Electrochemical Investigation of carbonyl group containing pesticide monalide in water samples by using differential pulse adsorptive stripping voltammetry

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ABSTRACT

In this investigation electrochemical behavior of carbonyl group containing pesticide monalide is studied and its residues in water samples is determined by using differential pulse adsorptive stripping voltammetry. In this investigation hanging mercury droop electrode is used as working electrode and universal buffer with pH range 4.0-6.0 is used as supporting electrolyte. Investigated compound was found to exhibit well defined peak at pH 5.0. Peak currents were linear over the concentration range of 1.0x10^{-5} M to 1.0x10^{-10} M with lower detection limit of 1.09x10^{-10} M. The relative standard deviation and correlation coefficients were found to be 1.15%, 0.998 respectively for 10 replicates. Calculations made by standard addition method.

Key words: Differential Pulse Adsorptive Stripping Voltammetry, universal buffer, hanging mercury droop electrode, water samples.
INTRODUCTION

Carbonyl group containing pesticides are playing vital role in the agriculture field. These pesticides are widely used as pre and post emergent weed control agents for a wide variety of crops, namely corn, sorghum, wheat, rice, sugar cane and for fruits, vegetables and wine yards, consequently, they are found in river water[1-5]. Monalide (4’-chlooro-2,2-dimethylvaleranilide) (C_{13}H_{18}ClNO) is herbicide Several analytical methods were used for the determination of traces of monalide in different matrices that is in biological and environmental. William C. steen and Timothy w. collette determined Microbial Degradation of Seven Amides by Suspended Bacterial Populations by using chromatographic techniques[6]. Khizar hayat et al. determined pesticide residues in blood samples of villagers involved in pesticide application at District Vehari (Punjab), Pakistan by using gas chromatography[7]. Guo-Fang Pang, determined 405 pesticide residues in grain by accelerated solvent extraction then gas chromatography-mass spectrometry or liquid chromatography-tandem mass spectrometry[8]. But there is no voltammetric method[9] in literature cited above so in the present article a selective and sensitive DP-ASV method were reported.

EXPERIMENTAL

Apparatus and electrodes

Voltametric assays were performed using a model 364 polarographic analyzer supplied by Princeton applied research corporation,(Princeton,NJ USA)coupled with a kipp and zonen BD8x-t recorder.a HMDE was used as working electrode and a saturated columnel electrode (SCE) as the reference electrode. Voltamograms were recorded with a unit supplied by metrohm (herisau,Switzerland)coupled with E 506 polarocardi and E 612 VA scanner. Cyclic voltammograms obtained by a digital electronics model 2000x-y/t recorder (Mumbai, India) in connection with the above unit. The DME used had an area of 0.223cm² at a drop time of 2s. A hanging mercury drop electrode (HMDE) used had an area of 0.223cm² in cyclic voltammetry. In all the above experiments platinum wire was used as auxiliary electrode all the experiments were performed at 25°C measurements were carried out with elico digital pH meter (Hyderabad, India).The millicoulometric apparatus used was supplied by radelkis (Budapest,hungary) controlled potential electrolysis was carried out using a techno potentiostat (tech.ini electronics, lucknow,India) in a modified cell with a mercury pool cathode saturated calomel reference electrode.

Reagents and solutions

Pure samples obtained from RANKEM india limited. The purity of sample was tested with tin layer chromatography and melting point determinations. Stock solution of pesticide under investigation was prepared in dimethyl formamide. Universal buffer containing 0.2Mboric acid, 0.05Mcitric acid and 0.1M trisodium orthophosphate were used as supporting electrolyte.

RESULT AND DISCUSSION

Fig. 1 exhibits voltammetric response for 1 x 10^{-5} M monalide at HMDE. The pH of a solution is critical factor affecting both the rate and equilibrium state of the reduction process and the rate of the electrode reaction. The influence of the pH on the DP-ASV response was studied at HDME of the 1 x 10^{-5} M monalide with, between the pH ranges 2.0 to 6.0. It can be observed from Fig. 2 that the maximum peak currents are obtained with pH 5.0.

Voltamograms obtaiend for increasing values of the scan rate showed the existence of a linear dependence of the peak current intensity on the scan rate between 10 to 60 mVs^{-1}. The peak currents were directly proportional to the scan rate indicating that the system was adsorption controlled.

Reduction mechanism of monalide has been studied over the pH range from 2.0 to 6.0. A single well resolved peak is observed throughout the pH range and this single peak is due to the reduction of carbonyl group in 2 electron process (scheme-1) to the corresponding hydroxyl group. Typical cyclic voltammogram is shown in Fig.3. Number of electrons involved in the electrode process determined by employing millicoulometric technique and it is found to be 2 in pH 4.0 for monalide, which indicates the final product to be hydroxyl compound.

Kinetic data

The values obtained for transfer coefficient, diffusion coefficient and heterogeneous forward rate constant for monalide are given in Table 1. The diffusion coefficient values evaluated from cyclic voltammetric technique were

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found to be in good agreement indicating the diffusion controlled. The diffusion coefficient values are decreasing with an increase in pH values. The reason may be due to the decrease in availability of protons with an increase in pH of the supporting electrolyte. The rate constant values in general found to decrease with an increase in pH indicating that the electrode reaction tends to become more and more irreversible with change in pH.

**Recovery experiments**

**Analysis**

The voltametric peak is due to the reduction of carbonyl group and therefore preferred for the analysis of water samples. The optimum pH for obtaining well resolve peak for quantitative determination of monalide are found to be 5.0.

Investigated compound was found to exhibit well resolved peak at pH 5.0, and the sharp well resolved peak was chosen for quantitative studies. Peak currents were linear over the monalide concentration range of $1.0 \times 10^{-5}$ M to $1.0 \times 10^{-10}$ M with lower detection limits of $1.09 \times 10^{-10}$ M. The relative standard deviation and correlation coefficients were found to be 1.15%, 0.998 respectively for 10 replicates.

**Recommended analytical procedure**

A standard solution of monalide ($1.0 \times 10^{-5}$ M) prepared in DMF. 1 mL of standard solution were transferred into a cell and made up with 9 mL of supporting electrolyte (pH 4.0) and deoxygenated with nitrogen gas for 10 min, subjected to voltammetry. After obtaining the voltammogram, a small increment of standard solution of monalide is added to voltammetric cell and deoxygenated for 10 min and voltammograms were recorded under similar conditions and validity of method was checked. In the same manner 10 voltammograms are recorded for 10 standard additions. The optimum conditions for analytical determination were found to be at pH 5.0.

**Determination of monalide in spiked water samples**

Known amount of pesticide is added to water sample collected from swarna mukhi river and from fields beside swarnamukhi river at vikadu, Nellore district Andhra Pradesh india. after 48 hours the aliquots separated and evaporated and then the residues dissolved in DMF filtered through a Whattman filter paper No.41 and filtrate was centrifuged at 1850g for 10 min The filtrate was quantitatively transferred into a 50mL calibrated flask and made up .Aliquots transferred into cell and analyzed by followin recommended analytical procedure. Results obtained for the determination of the herbicide in water samples are presented in Table 2. Mean recoveries obtained for monalide ranged from 97.50 to 98.00 %.

**CONCLUSION**

Electroanalytical procedures have been identified as powerful methods for the analysis of different pesticides down to $10^{-11}$ M level with reproducible results. The described electroanalytical method have conveniently been applied and which has been routinely adopted for the determination of pesticides in food grains, vegetables and other environemntal samples.

**Table.1: Cyclic voltammetric data of monalide, Concentration: $1.0 \times 10^{-5}$ M; Scan rate: 45mVs$^{-1}$**

<table>
<thead>
<tr>
<th>pH</th>
<th>$-E_p$</th>
<th>$i_p$</th>
<th>$\alpha n_a$</th>
<th>$D \times 10^6$</th>
<th>$k_{f_b}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>0.36</td>
<td>5.81</td>
<td>0.99</td>
<td>5.66</td>
<td>2.60 x $10^{-6}$</td>
</tr>
<tr>
<td>4.0</td>
<td>0.43</td>
<td>5.73</td>
<td>0.92</td>
<td>5.49</td>
<td>1.57 x $10^{-7}$</td>
</tr>
<tr>
<td>6.0</td>
<td>0.61</td>
<td>5.55</td>
<td>0.88</td>
<td>5.22</td>
<td>6.47 x $10^{-9}$</td>
</tr>
</tbody>
</table>
Table 2: Recoveries of monalide in spiked water samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Amount added µg/mL</th>
<th>Amount found µg/mL</th>
<th>recovery (%)</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>River water</td>
<td>1.0</td>
<td>0.975</td>
<td>97.50</td>
<td>0.055</td>
</tr>
<tr>
<td>Agriculture water</td>
<td>1.0</td>
<td>0.98</td>
<td>98.00</td>
<td>0.026</td>
</tr>
</tbody>
</table>

Scheme 1: Reduction mechanism of monalide at pH 4.0

Fig 1: Voltammogram of monalide at pH 5.0 concentration: $1.0 \times 10^{-5}$M.
Fig 2: Effect of pH on peak current in monalide

Fig 3: Typical cyclic voltammogram of monalide for an accumulation time of 80 sec at HMDE, accumulation potential: -0.6V; Rest time: 10 sec; stirring rate: 1500 rpm; scan rate: 45 mV s$^{-1}$; concentration: 1.0x10$^{-5}$M; pH: 5.0.

REFERENCES

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