



Preparation of a double-step modified carbon paste electrode for the voltammetric determination of prothionosulfonamide via bulk modification with fumed silica and drop-casting of maghemite-modified fumed silica nanocomposite



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ABSTRACT

In this study, a double-step modified carbon paste electrode (CPE) was prepared for the voltammetric determination of prothionosulfonamide (PRO). In the first step, modification of CPE was performed by incorporating 12.5% fumed silica (FS) into paste structure to obtain CPE-12.5FS. In the second step, CPE-12.5FS electrode was modified with drop-casting of maghemite-modified FS (MH@FS) dispersion to prepare CPE-12.5FS/MH@FS. The proposed modification process combined the advantages of both bulk modification and drop-casting techniques and showed synergistic effect on the voltammetric behaviour of the electrode. The electrode was characterized with cyclic voltammetry and electrochemical impedance spectroscopy. Scanning electron microscopy and X-ray diffraction analysis were used in the characterization of MH@FS. Electrode preparation and measurement conditions were optimized. The highest peak current for the oxidation of PRO was obtained at pH 6. PRO showed an irreversible oxidation on CPE-12.5FS/MH@FS. A linear relationship was obtained between oxidation peak current and PRO concentration in the range of 0.01 μM and 5.0 μM . The limit of detection value was calculated to be 4.4 nM. Measurement and fabrication reproducibility of the modified electrode was obtained as 2.95% (N: 9) and 4.80% (N: 6), respectively. The CPE-12.5FS/MH@FS allowed determining PRO in the presence of the carbamate pesticides of carbendazim and carbaryl. The determination of PRO in real samples such as potato, urine and river water was successfully tested with CPE-12.5FS/MH@FS. The results showed that the electrochemical sensor could be a very promising alternative to other methods of determining PRO.

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1. Introduction

Prothionosulfonamide (PRO) is a carbamate pesticide, one of pesticide groups widely used as insecticides or fungicides [1,2]. Carbamate pesticides have negative effects on the central nervous system by inactivating acetylcholinesterase [3,4]. At the same time, they prevent cell division and act on meristematic tissues [5,6]. Since carbamate pesticides are widely applied in agricultural activities, undesirable penetration of their residues into foods and environment is unavoidable leading to a potential risk for human health [7]. Therefore, there is a great demand for developing simple and rapid methods to detect the carbamate pesticides. The determination of carbamate pesticides in different samples was examined with different analytical methods which mainly concentrate on

chromatographic and spectroscopic techniques [5,8–12]. These methods require complicated equipments, and they are relatively expensive and time-consuming. In this sense, electroanalytical methods can be regarded as a promising alternative because of their properties such as low cost, simplicity and sensitivity [13–19]. Although these methods have been intensively investigated to determine different substances, there are only two studies on the electrochemical determination of PRO in related literature [20,21].

Among other carbon electrodes, carbon paste electrode (CPE) has gained particular attention lately due to its properties such as very low background current, low cost, easy preparation of a new surface and possibility to incorporate different substances during the paste preparation. Therefore, most of recent studies have investigated the preparation of modified CPEs for the determination of different substances [22–24].

Fumed silica (FS), composed of agglomerates of chain-like three-dimensional particles, is a form of silicon oxide. FS is a non-porous substance which has low density and high surface area. Thanks to its

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nanostructure, it is a great candidate for the preparation of modified electrodes. In this respect, FS was investigated as a modifier for the preparation of a modified CPE. As a modifier, FS may affect the rate of electrochemical reactions, increase the surface area of CPE and provide surface hydroxyl groups for molecular interactions.

Nowadays, various nanomaterials have been fabricated to increase the sensing performance of electrochemical (bio)sensors. In this context, preparation of iron oxides on different substances has been searched to obtain nanocomposites. These nanocomposites enhanced the adsorption behavior of organic substances and they catalyzed the electrochemical oxidation of some molecules [25–27]. In relation to this, we have investigated the preparation of maghemite ($\gamma\text{-Fe}_2\text{O}_3$) modified FS (MH@FS) to provide the related literature with a new nanocomposite. The MH@FS was characterized and used as a modifier for the preparation of a modified electrode. As a modifier, it is expected that MH@FS may interact with organic molecules by means of surface iron species ($\equiv\text{Fe}^{2+/3+}$) and surface hydroxyl groups. Moreover, MH@FS may show electro-catalytic activity in the electrochemical oxidation of organic molecules.

In this study, the preparation of a modified CPE in two steps was examined to develop a selective and sensitive voltammetric method for the determination of PRO in river water, potato and urine samples. In the first step, FS modified CPE was prepared by incorporating 12.5% FS into CPE (CPE-12.5FS). In the next step, MH@FS modified CPE-12.5FS was prepared with drop-casting method (CPE-12.5FS/MH@FS). The proposed two-step modification procedure brought additional properties to CPE such as chemical stability, high reproducibility and better electron transfer rates. These properties tremendously increased the oxidation peak currents of PRO. The performance of the electrode was evaluated for the determination of PRO in river water, potato and urine samples.

2. Experimental section

2.1. Chemicals and apparatus

Propham (Pestanal, 99%) and silica gel 60 (for column chromatography) were obtained from Fluka. Fumed silica (powder, 14 nm) was purchased from Sigma-Aldrich. The other reagents were obtained as a reagent grade and used without any pre-treatment.

A traditional electrochemical cell containing three electrodes was used in voltammetry experiments. A saturated calomel electrode (Gammy Instruments, USA) and a platinum wire were used as reference and auxiliary electrodes, respectively. Carbon paste and modified carbon paste electrodes were served as working electrodes. Electrochemical measurements were performed with the Autolab PGSTAT 204 model potentiostat (Eco Chemie, The Netherlands). Electrochemical impedance spectroscopy (EIS) measurements were performed using the CHI 660D Electrochemical Workstation. An ultra-high-resolution field emission scanning electron microscope (ULTRAFE-SEM) (Zeiss-Ultra plus) was used to obtain scanning electron micrograph images. X-ray diffraction measurements were performed with the BRUKER D8 Advance X-ray diffractometer.

2.2. Preparation of MH@FS and MH

MH@FS was prepared with a chemical precipitation method. In brief, 0.3125 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was dissolved in 12.5 mL water. Next, 0.125 mL concentrated H_2SO_4 and 0.125 g FS were added. After that, the mixture was stirred for 1 h in N_2 atmosphere. Then, 25 mL 1.32 M NH_3 solution was added slowly into the above mixture. A dark brown precipitate was formed after 1-h stirring. The precipitate

was separated magnetically with a magnet. The precipitate obtained was washed three times with water and dried at 140°C . MH was also prepared using the same method without FS.

2.3. Preparation of electrodes

CPE-12.5FS was prepared as follows: First, 0.625 g graphite, 0.125 g FS and 0.3 g paraffin oil were weighed and homogenized in a mortar. After that, the paste obtained was filled into a glass tube which had an internal diameter of 3.0 mm. Finally, the surface of the electrode was smoothed with a weighing paper. CPE was prepared in the same way without FS. In addition, CPE-12.5SG was prepared by replacing FS with silica gel (SG).

Aqueous dispersions of MH (1.0 mg mL^{-1}) and MH@FS (1.0 mg mL^{-1}) were prepared and dispersed in an ultrasonic cleaner for 10 min. Then, $10.0\ \mu\text{L}$ of these dispersions were dropped onto the CPE and CPE-12.5FS to prepare CPE/MH, CPE/MH@FS and CPE-12.5FS/MH@FS electrodes. Following this, the solvent was evaporated at 30°C under vacuum (600 mbar).

2.4. Preparation of real samples

The proposed method was tested with the determination of PRO in real samples. Three different real samples (urine, river water and potato) were used in the experiments. Urine samples were obtained from healthy volunteers and filtered with a membrane filter ($0.45\ \mu\text{m}$). River water samples were obtained from local sources and used after another filtration process. Potato samples were prepared according to the following procedure: A small amount of potato (0.5 g) was weighed and grinded. After that, 15 mL methanol was added and magnetically stirred for 2 h. Next, the liquid phase was separated with a membrane filter and diluted to 25 mL with water. Spiked-urine, spiked-river water and spiked-potato samples were prepared by mixing the samples with standard PRO solution.

2.5. Voltammetric measurements

Adsorptive stripping differential pulse voltammetry was used as a voltammetric method. CPE and modified CPEs were immersed into the analysis solution containing a certain amount of PRO for a definite time period. After that, differential pulse voltammetry measurements were performed in a pre-determined potential interval using modulation amplitude of 50 mV, step potential of 10 mV and scan rate of 20 mV s^{-1} .

3. Results and discussion

3.1. Evaluation of the voltammetric responses of the modified electrodes

Voltammetric performances of the CPE and of the modified CPEs were investigated via the differential pulse voltammetry measurements in a 0.1 M PBS (pH 7.4) containing $10.0\ \mu\text{M}$ PRO (Fig. 1). The voltammograms obtained in the presence of modified CPEs were compared with that of bare CPE to determine the best modification for the voltammetric determination of PRO. The oxidation potential and peak currents of PRO were used as comparison parameters. The oxidation of PRO took place at +0.994 V, +1.003 V, +0.993 V, +0.942 V and +0.953 V in the presence of CPE, CPE/MH, CPE/MH@FS, CPE-12.5FS and CPE12.5FS/MH@FS, respectively. The oxidation potential of PRO shifted slightly at both anodic and cathodic directions depending on the electrode used. The highest cathodic shift (0.052 V) was observed when the CPE-12.5FS was used in the measurements. The modified electrodes considerably changed the oxidation peak currents of PRO. While CPE/MH

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