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A disposable and inexpensive bismuth film minisensor for a voltammetric determination of diquat and paraquat pesticides in natural water samples

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ABSTRACT

The development of a bismuth film on a disposable minisensor for electroanalytical determination of Diquat (DQ) and Paraquat (PQ) using voltammetric techniques as square-wave (SWV) and differential-pulse (DPV) is reported. The disposable minisensor consisted of a bismuth film-working electrode, a silver-pseudo-reference and copper-counter electrodes. Copper boards of a printed circuit were used as substrate and nail varnish was used as an electrical insulator to limit the electrode area. The disposable proposed minisensor was applied for the determination of DQ using SWV and PQ using DPV. Under optimal experimental conditions, the cathodic peak current was linear in the DQ concentration range of 0.19×10^{-6}–9.3×10^{-6} mol L^{-1} with a detection limit of 8.9×10^{-8} mol L^{-1}, and, for PQ the peak current was linear in the concentration range of 0.12×10^{-6}–4.2×10^{-6} mol L^{-1} with a detection limit of 1.2×10^{-8} mol L^{-1}. The proposed method was applied for the determination of both pesticides in natural water samples and the obtained results are in good agreement with those results obtained using a high-performance liquid chromatography at a 95% confidence level.

1. Introduction

In the development of new architectures for sensors, researchers are always looking for low cost, robustness and easy modification. Thus, disposables sensors are examples of these new architectures that have been widely studied due their characteristics such as no regeneration of the surface and highly reproducible geometric area for all electrodes, these kinds of interesting properties can reduce the possible interferents and poisoning of electrode surface. In this way, the technique like “screen-printed” has been employed with great success to manufacture these electrodes [1–6].

Printed electrodes open a possibility of full automation in manufacturing of a complete system containing the working, counter and reference electrodes, all printed on the same support. In addition, there is a plenty of possibilities of modification [7]. The composition of the printing inks may be modified by the addition of different substances such as metals, enzymes, polymer, and other materials [2,8–11]. On the other hand, in the research for new materials, bismuth film electrode appears as good alternative for new studies in this area.

Bismuth film is an interesting material for the electrochemical field due present attractive vantages such as low residual current, large negative working potential range, good chemical stability, ability to form “fused alloys” with heavy metals, limited oxygen interference and high mechanical stability [12,13]. Furthermore, it is an environmentally friendly element with low toxicity which may successfully replace mercury based electrodes [14]. Because its properties, this material has been widely explored for fabrication of new sensors for the determination of different analytes such as heavy metals [15–18], organic compounds [19,20], pesticides [21–23], which are pollutants when used incorrectly.

Pesticides are substances used for the control, prevention and destruction of any kind of pest. However, due their high toxicity and their uncontrolled use on some populations the people’s understanding are changing about the use of this kind of substance. Two

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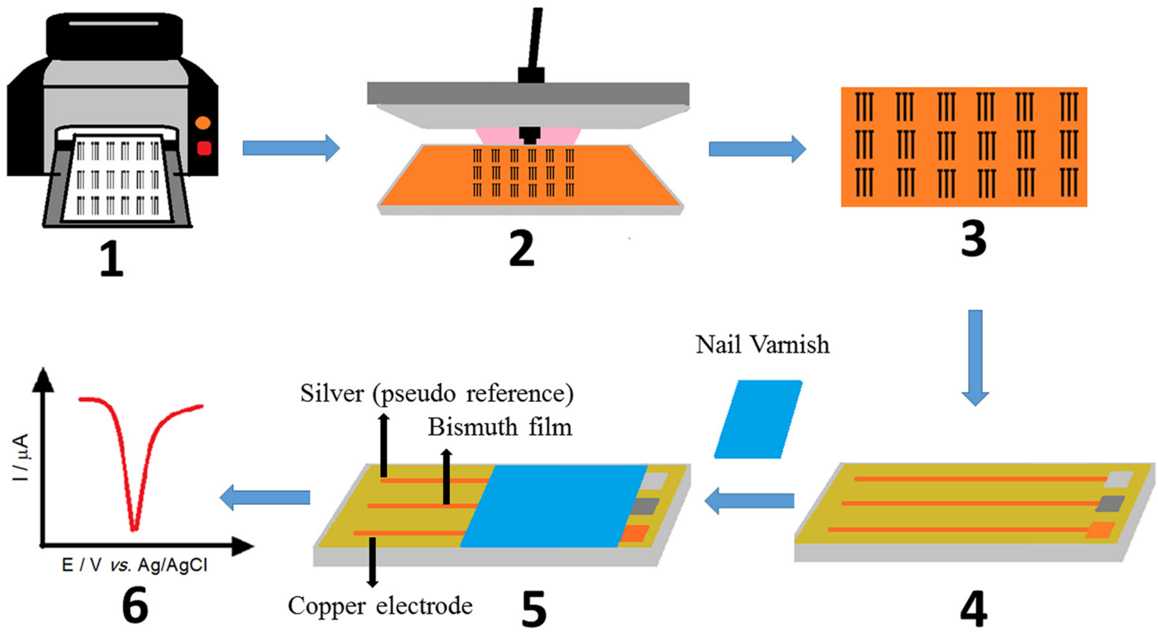

Fig. 1. Scheme of the disposable minisensor fabrication. Step 1: Print the layouts of the devices upon a polyester paper. Step 2: The design is transferred to the copper board at 120 °C for 240 s, using a thermal press. Step 3: The copper board with the layouts printed is washed with a concentrated $FeCl_3{\cdot}4H_2O$ solution to remove all the uncovered copper. Step 4: The board is cut out with the appropriate tools to obtain the electrodes and these are cleaned with acetone. Step 5: To define the electrode geometry, nail varnish is used as insulator and the *ex situ* bismuth film is electro-deposited. Step 6: The proposed minisensor is used for analytical applications.

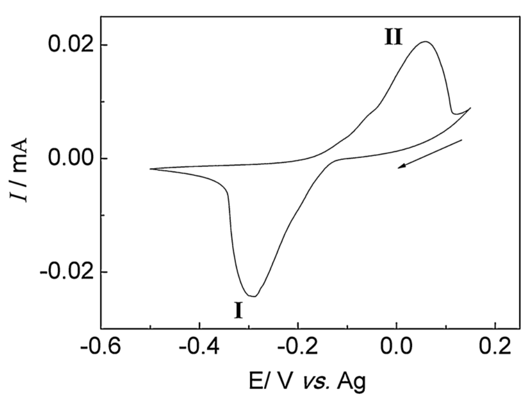

Fig. 2. Cyclic voltammogram obtained using a 0.02 mol L^{-1} $Bi(NO_3)_3$ solution in 0.1 mol L^{-1} acetate buffer solution (pH 4.5) as supporting electrolyte and copper electrode as working electrode at a potential scan rate of 10 mV s^{-1}.

examples of pesticides, which are used widely, are Diquat (DQ) and Paraquat (PQ). These dipyridyl compounds are non-selective herbicides and were introduced at decade of 50 on the market, being extremely applied nowadays in agriculture for control of weeds. Like other pest controllers, can be very toxic for human beings and animals, even in low concentrations [24,25].

Several methods have been reported in the literature for the determination of DQ and PQ such as spectrophotometry [26–30], electrophoresis systems [31,32], fluorimetry [33,34] and high performance liquid chromatography [35–38]. However, the use of electrochemical methods is an alternative for the determination of these analytes. The electrochemical procedures present advantages as easy instrumental manipulation, low operating costs, possibility of miniaturization and providing satisfactory and accurate results in detecting these substances [14,39–44].

In this work, pulse voltammetric techniques were used for determination of DQ and PQ herbicides in water samples, using a disposable printed minisensor modified with the bismuth film, resulting in an economical device with fast response, high sensitivity and good stability.

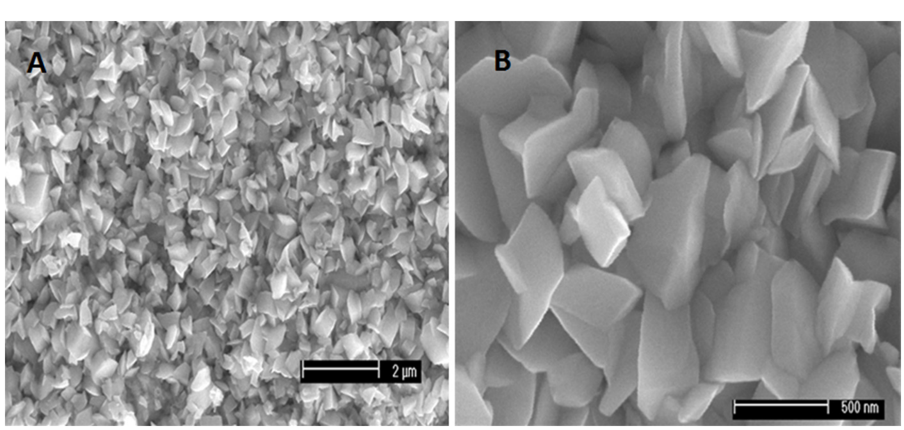

Fig. 3. FEG-SEM images of the bismuth film at different magnification: (A) 10000× and (B) 50000×.