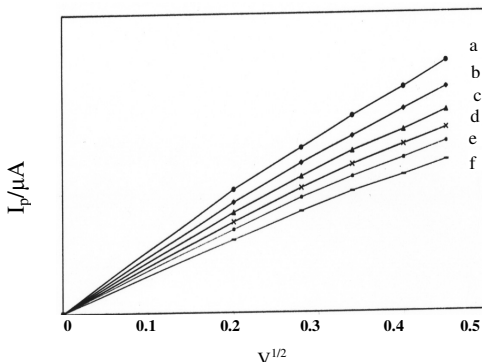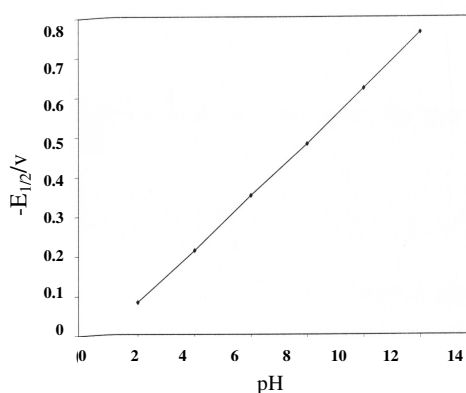

a=pH 2.0; b=pH 4.0; c=pH 6.0; d=pH 8.0; e=pH 10.0; f=pH 12.0

Figure 6. I_p *vs* $V^{1/2}$ plots of fluchloralin Con.0 0.5 mM
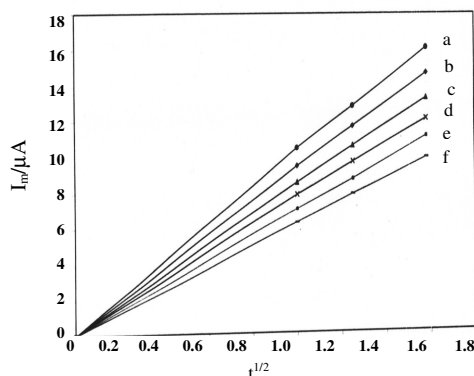
a=pH 2.0; b=pH 4.0; c=pH 6.0; d=pH 8.0; e=pH 10.0; f=pH 12.0

Figure 7. I_m *vs* $t^{2/3}$ plots of fluchloralin Con.0.5 mM

Figure 8. $E_{1/2}$ *vs* pH plots of fluchloralin Con.0.5mV, Drop Time: 3s

The ethereal layer was evaporated on water bath and the product was identified as the corresponding hydroxylamine. The isolation product was confirmed as hydroxylamine by I.R. spectral data (N-H stretch: 3420 cm^{-1}, O-H stretch: 3060-3000 cm^{-1} and N-H bend: 1575 cm^{-1}.

Kinetic data

The values obtained for transfer coefficient (α), diffusion coefficient (D) and heterogeneous forward rate constant ($k^o_{f,h}$), at various pH values in different techniques, are given in Tables 1 - 4. The diffusion coefficient values evaluated from all the techniques are in good agreement. This is evident particularly where no adsorption complication is involved in the electrode process. The reason for slight decrease in diffusion coefficient values with increase in pH may be due to the less availability of protons with increase in pH of the buffer solution.

The heterogeneous forward rate constant values calculated are, in general, found to decrease with increase in the pH of the solution. This trend shows that the electrode reaction tends to become more and more irreversible with increase in pH. The rate constant values obtained for the reduction of nitro group in fluchloralin is found to be high in acidic medium

in all the techniques, indicating that the rate of reaction is fast in acidic solution due to high proton involvement which makes the reduction process easier. But, in basic media, the reduction process does not easily occur owing to the lower availability of protons. Consequently, lower values are obtained for the rate constants in basic medium in contrast to acidic medium.

Table 1. Typical D.C. polarographic data of fluchloralin concentration 0.5 mM, Drop time: 3s

pH	$-E_{1/2}$/V	I_d/μA	$\acute{a}n_a$	$D \times 10^6$/cm^2 s^{-1}	$K^0_{f, h}$/ cm s^{-1}
2.0	0.09	8.8	1.67	9.12	1.86×10^{-4}
4.0	0.22	7.8	1.62	8.81	2.01×10^{-5}
6.0	0.38	7.0	1.59	8.60	2.90×10^{-8}
8.0	0.52	6.4	1.65	7.62	4.03×10^{-10}
10.0	0.64	5.6	1.61	7.12	9.86×10^{-12}
12.0	0.78	4.9	1.59	6.48	3.54×10^{-17}

Table 2. Typical cyclic voltmmetric data of fluchloralin concentration 0.5 mM, Scan rate: 40 mVms^{-1}

pH	$-E_p$/V	I_p/μA	$\acute{a}n_a$	$D \times 10^6$/cm^2 s^{-1}	$K^0_{f, h}$/ cm s^{-1}
2.0	0.12	10.3	1.53	9.01	1.70×10^{-4}
4.0	0.24	9.2	1.68	8.62	2.48×10^{-6}
6.0	0.38	8.4	1.62	8.20	6.30×10^{-8}
8.0	0.52	7.6	1.58	7.72	4.82×10^{-10}
10.0	0.67	6.8	1.61	7.46	8.20×10^{-12}
12.0	0.78	6.1	1.64	7.10	2.10×10^{-16}

**Table 3.** Typical A.C. polarographic data of fluchloralin concentration 0.5 mM, Drop time: 3s

pH	$-E_s$/V	I_s/μA	$\acute{a}$	$D \times 10^6$/cm^2 s^{-1}	K_s/ cm s^{-1}
2.0	0.12	10.2	0.81	8.84	1.70×10^{-3}
4.0	0.27	9.6	0.83	8.40	7.02×10^{-4}
6.0	0.40	8.4	0.79	8.12	5.80×10^{-7}
8.0	0.53	7.5	0.81	7.72	3.20×10^{-9}
10.0	0.68	6.6	0.81	7.65	2.96×10^{-11}
12.0	0.79	6.4	0.74	7.40	8.80×10^{-12}

Table 4. Typical differential pulse polarographic data of fluchloralin concentration 0.5 mM, Drop time: 3s, Pulse amplitude: 50 mV.

pH	$-E_m$/V	I_m/μA	$\acute{a}n_a$	$D \times 10^6$/cm^2 s^{-1}	$K^0_{f.h}$/ cm s^{-1}
2.0	0.08	13.1	1.63	8.82	1.74×10^{-4}
4.0	0.26	11.8	1.67	8.40	7.00×10^{-5}
6.0	0.42	10.2	1.65	8.01	5.84×10^{-8}
8.0	0.52	9.4	1.60	7.70	3.00×10^{-10}
10.0	0.68	8.5	1.62	7.63	2.80×10^{-12}
12.0	0.79	7.8	1.64	7.30	8.70×10^{-16}

Electrode mechanism

Based on the results obtained form different techniques, the reduction mechanism of the nitro group present in fluchloralin can be proposed (Scheme 1) as follows:
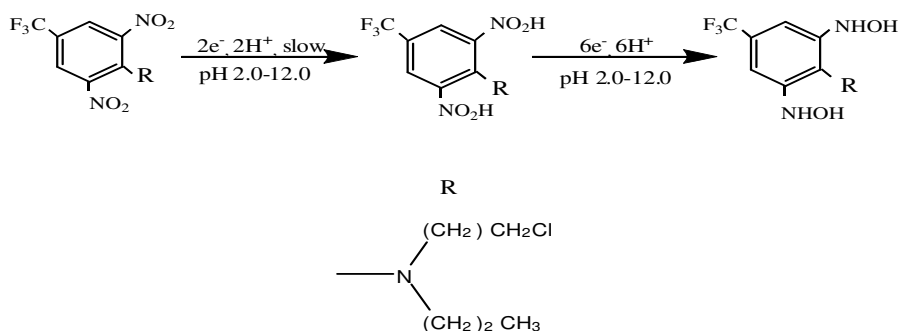
Scheme 1

Analysis

In the present study differential pulse polography (DPP) has been employed for the quantitative determination of fluchloralin in grain, soil and spiked water samples. The title compound is found to exhibit sharp and well resolved peaks in pH 4.0 and this peak is chosen for quantitative studies. Both standard addition and calibration methods are used. The peak heights are found to be linear over the concentration range 2×10^{-5} M to 2.62×10^{-8} M with lower detection limits of 1.5×10^{-8} M for fluchloralin. The correlation coefficients and relative standard deviation values are found to be 0.990 and 1.32% for 10 replicants.

Recommended analytical procedure

Standard stock solution (1×10^{-3} M) of the fluchloralin was prepared by dissolving an appropriate amount of electroactive species in ethanol. 1 mL of the standard solution was transferred into a polarographic cell, made up with 9 mL of the supporting electrolyte and then deoxygenated with nitrogen gas for 10 min. The polarogram was recorded. Later small increments (0.2 mL) of standard solution were added and the polarograms were recorded after each addition under the identical conditions. In the present study the best precision was obtained at pH 4.0 with a drop time of 2 sec, a pulse amplitude of 50 mV and applied potential of -0.22 V for fluchloralin. This method was successfully employed for the determination of the compound in agricultural formulations, grains, soil and water samples.

In the present analysis, fluchloralin formulations namely, Basalin was chosen. The required quantity of formulations corresponding to a stock solution of concentration 1×10^{-3} M was accurately measured and transferred into a 100 mL calibrated flask containing 50 mL of ethanol. A solution of 1×10^{-5} M was prepared by diluting this stock solution with the buffer solution and the above described procedure was employed. Assay results are given in Table 5.

Table 5. Determination of fluchloralin in agricultural formulations; pulse amplitude: 50 mV, Drop time: 2s

Compound	Labelled amount, mg	Average amount found, mg ±SD	Average recovery, %
	5.0	4.93 ± 0.038	98.60
Basalin	10.0	9.98 ± 0.081	98.90
	15.0	14.80 ± 0.065	98.67

Grain (rice) samples (50 g) and soil samples (25 g) were sprayed with known amounts of the fluchloralin and left for 2-4 h. The samples were extracted with acetone (2×50 mL) by shaking the flask for 5 min. The organic phase was filtered under suction through Whatmann No.1

filter paper. The solvent was removed through evaporation and the residues of the compounds were dissolved in ethanol and transferred into a 50 mL volumetric flask. The results obtained for the determination of fluchloralin in grain and soils samples are presented in Table 6.

Table 6. Recoveries of fluchloralin added to grains, soils and spiked tap water samples; pulse amplitude: 50 mV, Drop time: 2s

Sample	Amount added, mg	Average amount found, mg ±SD	Average recovery, %
Rice	10.0	9.76±0.036	97.60
	20.0	19.88±0.098	99.40
Soil	10.0	9.91±0.021	99.10
	20.0	19.85±0.082	99.25
Spiked tap water	4	3.97±0.033	99.25
	6	5.87±0.059	97.83
	8	7.86±0.060	98.25

A 1000 mL samples of tap water was spiked with the pesticide at different concentration levels (each concentration 3 times) taken into a 2 L separatory funnel and shaken for a few minutes. The solution was passed through Whatmann Nylon® memebrane filter (0.45 μm size). The elution was carried out with 3×50 mL dichloromethane. The organic solvent was filtered through anhydrous sodium sulfate and evaporated to dryness. Small volumes of hexane were added to remove dichloromethane completely. The residue was dissolved in ethanol and then transferred to a 50 ml volumetric flask. Table 6 gives the recovery of fluchloralin in spiked water samples.

Conclusion

The work describes the electrochemical behaviour of fluchloralin based on the reduction of the nitro group at DME and HMDE. The recovery result shows that DPP is a simple, reliable and inexpensive method for the determination of fluchloralin in environmental samples. 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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