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Electroanalysis of mevinphos in spiked human urine samples using polythiophene based nanosensor

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ABSTRACT

The electrochemical reduction behavior of Mevinphos has been studied by using, differential pulse voltammetry, cyclic voltammetry,. The determination of mevinphos in spiked human urine samples is carried out by using polythiophene modified glassy carbon electrode. Mevinphos exhibited single, well-defined peaks at pH 2.0 in Britton–Robinson (BR) buffer solution. The standard deviations of various spiked urine samples were found in between 0.060 to 0.20 and relative standard deviations were observed in between 0.50 to 1.21%. © 2013 Trade Science Inc. - INDIA

KEYWORDS

Mevinphos;
 Polythiophene coated
 glassy carbon electrode;
 Voltammetry;
 Spiked human urine
 samples.

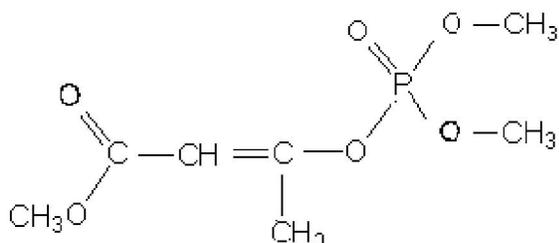
INTRODUCTION

Organophosphate pesticides used in agriculture are highly toxic to various crop pests and insects^[1]. Due to their toxicity, they present serious health hazards when enter food and water. Hence, accurate determination of these pesticides is more important to control pesticide pollution. The most widely used methods for the determination are based on GC^[2] LC^[3] and HPLC-UV-MS^[4]. Electroanalytical techniques offer simple and reliable methods for the analysis of pesticides^[5]. The sensitivity and selectivity of voltammetric techniques can be increased manifold by using chemically modified electrodes for their detection. OP pesticides are determined using electrode modified with clay^[6], hexadecane^[7], ZrO₂^[8], nafion^[9] Bismuth film^[10] and Nano Ag/nafion^[11]. Conducting polymers have attracted attention because of their well-defined electrochemical

properties. Conducting polymer modified electrodes provide enhanced sensitivities and fast electrochemical response based on increased surface area of the electrode and electrical conductivities. A large number of investigations are available on the use of conducting polymer based sensors and biosensors for the determination of pesticides. Acetylcholine esterase biosensor based on CNT/Polypyrrole-polyaniline copolymer is developed for the determination of OP pesticides^[12]. Au-polypyrrole nanocomposite based on acetylcholine esterase is used for the determination of methyl parathion^[13]. Conducting polymer/multi walled carbon nanotube based electrodes are employed for the determination of some common pesticides^[14]. Polypyrrole modified electrode is used for the determination of pesticides, carbendazim and isoproturon^[15].

Mevinphos (2-methoxycarbonyl-1-methylvinyl dimethyl phosphate) is an organophosphate insecticide

which is most commonly used for the control of mites and insects. The structure is shown in Scheme 1. It acts as an acetylcholinesterase inhibitor to control insects in a wide range of crops. The present work is focussed on the determination of mevinphos in spiked human urine samples by using polythiophene coated glassy carbon electrode by differential pulse adsorptive stripping voltammetry and cyclic voltammetry.



Scheme 1 : Structure of mevinphos

EXPERIMENTAL

Apparatus and reagents

Electrochemical studies were carried out by Autolab PGSTAT 101 supplied by Metrohm Autolab B.V., The Netherlands. A three electrode system comprising of a glassy carbon electrode (GCE) as working electrodes, Ag/AgCl as a reference electrode and Pt wire as a counter electrode obtained from Metrohm, The Netherlands was employed. An Elico LI-120 pH meter supplied by Elico LTD, Hyderabad, India was used to determine the pH of the buffer solution.

All the reagents used in this study were analytical grade. Double distilled water was used throughout the experiment. Mevinphos pesticide and thiophene was obtained from Sigma Aldrich, India. Britton-Robinson buffer was prepared from the appropriate amounts of orthophosphoric acid, boric acid, sodium hydroxide monohydrate and acetic acid. all other chemical were obtained from E-Merck (India).

Preparation of polythiophene modified electrode

Conducting polymers are generally used for the preparation of electrochemical sensors because they have good electrical conductivities and high surface areas. Among the different polymers, polythiophene films appear to be an alternative method for electrochemical studies. Prior to use the working electrode (glassy car-

bon) was polished with alumina powder (Al_2O_3 , 5 μm) on a polishing cloth and rinsed with double distilled water. Using cyclic voltammetry, polythiophene was deposited by scanning the potential of the electrode from -0.1 V to +1.8 V vs. Ag/AgCl in a solution of 0.1 M thiophene and 0.02 tetrabutyl ammonium perchlorate in acetonitrile solution. The thickness of the polymer film (100 nm) was controlled by the number of potential cycle sweeps. The electrode was rinsed with double distilled water and taken in the electrolytic cell.

Voltammetric determination of mevinphos

A suitable amount of mevinphos was accurately weighed and then dissolved in ethanol. The content was allowed to settle after stirring magnetically for 10 minutes. The sample solution was filtered through a whatman no.42 filter paper. Appropriate solutions were prepared by taking suitable aliquots of the clear supernatant liquid and diluting them with B-R buffer solution in order to obtain a final solution of 1.0×10^{-5} M mevinphos. The solution was transferred to a voltammetric cell and the voltammograms were subsequently recorded following the optimized conditions. Typical differential pulse adsorptive stripping voltammogram and blank signal were shown in Figure 2.

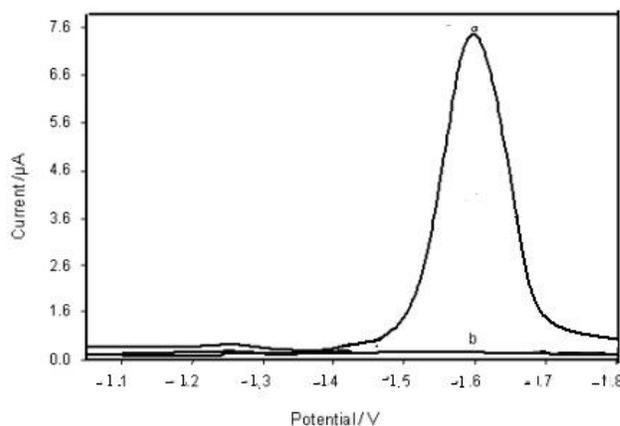


Figure 1 : Differential pulse stripping voltammogram of Mevinphos (a) at pH 2.0. Concentration: 0.01 mM, Deposition time: 30 sec., Pulse amplitude: 50 mV and blank solution (b)

RESULTS AND DISCUSSION

Effect of pH

Electrochemical reduction behaviour of mevinphos has been examined over the pH range of 2.0 to 12.0.

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In acidic solutions ($\text{pH} < 7$) mevinphos was found to give a single well defined cathodic wave/peak which was attributed to the reduction of the carbonyl group to the corresponding hydroxyl derivative in a two electron process. No waves are observed in the basic medium ($\text{pH} > 7$) due to the precipitation of the electro active species. The slight variation of the wave potential values of the title compound was found to be pH dependent and potential shifts towards more negative values along with an increase in the pH of the buffer system indicating the electrode process to be irreversible. The diffusion current and diffusion coefficient values are found to decrease with increase in the pH the solution. This trend shows that the reaction scheme involves successive proton and electron transfers in acidic media.

Cyclic voltammetric studies

Typical CV plot for title compound was shown in Figures 2. Millicoulometry employed at $\text{pH} 2.0$ to find out the number of electrons involved in the electrode process.

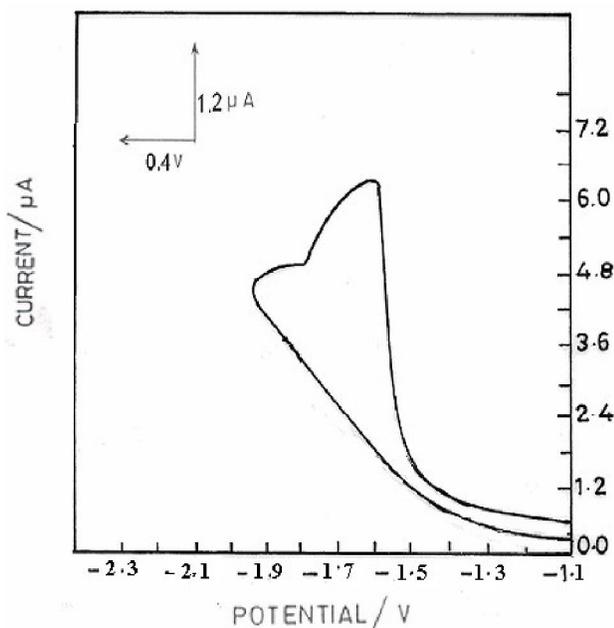


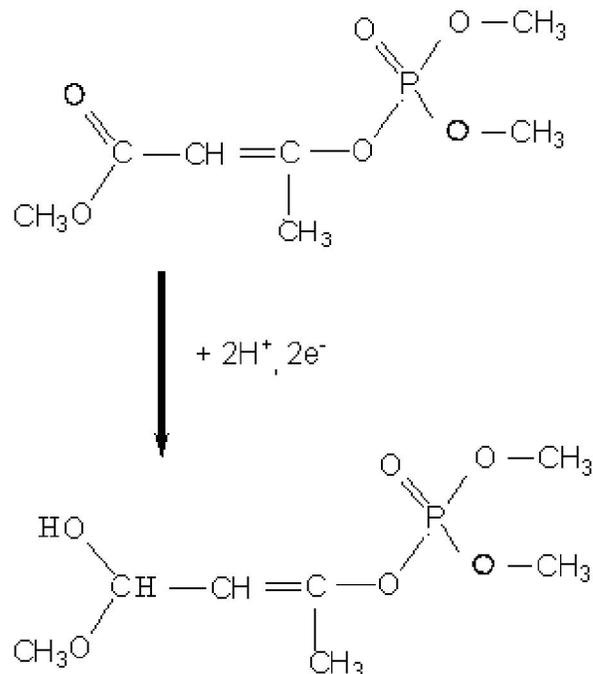
Figure 2 : Cyclic voltammogram of mevinphos at $\text{pH} 2.0$; concentration: 0.01 mM ; scan rate: 50 mVs^{-1}

A peak at was found due to the reduction of $>\text{C}=\text{O}$ group of the compound under study. There was no anodic peak observed in reverse direction which indicates that the reaction is irreversible in nature. Based on the results obtained, the electrochemical reduction mechanism of mevinphos can be proposed as in Scheme 2.

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The number of electrons involved in the reduction process was found to be 2.



Scheme 2 : Electrode reduction mechanism of mevinphos

Standard addition method was used for the analysis of the mevinphos. The peak current was found to vary linearly with the mevinphos concentration over the range of 1.0×10^{-5} to $1.25 \times 10^{-9} \text{ M}$. The detection limit was calculated using the expression $\text{dl} = 3 \times \text{Sd}/m$ (where Sd was the standard deviation and m was the slope of the calibration plot) is found to be $0.32 \times 10^{-9} \text{ M}$.

Determination of mevinphos in spiked human urine samples

Mevinphos was analysed by the standard addition method. The standard solution ($1.0 \times 10^{-5} \text{ M}$) was prepared by dissolving the appropriate amount of the mevinphos in Ethanol. One ml of the standard solution is transferred to the polarographic cell and made up to 10 ml with the supporting electrolyte to get the required concentration and then deoxygenated by purging nitrogen gas for 10 min. After recording the polarogram, small increments of the standard solutions (0.5ml) were added and then polarograms were recorded for each addition under similar conditions. The optimum conditions for the determination of mevinphos at $\text{pH} 4.0$ were found to be a drop time of 2 sec, a pulse amplitude of 50 mV and an accumulation potential of -0.27 V . The

relative standard deviation and correlation coefficient values were found to be 1.64% and 0.9423 respectively for 6 replicate determinations.

For analysis of mevinphos in spiked human urine samples, different amounts of mevinphos were added to a fixed volume of urine sample. A small portion of these spiked urine samples were diluted with supporting electrolyte and polarogram recorded. The recovery was found to be 97.6-99.0% with relative standard deviation of 0.60-1.21%. The determination of mevinphos in urine samples are presented in TABLE 1.

TABLE 1 : Recoveries of mevinphos in spiked human urine samples

Sample	Amount added in mM	Found mM	Recovery ^a (%)	Standard deviation	Relative Standard deviation (%)
sample A	10	9.87	98.7	0.0919	0.925
	20	19.76	98.8	0.1697	0.854
sample B	10	9.76	97.6	0.1697	1.718
	20	19.6	98.0	0.2828	1.428
sample C	10	9.88	98.8	0.0849	0.854
	20	19.8	99.0	0.1414	0.711

a. number of determinations = 6

To assess the reliability of the proposed method we evaluated the critical factors such as detection limits, range of calibration, accuracy and precision. The surface adsorption and catalytic activity of the polythiophene coated GCE provided high sensitivity that can be applied for the determination of mevinphos.

Interferences studies

The required quantity of mevinphos was dissolved in Ethanol to achieve stock solution concentration of 1.0×10^{-5} M and 1.0 ml of stock solution was added to each human urine samples. They were stirred magnetically for 10 minutes and filtered through a filter paper (whatman no.42) and added 9.0 ml of B-R buffer solution. The samples were determined by above described method without any significant deviation of signal in the presence of 500 ppm of uric acid, ascorbic acid and dopamine.

CONCLUSION

The voltammetric study and determination of

mevinphos is carried out using polythiophene based nanosensor in human urine samples. The accuracy and precision of the present method was checked by the analysis of known amount of mevinphos pesticide in spiked human urine samples. The results obtained imply that the developed method is simple, rapid, very sensitive and selective with good cost effectivity.

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