Research Article

VOLTAMMETRIC BEHAVIOR OF DIMETHAMETRYN AND ITS DETERMINATION IN SOIL AND WATER USING ADSORPTIVE STRIPPING VOLTAMMETRY AT HANGING MERCURY DROP ELECTRODE

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A B S T R A C T

A sensitive method for the determination of the herbicide dimethametryn by adsorptive stripping voltammetry using a hanging mercury drop electrode at pH 4.0 was described. The cyclic voltammogram of dimethametryn demonstrate that compound was adsorbed at the surface of mercury electrode and the overall reduction process was under controlled diffusion. The adsorptive peak was observed at -0.9V and peak response was measured with respect to pH, accumulation time, potential, and scan rate. The calibration plot was found to be linear from the concentration range 3.0×10^{-9} to 4.0×10^{-7} mol/L with a detection limit 2.0×10^{-9}. Also interference of some other pesticides on dimethametryn determination was evaluated. Finally the developed method was potentially applied for determination of dimethametryn in soil and water samples.

INTRODUCTION

Herbicides such as triazines are used in agriculture for crop protection and for fighting seaweed and plants on wet grounds, water reservoirs and drainage ditches. The extend utilization of triazine herbicides in agriculture makes possible their access to the environment.

Dimethametryn [(2-methyl thio-4-ethyl amino-6-(1,2-dimethyl propyl) amino-1,3,5 triazine)] is herbicide which belongs to the 5-triazine family. It has been demonstrated that 1,3,5 triazines are high stable compounds and have mutational and sometimes pathological effects on living organisms[1]. They have long persistence which leads to accumulation in soil and crops that have been treated directly[2]. Prevention of negative effects of herbicides requires a systemic control of their remains in soil, water and agricultural samples.

In recent years, various analytical methods have been developed for the determination of herbicides. The determination of triazine herbicides by micellar electrokinetic capillary chromatography with diode array detection was developed[3]. Five classes of triazine herbicides were studied by combined high performance liquid chromatography-mass spectrometry were done on a reversed phase C_8 column[4]. High performance thin-layer chromatography with automated multiple development was used to screen water samples for pesticides[5].

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Megersa *et al.* reported trace enrichment and sample preparation of alkyl thio-s-triazine herbicides in environmental water using a supported liquid membrane technique in combination with HPLC[6]. Tanabe *et al.* developed a gas chromatography-mass spectrometry method for the determination of concentration of herbicides in both dissolved phase and the suspended phase of river water[7]. Pesticide residue analysis in food stuffs by applying capillary gas chromatography with atomic emission[8].

However in the above mentioned methods are often complex time consuming and involves expensive apparatus. For these reasons, there is need a method which is faster, simple and accurate for the determination of dimethametryn in environmental samples. Electrochemical methods, such as DC and DPP have also been reported in the literature[9]. In electroanlytical chemistry Adsv is widely recognized as one of the most sensitive methods[10]. Adsv is often an appropriate electroanalytical technique for trace determination of pesticides including biological active substances and environmental samples[11-15]. In contrast to the conventional voltammetry, the enhanced sensitive of stripping voltammetry is attributed to the accumulation of surface concentration of analyte from pre-concentration procedure.

In the present investigation dimethemetryn has been selected to get more information on the reduction mechanism of azo-methine groups and electrode kinetics concerned using cyclic voltammetry. In addition, differential pulse adsorptive stripping voltammetry has also been employed to work out

analytical procedure in trace level estimation of the herbicide in soil and water samples.

MATERIALS AND METHODS

Materials

Dimethametryn was obtained from Sigma-Aldrich with declared purity of 99.4%. Dimethametryn (1×10^{-3} mol/L) stock solution were prepared by dissolving an appropriate amount of herbicide in dimethylformamide. The supporting electrolyte was universal buffers of pH range from 2.0 to12.0 was prepared by using 0.2 mol·L^{-1} boric acid, 0.05 mol·L^{-1}citric acid and 0.1 mol·L^{-1} trisodium orthophosphate(Merck). All the chemicals used were of analytical grade and used without further purification. Throughout the experiment double distilled water was used.

Methods

Appropriate amounts of dimethametryn stock solution were placed in a cell containing a buffer solution. A stream of oxygen free nitrogen gas was purged through the solution for 10 min. The voltammetric response was obtained using a pulse repetition time of 2s, with amplitude of 50mV and a scan rate of 20mV/s. For multi-step standard addition experiments, small increments of the standard solution (0.2 mL) are added and the voltammograms are recorded for each addition under similar conditions. To select a suitable medium for Dp-Adsv studies various supporting electrolytes such as 0.1 mol.dm^{-3} HCl, 0.1 mol.dm^{-3} HClO$_4$, and universal buffer were tested. The most well defined signal with a reasonably high sensitivity was obtain with a universal buffer of pH 4.0. The optimum conditions for the determination of dimethametryn at pH 4.0 were found to be pulse amplitude of 50 mV and applied potential of -0.9V respectively. The above described procedure was successfully employed for the determination of dimethametryn in their formulations, environmental samples like vegetable, soil and water samples.

Differential pulse adsorptive stripping voltammetry (Dp-Adsv) and cyclic voltammetry measurements were carried out using metroham E-506 (Herisau, Switzerland) polarecord in combination with a metroham 663VA stand and 612VA scanner in conjunction with a HMDE. Cyclic voltammetric studies were performed with 797VA computrace. The three-electrode system was completed by means of a pt wire as a counter electrode and saturate calomel electrode as the reference electrode. All experiments were performed at room temperature. The pH measurements were made by a Metrohm 632 pH-meter. The synthesized compounds were characterised by Fourier transform infra-red (FTIR) spectrometer (Perkin Elmer, Model: Spectrum Two). The compounds were thoroughly grounded with potassium bromide to prepare a pellet under a hydraulic pressure of 600 dynes/m^2, and the spectra were scanned from 400 to 4000 cm^{-1}.

RESULTS AND DISCUSSION

Cyclic voltammetric studies

Typical cyclic voltammograms of dimethametryn are depicted in Fig.1. Cyclic voltammetric behaviour of dimethametryn shows one irreversible cathodic peak. According to the molecular structure of dimethametryn this peak corresponds to the cathodic reduction of the azomethine group >CH=N in four

electron process (Scheme I). The reduction process of these compounds was found to be diffusion controlled and adsorption on the electrode surface in the buffer systems studied as evidenced from linear plots i_p *vs.* $v^{1/2}$ passing through origin. The shift of peak potential *(E$_p$)* towards more negative values with increase in concentration of depolarizer, shows that the electrode processes 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 that the irreversible nature of the electrode processes. The experimental constancy of $i_p/Cv^{1/2}$ with scan rate (v) has shown the electrode process to be free from any kinetic complications. The number of electrons involved in the electrode process to be four for the dimethametryn by employing the millicoulometry. The number of protons involved in the rate determining step of the electrode process found to be four. Controlled potential electrolysis experiments were carried out at -0.3 V *versus* SCE at pH 4.0 for both compounds. The reduction products were confirmed by FTIR spectral analysis. The significant N-H stretching frequency appears above 3300 cm^{-1} and C=N stretching frequency of peak appears from 1640 cm^{-1} to 1700 cm^{-1}.
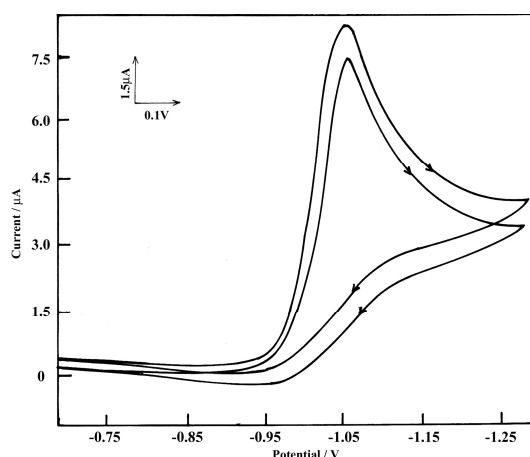

Figure 1 Typical cyclic voltammograms of dimethametryn at pH 4.0.Concentration: 0.5 mM; Scan rate: 50 mVs^{-1}

Differential pulse-adsorptive stripping voltammetric studies

Differential pulse-adsorptive stripping voltammetric studies were performed with hanging mercury drop electrode. From the Fig. 2, results demonstrate that an adsorption process occur on the mercury electrode surface which can be used as an effective pre-concentration step prior to voltammetric measurement. An exhaustive study of dependence of adsorptive peak currents on pH, accumulation potential, accumulation time and scan rate was performed using dimethametryn concentration at 1.0 x 10^{-7} mol/L.
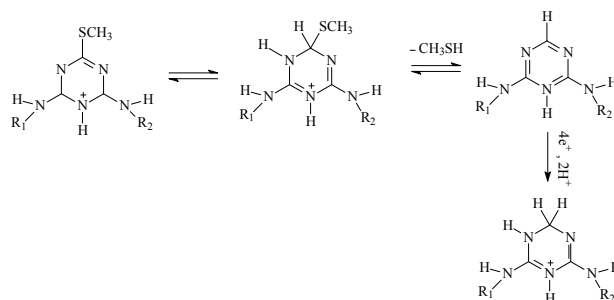

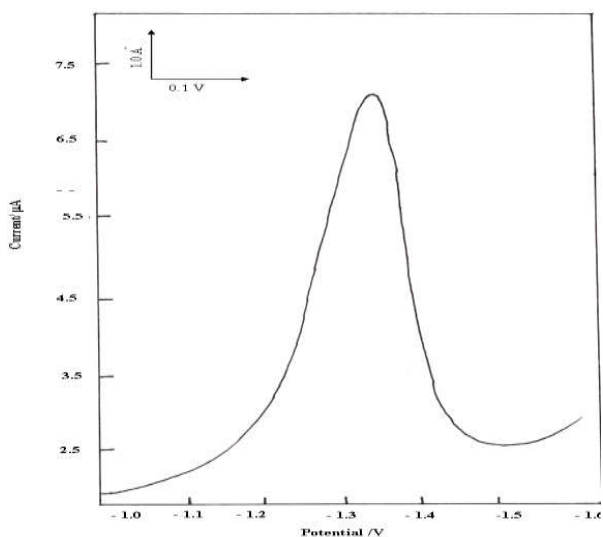**Figure 2** Reduction mechanism of Dimethametryn

Figure 3 Typical differential pulse adsorptive stripping voltammogram of dimethametryn at HMDE (pH 4.0). (a) Accumulation time: 60s. Accumulation potential: -0.9 V; rest time: 10s., stripping rate : 2000 rpm, scan rate : 20 mVs⁻¹, concentration : 1 × 10⁻⁷ mol.dm⁻³

Influence of pH

The pH of a solution is a critical factor affecting the rate and equilibrium state of the accumulation process and rate of the electrode reaction. The influence of the pH on peak current of dimethametryn was studied in the pH range of 2-6. Maximum peak current was obtained in the pH range 2-4 (Fig.3). When the pH value exceeded 4.5, the peak potentials shifted towards more negative values, indicating proton participation in the reduction process. In this work a pH value of 4 was selected for further experiments, because the optimum pH for production of homogeneous mercury film was found to be pH 4 and this pH was also near to the optimum pH for determination of dimethametryn. The influence of the pH on the Dp-AdSV response was studied at HMDE at 1×10^{-7} mol/L with accumulation times 60s.
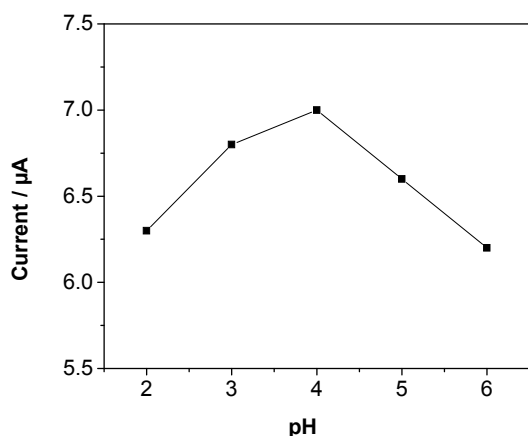

Figure 4 Effect of pH on dimethametryn solution at HMDE. Accumulation time: 60s; accumulation potential: -0.9V; rest time: 10s; stirring rate: 2000 rpm; Scan rate: 20 mVs⁻¹; pulse amplitude: 50 mV

Influence of accumulation potential

The accumulation potential also plays a major role in affecting the curve sensitivity. The optimal pre-concentration potential condition is between -0.7 to -1.5 V. Fig.4 shows the effect of the accumulation potential on the magnitude of the stripping peak current. It can be seen that the largest peak current was

obtained at a potential of -0.9V for dimethametryn. The sensitivity decreases sharply at potential less than -0.9 V. Thus an optimum pre-concentration potential -0.9 V are used in the s
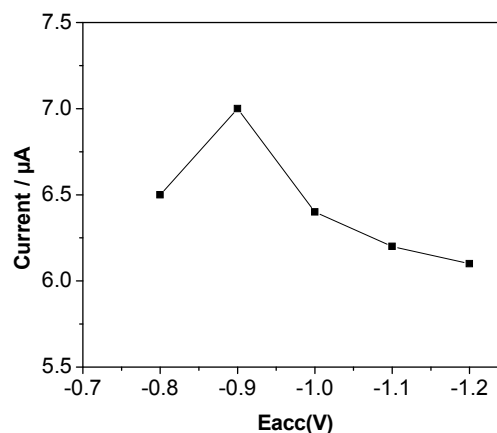

Figure 5 Effect of accumulation potential on the DP-AdSV response of dimethametryn

Influence of accumulation time

The adsorption behavior of dimethametryn is particular importance to be used to enhance the sensitivity of voltammetry. The effect of accumulation time on peak currents for 1x10⁻⁷ mol/L dimethametryn in universal buffer pH 4.0 was investigated. Maximum peak current was obtained at 60s. Therefore accumulation time of 60s was chosen for further a
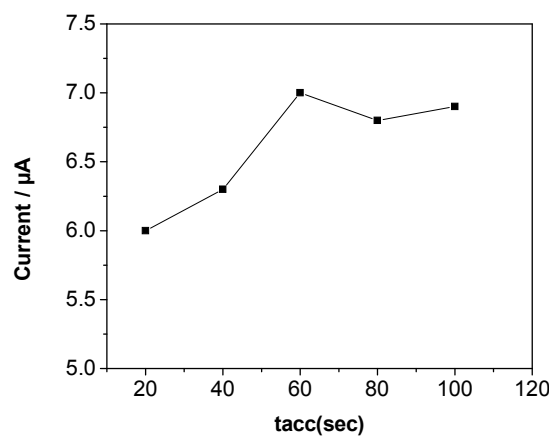

Figure 6 Effect of accumulation time on the DP-AdSV response of dimethametryn at HMDE. Accumulation potential: -0.9V; rest time: 10s; Scan rate: 20 mVs⁻¹

Influence of Scan rate

The effect of scan rate on the peak current was studied over the range of 5-80mVs⁻¹. When scan rate was increased from 5 to 20mVs⁻¹, the peak current increased. However, at scan rate higher than 20mVs⁻¹ no remarkable increase in peak current was observed. In addition, at scan rates above 25mVs⁻¹ baseline increased. So, a scan rate of 20mVs⁻¹ was selected as the optimum value. The stripping currents were not modified when varying the rest period. The chosen value, 15 s, is sufficient to allow the formation of a uniform concentration of the analyte in the mercury drop and to ensure that the subsequent stripping step is performed in a quiescent solution. Other instrumental parameters, such as drop size and pulse

amplitude, which directly affect the voltammetric response, were optimized. Under the optimum conditions of pH 4, 60s of accumulation time, -0.9V accumulation potential, $20mVs^{-1}$ scan rate and 50mV pulse amplitude a linear relationship was obtained between concentration range 3.0×10^{-9} to 4.0×10^{-7} mol/L. The calibration plot was found to be linear with correlation coefficient of 0.9997. A detection limit of 2.0×10^{-9} was estimated from quantization of dimethametryn under the optimum conditions.

Table 1 Statistical parameters

Parameter	Dimethametryn
Linearity range	3×10^{-9} to 4×10^{-7} mol/M
Correlation Coefficient	0.9997
LOD	2.0×10^{-9}

Determination of dimethametryn in water samples

A 1000 mL sample of tap water was spiked with different concentrations of dimethamertyn and shaken for few minutes. The sample was then filtered through a Whatmann Nylon membrane filter and filtrate passed through a sep-pak C^{18} cartridge previesouly activated with 10 mL of dichloromethane, elution was carried out with 30 mL of dichloromethane. The organic phase was evaporated in an ordinary rotatory vacuum evaporator. The residues was dissolved in acetonitrile and added to cell containing a buffer solution. The determination of dimethametryn is carried out by DP-AdSV using a calibration graph obtained by adding aliquots of a stock solutions to a blank solution subjected to the above treatment. Recovery studies yielded the results are furnished in Table 2. These results indicate that the DP-AdSV method may serve as a screening protocol for the determination of dimethametryn in spiked water samples.

Determination of dimethametryn in soil samples

Collected soil sample was dried and allowed to pass through a 2.8 mm sieve and subsequently homogenized in a ball mill. Aliquots (50g) of soil sample were added with known amount of both solutions and kept in contact for 24 h. After this period, the mixture was extracted with 20 mL of dichloromethane three times. The solvent evaporated and the residue was dissolved in acetonitrile and subjected to voltammetry by means of standard addition method. The quantity of herbicide was estimated.

Table 2 Recovery studies for dimethametryn in spiked soil and water samples by DP-AdSV

Name of the Sample	Labelled amount (mg)	Amount found (mg)	Recovery (%)	Standard deviation
Soil	5.0	4.71	94.20	0.014
	10.0	9.70	97.00	0.021
	15.0	14.37	95.80	0.028
Water	5.0	4.91	98.20	0.023
	10.0	9.91	99.10	0.014
	15.0	14.92	99.46	0.012

Quantitative determination of dimethametryn in spiked Vegetable samples

In the present investigation, vegetables such as tomato and potato have been chosen for the determination of dimethametryn. Known amount of dimethametryn was sprayed on tomato and potato and left for 1-2 h. The extracts were prepared by the treatment of a crushed sample with 100 mL of

acetone. Then the extract was allowed to dry. The residue of dimethametryn was dissolved in DMF and transferred into a 50 mL volumetric flask. Then the voltammograms were recorded in the same manner as described earlier. The results obtained by the DP-AdSV are shown in Table 3.

Table 3 Recovery studies for dimethametryn in vegetable samples

Name of the Sample	Labelled amount (mg)	Amount found (mg)	Recovery (%)	Standard deviation
Tomato	2.0	1.82	91.00	0.014
	4.0	3.70	92.50	0.021
	6.0	5.47	91.16	0.028
Potato	2.0	1.71	85.50	0.023
	4.0	3.81	95.25	0.014
	6.0	5.79	96.50	0.012

Quantitative determination of dimethametryn in spiked irrigation water samples

An attempt has also been made to estimate dimethametryn quantitatively in spiked irrigation water samples by using the above procedure. Results obtained for the determination of dimethametryn in irrigation water samples are given in Table 4.

Table 4 Recovery studies for dimethametryn in spiked irrigation water samples

Name of the Sample	Amount added (mg)	Amount found (mg)	Recovery (%)
Irrigation water (Dimethametryn)	2.0×10^{-8}	1.77×10^{-8}	88.50
		1.87×10^{-8}	93.50
		1.88×10^{-8}	94.00

Interferences

The interferences of some inorganic cations (Zn^{+2}, Cd^{+2}, Co^{+2}, Cu^{+2}) and some anions (NO^{-3}, SO^{-2}_4 ClO^{-2}_4, I^-) most of these species are commonly present in soil and irrigation water. The reduction potential of Pb^{+2} is close to those of dimethametryn and decreases the stripping signal of both compounds by 30%. The remaining cations do not show any appreciable change in the stripping signals of both compounds. In the presence of Cl^- or I^- metal ions, interference effect was observed at 1×10^{-2} mol/L .The peak heights decreases by 10 and 16% respectively.

CONCLUSIONS

The electrochemical reduction of dimethametryn under experimental conditions described in this work is an irreversible diffusion controlled process. An adsorption process of two compounds occurs on the mercury electrode surface that can be used as an effective pre-concentration step prior to the voltammetric measurement. The percentages of recoveries in soil and water samples are 94.20% to 97.00% and 98.20% to 99.46%, respectively. Recovery water samples are comparatively more than the soil samples. This indicates the potentiality, accuracy and reproducibility of the proposed differential pulse adsorptive stripping voltammetric method in determination of trace amounts of herbicide.

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