

Determination of the Herbicide Fenclorim by Adsorptive Stripping Voltammetry at Carbon Nano Tubes Paste Electrodes (CNTPE)

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Abstract

In this investigation a sensitive method for the determination of the herbicide fenclorim by adsorptive stripping voltammetry (AdSV) at carbon nano tubes paste electrodes (CNTPE) at pH 4.0 was described. The cyclic voltammograms demonstrate the adsorption of these compounds at the working electrode. A symmetric study of the various operational parameters such as Accumulation potential (-0.8V) and (60s) accumulation time that affect the stripping response was carried out by differential pulse voltammetry. Universal buffer with pH range 2.0-6.0 used as supporting electrolyte. The peak heights are in linear trend over the concentration range of 1.0×10^{-8} to 1.0×10^{-5} M. The relative standard deviation and correlation coefficient for fenclorim was 0.97% and 0.998 respectively. The lower detection limit for fenclorim was 0.92×10^{-7} M. The degree of interference of some other pesticides on the differential pulse adsorptive stripping signal for fenclorim was evaluated. Finally the proposed method was applied for determination of fenclorim in grains (wheat and rice) and water samples.

Keywords: Fenclorim; Carbon nano tubes paste electrodes; Wheat; Rice and water samples

Introduction

Modern agriculture production depends considerably on the use of herbicides to control weeds in crops. Many herbicides are potentially toxic to higher animals. The increasing use of herbicides exerts their toxic effects through repeated exposure. The azomethine group containing herbicides were introduced in agriculture in 1954. The azomethine group containing herbicides are used worldwide as selective pre and post emergence herbicides [1-4].

Fenclorim (4, 6-dichloro-2-phenylprimidine) is abroad spectrum herbicide used to control of weeds. Luciano et al. [5-7] studied the influence of fenclorim on glutathione S-transferase (GST) activity in plants by using UV-Vis spectro photometry. Zhang Q, Riechers DE [8] reported protamic methods such as two dimensional gel electrophoresis and LC-MS to identify the residues of fenclorim in triticumtauschii.

Using herbicides at below-labeled rates has the potential risk of weed control failures and yield reductions. Herbicide resistance.... In the end, it all depends on weighting the potential benefits of reduced rates and degree to which you are willing to accept the risks associated with this weed management approach.

Electro analysis is perhaps the branch of analytical chemistry with a number of practical applications. In the analysis of pesticides in environmental samples [9-12] electro analytical technique has been shown to be an exceptional method and quite often superior to classical wet methods or spectrophotometric method and other analytical tools such as gas chromatography, liquid-liquid chromatography, thin layer chromatography, high performance liquid chromatography (HPLC), infrared (IR), nuclear magnetic resonance (NMR) and mass spectrometry (MS).

Experimental

Apparatus and electrodes

Voltammetric determinations were performed using a model meterohm Auto Lab 101 PG stat (Netherlands). CNTPE was used as working electrode for differential pulse adsorptive stripping voltammetry and cyclic voltammetry. pH measurements were carried

out with an Eutech PC_510 cyber scan. Meltzer Toledo (Japan) Xp26 delta range micro balancer were used to weigh the samples during the preparation of standard solutions. All the experiments were performed at 25°C.

Reagents and solutions

All reagents used for this work are analytical grade obtained from Merck, INDIA, Ltd. Double distilled water was used throughout the analysis. In the present investigation universal buffers of pH range 2.0 to 6.0 are used as supporting electrolytes and are prepared by using 0.2 M boric acid, 0.05M citric acid and 0.1M tri sodium orthophosphate solutions. Pesticide Samples obtained from Bayer crop, India.

Measurement step

In the standard addition method, the voltammogram of the unknown is first recorded after which a known volume of standard solution of the same electro active species is added to the cell and second voltammogram is taken. From the magnitude of the peak height, the unknown concentration of species was calculated using the equation.

$$Cu = \frac{C_s \times V}{V_1 \times i_2} \times i_1$$

Where, i_1 = The observed maximum current of voltammogram in microamperes of unknown solution.

i_2 = The maximum current of the voltammogram after adding volume of V ml of unknown concentration.

C_s = Concentration of the standard solution in mM

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C_u = Concentration of the unknown solution in mM

V_t = Total volume of the solution (V + v)

Result and Discussion

The effect of pH on the voltammograms has been investigated by recording the current voltage curves of fenclorim at a concentration of 0.5 mM in universal buffer systems over the pH range of 2.0 to 6.0. Fenclorim exhibits a single well-defined wave / peak obtained in pH 2.0 to 6.0 in all the techniques, corresponding to the reduction of azomethine group in two electron process. Typical cyclic voltammogram are shown in Figure 1.

Based on the linear plots i_p vs $v^{1/2}$ passing through origin (Figure 2) the reduction process is found to be diffusion controlled and adsorption free. The shift of peak potential (E_p) towards more negative values with increase in concentration of depolariser, indicates that the electrode process is irreversible. This is further confirmed by log-plot analysis. The variation of peak potentials with scan rates and absence of anodic peak in the reverse scan in cyclic voltammetry indicates the irreversible nature of the electrode process. The dependence of i_p / pH curves shows a behavior in accordance with a process in which a proton transfer provides the electrochemical reduction of the acid form to form an electro active species. The number of protons involved in the rate determining step is found to be two.

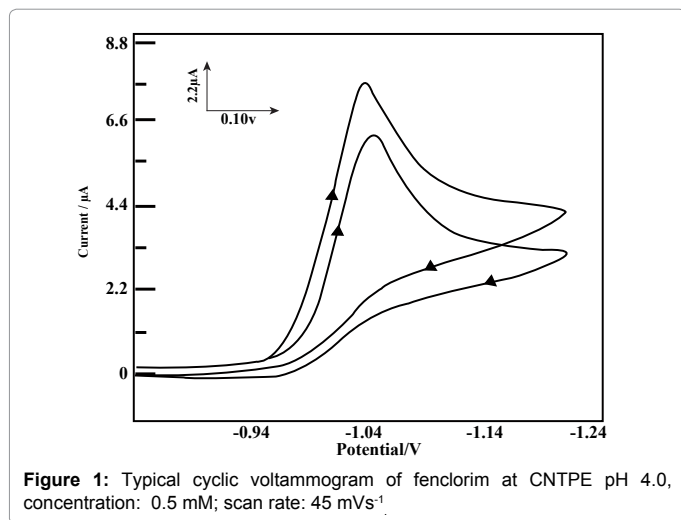


Figure 1: Typical cyclic voltammogram of fenclorim at CNTPE pH 4.0, concentration: 0.5 mM; scan rate: 45 mVs⁻¹.

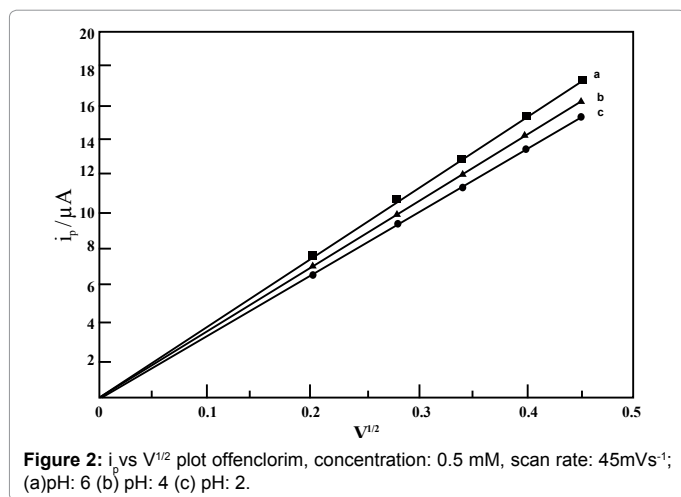


Figure 2: i_p vs $V^{1/2}$ plot of fenclorim, concentration: 0.5 mM, scan rate: 45mVs⁻¹; (a) pH: 6 (b) pH: 4 (c) pH: 2.

Number of electrons involved in the overall reduction process of fenclorim (Scheme 1) is found to be two and it is evidenced by millicoulometric technique. Controlled potential electrolysis conducted at -1.0V vs. SCE at pH 4.0 and the corresponding decay noted by using the galvanometer. The electrolysis is allowed to proceed virtually to completion. The product formed after controlled potential electrolysis was identified and confirmed by I.R. spectral data (N-H stretching frequency appears above 3300 cm⁻¹ and C=N stretching frequency of peak appear at 1630 cm⁻¹ to 1710 cm⁻¹).

Kinetic parameters such as diffusion coefficient, transfer coefficient and heterogeneous forward rate constant values evaluated and reported in Table 1. The diffusion coefficient values were noticed to be in good agreement from cyclic voltammetry. The heterogeneous forward rate constants were decreasing with an increase in pH of the supporting electrolyte, which may account for the shift of reduction potentials towards more negative values with increase in pH. This trend was particularly evident where proton transfer was involved in the electrode process.

Based on the results obtained from all the techniques, the electrochemical reduction mechanism is evaluated as shown in Scheme 1.

Fenclorim exhibits a single well-defined peak in the pH range 2.0 to 6.0, when potential was scanned from -1.05 V and so on at CNTPE (Figure 3) which is due to the reduction of the azomethine group. The experimental parameters that affect the AdSV signal carried out by considering stripping peak in order to establish the optimum conditions. Both standard addition and calibration methods are employed for the determination of fenclorim in grains and water.

The peak current i_p , increased gradually with the increase of pH of the solution till it reaches the maximum value at pH 4.0 (Figure 4). A shift of the peak potential towards more negative value with increase in pH indicates the existence of a protonation reaction coupled with the fenclorim reduction process. The best curve and highest peak current are obtained in universal buffer at pH 4.0.

The influence of accumulation potential from -0.5 V to -1.0 V on the peak height for 0.5 mM fenclorim was tested using AdSV technique in the presence of universal buffer (pH 4.0) an enhanced adsorption peak at potential -0.80V obtained as shown in Figures 5 and 6.

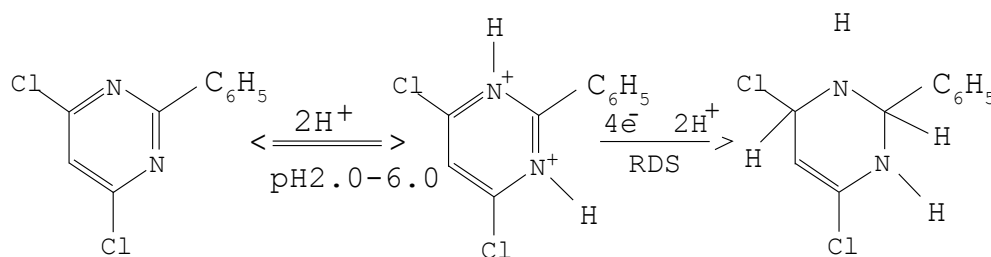
The adsorption behavior of fenclorim has a particular importance to enhance the sensitivity of voltammetry. At first, peak current increased linearly with accumulation time which indicates that before adsorptive equilibrium is reached, the longer the accumulation time, the more the fenclorim becomes adsorbed and larger is the peak current. However, after 60 sec. accumulation time, the peak current tended to level of, illustrating that adsorptive equilibrium of fenclorim on the mercury electrode surface is achieved. Fig.6.0 shows the effect of accumulation time on peak currents for 0.5 mM of fenclorim. The accumulation time of 60 sec. is used for further studies.

The effects of varying the potential scan rate on the reduction peak current of fenclorim were examined. The reduction peak current increased linearly with the scan rate over the range from 30 mVs⁻¹ to 80 mVs⁻¹. Better sensitivity was observed at 45 mVs⁻¹.

Recovery Experiments

Analysis

Adsorptive stripping voltammetry is a suitable technique for the analysis of fenclorim due to its high sensitivity and resolution. The well resolved stripping voltammetric peak for the analytical purpose



Scheme 1: Electrode Mechanism of Fenclorim.

pH of the supporting electrolyte	$\frac{-E_p}{V}$	$\frac{i_p}{\mu A}$	αn_a	$\frac{D \times 10^6}{cm^2 s^{-1}}$	$\frac{k_{th}^0}{cm s^{-1}}$
2.0	0.90	8.2	0.43	1.50	4.10×10^{-9}
4.0	0.98	7.5	0.32	1.48	8.92×10^{-10}
6.0	1.04	7.1	0.24	1.28	6.23×10^{-12}

Table 1: Typical cyclic voltammetric data of fenclorim at CNTPE; accumulation potential: -0.8V; rest time: 10 sec., stirring rate: 2000 rpm; scan rate: 45 mVs⁻¹; Concentration: 0.5 mM.

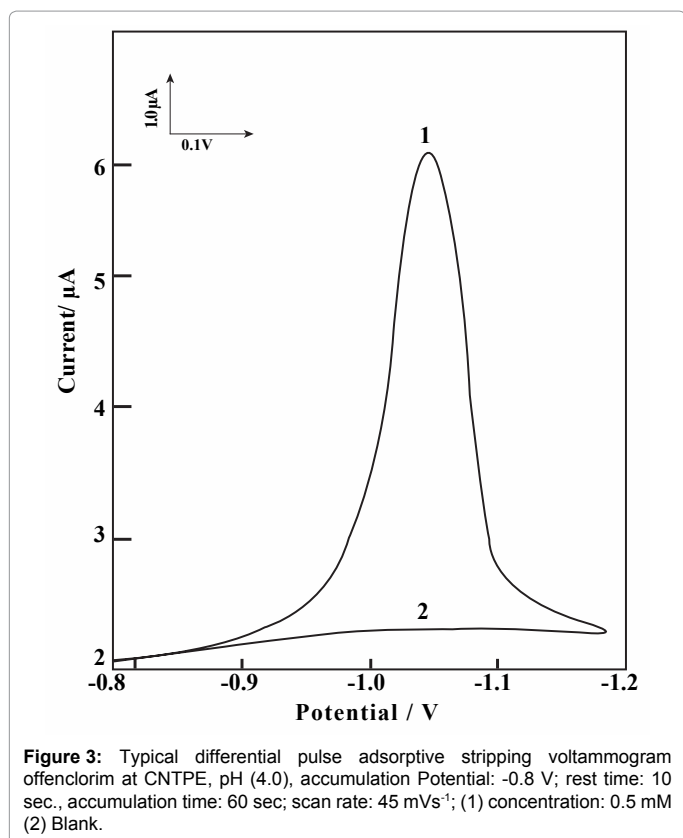


Figure 3: Typical differential pulse adsorptive stripping voltammogram of fenclorim at CNTPE, pH (4.0), accumulation Potential: -0.8 V; rest time: 10 sec., accumulation time: 60 sec; scan rate: 45 mVs⁻¹; (1) concentration: 0.5 mM (2) Blank.

was obtained at pH 2.0 to 6.0, because in the buffer solution of higher alkalinity (pH < 8) the reduction of azomethine group is not easily facilitated owing to the less availability of protons. The peak heights are in linear trend over the concentration range of 1.0×10^{-8} to 1.0×10^{-5} M. The relative standard deviation and correlation coefficient for fenclorim was 0.97% and 0.998 respectively. The lower detection limit for fenclorim compound was 0.92×10^{-7} M.

Recommended analytical procedure

Analytical procedure for the voltammetric determination of

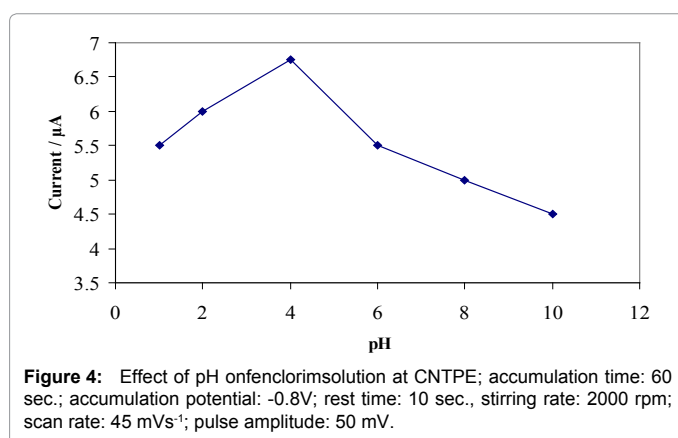


Figure 4: Effect of pH on fenclorim solution at CNTPE; accumulation time: 60 sec.; accumulation potential: -0.8V; rest time: 10 sec., stirring rate: 2000 rpm; scan rate: 45 mVs⁻¹; pulse amplitude: 50 mV.

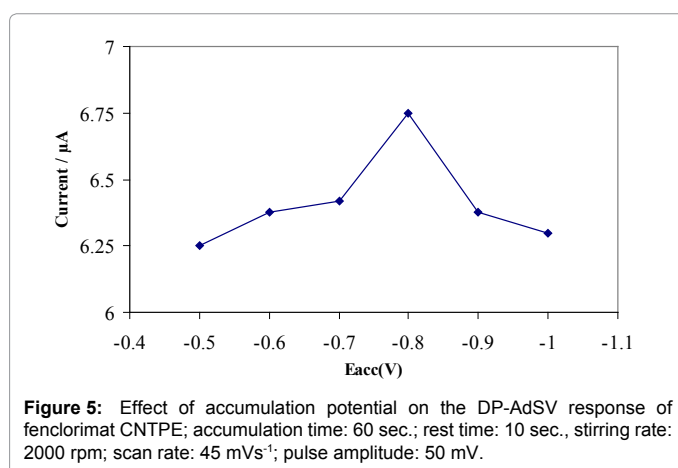
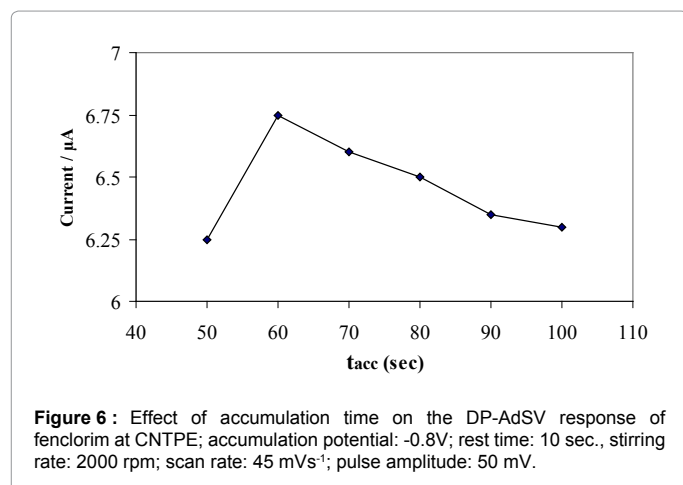


Figure 5: Effect of accumulation potential on the DP-AdSV response of fenclorim at CNTPE; accumulation time: 60 sec.; rest time: 10 sec., stirring rate: 2000 rpm; scan rate: 45 mVs⁻¹; pulse amplitude: 50 mV.

fenclorim as follows. A standard solution of fenclorim (0.5 mM) is prepared in methanol. 1 mL of standard solution is transferred in to cell and made up with 9 mL of supporting electrolyte and then purged with oxygen free N₂ gas for 10 min. prior to each run. After obtaining the voltammogram, small addition of standard solutions are added and voltammogram recorded after each addition under



similar experimental parameters. The optimum conditions for the determination of fenclorim in pH 4.0 with a drop time of 2 sec., pulse amplitude of 50 mV and applied potential of -1.05 V vs. SCE.

Determination of fenclorim in spiked grain samples

The developed analytical procedure has been applied to the quantitative estimation of fenclorim in grain samples. Known amounts of fenclorim were sprayed on grain (wheat, rice) samples (25 g) and left for 1-2 hours. Then the samples are weighed, crushed and homogenized. The extracts were prepared by treatment of the above sample with two 50 mL portions of acetone and evaporated to dryness. The residue of fenclorim dissolved in methanol and transferred to a 100 mL volumetric flask. Results obtained for the determination of fenclorim in grains by DP-AdSV method, range from 98.00 to 99.20% is obtained for two samples, which indicates the high accuracy and reproducibility of the proposed DP-AdSV method. The results are summarized in Table 2.

Determination of fenclorim in spiked water samples

River water samples, which received run-off water from agricultural field, were collected from swarnamukhi river belt, Vakadu, Nellore district, A.P., India. These samples were filtered through a Whatman No.41 filter paper and added with known amount of fenclorim. Aliquots of water samples were taken in a 25 mL graduated tube, to its buffer solution was added and analysed as described above. The average recoveries obtained for fenclorim in two samples ranged from 98.0 to 99.33% and the results are furnished in Table 3.

Conclusion

Analytical procedures are described for the quantitative determination of this compound by using DP-ASV. In the present investigation both standard addition and calibration methods are utilized for the determination of this pesticide in water samples. From the recoveries it has been observed that the proposed method described the successful application of electro analytical techniques for analysis of these pesticides. It also demonstrates that DP-ASV at CNTPE can be conveniently used for the quantitative determination of these pesticides in above described experimental conditions. Hence, the method proposed is crucial and may become an attractive alternative to chromatographic techniques which are more tedious and time consuming.

Sample	Amount added (μg/mL)	Amount found (μg/mL)	Recovery (%)	Standard deviation
wheat	2.0	1.96	98.00	0.0212
	6.0	5.95	99.16	0.0252
	10.0	9.92	99.20	0.0282
	15.0	14.80	98.66	0.0180
rice	3.0	2.96	98.66	0.007
	5.0	4.92	98.40	0.021
	7.0	6.94	99.14	0.007
	10.0	9.90	99.00	0.010

Table 2: Recoveries of fenclorim in spiked grain samples.

Sample	Amount added (μg/mL)	Amount found (μg/mL)	Recovery (%)	Standard deviation
Water-1 (Tank)	2.0	1.97	98.50	0.0312
	6.0	5.96	99.33	0.0152
	10.0	9.93	99.30	0.0382
Water-2 (Irrigation)	3.0	2.95	98.33	0.007
	5.0	4.90	98.00	0.031
	7.0	6.93	99.00	0.017

Table 3: Recoveries of fenclorimin spiked water samples.

References

1. E Smolkova Jr, U Pacakova (1978) Liquid chromatographic separation and behaviour of some substituted s-triazines on a CN-bonded stationary phase. *Chromatographia* 11: 698-702.
2. Vischetti C, Del Buono D, Scarponi L (2003) Italian ryegrass (*Lolium multiflorum* L) to remove terbuthylazine (TBA) from aqueous solution. *Fresenius Environmental Bulletin*.
3. Luciano Scarponi, Daniele Del Buono, Costantino Vischetti (2003) Persistence and detoxification of Pretilachlor and Fenclorim in rice (*Oryza sativa*). *Agronomie* 23: 147-151.
4. Luciano Scarponi, Piero Perucci, Luca Martientti (1991) Conjugation of 2-chloroacetanilide herbicides with glutathione: role of molecular structures and of glutathione S-transferase enzymes. *J Agric Food Chem*.
5. Luciano Scarponi, Daniele Del Buono, Elisa Quagliarini, Roberto D (2012) *Festuca arundinacea* grass and herbicide safeners to prevent herbicide pollution. *Agron Sustain Dev* 29: 313-319.
6. Del Buono D, Prinsi B, Espen L, Scarponi L (2011) Triosephosphate Isomerases in Italian Ryegrass (*Lolium multiflorum*): Characterization and Susceptibility to Herbicides. *J Agric Food Chem* 59: 12109-12115.
7. Scarponi L, Quagliarini E, Del Buono D (2006) Induction of wheat and maize glutathione S-transferase by some herbicide safeners and their effect on enzyme activity against butachlor and terbuthylazine. *Pest Manag Sci* 62: 927-932.
8. Zhang Q, Riechers DE (2004) Proteomic characterization of herbicide safener-induced proteins in the coleoptile of *Triticum tauschii* seedlings. *Proteomics* 4: 2058-2071.
9. Babu TR, Reddy SR, Sujana P (2014) Comparative voltammetric study and determination of carbamate pesticide residues in soil at carbon nanotubes paste electrodes. *J Electrochem Sci Eng* 4: 19-26.
10. Reddy SR, Sreedhar NY, Mohan KC, Nagaraju M (2012) Voltammetric behaviour of carbonyl group containing pesticides topramezone, fenomidone and methiocarb. *Global journal of Science Frontier Research* 12: 45-50.
11. Reddy SR, Mohan KC, Sreedhar NY (2011) Differential Polarographic Behaviour of Nitrogroup Containing Pesticides Dinitramine, Bromethalin and Isopropalin. *International Journal of Scientific and Engineering Research* 2: 1-5.
12. Reddy SR, Babu TR (2013) Voltammetric Determination of Acetophos in Water Samples at CNTPE. *Int J Nanoscience* 12.