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A SENSITIVE DIFFERENTIAL PULSE ADSORPTIVE STRIPPING VOLTAMMETRIC METHOD FOR THE DETERMINATION OF FENOMEDONE

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Abstract:

A sensitive differential pulse adsorptive stripping voltammetric method for the determination of fenomedone with universal buffer solution was described. The method was based on the adsorptive accumulation of fenomedone at Hanging Mercury Drop Electrode (HMDE). The cyclic voltammograms demonstrate the adsorption of this compound at the mercury electrode. A systematic study of various operational parameters that affect the stripping response was carried out by DP-AdSV with accumulation potential of -0.32V and accumulation time 80 sec. From the calibration method, it is observed that the peak height vs concentration plot is found to be linear over the concentration range 1.25×10^{-5} M to 1.25×10^{-9} M. The lower detection limit was found to be 1.05×10^{-9} M.

Key Words: Fenamidone, Dp- Asv, Cereal grains, HMDE, Universal buffer, Cyclic voltammeter

Introduction:

Fenamidone ((S)-1-anilino-4-methyl-2-methylthio-4-phenylimidazolin-5-one) is imidazole fungicide. It is broad spectrum pesticide used to protect crops from fungal diseases.

Susana et al^[1] reported GC/MS for analysis of fenamidone in grapes and wine. De mello et al^[2] reported LC with diod array detection (DAD) method for screening of pesticides including fenamidone in grapes and wines. Danion et al^[3] reported solid phase extraction method coupled with LC/MS for isolation of fenamidone from plants. Luigi et al^[4] analyzed three fungicide residues including fenamidone by applying pseudo first order kinetics and half life method in wine. Schreiber et al^[5] reported triple quadropole

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mass spectroscopy with liquid chromatographic (LC/MS/MS) method for analysis of residues in food stuffs. Lutz alder et al^[6] reported GC/MS, LC/ MS/ MS, GC/ EI/ MS and LC/ ESI/ MS/MS methods for analysis of 500 high priority pesticide residues including fenamidone. Donbroun^[7] reported GC/MS/MS and LC/MS/MS methods for analysis of pesticide residues in fruits and vegetables. Lambropoulou et al^[8] reported coupling of head space solid space micro extraction with ultra sonic extraction for determination of fenamidone residues in birds by using GC.

So far we have not come across any such study in the literature on the electrochemical reduction behaviour of fenamidone. Therefore, we have under taken the present work to establish the experimental conditions for understanding the electro chemical behaviour of fenamidone from the measurement of cyclic voltammetry, differential pulse adsorptive stripping voltammetry, controlled potential electrolysis and milli coulometry. it is also aimed to devlope DP-Asv method for analysis of fenamidone in its pure form and in spiked water samples.

Materials and methods

The electrochemical measurements were carried out with model Metrohm 757 VA computrace. Three electrode systems consisting of hanging mercury electrode (HMDE) as working electrode, Ag/AgCl (salt KCl) was used as a reference electrode and a platinum wire as an auxiliary electrode which displays negative potential range. Elico Li-129 model glass calomel combined electrode was employed for measuring pH values. All reagents used were of analytical reagent grade. Double distilled water was used throughout the. In the present investigation universal buffers of pH range 2.0 to 12.0 are used as supporting electrolytes and are prepared by using 0.2 M boric acid, 0.05M

citric acid and 0.1M trisodium orthophosphate solutions.

Result and discussion

The electrochemical reduction of fenamidone was studied in universal buffer and consisted of a single step process in the pH range 2.0-6.0. The effect of pH on the voltammograms have been investigated by recording the current voltage curves of fenamidone at concentration of 1.0×10^{-7} M. For experimental results obtained by CV and DP-Asv, the facile simultaneous reduction of carbonyl group in fenamidone in the present study found to proceed with a 2 electron addition. Typical voltammograms are shown in figures 1-2. The DP-AdSV behaviour of fenamidone (1×10^{-7} M) was investigated over pH range 2.0 to 6.0 at the HMDE. The Faradic response exhibited is an adsorptive reduction peak (Fig. 1) which corresponded to the reduction of carbonyl group ($>C=O$) of fenamidone. Both standard addition and calibration methods are employed for the determination of fenamidone in spiked water and soil samples. The effect of pH on the voltammograms has been investigated by recording the current-voltage curves for fenamidone at a concentration of 0.5 mM in universal buffer systems over the pH range 2.0 to 6.0. Fenamidone exhibits a single well defined wave/peak at pH 2.0 to 6.0 in all techniques corresponding to the reduction of carbonyl group. Typical cyclic voltammograms have been shown in Fig. IV.8. Reduction wave is not obtained for fenamidone in basic medium due to the precipitation of electro active species.

Effect of pH

The DP-AdSV current of fenamidone is recorded as a function of potential in universal buffer solutions of varying pH (2.0 to 6.0). The reduction of fenamidone at HMDE is found to be pH dependent. The

recorded DP-AdSV peak is mainly due to the reduction of the carbonyl group to the corresponding hydroxy product. It can be observed from (Fig. 3) that the maximum peak current is obtained with pH 4.0. Reduction peak is not obtained for fenamidone in basic medium due to the precipitation of electro active species.

Effect of accumulation potential

The effect of accumulation potential on the peak current is studied over the potential range -0.62 V to -0.02 V. The highest peak current is observed for an accumulation potential of -0.32 V. A gradual decrease in the peak height was observed with the change in the potential to more negative or less negative potentials than -0.32 V. Therefore, an accumulation potential of -0.32 V offered the best signal to background characteristics and was used in all subsequent studies.

Effect of accumulation time

DP-AdSV peak height of 0.5 mM fenamidone after different accumulation times and a plot of the resulting current versus accumulation time have been shown in fig. At first the current increases linearly with time and then starts to level off. The deviation from linearity occurs after the accumulation time of 80 sec.

Effect of scan rate

The effect of varying potential scan rate on the reduction peak current of fenamidone are examined. The reduction peak current increased linearly with the scan rate over the range from 25 mVs⁻¹ to 100 mVs⁻¹. Better sensitivity is observed at 45mVs⁻¹.

Analysis

Well defined and well resolved wave / peak of fenamidone obtained at pH 4.0 is used for the quantitative determination of fenamidone in water and grains. Both standard addition and calibration methods are used for the quantitative estimation of the above said

compound. From the calibration method, it is observed that the peak height vs concentration plot is found to be linear over the concentration range 1.25×10^{-5} M to 1.25×10^{-9} M. The lower detection limit was found to be 1.05×10^{-9} M.

Recovery experiments

Recommended analytical procedure

1 mL of standard solution of fenamidone (0.5 mM) is taken in voltammetric cell and 9 ml of the supporting electrolyte (pH 4.0) is added and purged with O₂ free N₂ gas for 10 minutes prior to each run. The optimum conditions for the analytical determination at pH 4.0 were found to be a drop time of 2 sec., a pulse amplitude of 50 mV and an applied potential of -0.32 V. The correlation coefficient and relative standard deviation obtained using the procedure are found to be 0.996 and 1.25% respectively for 10 replicants.

Fenamidone in cereal grains

The above mentioned AdSV procedures were applied for the determination of fenamidone in cereal grains such as maize and barley. Grain (maize and barley) samples (50 g) were spiked with known amount of fenamidone and left for 2-3 hrs. Then the samples are crushed into a fine powder. Then extracted with acetonitrile. The organic solvent was evaporated to dryness. The residue of fenamidone dissolved in DMF and transferred into a 50 mL volumetric flask. Voltammograms recorded for the solution. The results obtained for the estimation of fenamidone in cereal grain by DP-AdSV are reported in table 2. The average recovery obtained for fenamidone in maize and barley ranged from 97.80 to 99.80%.

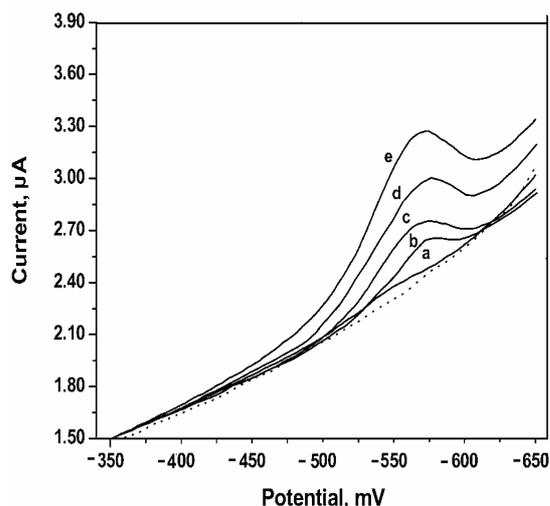


Fig-1, Voltammograms of fenomidone at HMDE

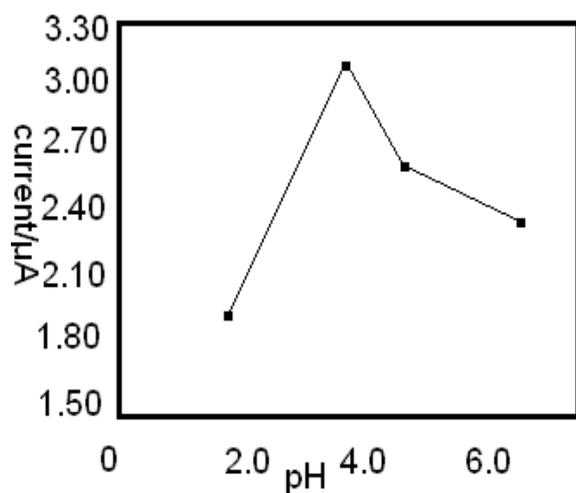


Fig-2, Cyclic Voltammograms of fenomidone at HMDE

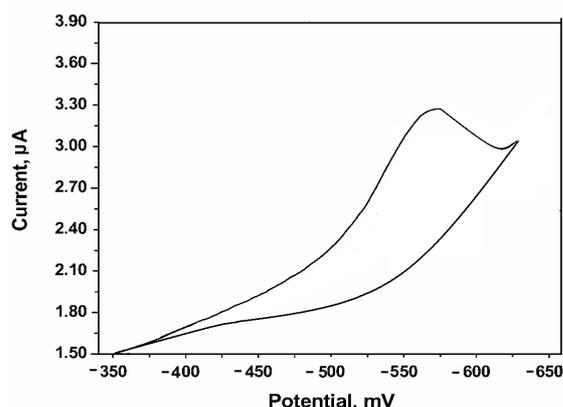


Fig-3, Effect of pH on Peak Current

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