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CONTENT

QUANTIFICATION OF ORGANOPHOSPHORUS PESTICIDE AZAMETHIPHOS USING ELECTROANALYTICAL APPROACH

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ABSTRACT

In this work, for the first time, we proposed electrochemical behavior and development of analytical procedure for quantification of pesticide azamethiphos, using boron doped diamond (BDD) electrode. It was found that azamethiphos electrochemical behavior is irreversible oxidation at potential of around 1.70 V, in 1M nitric acid. Square wave voltammetric technique was most appropriate for azamethiphos quantification. Under optimized experimental conditions linear working range from 2 to 100 μM was estimated with detection limit of 1.38 μM. Negligible effect of possible interfering compound was observed. Obtained results clearly show that developed analytical methodology can be adequate replacement for the, up to date, used methods for detection of organophosphorous pesticide.

INTRODUCTION

Azamethiphos (AZA) is an organophosphorus pesticide which is used as spray for control flays and cockroaches or in veterinary medicine, in fish farming. Determination of this pesticide is mainly done by liquid chromatography or mass spectrometry [1]. Due to the high instrument costs, sometime complicated sample preparation of chromatographic methods and, on the other hand, low cost instrumentation and very often direct measurements of electrochemical methods only by sample dilution, the aim

of this paper was to offer rapid, sensitive and selective method for quantification of selected pesticide using electroanalytical detection.

In our work we used boron doped diamond (BDD) electrode, primarily due to its properties such as: wide potential window in aqueous solutions, low background current and negligible adsorption on electrode surface. This electrode has been widely used in electrochemical studies regarding vitamins, drugs and different class of pesticides [2,3]. Electrochemical behavior of AZA was studied using cyclic voltammetry and for quantification of this compound square wave voltammetry was used.

EXPERIMENTAL

All electrochemical experiments were done in conventional three electrode glass cell consist of boron doped diamond (BDD) electrode as working electrode, an Ag/AgCl electrode (3 M KCl) as reference electrode and Pt wire as counter electrode. For all electrochemical measurements CHI 760b (USA) potenciostat/galvanostat was used. All chemical used in this work were purchased from Sigma Aldrich and used as received. As supporting electrolyte Britton–Robinson buffer solutions and nitric acid solutions of different concentrations were examined.

RESULTS AND DISCUSSION

We examine electrochemical behavior of AZA at a BDD electrode using cyclic voltammetry (CV). AZA shows a well-defined oxidation peak with a potential of around +1.7 V in the anodic scan. In the reverse scan, no cathodic peak was observed indicating that the oxidation of this compound is electrochemically irreversible.

The effect of the pH value of the supporting electrolyte solution was investigated in the range from 0 to 12 using CV. For this purposes Britton–Robinson buffers (pH 2.0–12.0) and 0.1M and 1M solutions of nitric acid (pH 1 and 0) were used. The highest magnitude of peak current and the best peak shape, was achieved using 1M nitric acid, thus it was chosen as support electrolyte.

The effect of the scan rate (10-200 mV/s) on the oxidation peak current of AZA was also investigated (Figure 1). Dependence of peak current on the square root of the scan rate is linear, which indicate that the electrochemical reaction is controlled by diffusion.

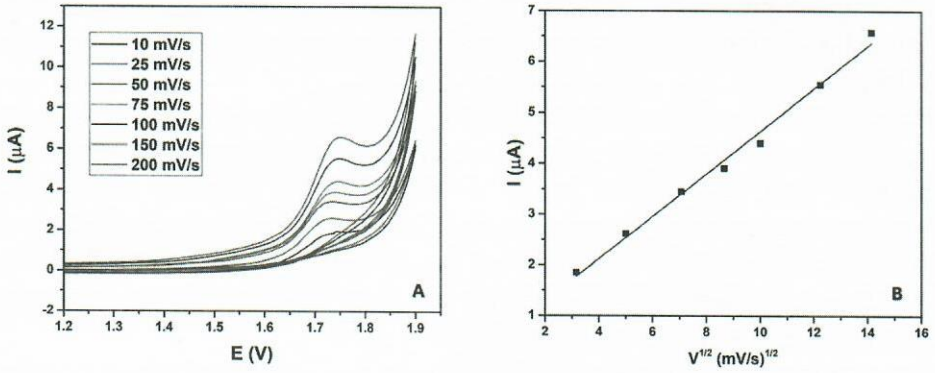

Figure 1. A) Cyclic voltammograms of 0.1 mM of AZA at BDD electrode in 1M nitric acid at various scan rates (10-200 mV/s). B) Dependence of the peak current from the square root of the scan rate.

Oxidation response of 0.1 mM AZA was investigated using differential pulse voltammetry (DPV) and square wave voltammetry (SWV). Significantly better response was obtained using SWV and this technique was chosen for all futher experiments. SWV operating parameters, pulse amplitude and frequency, were optimized. The best analytical response was obtained with pulse amplitude of 30 mV and frequency of 80 Hz and these parameters values were used in further studies.

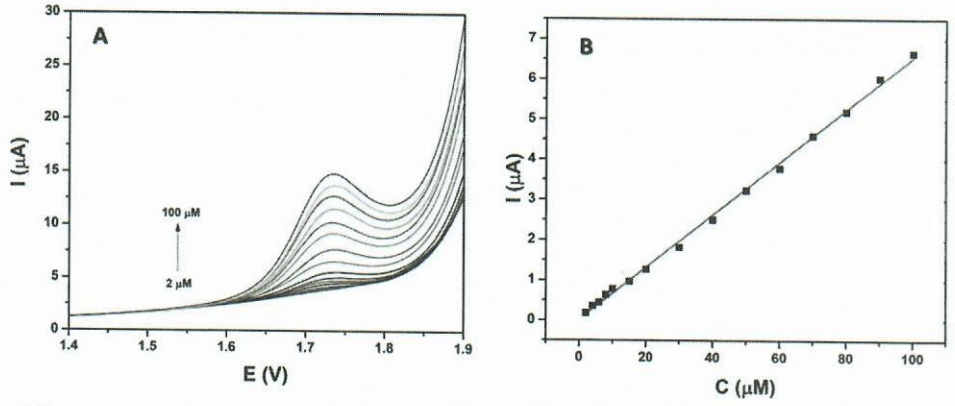

Figure 2. (A) Voltammograms obtained for different concentrations of AZA at BDD electrode in 1M nitric acid (SWV, pulse amplitude 30 mV, frequency 80 Hz). (B) Corresponding calibration curve.

Voltammograms for different AZA concentrations and corresponding calibration curve are shown in Figure 2. It was found that oxidation current

shows linear dependence with increase of AZA concentrations in the range of 2-100 μM. Calculated limit of detection (as 3σintercept/slope), was found to be 1.38 μM.

Selectivity of the proposed procedure toward detection of AZA was tested using SWV under optimized experimental conditions. Some other pesticides, clomazone and sulcotrione were investigated as possible interfering substances. Presences of clomazone significantly interfere determination of AZA and have influence on analytical performances of our method. In the case of the second tested compound, the presence of an interfering substance did not significantly effect on the signal of analyte.

The application of proposed method was examined on real water samples from the Danube River. Our sample did not show any pesticide content, so they were spiked with the analyte. Experiments were performed in triplicate. recoveries from our experiment were between 98% and 103%. From obtained results. can be concluded that our method can be used for detection of AZA in real samples.

CONCLUSION

In our work, we have developed a method for rapid, simple and reliable detection and quantification of azametiphos. Analytical characteristics of proposed method were quite good, with detection limit of 1.38 μM and wide linear range (2-100 μM). Also, this method was used for determination of AZA in three spiked real samples. In comparison with some other methods, such as HPLC, our method is simpler, less expensive and no complex preparation of samples is required.

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