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Electrochemically pretreated glassy carbon electrode for electrochemical detection of fenitrothion in tap water and human urine

Welesamel Geremedhin [a], Maereg Amare [b,*], Shimelis Admassie [a]

[a] *Department of Chemistry, Addis Ababa University, P.O. Box 1176, Addis Ababa, Ethiopia*
[b] *Department of Chemistry, Bahir Dar University, P.O. Box 79, Bahir Dar, Ethiopia*

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ABSTRACT

A simple, inexpensive and highly sensitive electrochemical method for the detection of fenitrothion in tap water and human urine was developed using electrochemically pretreated glassy carbon electrode. Compared to untreated glassy carbon electrode, the electrochemically pretreated glassy carbon electrode showed a significantly enhanced peak current and peak potential shift indicating its catalytic activity towards fenitrothion reduction. Cyclic voltammetry was used to study the effect of pH, the dependence of peak current and peak potential on scan rate and to extract kinetic parameters (n, α, k_s, Γ, E^0 and $\Delta E_{pc,1/2}$). The peak current showed linear dependence on the concentration of fenitrothion with a linear regression equation, correlation coefficient (R^2) and limit of detection (LoD) of I_{pc} (μA) = 0.796 C (μM) − 0.043, $R^2 = 0.9972$ and 7.8×10^{-8} M (S/N = 3), respectively. Recoveries in the range 93.3–96.7% from spiked tap water and 85.73–93.3% from human urine signified the applicability of the developed method for determination of fenitrothion in environmental samples.

1. Introduction

Organophosphorus pesticides (OPs) are phosphoric acid esters or thiophosphoric acid esters which are among the most widely used pesticides for insect control [1]. OPs are extensively used in agriculture due to their high toxicity to insects and limited persistence in the environment [1,2].

These pesticides are toxic because they act as inhibitors of acetylcholinesterase, an enzyme that catalyzes the hydrolysis of the neurotransmitter acetylcholine in a very efficient way. This enzyme is present in vertebrates and insects and its inhibition can disrupt the transmission of nerve impulses [3,4].

Fenitrothion, O,O-dimethyl O-(3-methyl-4-nitrophenyl) phosphorothioate (Scheme 1), which is one of the OPs, is a contact and stomach poison [5,6]. It is widely used to control penetrating, chewing, and sucking insect pests (coffee leafminers, locusts, rice stem borers, wheat bugs, flours beetles, grain beetles, and grain weevils) on cereals, cotton, rice, and vegetables [6–9]. It is also used on farms and in public health programs as a residual contact spray for flies, mosquitoes, and cockroaches [7,10].

Due to its indiscriminate application, it finds a way into surface water bodies, through agriculture runoff and municipal waste water systems by ingestion and inhalation reaching the human system. Therefore, the presence of residues of such pesticides in natural waters and in foodstuffs is of major concern for public health reasons [5], which necessitated the development of methods that can be used to determine fenitrothion in environmental samples at trace levels.

Gas chromatography [11–13] and liquid chromatography [12–16] are among the frequently reported sensitive and specific analytical methods. Nonetheless, these techniques involve compound extraction, preconcentration and clean-up steps, which make them tedious, time-consuming, expensive, not environmentally friendly and not suitable for in-field analysis. Moreover, highly trained technicians and specialized laboratories are required [17].

On the other hand, electroanalytical techniques have been of great interest due to their advantages, including high sensitivity, comparative simplicity, rapid response and low cost [18]. Although reports have been made on the application of electroanalytical methods for determination of fenitrothion [4,6,8,9,19–21], many of which used mercury as working electrode whose toxicity cannot be overlooked while the remaining used polymer modified-electrodes.

Glassy carbon electrodes are currently in widespread use in electroanalysis, primarily because of their broad potential window, low background current, rich surface chemistry, low cost, easy surface modification, excellent mechanical and electrical properties, chemical inertness, availability in various forms and shapes and suitability for various sensing and detection applications [22–24].

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* Corresponding author.
E-mail address: maerega@yahoo.com (M. Amare).

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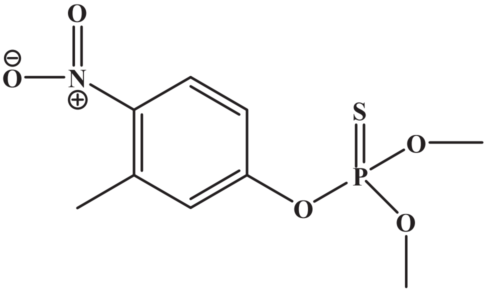

Scheme 1. Chemical structure of fenitrothion.

Pretreatment of GCEs is an important way to improve their performance. Various kinds of pretreatment methods such as electrochemical pretreatment [25–30], radio frequency plasma [31] and in situ laser irradiation [32] have been reported. Among these activation methods, electrochemical pretreatment is one of the most commonly used methods to improve electrochemical responses to biological compounds due to its good reproducibility and simple operation.

The present paper deals with the development of a simple, sensitive, selective and reproducible electrochemical method based on electrochemically pretreated glassy carbon electrode applied for determination of fenitrothion in tap water and human urine samples.

2. Experimental

2.1. Apparatus and chemicals

Voltammetric measurements were carried out using electrochemical analyzer (BAS CV-50 W) while electrochemical impedance spectroscopic experiments performed with an Autolab PGSTAT30 analyzer (Eco Chemie B.V. Netherlands) controlled by GPES/FRA 4.9 software. A conventional three-electrode system consisting of untreated glassy carbon electrode (UGCE) or pretreated glassy carbon electrode (PGCE) (3 mm diameter) as working electrode, platinum wire as auxiliary electrode and saturated calomel electrode (SCE) as reference electrode was used. Fenitrothion (FT) solutions were prepared from standard fenitrothion supplied by Fluka Chemika, Switzerland. Acetate buffer solution (ABS) prepared by mixing appropriate amounts of 0.1 M sodium acetate ($CH_3CO_2Na{\cdot}3H_2O$) and 0.1 M acetic acid (CH_3CO_2H) solutions was used as supporting electrolyte. The pH of the ABS was adjusted using pH meter (Digital JENWAY model 3510). All chemicals used were of analytical reagent grade and were used without further purification. All aqueous solutions were prepared with distilled water unless stated. All experiments were carried out at 19 ± 2 °C.

2.2. Analytical procedure

Stock solution of FT (0.534 mM) in ethanol (C_2H_5OH) was prepared and kept in the dark under refrigeration. Cyclic voltammetry was used to investigate the electrochemical behavior of FT at the working electrodes. The irreversible reductive peak of FT was used for the analyses. Analysis of the fenitrothion content of aqueous samples was performed using square wave voltammetry. Linear regression equation was used to calculate the recoveries of FT from different samples and hence the applicability of the method developed. 10 mM $Fe(CN)_6^{3+}/Fe(CN)_6^{4+}$ in pH 7 PBS containing 0.1 M KCl supporting electrolyte was used for the electrochemical impedance spectroscopic characterization of the working electrodes.

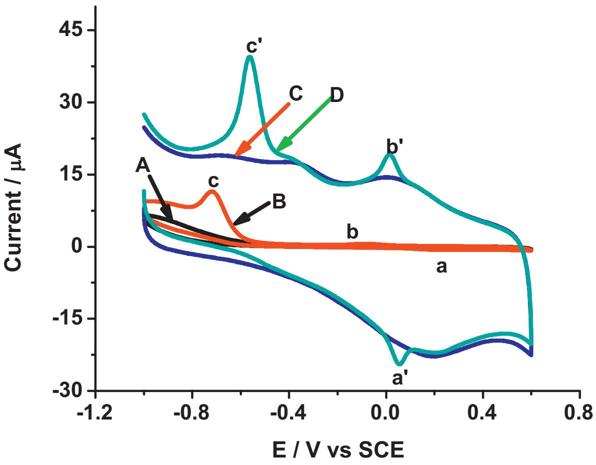

Fig. 1. Cyclic voltammograms of pH 5.0 ABS in the presence of 50×10^{-6} M FT (curves B and D) and in the absence of FT (curves A and C) at UGCE (curves A and B) and PGCE (curves C and D) at 100 mV s^{-1}.

2.3. Electrochemical pretreatment of the glassy carbon electrode

The glassy carbon electrode was polished carefully with alumina powder of different particle size (1.0, 0.3 and 0.05 μm size) to a mirror finish and then rinsed with distilled water to remove residual particles. The polished GCE was electrochemically pretreated following previously reported procedure [29]. Briefly: a constant oxidative potential of +1.75 V was applied on the polished electrode in pH 5 ABS for 200 s time. The pretreated electrode was then scanned between −0.4 and −1.0 V in pH 5 ABS at a scan rate of 0.1 V s^{-1} until a stable voltammogram was obtained. After each electrochemical determination, the electrode surface was cleaned prior to the next measurement by running a linear sweep in the reverse direction.

2.4. Preparation of human urine samples

Human urine collected from a volunteer was suction filtrated using a 0.45 μm pore size filter paper. The filtrate was then diluted with pH 5.4 ABS in a 1:20 (urine:buffer) volume ratio. The diluted urine was used to prepare three samples (b–d) with 20, 10 and 5 μM FT, respectively.

3. Results and discussions

3.1. Voltammetric behavior of fenitrothion at pretreated glassy carbon electrode

Fig. 1 depicts the cyclic voltammograms of UGCE (curves A and B) and PGCE (curves C and D) in pH 5.0 ABS in the absence (curves A and C) and presence of 50×10^{-6} M FT (curves B and D). Cyclic voltammogram of FT at the UGCE (curve B) showed an irreversible weak reductive peak at about −0.71 V and diffused quasireversible reductive and oxidative peaks centered at about −0.08 and +0.21 V, respectively. At the PGCE (curve D), similar peaks but with significantly enhanced peak current and peak potential shift were observed. Over 2-folds of peak current and a potential shift of about 140 mV was observed for the irreversibly reductive peak (peak c′ of curve D) at the PGCE. These effects clearly prove the catalytic effect of the electrochemically pretreated glassy carbon electrode for the reduction of FT. The peak current enhancement and peak potential