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Electrochemical Sensor for Determination of Fenitrothion at Multi-wall Carbon Nanotubes Modified Glassy Carbon Electrode

M. Tefera[a,b,]*, M. Tessema[a], S. Admassie[a] and S. Mehretie[a]
[a]*Department of Chemistry, Addis Ababa University, P. O. Box: 1176, Addis Ababa, Ethiopia*
[b]*Department of Chemistry, University of Gondar, P. O. Box: 196, Gondar, Ethiopia*

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A sensor, based on multi-wall carbon nanotubes modified glassy carbon electrode (MWCNT/GCE), was developed for determination of fenitrothion. Determining the surface area of MWCNT/GCE showed that this surface is three times more active than that of a glassy carbon electrode. The experimental parameters, such as the amount of MWCNTs, pH of the fenitrothion solution, preconcentration potential and preconcentration time were optimized. Under these conditions, reduction current showed a linear relationship with the concentration of fenitrothion in a range of 0.01-5.0 μM, with a detection limit of 6.4 nM. The modified electrode also exhibited good stability and reproducibility. The effects of possible interferents were studied and found to be negligible, indicative of high selectivity of the electrode. This sensor was also successfully employed for determination of fenitrothion in soil and Teff samples with recovery values in the range of 88.0-93.3% and 86.7-91.4%, respectively.

Keywords: Fenitrothion, Multi-wall carbon nanotube, Square wave voltammetry, Soil, Teff

INTRODUCTION

Organophosphorus compounds (OPs) are pesticides commonly applied to kill a wide range of insects on fruits, vegetables and commercial crops and chemical warfare agents [1-3]. The principal function of organophosphorus is to inhibit the activity of acetylcholinesterase (AChE) that regulates acetylcholine release [4,5], which leads to negative effect on the nervous system in both animals and humans [6]. As a result, the presence of pesticide residues and metabolites in food, water and soil currently represent one of the major issues for environmental chemistry [4]. Fenitrothion (O,O-dimethyl O-4-nitro-m-tolyl phosphorothionate) is a contact and non-persistent organophosphorus pesticide (Fig. 1), used in agriculture, horticulture, forestry and public health against chewing and sucking insects on cereals, cotton, orchard fruits, rice, vegetables and forests [7-9].

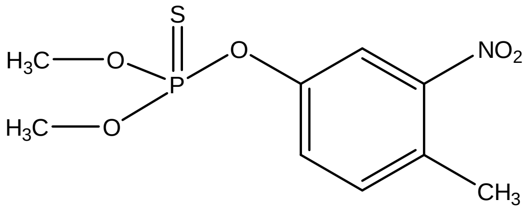

Fig. 1. Structure of fenitrothion.

With introduction of OPs to the market in the 1970s and increasing concerns on health and their potential environmental impact, many analytical methods such as soxhlet extraction (SE) followed by gas chromatography (GC) [10], paper bio-chromatographic method [11], spectrophotometric [12], solid-phase extraction and solid-phase microextraction followed by GC and GC/MS method [13-15] and high performance liquid chromatography [10,16,17] were developed to detect these compounds. However, these methods require complex separation processes in sample pretreatment process, expensive equipments and toxic solvents, time consuming, complex

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*Corresponding author. E-mail: mollatef2001@gmail.com and require trained personnel. Due to high sensitivity, good stability and cost-effectiveness, electrochemical methods are more advantageous [18].

Glassy carbon electrodes (GCE) were used extensively in electrochemistry and often as the base for surface modified electrodes [19]. However, low sensitivity and reproducibility, slow electron transfer reaction, low stability over a wide range of solution composition and high overpotential, bare electrodes have limited electrochemical applications. Modification of the electrode surfaces helps to enhance the sensitivity and selectivity of electrochemical sensors and prevents surface fouling [20,21]. Different materials were used for modification of electrode surfaces, such as carbon nanotubes, metal oxides, conductive polymers, and inorganic catalysts [22].

Carbon nanotubes (CNTs) having two distinct types of structures, namely single wall and multi-wall [23], are important classes of nanomaterials [24], used for modifying bare electrodes. Due to high mechanical strength, high electrical conductivity, high surface area, good chemical stability in both aqueous and non-aqueous solutions, relative chemical inertness in most electrolyte solutions and a wide potential window [25-27], the use of CNTs as modifier has recently received much attention [28-30]. Large aspect ratios and strong π-π interactions between the tubes, cause the aggregation of CNTs and further prevent their dispersibility in common solvents and matrices [31]. However, on functionalization of nanotubes both the interfacial interaction and hydrophilic nature can be improved [22].

Hanging mercury drop electrode [5,7], static mercury drop electrode [32] and activated glassy carbon electrode [33] were commonly used for detecting fenitrothion. Recently, few modified electrodes have been reported for the electrochemical detection of fenitrothion, like polyaniline modified glassy carbon electrode [9], nano-TiO_2 modified glassy carbon electrode [34] and poly(4-amino-3-hydroxynaphthalene sulfonic acid) modified glassy carbon electrode [35].

In this paper, determination of fenitrothion using MWCNT/GCE is described. MWCNT/GCE exhibits excellent electrocatalytic activity towards fenitrothion with high sensitivity and selectivity. Furthermore, the method was successfully utilized for the quantitative determination of fenitrothion in soil and Teff samples.

EXPERIMENTAL

Apparatus and Reagents

Electrochemical experiments were performed with a CHI760D electrochemical Workstation, at which CHI instruments (Austin, Texas, USA) were controlled by personal computer. Glassy carbon electrode (GCE) or MWCNT/GCE, platinum wire and Ag|AgCl (saturated KCl) used as working electrode, counter electrode and reference electrode, respectively. All pH measurements were determined by digital Jenway model 3345 ion meter. Ultrasonic cleaner YJ 5120-B (Shanghai, China) used for dispersed MWCNTs.

Fenitrothion, methanol, multi-wall carbon nanotubes (density ~2.1 g ml^{-1} at 25 C, diameter: 7.5-15 nm, length: 0.5-10 μm, purity > 99%), potassium ferrocynide, potassium chloride, dipotassium hydrogen phosphate and potassium dihydrogen phosphate were purchased from Sigma Aldrich. Stock standard solutions of fenitrothion were prepared with methanol. Phosphate buffer solution was prepared using 0.1 M K_2HPO_4 and 0.1 M KH_2PO_4 and the pH of the solutions were adjusted with 0.1 M NaOH and 0.1 M HNO_3. The working solutions of fenitrothion were prepared by diluting the stock solutions with phosphate buffer solutions.

Preparation of MWCNT/GCE

Before modification, glassy carbon electrode was carefully polished with 1.0, 0.3 and 0.05 μm alumina slurry in sequence until a mirror like surface obtained and then it was washed with deionized water. A 2.0 g of MWCNT was allowed to oxidize in a conc. HNO_3 and H_2SO_4 (1:3, V/V) at 90 °C for 8 h to remove impurities and to generate surface functional groups. Then, the functionalized MWCNT was allowed to cool down to room temperature and the resulting slurry was decanted consecutively and finally washed thoroughly with deionized water followed by filtration until the water pH reached 7 and then dried. Finally, the precipitate was dried at 90 °C in an oven for 10 h.

Multi-wall carbon nanotube solution was prepared by mixing 1 mg acidified MWCNTs in 1 ml double deionized water (1 mg ml^{-1}) and sonicated to debundling and dispersing the nanotubes [36]. MWCNT solution was dropped onto the surface of the polished glassy carbon electrode and dried under sun light until the solvent evaporated. Finally, the surface of the modified electrode was rinsed thoroughly with double-deionized water.

Sampling and Sample Preparation

Soil and Teff samples used in this study were collected from different farm sites in Alamata Woreda, South Tigria Administer Zone, Tigria Regional State, on the main road to Addis Ababa. Before analysis, soil samples were dried in a dish at room temperature for 5 days and then ground in a mortar to homogenize. Anhydrous sodium sulfate (200 mg) and dichloromethane-acetone mixture (2:1, v/v; 50 ml) were added to the soil sample. The mixture was sonicated for 5 min and shacked vigorously by hand for 10 min. The mixture then centrifuged to obtain the supernatant layer followed by suction filtration through Buchner funnel. Finally, the solvent was evaporated to dryness using rotatory evaporator.

To the dry sample 4 ml methanol was added and the solution was diluted with phosphate buffer (pH 6) and this sample solution was analyzed using square wave voltammetry. After homogenization and powdering, 15 g Teff was twice extracted with 50 ml of dichloromethane and transferred into Buchner funnel and filtered under suction.

To the extract 50 ml water, 15 ml saturated sodium chloride and 50 ml dichloromethane were added. Then, the mixture was thoroughly shaked for 5 min in a separatory funnel. The combined extracts were filtered over 50 g of anhydrous sodium sulphate and the solvent was evaporated through rotatory evaporator. Methanol was added to the residue and further diluted with phosphate buffer for voltammetry analysis.

RESULTS AND DISCUSSION

Electrochemical Characterization of MWCNT/ GCE

The electrochemical behaviors of MWCNT modified GCE were investigated using cyclic voltammetry in 0.1 mM

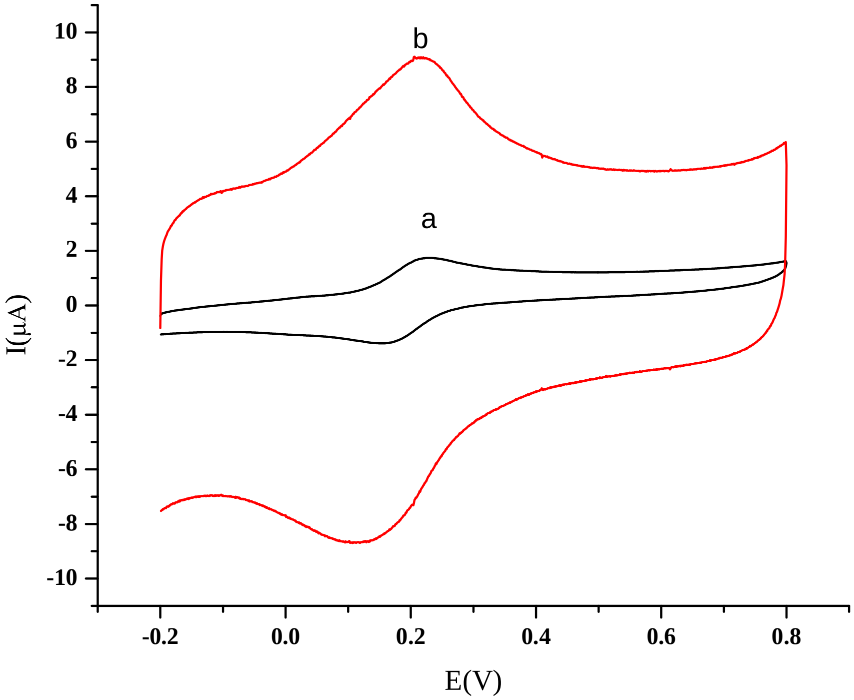

Fig. 2. Cyclic voltammograms of 0.1 mM $Fe(CN)_6^{4-}$ in 0.1 M KCl on (a) GCE and (b) MWCNT/GCE at a scan rate of 100 mV s^{-1}.

potassium ferrocyanide in the presence of 0.1 M KCl. The electrochemical response of 0.1 M $K_4[Fe(CN)_6]$ at MWCNT modified GCE exhibits a reversible reaction (Fig. 2). Both the anodic and cathodic peak currents at the multi-wall carbon nanotube modified electrode show three-fold increment compared to those of the bare glassy electrode. The enhancement of the peak current demonstrates the modification of GCE by MWCNT.

The influence of scan rate on ferro/ferric probe at MWCNT/GCE was also studied in the range between 40 and 200 mV s^{-1}. It was found that the peak current increases linearly with the square root of scan rate [37], suggesting that the electrode process is diffusion controlled.

Under the same measurements, the surface active area of GCE and MWCNT/GCE was estimated using the Randles-Sevcik equation [38]:

$$i_p = (2.69 \times 10^5)n^{3/2}ACD^{1/2}\,v^{1/2} \qquad (1)$$

where, i_p is the peak current, A is the surface area of the electrode, v is the scan rate and C is the concentration of $K_4Fe(CN)_6$, and D is the diffusion coefficient (6.2×10^{-6} cm^2 s^{-1}). Thus, the slope of i_p *vs.* $v^{1/2}$ was 15.6×10^{-6} A $(V\ s^{-1})^{-1/2}$ and the electrochemical active surface area of the MWCNT/GCE was found to be 0.232 cm^2, which is about five times higher than that of the bare GCE (0·047 cm^2). The significant increment in the surface active area suggests that MWCNT/GCE would be useful for electrochemical sensing.

Electrochemical Behavior of Fenitrothion

The electrochemical behaviors of fenitrothion at bare GCE and MWCNT/GCE were examined in the potential range of -0.9 V to 0.5 V at scan rate of 100 mV s^{-1}. Fenitrothion exhibits an oxidation peak at -0.083 V(O_2) and two reduction peaks at -0.121 V (R2) and -0.671 V (R1) with a remarkable increment at MWCNT/GCE compared to

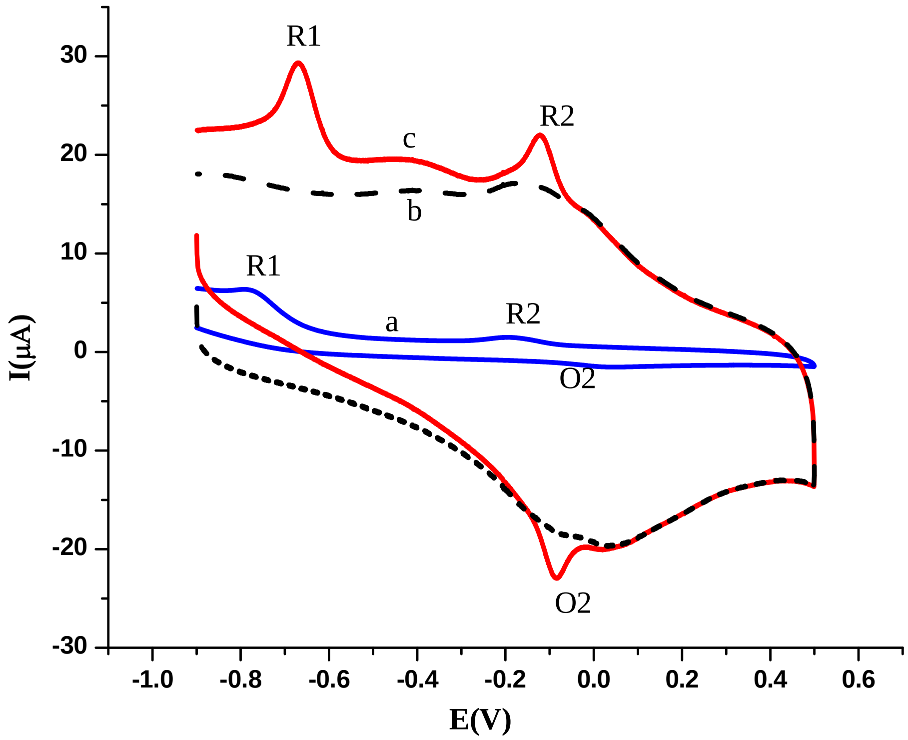

Fig. 3. Cyclic voltammograms of 40 μM fenitrothion solutions at GCE in 0.1 M PBS pH 7 (a), 0.1 M phosphate buffer solution (pH 7.0) at MWCNT/GCE (b) and 40 μM fenitrothion solution in 0.1 M PBS pH 7 at MWCNT/GCE(c). Scan rate: 100 mV s^{-1}.

that at bare GCE (Fig. 3). The reduction peak R1 can be designated as the irreversible reduction of the nitro group (NO_2) on fenitrothion to hydroxylamine group (NHOH), which is responsible for the formation of the redox couple (O2/R2). A pair of redox peaks (O2 and R2) relates the reversible conversion of hydroxylamine group into nitric oxide [9,33-35]. The increased currents as well as the potential shifts of anodic peak to more negative and reduction peaks to more positive values demonstrated the catalytic behavior of MWCNT/GCE towards fenitrothion. This behavior can be attributed to the larger surface active area of MWCNT to trap fenitrothion [39].

Effect of Varying Amount of MWCNTs on Fenitrothion

The quantity of MWCNT needed to modify GCE was optimized to obtain a better electrochemical response. Figure 4 shows the effect of various volumes of MWCNTs coated on the surface of GCE towards the response of fenitrothion. The reduction peak current increased as the volume of MWCNT suspension increased until reached to the maximum value of 10 μl. Then, the reduction peak current remains nearly constant when the amount of MWCNT exceeds to 10 μl. Therefore, 10 μl of MWCNTs suspension was used to modify the surface of glassy carbon electrode in this study.

Effect of pH

The effect of solution pH on the reduction peak current and the peak potential of $-NO_2$ group of fenitrothion were investigated using cyclic voltammetry in phosphate buffer over the pH range 5-7.5. The peak current increased with

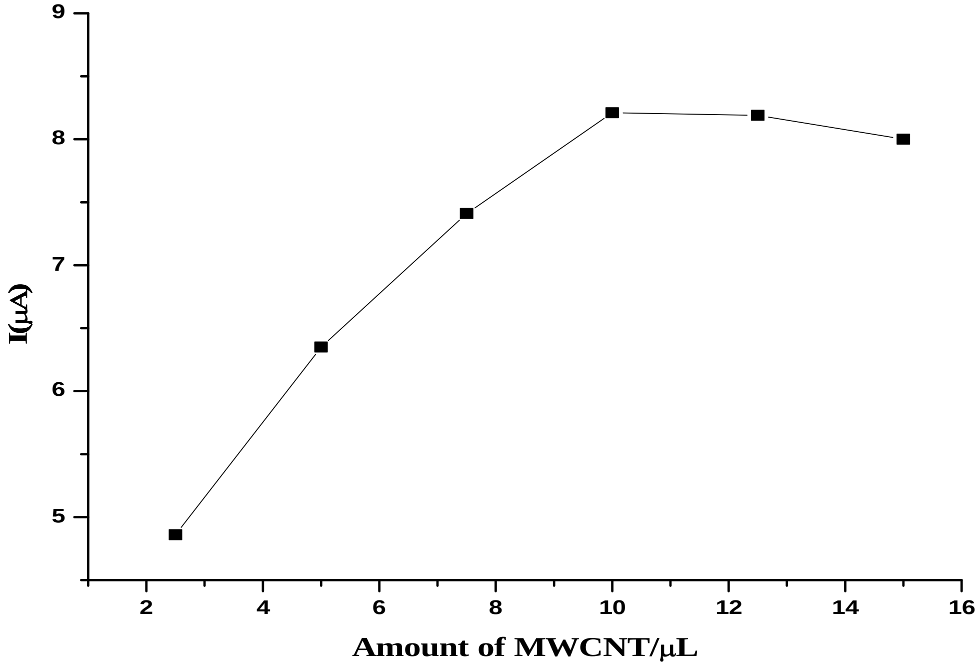

Fig. 4. Effect of MWCNTs on reduction peak current of 40 μM fenitrothion in 0.1 M phosphate buffer solution (pH 7.0) at 100 mV s^{-1}.

the pH value until it attained the maximum value at pH 6.0 and then decreased with further increase in the pH value (Fig. 5A). The reduction peak potential was also affected by the solution pH and it shifted negatively with increasing pH values (Fig. 5B). Peak potential shows a linear relationship with solution pH with a regression equation E(V) = 0.040 pH + -0.399 (R^2 = 0.9997), indicating that reduction of the nitro-group to hydroxylamine group occurs by proton transfer. Therefore, pH 6.0 was selected as the optimum pH.

Effect of Scan Rate

The influence of scan rate on the reduction peak current of 40 μM fenitrothion on MWCNT/GCE was studied within the range of 40 to 225 mV s^{-1}. Figure 6 shows that the reduction peak current increases linearly with increasing the scan rate, with linear equation i_{pc} = 0.118v + 15.91 and regression coefficient of 0.9966. The result indicates that the electrochemical reaction of fenitrothion at MWCNT/GCE exhibits an adsorption controlled process. The reduction peak potential was also dependent on scan rate. The peak potential shifted to the more negative values with increasing the scan rate, further confirming the irreversibility of fenitrothion reduction (R1).

Effect of Accumulation Time and Potential

Because of the adsorption nature of fenitrothion electrochemical process at MWCNT/GCE, the effects of accumulation parameters of the peak current were required to be optimized. The influence of accumulation potential on reduction current of 40 μM fenitrothion was examined in the range of -100 to -550 mV for an accumulation time of 40 s. The reduction peak current apparently increases as the accumulation potential becomes more positive (Fig. 7A). The maximum peak current was obtained at -400 mV and then decreased with further increasing of accumulation potential. Thus, an accumulation potential of -400 mV was used in subsequent studies.

The effect of accumulation time on the reduction peak current of fenitrothion was also examined. The peak current increased as the accumulation time increased up to 80 s and no significant change was observed after this time (Fig. 7B), indicating that the accumulation of fenitrothion at the MWCNT/GCE surface nearly has reached to a saturation state at 80 s. Therefore, 80 s was considered as the optimum

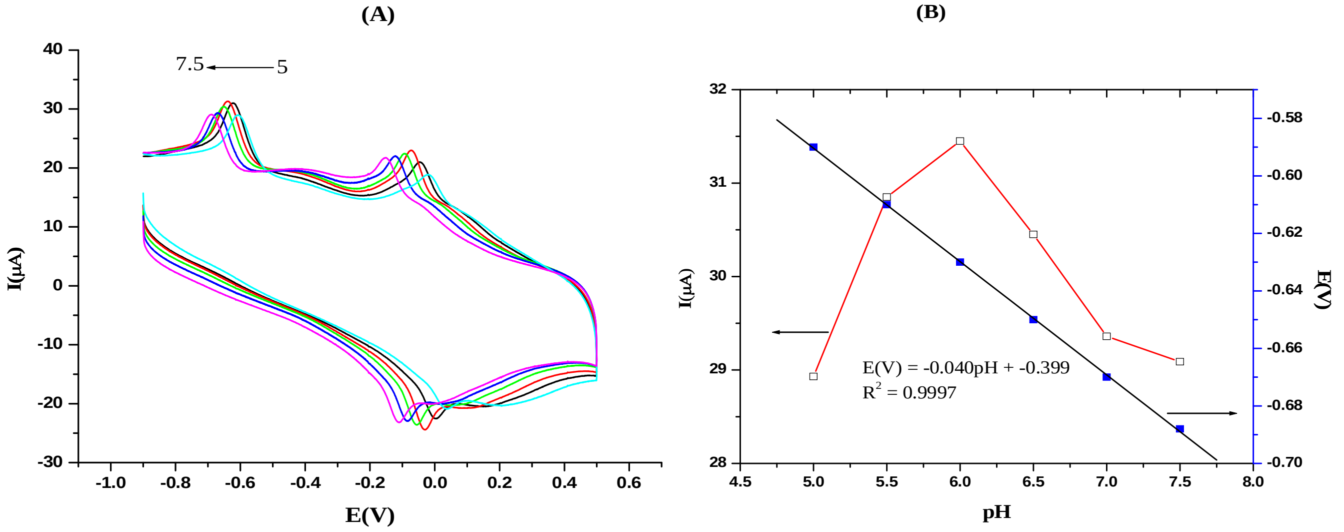

Fig. 5. (A) Cyclic voltammograms of 40 μM fenitrothion in 0.1 M phosphate buffer solution at various pH values (B) Plots of current *vs.* pH and peak potential *vs.* pH of 40 μM fenitrothion at MWCNT/GCE.

accumulation time for the measurement.

Effect of Square Wave Parameters

The effect of step potential for the reduction of fenitrothion was studied over the range of 2-20 mV by fixing the amplitude and frequency at 50 mV and 15 Hz, respectively. The peak current was increased significantly up to 10 mV with the best shape for the peak. The influence of amplitude on the reduction of 40 μM fenitrothion was also investigated in the range of 20-110 mV, the peak current was found to increase with increasing amplitude and reached to a maximum at 90 mV and then decreased. Thus, 90 mV was fixed as the best amplitude in detection of fenitrothion. In addition, the impact of square wave frequency on the peak current was evaluated at 10 mV step potential and 90 mV amplitude. The frequency was varied in the range between 5 and 30 Hz, the peak currents became maximum at 20 Hz and gradually decreased thereafter. Hence, for further electrochemical investigation, step potential 10 mV, amplitude 90 mV and 20 Hz frequency were selected as the optimal values in this study.

Performance of MWCNT/GCE

A calibration curve was constructed under the optimum conditions to demonstrate the relationship between square wave voltammetry peak current and the concentration of fenitrothion. Figure 8 shows that peak current increases with increasing fenitrothion concentration in the range of 0.01-5.0 μM at MWCNT/GCE. The linear relationship can be expressed with a linear regression equation i_p (μA) = 7.20C (μM) + 0.762 and R^2 = 0.9975 (inset of Fig. 8). The sensitivity of MWCNT/GCE was 7.2 (μA/μM) and the detection limit was obtained 6.4 nM based on the signal-to-noise ratio of 3.

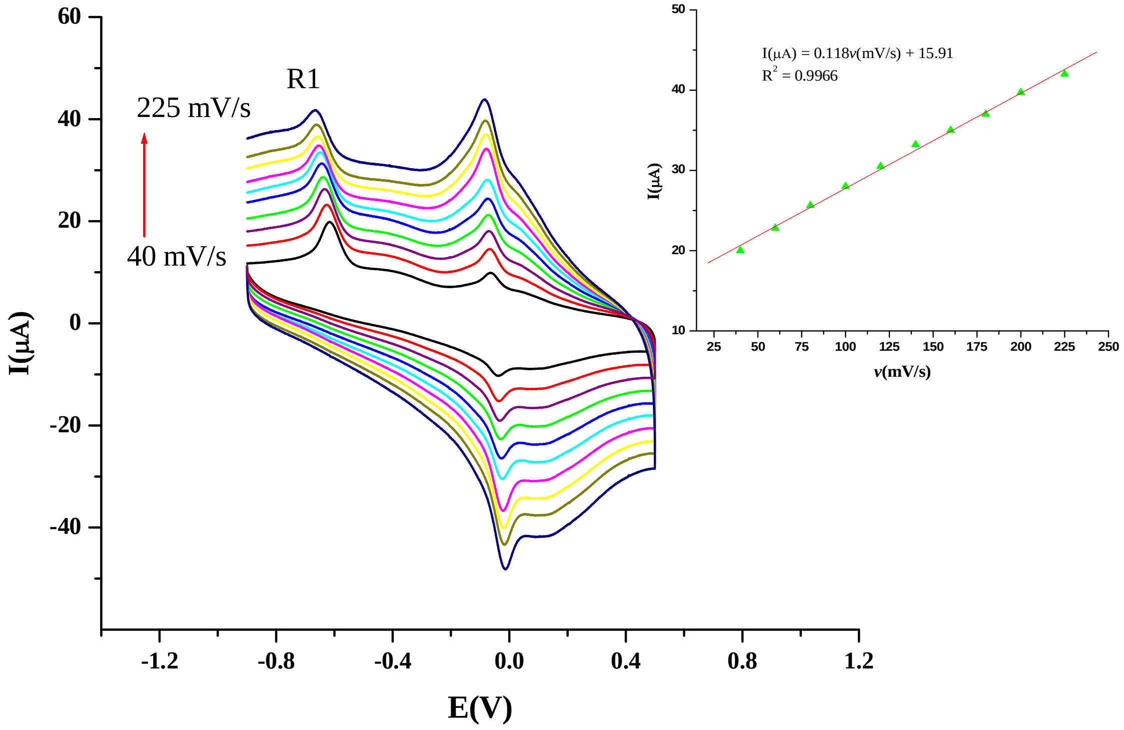

Fig. 6. The cyclic voltmmograms of 40 μM fenitrothion in 0.1 M phosphate buffer solution (pH 6.0) on MWCNT/GCE at various scan rates (40, 60, 80, 100, 120, 140, 160, 180, 200 and 225 mV s^{-1}). Inset: plot of reduction peak current *vs*. scan rate.

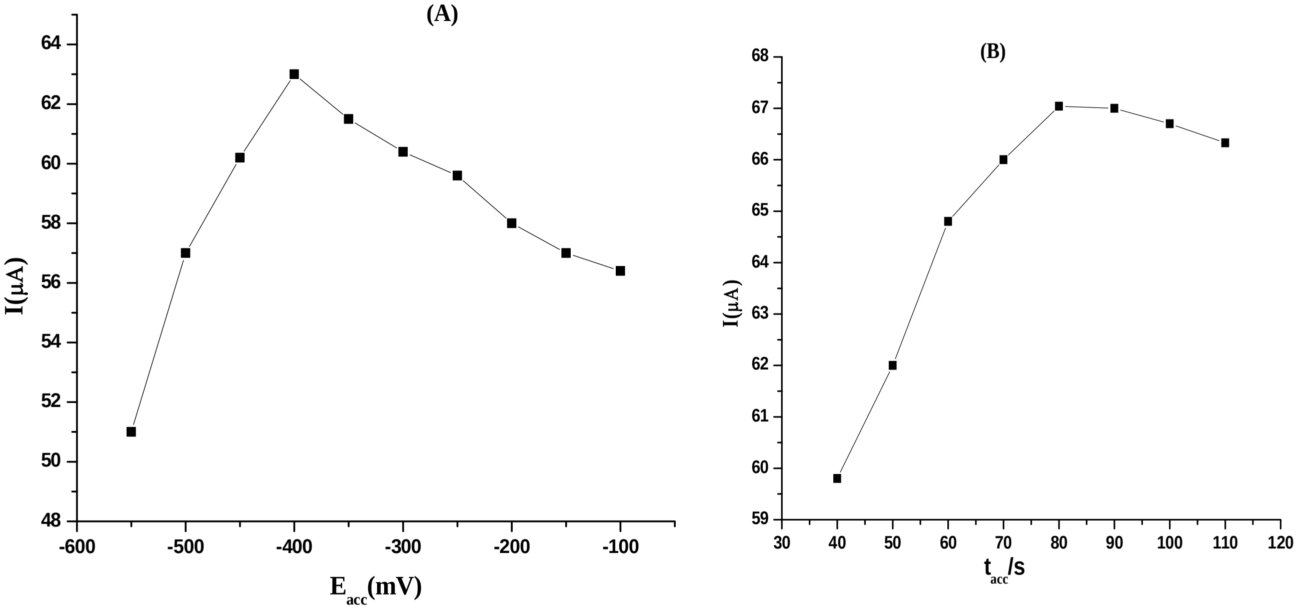

Fig. 7. Effects of (A) accumulation potential and (B) accumulation time on peak current of 40 μM fenitrothion in 0.1 mM phosphate buffer solution of pH 6.0 at MWCNT/GCE.

Performances of the modified electrode are compared with those previously reported in literature as shown in Table 1 [5,7,9,32-35]. The results obtained in this work shows a lower detection limit than most other results reported from other electrochemical methods in determination of fenitrothion at the surface of different bare and modified electrodes.

The repeatability of the MWCNT/GCE was evaluated in replicating measurements of 40 μM fenitrothion solution under optimized conditions in one day and the relative standard deviation (RSD) was found 2.88% (n = 10), indicating excellent repeatability of the response at MWCNT/GCE. The reproducibility of the sensor was also examined by measuring 40 μM fenitrothion for three MWCNT/GCEs under the same experimental conditions, and the relative standard deviation of the responses of modified electrodes was 4.5%, which is less than 5%. Furthermore, the long-term stability of the electrode was evaluated by measuring the current responses at 40 μM fenitrothion after keeping in phosphate buffer solution (pH 6.0) over a period of 10 days. The electrochemical responses indicated that the current responses decreased only 7.2% compared to the initial response, supporting the long-term stability of MWCNT/GCE.

The effects of interfering substances on determination of fenitrothion were investigated at the surface of MWCNT/GCE by addition of various species to 2 μM fenitrothion in pH 6.0 phosphate buffer solutions. The experimental results show that the voltammetric determination of fenitrothion was not affected by 1000-fold excess concentration of Na^+, Co^{2+}, ascorbic acid and phenol as presented in Table 2. Moreover, 100-fold increment in a concentration of 4-aminophenol, 10-fold of nitrobenzene and 1:1 ratio of 4-nitrophenol had no influence on the current response of fenitrothion (signal change below 5%). NO_2-group containing interferents exhibited a strong tendency to interfere with fenitrothion at higher concentration. This can be attributed to the electron withdrawing group $-NO_2$ tending to reduce to hydroxylamine-group (R-NHOH) at the surface of MWCNT and consequently abrupt changing of electrochemical response of the analyte [40]. In general, the results reveal that MWCNT/GCE electrode exhibits a good selectivity towards determination of fenitrothion.

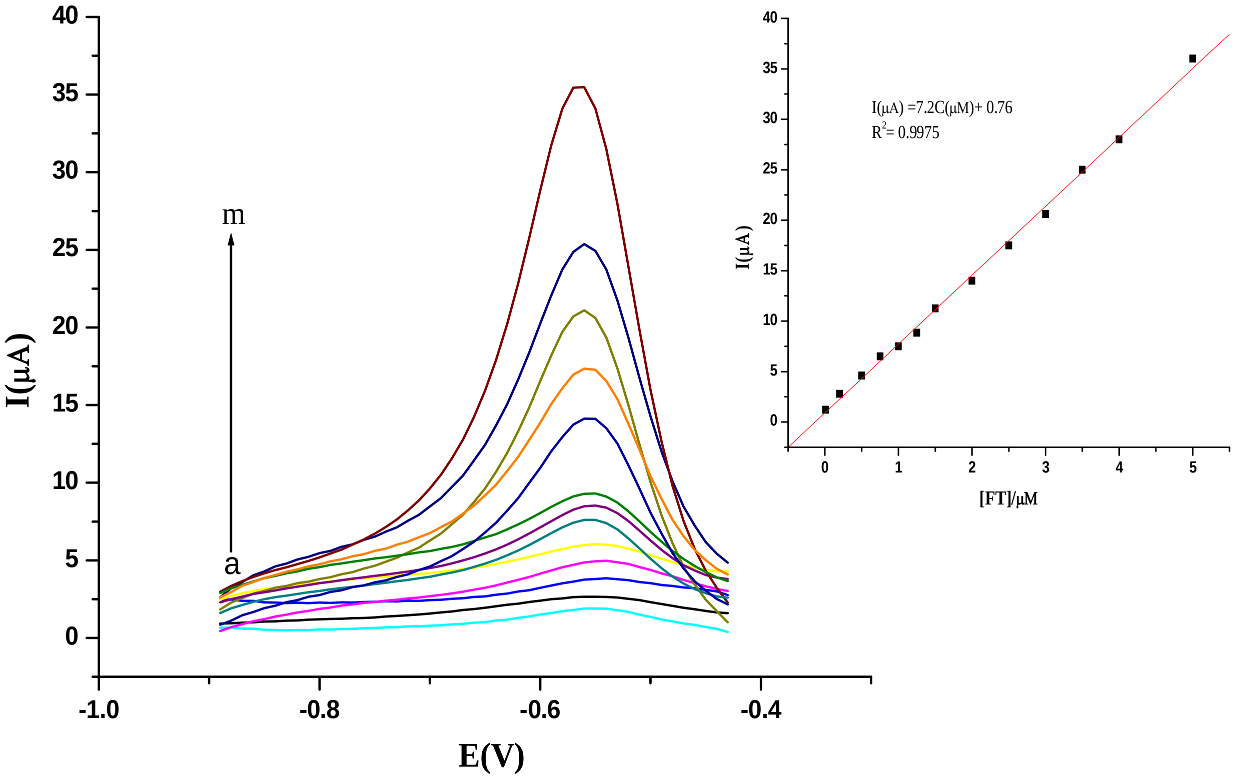

Fig. 8. Square wave voltammograms of various concentrations of fenitrothion (a) 0.01 µM, (b) 0.2 µM, (c) 0.5 µM, (d) 0.75 µM, (e) 1.0 µM, (f) 1.25 µM, (g) 1.5 µM, (h) 2.0 µM, (i) 2.5 µM, (j) 3.0 µM, (k) 3.5 µM, (l) 4.0 µM and (m) 5.0 µM.

Table 1. Comparison of Analytical Parameters for Reduction of Fenitrothion at MWCNT/GCE and other Sensors

Electrode	Modifier	Linear Range (µM)	LOD (nM)	Ref.
HMDE	-	0.01-1.0	0.13	[5]
HMDE	-	0.093-0.89	5.2	[7]
GCE	Polyaniline	0.01-100	7.2	[9]
STMDE	-	0.01-6.2	10	[32]
GCE	Activated	0.4-50	78	[33]
GCE	Nano-TiO_2	0.025-10	10	[34]
GCE	Poly(AHNSA)	0.001-6.6	0.8	[35]
GCE	MWCNT	0.01-5.0	6.4	This work

STMDE-Static mercury drop electrode. HMDE- Hanging mercury drop electrode.

Table 2. Effect of Interferents on Detection of Fenitrothion at MWCNT/GCE

Interferent	[Interferent] (μM)	Current response (%)[a]	RSD (%)
Na^+	2000	99.2	3.4
Co^{2+}	2000	97.7	4.8
Ascorbic acid	2000	98.7	3.2
4-Aminophenol	200	94.6	3.4
4-Nitrophenol	2	95.3	78
Nitrobenzene	20	95.5	1.0
Phenol	2000	97.6	3.6

[a] Average of three replicate determinations

Table 3. Recovery Study of Fenitrothion in the Soil and Teff Samples (n = 3) at the MWCNT/GCE

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Samples	Added (μM)	Found (μM)[a]	Recovery (%)	RSD (%)
Soil	2.5	2.2	88.0	2.3
	3.0	2.8	93.3	3.1
	3.5	3.1	88.6	1.3
Teff	2.0	1.8	90.0	1.8
	3.0	2.6	86.7	2.5
	3.5	3.2	91.4	1.5

Application to Real Sample

The practical applicability of MWCNT/GCE was evaluated by applying it in determination of fenitrothion in soil and Teff samples collected from Alamata Woreda. The procedure for the fenitrothion analysis was followed as described in the procedural section (2.3). No voltammetric peaks corresponding to fenitrothion were observed over analyzing the samples. Thus, in recovery tests, we adopted the standard additions approach to estimate the reliability. Different amounts of fenitrothion were spiked into the soil and Teff samples, and adjusted to a certain concentration. The results obtained have been summarized in Table 3. The recoveries of soil were in the range of 88.0-93.3% and for Teff were in the range of 86.7-91.4%. These results indicate that the proposed method can be efficiently used for determination of fenitrothion in soil and Teff samples.

CONCLUSIONS

High surface active area, subtle electronic properties and strong adsorptive ability of MWCNT alter the electrochemical performance of GCE. The MWCNT/GCE exhibits an excellent electrocatalytic activity in lowering overpotential and a significant enhancement in peak current of fenitrothion as compared to those of the bare electrode, with a wider linear range, higher sensitivity and less than 5% reproducibility. The developed sensor was successfully applied for determination of fenitrothion in soil and Teff samples with a good recovery (88.8-93.3% and 86.7-91.4%, respectively) without the interference of coexisting species. Therefore, the MWCNT modified glassy electrode could be a potential candidate for determination of fenitrothion in environment samples.

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