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Electrochemical behavior of metribuzin based on L-Norvaline modified electrode and its sensitive determination

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ABSTRACT

The electro-polymerization of L-Norvaline was investigated for the first time on glassy carbon electrode. The polymeric conditions and mechanism were discussed in detail. The electrochemical behaviors of metribuzin were studied systematically at this sensor and the dynamic parameters of electrode process were calculated. This electrochemical sensor, fabricated simply and very easy surface update, showed good response for metribuzin with a wide linear range from 6.43×10^{-3} to 1.07 μg/mL and a low detection limit of 2.14×10^{-3} μg/mL (S/N = 3). The proposed method was successfully applied to determine metribuzin in soil sample with satisfactory results. This work promoted the potential applications of amino acid materials in electrochemical sensors.

1. Introduction

Pesticide contamination in environment is one of the major health concerns. These contaminants, for example, have been detected in the milk from lactating women [1]. Therefore, it is important to monitor their residues in all environmental segments. Triazine and organophosphorus pesticides are detected in the environment and their environmental behaviors are of great concern, although several members of these classes have been banned for years [2–6].

Metribuzin, [4-amino-6-(1-1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4H)-one], is a s-triazine herbicide. Its molecular structure is shown in Scheme 1(a). This herbicide is considered to be moderate persistence in soils. Metribuzin have received a great deal of attention. Various studies about determination of metribuzin have been investigated by using chromatographic methods, such as liquid chromatography [7–10], gas chromatography [11], micellar electro kinetic chromatography [12,13], capillary zone electrophoresis [14], molecularly imprinted polymer [15,16] and the spectrophotometric method based on its complexation with copper [17]. Nevertheless, chromatographic method is accurate but time-consuming, expensive, cumbersome operation. For now, researchers have paid attention to electroanalytical technique due to its advantages, such as high sensitivity, good selectivity, rapid response and low cost. So far as we know, there have four literatures for determination of metribuzin by electroanalytical method [18–21]. However, the literature [19–21] was no enough sensitivity and the other literature [18] used mercury electrode as the electrochemical sensor for determination of metribuzin. Mercury is toxic and the use of mercury electrode has been banned in several situations due to environmental concerns and safety regulations. Therefore, to develop a more sensitive and environmentally friendly electroanalytical method for determination of metribuzin is still interesting and significant.

Up to now, conducting polymer has attracted considerable interest because of their actual and potential applications in different fields. In addition, plenty of conducting polymers have been employed in the fields of ion recognition [22], electron transfer [23] and electrochemical sensor [24,25]. Among them, there are quite a few reports about amino acid as material to build sensing interface for analytical application [26–28], which reveal that amino acids are promising materials for electrochemical sensors. L-Norvaline ($C_5H_{11}NO_2$, Scheme 1(b)), also called L-(+)-2-Aminovaleric acid, is a white crystalline powder. It is soluble in hot water and dilute hydrochloric acid, but is insoluble in ethanol and ether. As far as we know, there has no report about L-Norvaline applied to electrode modified material so far.

In this approach, a poly-L-Norvaline modified glassy carbon electrode (poly(L-Norvaline)/GCE) was prepared by cyclic voltammetric method, and used as a voltammetric sensor for sensitive determination of metribuzin. The electro-polymerization parameters of poly(L-Norvaline)/GCE were discussed in detail. Using this sensor, the electrochemical behavior of metribuzin was investigated systematically and dynamic parameters of electrode process were determined using various electrochemical techniques. The electrode exhibited a good response on the electrochemical reduction of metribuzin, decreasing the peak potential and also increasing the peak current. A simple, sensitive

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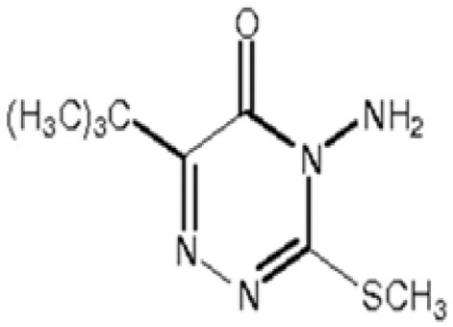
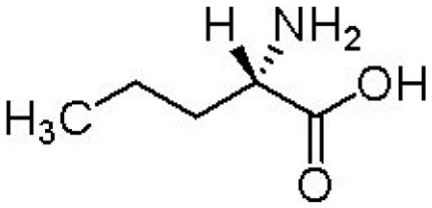


(a). Chemical structure of metribuzin



(b). Chemical structure of L-Norvaline

Scheme 1. (a) Chemical structure of metribuzin. (b) Chemical structure of L-Norvaline.

and stable electroanalytical method of metribuzin was proposed with wide linear range and low detect limit. Besides, the proposed method was used for metribuzin determination in natural soil with satisfactory results.

2. Experimental

2.1. Instruments and reagents

Electrochemical measurements were performed using a RST3000 electrochemical workstation (Zhengzhou Shiruisi Instrument Co., Ltd., Zhengzhou, China) with conventional three-electrode cell. A bare GCE (3 mm diameter) or modified GCE was used as the working electrode. An Ag/AgCl and a platinum (Pt) wire were used as reference and counter electrodes, respectively. All the potentials in this paper refer to Ag/AgCl. Electrochemical experiments were performed in 10 mL supporting electrolyte at room temperature.

L-Norvaline and metribuzin were purchased from Aladdin (http://www.aladdine.com/). Standard stock solution of metribuzin (2.14×10^3 μg/mL) was prepared with methyl alcohol and kept under 4 °C. It was diluted to necessary concentration before use. Working solutions were prepared daily by dilution with 0.1 mol L^{-1} Britton–Robinson buffer (B–R). All other reagents were of analytical grade and were used directly without further purification. 0.1 mol L^{-1} B–R buffer was prepared using a mixed acid (0.04 mol L^{-1} H_3PO_4 + 0.04 mol L^{-1} HAc + 0.04 mol L^{-1} H_3BO_3) that was titrated to the desired pH with 0.2 mol L^{-1} NaOH. A pH 8.0 (phosphate buffer solution) aqueous L-Norvaline solution was used for electro-polymerization.

2.2. Fabrication of poly(L-Norvaline)/GCE

Prior to modification, the GCE was polished to a mirror finish using finer emery-paper and 0.5 μm alumina slurry respectively. After rinsing thoroughly with water, the GCE was washed ultrasonically in absolute alcohol and double-distilled water again. Then L-Norvaline (2.5×10^{-3} mol L^{-1} in phosphate buffer solution, pH 8.0) was electrodeposited on the cleaned GCE surface by cyclic scanning between −1500 and +2500 mV with 100 mV s^{-1} for four cycles. This was the optimal polymeric condition for fabricating the poly(L-Norvaline)/GCE from test. Prior to use, the poly(L-Norvaline)/GCE was pretreated in a 0.1 mol L^{-1} B–R buffer solution by cyclic scanning between potentials of −400 and −1000 mV (5 cycles).

2.3. Analytical procedure

All electrochemical performances were carried out in B–R buffer solution (pH 1.82) at room temperature unless otherwise specified. Before measure, the poly(L-Norvaline)/GCE was put in pH 1.82 B–R solution for successive cyclic sweeps between −0.4 and −1.0 V at 100 mV s^{-1}. When the voltammogram became steady, a known volume of metribuzin standard solution was added into the electrochemical cell. Following each measurement, the poly(L-Norvaline)/GCE was put in the original solution for two cyclic scanning to renew the electrode surface.

3. Results and discussion

3.1. Electro-polymerization of L-Norvaline on GCE

For a polymer film modified electrode, its electrochemical response to the analyte was greatly affected by its polymerization conditions: polymeric potential window, pH of polymeric solution and thickness of polymer film. In current research, the polymerization conditions of poly(L-Norvaline) were investigated in detail. The evaluation criteria was its electrochemical response for metribuzin (10.7 μg/mL in 0.1 mol L^{-1} B–R, pH 1.82) by cyclic voltammetry.

3.1.1. Effects of electro-polymerization potential window

By selection, the suitable potential window for electropolymerization of L-Norvaline was between −1500 mV and +2500 mV. Fig. 1A showed the cyclic voltammograms for repetitive sweep 15 cycles. In the first cycle, two relatively weak anodic peaks (marked P1 and P2) at +180 mV and +1500 mV and a large cathodic peak (P3) at −694 mV were observed. From the second cycle on, the three peaks increased concurrently in subsequent cycles, suggesting that the amount of electroactive polymer increased on GCE surface. At the same time, it was also observed that the film growth was faster in the initial six cycles than that in subsequent cycles. From the tenth cycle on, the film grew more slowly. After electropolymerization, a uniform and greenish blue film of poly(L-Norvaline) could be seen by bare eyes on the GCE surface.

During the potential selection, we found that if the negative potential was put less than −1000 mV, the electropolymerization of L-Norvaline could not take place on the electrode surface. It was also found that the smallest positive potential was +1500 mV for the electropolymerization of L-Norvaline on GCE. And the more positive potential was set, the faster electropolymerization of L-Norvaline took place and more sensitive electrochemical response for metribuzin was observed. Fig. 1B displayed the current response of metribuzin at poly(L-Norvaline)/GCE obtained under different positive potential ranged from +2000 to +2600 mV (negative potential of −1500 mV), each for 5 cycles. This might be attributed to the more positive potential was, the more amino acid cation radicals generated, contributing to polymer fixed on the electrode surface. Considering the tolerance of GCE to the applied positive potential, +2500 mV was chosen as the positive polymerization potential.

3.1.2. Effects of supporting electrolyte pH

Next, the influence of polymerization solution pH was investigated in 0.2 mol L^{-1} phosphate buffer solution (PBS) containing 2.5×10^{-3} mol L^{-1} L-Norvaline. The solution pH was changed from 5.5 to 8.0 and the electro-polymerization potential window was