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SHORT COMMUNICATION

Stearic acid modified glassy carbon electrode for electrochemical sensing of parathion and methyl parathion

J. Nancy Nirmala · A. Kumaravel · M. Chandrasekaran

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Abstract Stearic acid modified glassy carbon electrode for the sensing of parathion and methyl parathion was fabricated. The electrochemical responses for parathion and methyl parathion were investigated by cyclic voltammetry, differential pulse voltammetry and amperometry. The results on stearic acid modified electrode and bare glassy carbon electrode were compared. Higher sensing current was obtained on stearic acid modified glassy carbon electrode. Analytical characteristics of the sensor such as sensitivity, linear dynamic range, lower detection limit and response time were evaluated.

Keywords Parathion · Methyl parathion · Electrochemical sensor · Stearic acid · Glassy carbon

1 Introduction

Organophosphorus (OP) pesticides include variety of toxic chemicals, e.g. parathion, methyl parathion, fenitrothion and malathion. For the sake of human health and environmental protection, it is important to develop a rapid, selective and sensitive method for the detection of OP pesticides [1]. Analysis of these pesticides are routinely carried out by using mass spectrometry and gas or liquid chromatography [2]. These analytical instruments are available only in centralized laboratories. Moreover, these analytical techniques cannot be applied in the field conditions. Biological methods, such as immunoassay, have also been reported [3, 4]. The major drawback of these methods is time consuming. Electro analytical method is an alternative and viable method to meet these requirements because of its low cost, compact nature, field deployment and produce selective and sensitive responses within a very short time. The major problem encountered in the electrochemical techniques is the fouling of the electrode surface due to the coverage of bulky pesticide molecules on its surface, which affects the reproducibility of the sensor. This problem is avoided by applying suitable modifier on the electrode surface, which also offers multifunction simultaneously [5–15]. Hexadecane is the neutral organic compound, which was used as the modifier for the detection of parathion [16]. Stearic acid is the non-electro active compound, which was used as the modifier for the detection of paraquat [17]. Parathion and methyl parathion possess similar structure with paraquat, which are extensively used in agricultural field. In this paper we report a stearic acid modified glassy carbon electrode for the sensing of parathion and methyl parathion. Cyclic voltammetry, differential pulse voltammetry and amperometry were used for electrochemical detection.

2 Experimental

Methyl parathion and parathion were purchased from Accu Standard, USA. Stock solutions of parathion (2540 μM) methyl parathion (2070 μM) were prepared from methanol. Working solution was prepared by dilution with Britton-Robinson buffer (B-R) of pH 2.56. The B-R buffer solution of pH 2.56 was prepared by adding 15 mL of 0.2 M sodium hydroxide solution into 100 mL of a mixed acid,

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containing 0.04 M of each boric, ortho-phosphoric and acetic acids. Stearic acid was purchased from Merck India Limited, Bombay. Other reagents used were of analytical reagent grade and double distilled water was used to prepare aqueous solutions. Cyclic voltammetry, differential pulse voltammetry and amperometry were performed with computer controlled Autolab PGSTAT 30 (Eco Chemie, Netherlands) electrochemical system. A three-electrode configuration was employed, consisting of stearic acid coated GCE (Alfa Aesar GC 3 mm diameter) served as a working electrode, platinum foil and platinum wire served as the counter and reference electrodes respectively. Electrochemical experiments were carried out in a 20 mL voltammetric glass cell at room temperature (25 ± 1 °C). Prior to electrochemical measurements, the solution was deoxygenated by purging with pure nitrogen for 15 min. The GC electrode was hand polished to a mirror finish by using Premier emery papers 2/0, 3/0 and 4/0. The polished electrode was thoroughly rinsed with doubly distilled water and then cleaned with trichloroethylene. The electrode was coated with 2 μL solution of 1% stearic acid dissolved in dichloromethane by drop dry method. The solvent was left to evaporate for 10 min in air, whereupon a uniform film was formed over the entire surface. It was used for electrochemical measurements.

3 Results and discussion

Parathion is reduced around at −0.873 V at stearic acid modified glassy carbon electrode. The peak current increases with the increase in the concentration of parathion. About 20% increase in the peak current was observed compared with the current obtained at bare glassy carbon electrode under identical conditions. The enhancement occurs because parathion penetrates through the stearic acid layer and reaches the surface of the electrode thereby increasing the concentration near the electrode surface whereas it can reach the surface of the bare electrode by diffusion only [15, 16]. Figure 1A shows the cyclic voltammetric response of different concentrations of parathion at stearic acid modified glassy carbon electrode. The peak potential is negatively shifted slightly with increasing the concentrations of parathion. This is due to the weak adsorption of parathion on the electrode surface which is commonly observed for the modified electrode surfaces [8]. The reduction peak obtained at stearic acid modified electrode was sharp when compared with the reduction peak obtained at bare glassy carbon electrode. Methyl parathion possesses similar structure with parathion, which is reduced around at −0.900 V at stearic acid modified GCE. This reduction peak is due to irreversible $4e^-$ transfer reduction of nitro group into hydroxylamine group [18]. A linear relationship between the peak currents and the square root of the scan rate was obtained for both parathion and methyl parathion, which shows that they undergo diffusion controlled reduction process [19]. The non linear relationship between the peak current and the different concentrations of methyl parathion reveals that there is electrode fouling (Fig. 1B). This may be due to strong blocking/adsorption of methyl parathion on stearic acid film. Hence cyclic voltammetric method can conveniently be used for the detection of parathion.

Differential pulse voltammetry (DPV) is more sensitive technique than cyclic voltammetry and linear scan voltammetry. DPV was recorded with the following optimized

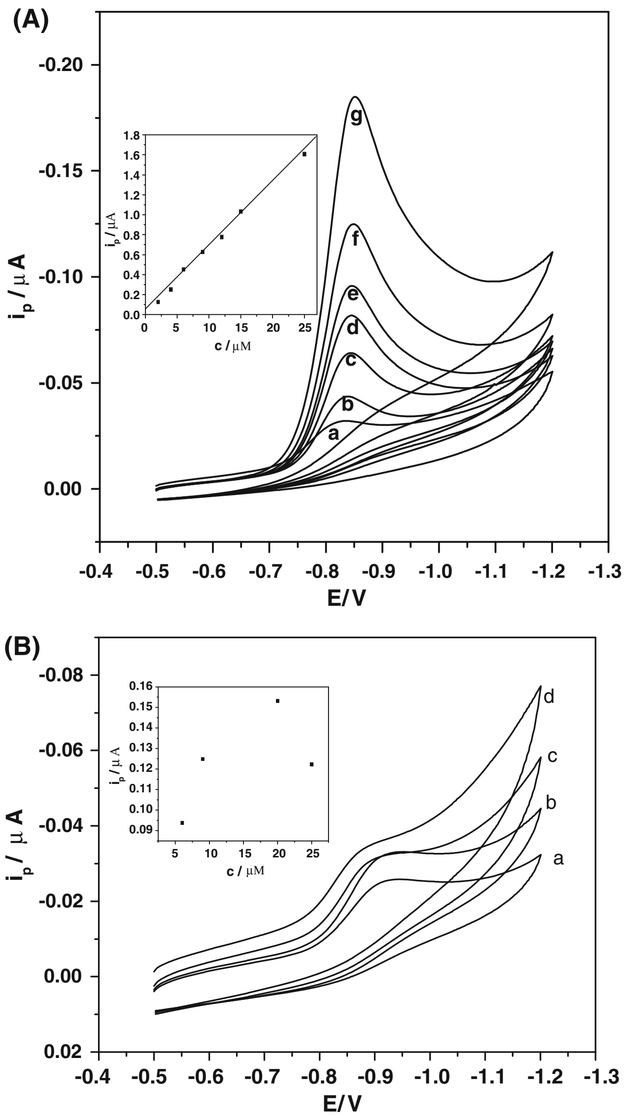

Fig. 1 Cyclic voltammograms of parathion (**A**) at different concentrations: (*a*) 2, (*b*) 4, (*c*) 6, (*d*) 9, (*e*) 12, (*f*) 15, (*g*) 25 μM and methyl parathion (**B**) at different concentrations: (*a*) 6, (*b*) 9, (*c*) 20, (*d*) 25 μM at stearic acid modified GCE in 2.56 pH B-R buffer solution. Scan rate: 20 mV s^{-1}. *Insets* show the respective calibration graphs

instrumental settings: modulation amplitude, 40 mV; modulation frequency, 30 Hz; modulation step, 4 mV. Figure 2A, B shows the differential pulse voltammetric response of parathion and methyl parathion. The peak current increases with the increase in the concentration of parathion and methyl parathion. The linear relationship was observed for the concentration ranging from 2 to 9 μM with the correlation coefficient of 0.9998 for parathion and from 2 to 25 μM for methyl parathion with the correlation coefficient of 0.9987. The detection limit was found to be 0.02 μM for parathion and 0.6583 μM for methyl parathion.

Amperometry is a voltammetric technique in which the potential is kept constant for the measurement of steady state current [20]. The obtained current is a linear function of analyte concentration in the solution. Figure 3 shows the amperometric relationship between the concentration and the current at bare GCE for parathion. It reveals that the variation of current with the concentration was linear only at lower concentrations and at higher concentrations the current decreased, this is due to the coverage of pesticide molecules on the electrode surface and also produce noise during measurements. The fouling of the electrode was not observed for stearic acid modified GCE. This is due to the prevention of strong blocking/adsorption of pesticide molecules on stearic acid film. Noise level was also low during measurements.

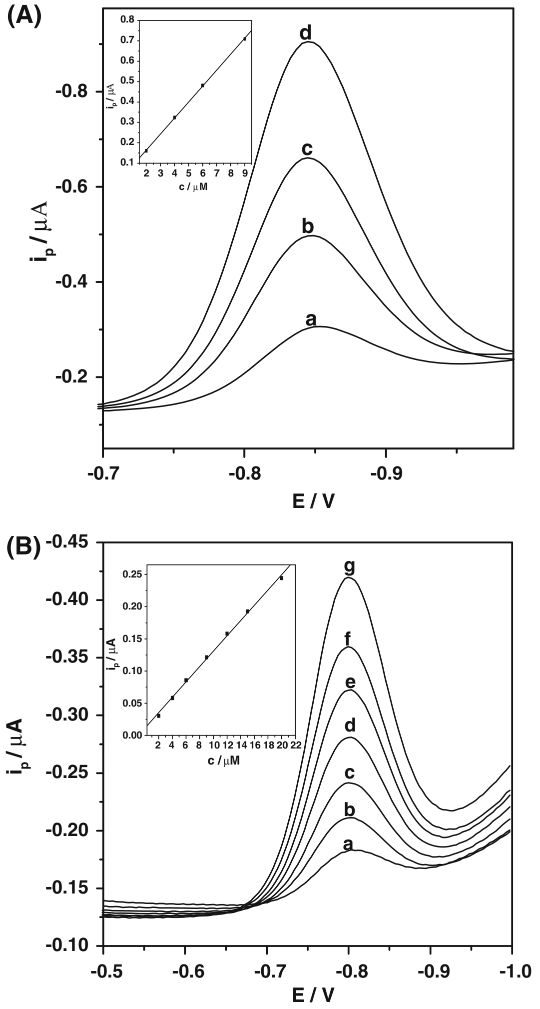

Fig. 2 Differential pulse voltammograms of parathion (**A**) at different concentrations: (*a*) 2, (*b*) 4, (c) 6, (*d*) 9 μM and methyl parathion (**B**) at different concentrations: (*a*) 2, (*b*) 4, (*c*) 6, (*d*) 9, (*e*) 12, (*f*) 15, (*g*) 25 μM at stearic acid modified GCE in 2.56 pH B-R buffer solution. *Inset* shows the respective calibration graphs

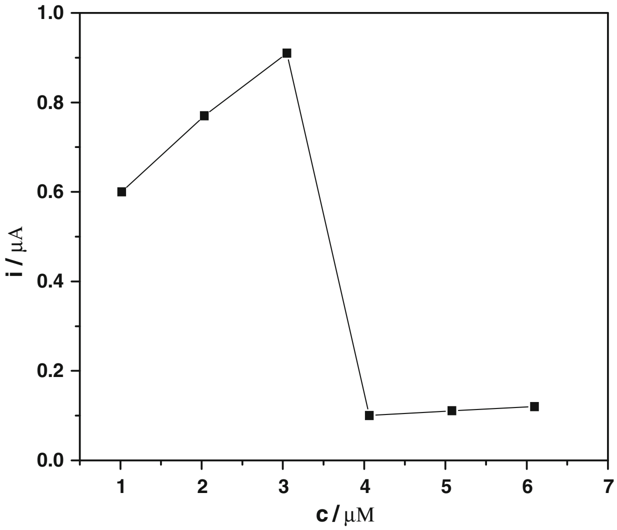

Fig. 3 Amperometric relationship between the concentration and the current for parathion at bare glassy carbon electrode in 2.56 pH B-R buffer solution

Figure 4A, B shows the amperometric response of parathion and methyl parathion at stearic acid modified GCE. The i–t curves obtained for the constant addition of 1.016 μM for parathion and 2.07 μM for methyl parathion to the 2.56 pH B-R buffer solution. The operating potential was −0.900 V. The solutions were stirred during measurements. The sensor attains the steady state within 10 s. The calibration graph for parathion and methyl parathion were constructed. The variation of the analyte concentration on the current was linear for the concentrations ranging from 1.016 to 6.096 μM with the correlation coefficient of 0.9997 for parathion and from 2.07 to 12.42 μM for methyl parathion with the correlation coefficient of 0.9992. The detection limits were found to be 0.7929 μM for parathion and 0.95 μM for methyl parathion.

4 Conclusions

In this work, the stearic acid modified glassy carbon electrode for the sensing of parathion and methyl parathion

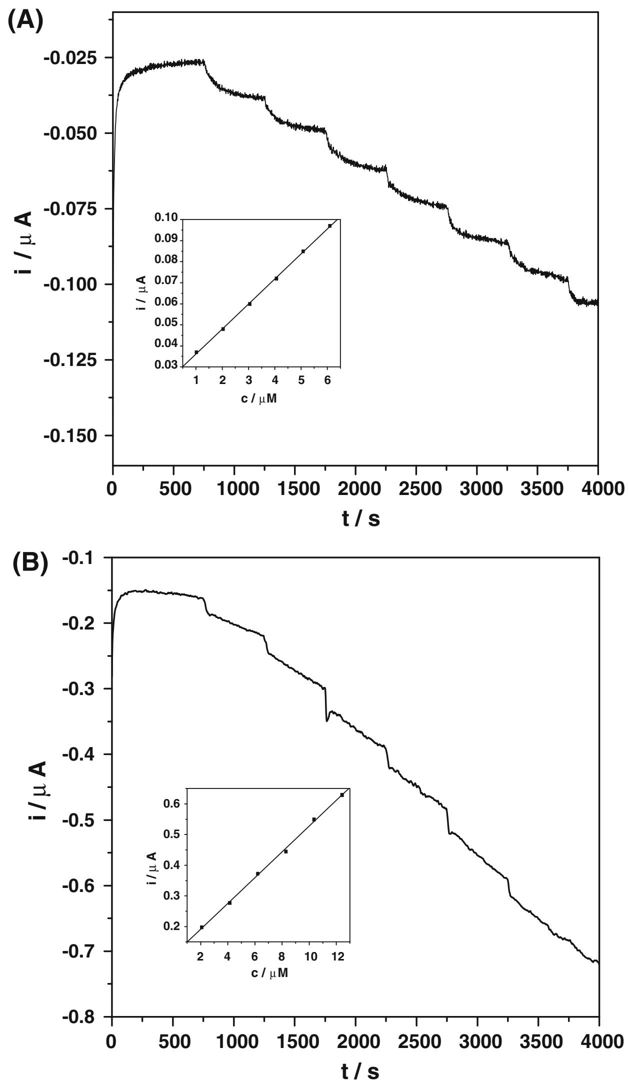

Fig. 4 Amperometric response of parathion (**A**) and methyl parathion (**B**) for the constant addition of 1.016 µM for parathion and 2.07 µM for methyl parathion at stearic acid modified GCE in 2.56 pH B-R buffer solution. *Insets* show the respective calibration graphs

was fabricated. The modification of the electrode surface is carried out by simple drop dry method. The stearic acid film can easily be removed for further modifications to give reproducible results. Moreover, this modification process is inexpensive. The electrochemical behavior of parathion and methyl parathion was investigated by using various electrochemical techniques such as cyclic voltammetry, differential pulse voltammetry and amperometry. The results were compared with that obtained at bare glassy carbon electrode. It suggested that the electrode reaction process of parathion and methyl parathion at stearic acid modified electrode is diffusion-controlled process. Improved sensing current was obtained. Analytical characteristics of the sensor such as sensitivity, linear dynamic range, lower detection limit and response time were evaluated. This proposed method would be very useful for the sensing of parathion and methyl parathion.

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