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 x 10^{-8} to 1.0 x 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 ingrans (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 a broad 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 triticumtauschi.

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] electroanalytical 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.

\[
C_u = \frac{C_s \times V}{i_1 \times i_2} \times \frac{V}{i}
\]

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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Number of electrons involved in the overall reduction process of fenclorim (Scheme 1) is found to be two and it is evidenced by millimicroumolemetric technique. Controlled potential electrolysis conducted at -1.0 V 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=\(\text{N}\) 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 is

\[
C_n = \text{Concentration of the unknown solution in mM}
\]
\[
V_i = \text{Total volume of the solution (V + v)}
\]
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 $1.0 \times 10^{-8}$ to $1.0 \times 10^{-5}$ 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 $0.92 \times 10^{-7}$ M.

**Recommended analytical procedure**

Analytical procedure for the voltammetric determination of fenclorim is as follows. A standard solution of fenclorim (0.5 mM) is prepared in methanol. 1 mL of standard solution is transferred to cell and made up with 9 mL of supporting electrolyte and then purged with oxygen free N$_2$ 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. 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 form 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 fenclorin 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 quantitave 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 tech-niques which are more tedious and time consuming.

References