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In situ bismuth-film electrode for square-wave cathodic voltammetric detection of pendimethalin at nanomolar level

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ABSTRACT

An *in situ* plated bismuth-film electrode (BiFE) was used for the study of the herbicide pendimethalin. A single peak was observed by cyclic voltammetry at −0.520 V associated with the reduction of pendimethalin in HCl solution at pH 3.0. Square-wave cathodic voltammetry (SWCV) was used for the analytical procedures after the preparation of the BiFE using 10.0 μmol L^{-1} Bi(III) for 80 s at −0.250 V. A peak current at −0.585 V related to the reduction of the herbicide was obtained, which increased linearly with the pendimethalin concentration in the range of 0.3 to 1.0 μmol L^{-1}. The limit of detection attained was 37.0 nmol L^{-1}. The sensor prepared *in situ* was applied for the determination of pendimethalin in simulated samples of tap water and sea water with satisfactory results being obtained compared with the UV–vis spectroscopy technique. In addition, pendimethalin was spiked and determined at nanomolar level in samples of water collected from a local river. The recovery values for such experiments were between 93% and 96%.

1. Introduction

Bismuth-film electrodes (BiFEs) [1] have been widely accepted by the scientific community and are used in various electroanalytical laboratories since they offer many advantages including simple preparation, high selectivity, well-defined signals, sensitivity and low toxicity [2]. Bismuth has been recognized as a "green" element exhibiting comparable electroanalytical performance to mercury [3]. Bismuth electrodes have been used in different configurations, *e.g.* bismuth-film prepared on glassy carbon [4,5], carbon paste [6,7], carbon fiber [8] boron-doped diamond [9] or screen printed substrates [10]. They can be used for the determination of inorganic [11–17] as well as organic [18–20] analytes. BiFEs can be used for analytical purposes in conjunction with any of the electroanalytical techniques available [21]. In addition, with the advancement of the technology, it is possible to carry out *in loco* analysis due to the portability of new potentiostats and accessories.

Aromatic nitrocompounds are used in a wide range of industries, for instance, in pharmaceuticals, pesticides and explosives [22–24]. However, it is well known that some nitrocompounds are toxic and are considered harmful to humans and to the environment [25,26]. Herbicides play an important role in crop production, but their residues can cause various environmental problems, such as the pollution of surface waters. Pendimethalin (3,4-dimethyl-2,6-dinitro-N-pentan-3-yl-aniline – Fig. 1) is a dinitroaniline used as a selective herbicide [27] for the control of annual grasses and certain broadleaf weeds in the cultivation of corn, potato, rice, cotton, soybeans, tobacco, peanuts and sunflowers [28]. This herbicide interrupts the sequence of mitosis by inhibiting the production of the microtubule protein tubulin, which forms part of the cytoskeleton in cells [29]. Recently, it has been found to be interrelated with several physiological changes and endocrine effects, including liver and kidney damage and mutagenic effects [30]. Therefore, it is important to monitor pendimethalin residues. However, few authors have reported the electroanalytical determination of pendimethalin [31–34]. In addition, reports are scarce on the use of BiFEs prepared *in situ*, i.e., in the same solution as the analyte, for the determination of organic compounds. To achieve this, the reduction potential of the analyte needs to be more negative than the BiFE plating potential and the experimental conditions should be favorable, as in the case of the study reported herein. In this context, we describe herein, for the first time, the successful application of a BiFE prepared *in situ* for the detection of pendimethalin at nanomolar levels. Cathodic voltammetry was applied in the square-wave mode, which was designated as square-wave cathodic voltammetry (SWCV).

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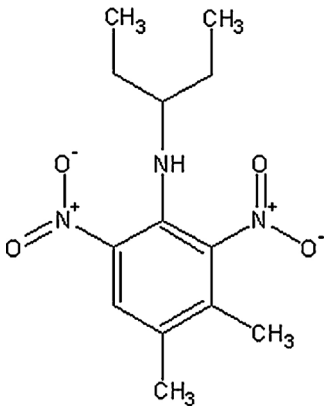

Fig. 1. Chemical structure of pendimethalin.

2. Experimental

2.1. Reagents and solutions

All reagents used in this study were of analytical grade. The solutions were prepared with water purified using a Milli-Q system manufactured by Millipore (Bedford, MA, USA). A solution of 2.0 mmol L^{-1} $Bi(NO_3)_3$ was obtained by dissolving the salt in 1.0 mol L^{-1} HCl. The solution was employed for the deposition of the bismuth-film onto a glassy carbon electrode. Britton–Robinson (B–R) and citrate buffers and HCl solutions at an initial concentration of 0.1 mol L^{-1} were tested as supporting electrolytes. The pH was adjusted to the desired level with 1.0 mol L^{-1} HCl or NaOH. A stock solution of 5.0 mmol L^{-1} pendimethalin was prepared by dissolving the pesticide in ethanol. Less concentrated solutions were obtained by dilution in the supporting electrolyte.

2.2. Electrochemical apparatus

The electrochemical studies were carried out with a PGSTAT101 potentiostat/galvanostat interfaced with a personal computer using the "NOVA 1.7" software for data acquisition and analysis. Cyclic and square-wave voltammograms were recorded using an electrochemical cell with three electrodes: the BiFE as the working electrode, platinum wire as the auxiliary electrode and Ag/AgCl saturated with KCl as the reference electrode. All of the potentials measured are quoted *versus* the reference electrode.

2.3. In situ preparation of BiFE

The surface of a glassy carbon electrode (area: 0.031 cm^2) was employed as the substrate for deposition of the film. In a typical procedure, the glassy carbon surface was hand polished using alumina slurry with a particle size of 0.03 μm, followed by washing and sonication for 2 min in purified water. The bismuth-film was deposited from an electrochemical cell containing HCl at pH 3.0 and both 10.0 μmol L^{-1} Bi (III) and pendimethalin in the concentration range of 0.3 to 6.0 μmol L^{-1} (*in situ* deposition). An oxygen-free solution was obtained by purging N_2 gas for 10 min before the bismuth deposition. The electrolysis was carried out at −0.250 V for 80 s under stirring. After each voltammetric experiment, a potential of +0.200 V was applied for 20 s under stirring as a clean-up step to remove the bismuth-film. This procedure was repeated without mechanical polishing of the glassy carbon substrate. The optimization of the experimental conditions for *in situ* preparation will be discussed in Section 3.2.

2.4. Square-wave cathodic voltammetry – SWCV

The SWCV experiments were carried out with 1.0 μmol L^{-1} pendimethalin, except for the construction of the calibration curve, which was performed in the concentration range of 0.3 to 6.0 μmol L^{-1} pendimethalin. After the deposition step, square-wave cathodic voltammograms were obtained by the simple application of potentials from −0.200 to −1.00 V with the BiFE in HCl at pH 3.0 in the presence of pendimethalin. No accumulation step was necessary to achieve reproducible data. Thus, the dependence of the SWV response on the parameters frequency (f), amplitude (a) and scan increment (ΔE_s) was analyzed in order

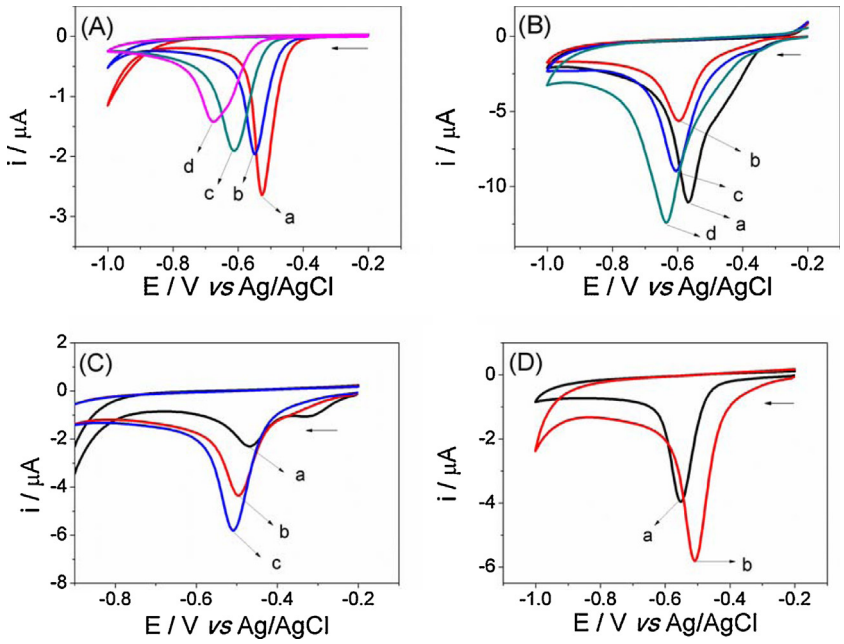

Fig. 2. Effect of supporting electrolyte and solution pH. Cyclic voltammograms for the BiFE in 5.0 μmol L^{-1} pendimethalin and different supporting electrolytes with different solution pH values. (A) B–R buffer (pH of (a) 2.0; (b) 3.0; (c) 4.0; (d) 5.0), (B) citrate buffer (pH of (a) 3.5; (b) 4.0; (c) 4.5; (d) 5.0) and (C) HCl solution (pH of (a) 2.0; (b) 2.5; (c) 3.0). (D) Comparison between data obtained using (a) CGE and (b) BiFE in HCl solution at pH 3.0, $\nu = 0.100$ V s^{-1}.