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Electrochemical study of fenitrothion and bifenox and their simultaneous determination using multiwalled carbon nanotube modified glassy carbon electrode

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ABSTRACT

Electrochemical behavior of fenitrothion (FT) and bifenox (BF) was investigated using cyclic voltammetry on the glassy carbon electrode. Cathodic peaks for the reduction of an Ar–NO_2 group in both fenitrothine (*o,o*-dimethyl *o*-(3-methyl-4-nitrophenyl) phosphorothioate) (FT) and bifenox (methyl 5-(2,4-dichlorophenoxy)-2-nitrobenzoate) (BF) overlap strongly, and it is difficult to determine the compounds individually from their mixtures by these cathodic peaks. By an electrochemical irreversible reduction of Ar–NO_2 in FT and BF it was transformed into a reversible redox couple (Ar–NHOH/Ar–NO) which can be used for simultaneous determination of fenitrothion (FT) and bifenox (BF) by square wave voltammetry (SWV). The experimental parameters, such as pH value, prepotential magnitude, time of the applied prepotential and pulse amplitude of SWs were optimized. To obtain better detection limit and sensitivity, the surface of the glassy carbon electrode was modified by a pretreated multi-walled carbon nanotube. Scanning electron microscopy (SEM) and square wave voltammetry (SWV) were used to characterize the performance and structure of the modified electrode. Under the optimized experimental conditions FT and BF give linear response over the range of 0.2–60.0 μM. The detection limit for both FT and BF was found to be 0.08 μM. The practical application of the modified electrode was demonstrated by measuring the concentration of FT and BF in river water samples.

1. Introduction

Organophosphorus (Ops) and nitro diphenyl ether (NDPE) compounds are the well-known toxic substances. They are used as insecticide, herbicide and pesticide agents. The high toxicity of these compounds and their use in agriculture activities increases public concerns. Because of extensive uses in agricultural areas, the residue of these compounds remains in our environment [1,2]. For the protection of human health and control of the environment, developing a rapid, selective and sensitive method for detection of these pesticides in soils, water, plants, etc. is important.

Analytical techniques such as gas or liquid chromatography and mass spectrometry have been used for analysis of pesticides in environmental and biological samples [3]. Despite having high sensitivity, these techniques are complex, costly and require skilled technicians and large laboratory based instrumentation. Furthermore, complex and time consuming extraction procedures such as liquid solid extraction or solid phase micro extraction are needed for most of these techniques [4–6]. On the other hand, biological and immunoassay methods have been used in many investigations [7,8] and offer better specificity and sensitivity [9]. Nevertheless, these methods require a labeling process, long analysis time and extensive sample handling with multiple washing steps which limit their applications. Also total biological receptors which are used in biosensors have well-known limitations, including low stability, difficult immunization, low temporal, chemical and thermal stabilities and high price [10–13].

On the other hand, determination of organophosphorus (Ops) and nitro diphenyl ether (NDPE) compounds using electrochemical procedures based on modified electrodes has proved to be a sensitive and selective method [14–16]. Electrochemical detection can be done rapidly without tedious separation, and its application is very promising in continuous monitoring.

In this paper, we report the results concerned with the electrochemical study of pesticides, fenitrothion (FT) and bifenox (BF), and their simultaneous determination by using a multiwalled carbon nanotube modified glassy carbon electrode (MWCNT/GCE) based on the voltammetry technique. Since the reduction peak potentials of the voltammograms for the individual pesticides are close, the voltammogram of mixtures of these compounds in the reductive region is composed of overlapping peaks. Our work describes the research of the redox behavior of the pesticides and presents a condition in which two pesticides

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can be electrochemically determined. The chemical structure of both FT and BF are shown in Fig. 1.

2. Experimental

2.1. Chemicals and apparatus

FT and BF were obtained from Sigma-Aldrich (Germany). Other chemicals used were of analytical regent grade purchased from Merck Company (Darmstadt, Germany). Distilled water was used throughout. Stock solutions of FT (1.0×10^{-2} M) and BF (1.0×10^{-2} M) were prepared in a 50:50 (*v*/*v*) mixture of water and ethanol and stored in a refrigerator at 4 °C. In the present study, acetate and phosphate buffer solutions were used for different pH values. The multi-walled carbon nanotube (MWCNT) (purity more than 90%, outer diameter 70–90 nm and inner diameter 5–9 nm) used for the modification of the GCE was from Neutrino Company (Iran).

An Autolab model PGSTAT 302N potentiostat/galvanostat with a three electrode configuration including a glassy carbon electrode (GCE) as the working electrode, a platinum wire as the counter electrode, and an Ag/AgCl electrode (saturated KCl) as the reference electrode was used for all the electrochemical experiments.

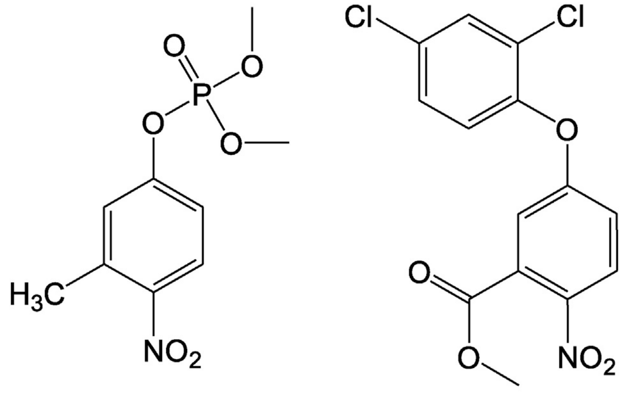
2.2. Dispersion and functionalization of CNTs and modification of GCE

A homogeneously dispersed CNT solution (0.5 mg/ml) with multiple hydroxyl groups was obtained by functionalization and dispersion of CNTs in absolute ethanol (EtOH) according to procedures reported previously [17–19].

After the polishing of the glassy carbon electrode using an alumina slurry, it was sonicated with ethanol and water and dried at room temperature. Then, 20 μl of the homogeneously dispersed ethanol–CNT solution was carefully dropped on the surface of the polished GCE and dried in air. The MWCNTs/GCE were thus obtained. Finally, activation of the modified electrode was done by successive potential scans from 0.1 to 1.2 V with a scan rate of 100 mV/s in acetate buffer solution (pH 5.0).

3. Results and discussion

3.1. Mechanistic studies of FT



fenitrothion

bifenox

Fig. 1. The chemical structure of FT (*o*,*o*-dimethyl *o*-(3-methyl-4-nitrophenyl) and BF (methyl 5-(2,4-dichlorophenoxy)-2-nitrobenzoate).

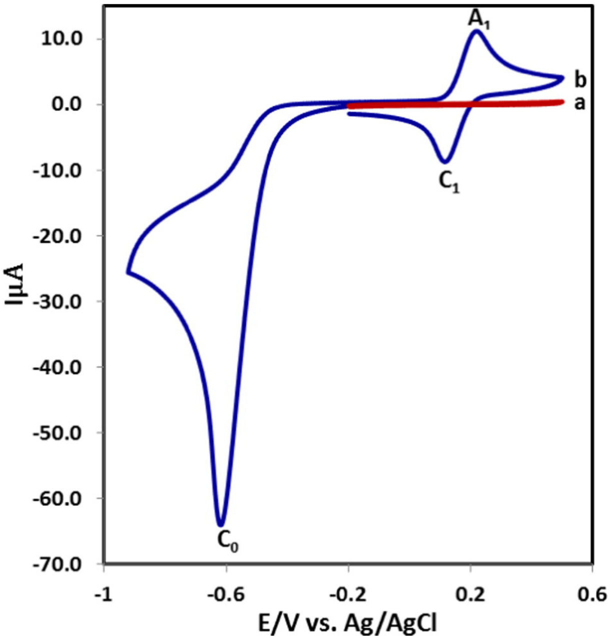


Fig. 2. Cyclic voltammograms of 1.0 mM FT in aqueous solution containing phosphate buffer (pH = 2.0, 0.2 M) and 20% ethanol (*v*/*v*) at the glassy carbon electrode. (a) Starting potential −0.2 V and switching potential 0.5 V vs. Ag/AgCl. (b) Starting potential −0.2 V, first switching potential −0.9 V and second switching potential 0.5 V vs. Ag/AgCl. Scan rate 100 mV/s.

Fig. 2 shows the cyclic voltammograms of 1.0 mM FT in water/ethanol (80/20 *v*/*v*) solution containing phosphate buffer (0.2 M, pH = 2.0) in two different potential scan ranges. In cyclic voltammogram "a" scanning of the potential is started at −0.2 V and is switched at 0.5 V vs. Ag/AgCl. As can be seen there are no anodic and cathodic peaks for FT at this potential range. Upon the scanning of the GCE to negative potentials, a large cathodic peak (C_0) is observed at −0.60 V vs. Ag/AgCl. It corresponds to the irreversible reduction of the NO_2 group of FT ($Ar–NO_2$) to hydroxyl amine (Ar–NHOH) (Scheme 1). On reversing the scan direction no oxidative process corresponding to this cathodic peak can be observed, but a new anodic peak (A_1) is observed at 0.19 V vs. Ag/AgCl. On a subsequent scan the corresponding reduction peak (C_1) is observed with a peak to peak separation of 0.47 mV. This reversible system is related to the FT_{red} (ArNHOH)/FT_{ox} (ArNO) couple (Scheme 1) [20–23].

3.2. Effect of pH on the cyclic voltammograms of FT

Cyclic voltammograms of FT at various pH values are shown in Fig. 3. In these voltammograms, by scanning of the potential to the negative value, the NO_2 group of FT was first reduced to the related hydroxyl amine group and then the influence of pH on the cyclic voltammetric behavior of the in situ produced redox couple, FT_{red} (ArNHOH)/FT_{ox} (ArNO), was studied in the pH range of 2.0–8.0 with a scan rate of 100 mV/s. As can be seen, the potential of anodic peak A_1 (E_{pA1}) and its cathodic counterpart (E_{pC1}) depends on the solution pH and shifts to the negative values by increasing pH. This is due to the participation of proton(s) in the oxidation of FT_{red} (ArNHOH) to FT_{ox} (ArNO) [24].

$$\mathrm{ArNHOH} - 2e^- - m\mathrm{H}^+ \rightleftharpoons \mathrm{ArNO}$$

where m is the number of protons. The formal potential (E_f) is given by the below equation:

$$E_f = E_f^0 - \left(\frac{2.303mRT}{2F}\right)\mathrm{pH}.$$

E_f^0 is the formal potential at pH 0.0. R, T and F have their usual meanings. In Fig. 3, part II, a potential–pH diagram (plotting of the calculated E_f values as a function of pH) is shown for FT_{red} (ArNHOH) to FT_{ox} (ArNO) redox couples. As can be seen, the slope of the diagram (~59 mV/pH) is in agreement with the theoretical slope (2.303mRT/2F) of 59 mV/pH with m about 2. Thus, it can be concluded that, the electron