

A Methyl Parathion Electrochemical Sensor Based on Poly(glutamic acid) Modified Glass Carbon Electrodes

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Abstract A simple electrochemical sensor was developed for detecting methyl parathion (MP) based on electropolymerization of *L*-glutamic acid on the glassy carbon electrode. The redox behavior of MP on the sensor was investigated by cyclic voltammetry, and the determination of methyl parathion was performed with differential pulse voltammetry. A highly linear current response to methyl parathion was obtained in the concentration range from 5.0×10^{-7} to 7.5×10^{-4} mol/L. A detection limit of 1.0×10^{-9} mol/L at a signal-to-noise ratio of 3 was attained. The method could be applied to the determination of methyl parathion in real samples.

Keywords methyl parathion, poly(glutamic acid), electrochemical sensor, electropolymerization

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Methyl parathion (MP) is one of the organophosphorus pesticides (OPs) and has been used widely^[1]. On the other hand, OPs can be easily transported by wind or water into environment, and contaminate ecological compartments such as lakes and rivers^[2-3]. Therefore, it is essential to develop a fast, simple, sensitive, and inexpensive method for the determination of OPs in environmental samples.

Many analytical methods, including gas and liquid chromatography^[4-5] have been applied to detect OPs residue. These analytical methods have the feature of high sensitivity and accuracy, but require tedious sample preparation and long analysis time that limit their application for on-site analysis. The electrochemical method has been widely applied to detect OPs^[6-8], because of its high sensitivity, good selectivity, fast response time and low-cost instrumentation. For example, acetylene black-chitosan composite film modified electrode was used for the detection of OPs and the detection limit was 2.0×10^{-9} mol/L^[9]. Poly(glutamic acid) (PGA) modified electrode has been also reported in the literature for fabricating sensors of catechol^[10], *L*-tryptophan^[11] and amoxicillin^[12]. However, it has not been utilized for the determination of OPs.

In this work, a simple electrochemical sensor was developed for detecting MP based on the electropolymerization of *L*-glutamic acid on glassy carbon electrode. The redox behavior of MP on the sensor was investigated by cyclic voltammetry, and the determination of MP was performed using differential pulse voltammetry (DPV). Such a sensor gave satisfactory results for the detection of MP in real water samples, therefore it has potential for practical applications.

1 Experimental

1.1 Reagents

L-Glutamic acid was purchased from Tianjin Damao Chemical Reagent Factory (Tianjin, China). Methyl

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parathion(MP) was obtained from the college of resources and environment of Hunan Agricultural University (Changsha, China). Other chemicals were analytical grade. The stock solution (0.1 mol/L MP) was prepared in ethanol and stored at 4 °C. Different pH values of phosphate buffer solution(PBS, 0.1 mol/L) were prepared using KH_2PO_4 and NaOH. Double distilled water was used throughout the whole experiment.

1.2 Apparatus

Electrochemical measurements were performed on a CHI760C electrochemical workstation (CH Instruments Co, Shanghai, China) with a conventional three electrode system comprising platinum wire as an auxiliary electrode, a saturated calomel electrode (SCE) as the reference electrode and the modified or unmodified glass carbon electrodes(2 mm diameter, GCEs) as working electrodes.

1.3 Preparation of PGA/GCE

The GCE was mechanically polished to a mirror by using 0.05 μm alumina slurries, rinsed, and sonicated in 30% HNO_3 , ethanol and distilled water for 3 min consecutively, and allowed to dry in air atmosphere. PGA/GCE was obtained by electropolymerization in 0.02 mol/L *L*-glutamic acid in the potential range of -0.2 and $+2.2$ V at 0.08 mV/s for 15 cycles. Then the modified electrode was rinsed with distilled water and allowed to dry in air also at room temperature.

1.4 Electrochemical experiments

The PBS (0.1 mol/L, pH = 7.0) was used as the supporting electrolyte. Before electrochemical measurements, the dissolved oxygen was removed from the solution by bubbling high purity nitrogen. PGA/GCE was used as a working electrode, and dipped into a 0.1 mol/L PBS(pH = 7.0) containing the desired concentration of methyl parathion under stirring for 5 min. Cyclic voltammetry (CV) was performed to determine methyl parathion in 0.1 mol/L PBS from -1.0 to 0.8 V at a scan rate of 100 mV/s. Differential pulse voltammetry(DPV) was performed from -0.4 to 0.1 V with an increase voltage of 4 mV, amplitude of 4 mV, pulse width of 60 ms and under room temperature. Other conditions of measurement are similar to those reported in literature^[13].

2 Results and discussion

2.1 Optimization of PGA/GCE on the response of MP

It is well known that the thickness of the polymer film is directly related to the number of cycles of CV during electropolymerization. A series of CV cycles was carried out for the polymerization of 0.02 mol/L *L*-glutamic acid in the potential range of -0.2 and $+2.2$ V at 0.08 mV/s. The influence of potential cycling on the thickness of polymer film on the electrode was evaluated by CV of PGA/GCEs in 5.0×10^{-4} mol/L MP in the potential range of 0.8 and -1.0 V at 100 mV/s as shown in Fig. 1. The peak currents (-0.117 V, peak 3 of Fig. 2) increased with increasing the number of cycles up to 15, then decreased. The behavior is most probably due to the increased barrier of electron transfer with the increased thickness of film. Therefore, cycle number 15 was considered as the optimum and used in further experiments.

2.2 Electrochemical behavior of MP on the PGA/GCE

As shown in Fig. 2, during the two successive CV

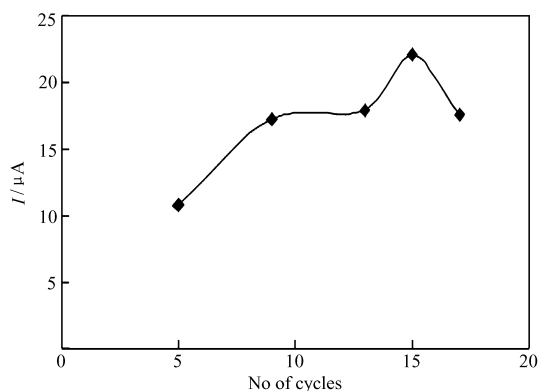
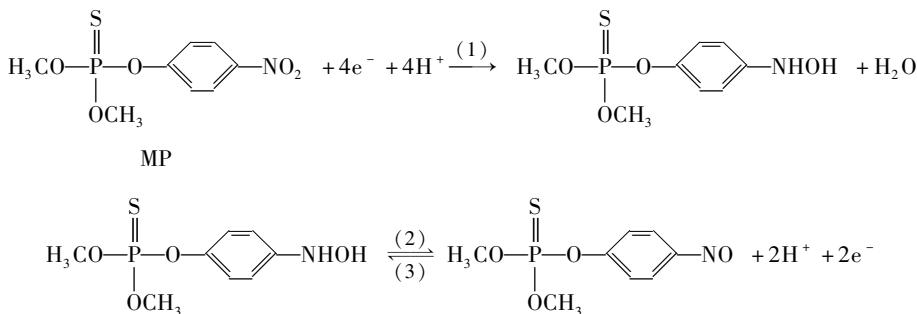


Fig. 1 The plot of peak currents of MP (5.0×10^{-4} mol/L) on PGA/GCEs and potential cycling numbers of electropolymerization of *L*-glutamic acid on GCEs

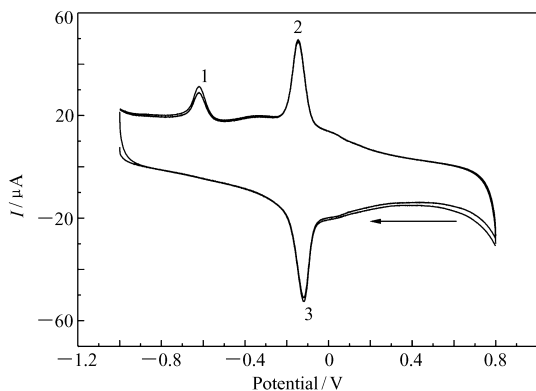
cycles of 5.0×10^{-4} mol/L MP on PGA/GCEs, there is no current or redox potential difference, suggesting that the electrocatalytic properties of PGA/GCE are stable. During the first cathodic scan, an irreversible reduction peak appeared at -0.622 V (reaction (1), peak 1) was observed, which could be ascribed to the reduction of the nitro group ($-\text{NO}_2$) to hydroxylamine ($-\text{NHOH}$) *via* a four-electron reduction process. Then an oxidation of hydroxylamine to nitroso ($-\text{NO}$) compound at -0.117 V (reaction (2), peak 3) occurred. In the successive cycles, the nitroso group is reversibly reduced to hydroxylamine with another reduction peak appeared at -0.147 V (reaction (3), peak 2). The reversible redox peaks should be attributed to a two-electron redox process, which is consistent with many reported results of nitroaromatic compounds^[14-17]. However, the potential difference between the reduction and oxidization peaks is about 30 mV (reversible redox reaction potential is $59/n$). Since the potential of the redox peaks is about 100 mV in literature^[16], therefore the electrocatalytic properties of PGA/GCE are excellent for the determination of MP.



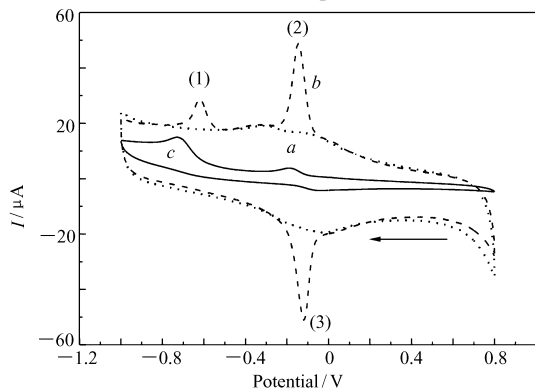
Scheme 1 chemical reaction mechanism of MP

Fig. 3 showed a comparison of the CVs between PGA/GCE (a) and bare GCE (b) in 0.1 mol/L PBS (pH = 7.0) containing 5.0×10^{-4} mol/L MP. Compared with the corresponding current of MP at bare GCE, PGA/GCE exhibited dramatically higher current response toward MP and the redox peaks were discernible. The experimental results supported the previous explanation toward this process^[18] which stated that the polymeric network film formed by well-defined nanofibres might undergo extensive swelling in solution, allowing an easier electron transfer and bearing opposite charges on the polymer film. A control experiment was also carried out under identical conditions using PGA/GCE in the absence of MP. As shown in curve c of Fig. 3, no obvious redox peak appeared in the scan potential range.

DPV possesses a higher sensitivity than CV. Fig. 4 shows corresponding DPV of MP at PGA/GCE (a). The MP at PGA/GCE exhibits a very sharp and

Fig. 2 CV of two successive cycles of 5.0×10^{-4} mol/L MP at PGA/GCE

Scanning potential range, 0.8 to -1.0 V; scanning rate: 100 mV/s

Fig. 3 CVs of PGA/GCE (a), bare GCE (b) in PBS (pH = 7.0) containing 5.0×10^{-4} mol/L MP, and PGA/GCE (c) in blank of PBS

Other conditions were identical to those in Fig. 2

well-defined stripping oxidization peak (peak 3 in Fig.1) in the potential range of -0.4 to 0.1 V. There is no obvious anodic stripping oxidization peak observed at the PGA/GCE in 0.1 mol/L PBS(*b*).

2.3 Effect of scan rate

The effect of scan rate on the redox peak current of MP was studied on the PGA/GCE by CV. As shown in Fig. 5A, in the range of $20 \sim 200$ mV/s, the redox peak current of MP increased linearly with increasing square root of scan rates ($v^{1/2}$) with correlation coefficient of 0.9975 and 0.9959 , respectively (Fig.5B). This strongly suggested that the redox reaction of MP at PGA/GCE was diffusion-controlled.

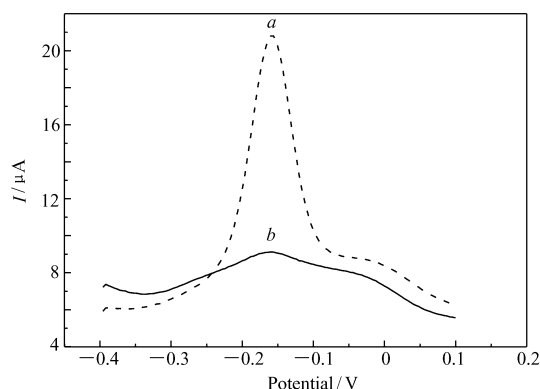
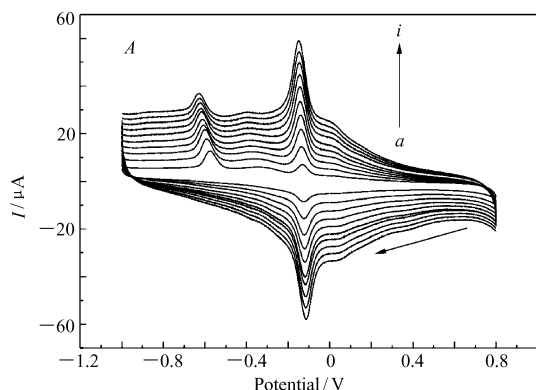


Fig.4 DPV of PGA/GCE in 5.0×10^{-4} mol/L MP (*a*) and in 0.1 mol/L PBS of pH 7.0(*b*)

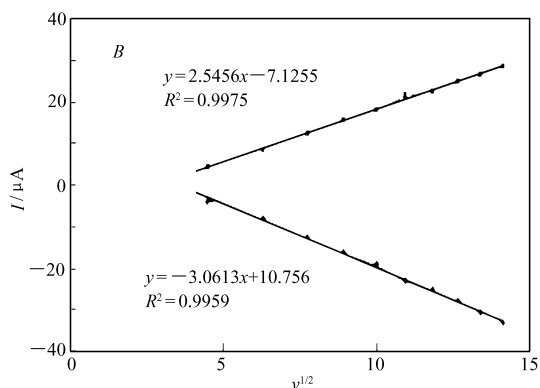


Fig.5 CVs of 5.0×10^{-4} mol/L MP at PGA/GCE at different scan rate (from inner to outer): $20, 40, 60, 80, 100, 120, 140, 160, 180$ and 200 mV/s, respectively(*A*), and the dependence of redox peak current on the square root of scan rate(*B*). Other conditions were defined in Fig.3

2.4 Effect of pH

The effect of solution pH value on the peak current of MP at PGA/GCE was investigated by DPV as shown in Fig. 6. In the range of pH $6.0 \sim 9.0$, the anodic oxidization peak current of MP increased with increasing pH firstly, then decreased after reaching the maximum value at pH = 7.0 .

The oxidization peak currents decreased rapidly with further increase of pH values. The reduction of hydronium ion (H_3O^+) might cause the decrease in intensity of peak current at pH values less than 7.0 . The pH = 7.0 PBS (0.1 mol/L) was chosen for subsequent experiments.

2.5 Linearity, stability and reproducibility of sensor

The analytical features of linearity, stability and reproducibility were investigated by DPV in the scan potential range from -0.4 to 0.1 V (0.1 mol/L PBS, pH = 7). As can be seen from Fig. 7A, the peak current increased linearly with the MP concentration in the

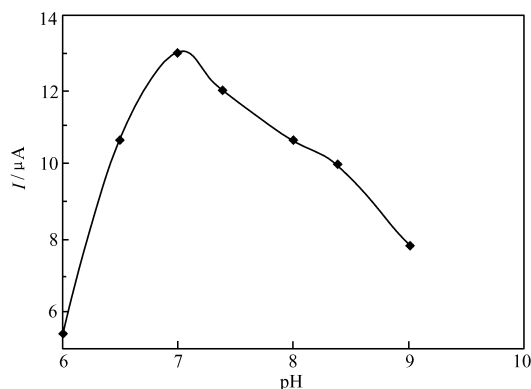


Fig.6 The effect of solution pH value on the peak current

The conditions were same as in Fig. 4

range of $5.0 \times 10^{-7} \sim 7.5 \times 10^{-4}$ mol/L (Fig. 7B). The linear equation was $i_{pc}(\mu A) = 0.207c(\mu mol/L) + 0.198$ with a correlation coefficient of 0.9921. The detection limit was estimated to be 1.0×10^{-9} mol/L based on signal-to-noise ratio of 3.

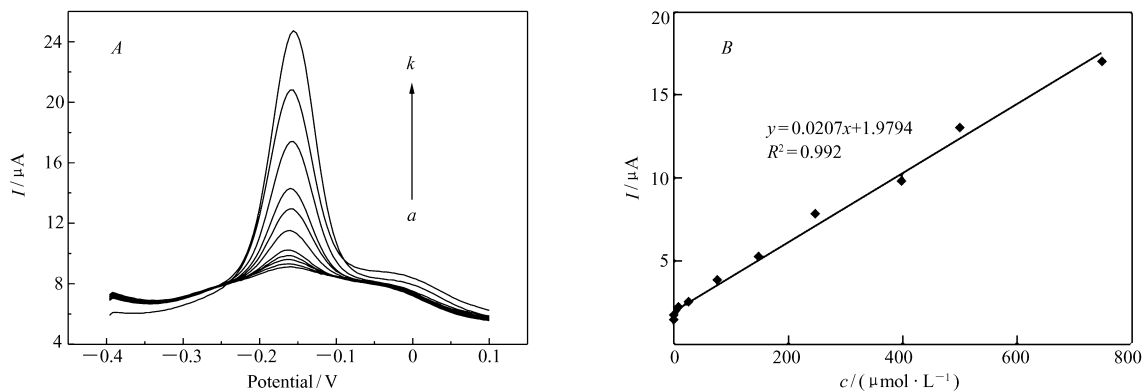


Fig.7 (A) DPVs of increasing methyl parathion concentration in 0.1 mol/L PBS (pH = 7.0) at PGA/GCE, from bottom to top, with concentrations of 0, 5.0×10^{-7} , 5×10^{-6} , 1.0×10^{-5} , 2.5×10^{-5} , 7.5×10^{-5} , 1.5×10^{-4} , 2.5×10^{-4} , 4.0×10^{-4} , 5.0×10^{-4} , 7.5×10^{-4} mol/L, respectively; (B) the calibration curve
Accumulation time: 2 min; supporting electrolyte solution: 0.1 mol/L PBS (pH = 7.0)

The stability and reproducibility of PAG/GCE were also investigated. For MP measurement, the sensor can be used continuously for at least 24 h, and the sensor remained 92.2% of its initial current intensity after it was kept in air for 2 week. After being kept in air for 30 days, such value decreased to 80%. Both indicate the good stability of the PAG/GCE electrode. The DPV responses of the sensors in 8 parallel measurements of 5.0×10^{-4} mol/L MP were nearly the same with a relative standard deviation (RSD) of 2.2%, which suggested that the sensor has a good reproducibility for the determination of MP.

2.6 Interference studies

The anti-interference capability of the sensor was also examined. The experiments were performed using 5.0×10^{-4} mol/L MP in 0.1 mol/L PBS (pH = 7.0). The results indicated that common inorganic ions, such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cu^{2+} , Cl^- , NO_3^- , SO_4^{2-} , CO_3^{2-} and PO_4^{3-} , with the concentration of 5.0×10^{-4} mol/L, had no interference for the MP detection. Some organic compounds containing phenolic hydroxy-groups and amino-groups, such as 4-hydroxy benzene sulfonic acid, *p*-aminophenol, carbofuran, omethoate and dichlorvos have been also tested. At the concentration of 5.0×10^{-3} mol/L, there is no interference in determining 5.0×10^{-4} mol/L MP.

2.7 Analytical application

To demonstrate the feasibility of the PAG/GCE, the proposed procedure was applied to the determination of MP in real water samples collected from Liuyang River in Hunan Changsha City. Since no DPV response corresponding to MP was observed, different quantity of MP was intentionally added to the samples. As can be seen from the results summarized in Table 1, the recoveries were 102%. It is believed that the proposed DPV procedure based on PAG/GCE can be applied for detecting MP in environmental water samples with good results.

Table 1 Determination of MP in water samples

Sample	Added MP/(mol·L ⁻¹)	Found MP/(mol·L ⁻¹)	Recovery/%
1	5.0×10^{-6}	5.13×10^{-6}	102.6
2	1.0×10^{-5}	1.025×10^{-5}	102.5
3	1.5×10^{-5}	1.53×10^{-5}	102.2

3 Conclusion

A simple and novel MP electrochemical sensor was fabricated based on poly (glutamic acid) modified glass carbon electrodes. The sensor exhibited high sensitivity, electrocatalytic activity and good reproducibility to MP detection. The detection linearity ranged from 5.0×10^{-7} to 7.5×10^{-4} mol/L, and the detection limit was estimated to be 1.0×10^{-9} mol/L for MP.

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基于聚谷氨酸修饰玻碳电极的甲基对硫磷电化学传感器

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摘 要 制备了一种简单的聚谷氨酸修饰玻碳电极的用于检测甲基对硫磷的电化学传感器。并应用循环伏安法研究了甲基对硫磷在该修饰电极上的氧化还原行为;甲基对硫磷的浓度检测采用差分脉冲伏安法,结果表明,甲基对硫磷在 $5.0 \times 10^{-7} \sim 7.5 \times 10^{-4}$ mol/L 浓度范围与响应电流有良好的线性关系。甲基对硫磷检测限($S/N=3$)可达 1.0×10^{-9} mol/L。该法制备的传感器有望应用于实际样品中的甲基对硫磷的检测。

关键词 甲基对硫磷,聚谷氨酸,电化学传感器,电聚合

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