



An electrochemical fungicide pyrimethanil sensor based on carbon nanotubes/ionic-liquid construction modified electrode



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ABSTRACT

In this study, a simple, rapid, sensitive and environmentally friendly electroanalytical detection method for pyrimethanil (PMT) was developed, which was based on multi-walled carbon nanotubes (MWCNTs) and ionic liquids (IL) 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆]) modified glassy carbon electrode (GCE). MWCNTs–IL modified electrode significantly enhanced the oxidation peak current of PMT by combining the excellent electrochemical properties of MWCNTs and IL, suggesting that the modified electrode can remarkably improve the sensitivity of PMT detection. Under the optimum conditions, this electrochemical sensor exhibited a linear concentration range for PMT of 1.0×10^{-7} – 1.0×10^{-4} mol L⁻¹ and the detection limit was 1.6×10^{-8} mol L⁻¹ (S/N = 3). The fabricated electrode showed good reproducibility, stability and anti-interference, and also it was successfully employed to detect PMT in real samples.

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1. Introduction

Contamination by agrochemicals due to spray-drift, leaching, run-off and accidental spills has been a worldwide problem and caused wide public concern (Ma et al., 2006; Miquel, Arben, & Salvador, 2001; Verdisson, Couderchet, & Vernet, 2001). Pyrimethanil [(PMT), *N*-(4,6-dimethylpyrimidin-2-yl)-phenylamine] belongs to the anilinopyrimidine class of fungicides. PMT plays an important role in agricultural activities, which is activities, and is effectively used for the control of gray mould, leaf scab and other postharvest diseases on pome fruits, vegetables and ornamentals (Chen et al., 2013). However, the intensive use of PMT can generate residues that may become a potential risk for both public health and environment. Owing to the toxicity of PMT, the European Union Directive on drinking water quality (98/83/EC) has established a maximum allowed concentration of $0.1 \mu\text{g L}^{-1}$ for PMT (Cheng, Xia, Zhou, Guo, & Chen, 2011). Therefore, developing a sensitive, rapid and accurate method for the determination of PMT residue in vegetables, fruits and water samples is very important. Currently, the determination of PMT is usually carried out by high performance liquid chromatography (HPLC), gas chromatography coupled with mass spectrometry (GC–MS), ultra-performance liquid chromatography coupled to triple quadrupole tandem mass spectrometry (UPLC–MS/MS) and liquid

chromatography tandem mass spectrometry (LC–MS/MS) (Baggiani, Baravalle, Giraudi, & Tozzi, 2007; Mezcua et al., 2006; Navalon, Prieto, Araujo, & Vilchez, 2002; Rodrigues, Ferreira, Cardoso, Ferreira, & Benoliel, 2007; Wang, Zhao, & Liu, 2008). These methods have high accuracy, good reproducibility and are reliable in qualitative, but they also suffer from inevitable disadvantages such as expensive experimental instruments, trained personnel and time-consuming extraction steps. In contrast, electrochemical methods for accurate quantification of pesticides residues have attracted a lot of attention because of their high sensitivity, rapid response and low cost (Li & Chi, 2009; Liu et al., 2014; Nigović, Sadiković, & Sertić, 2014; Ping, Wang, Wu, Ying, & Ji, 2012; Wan, Zou, Yan, Zhao, & Zeng, 2007). MWCNTs are highly electroconductive and are characterized by a large surface area, excellent chemical and physical stabilities. ILs are ion conductive, display a wide electrochemical potential window, and can be used as an excellent conductive binder to immobilize MWCNTs onto the surface of an electrode. As far as we know, MWCNTs–IL composite electrodes have not been reported for PMT determination.

In this study, a MWCNTs–[BMIM][PF₆] modified electrode was fabricated and used to study the electrochemistry of PMT. The electrochemical behaviors of PMT were examined by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Compared with the MWCNTs/GCE and bare GCE, the oxidation peak currents of PMT obviously increased on the MWCNTs–IL/GCE due to the synergistic effect between MWCNTs and IL. This kind of synergistic

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effect could promote the electron transfer in process of PMT oxidation. The proposed electrochemical method was successfully applied to determine PMT in real samples, and the results were satisfactory.

2. Experimental

2.1. Reagents and solutions

MWCNTs used (length 10–20 nm; specific surface area 100–160 m²/g; 97% purity) came from Shenzhen Nanotech Port Co., Ltd. IL (1-butyl-3-methylimidazolium hexafluorophosphate, [BMIM][PF₆]) was purchased from Chengjie Chemical Co., Ltd. (Shanghai, China). The analytical standard of PMT (95% purity) was purchased from Bepharma Co. Ltd. (Shanghai, China). The other chemical reagents were all of analytical purity and obtained from Shenyang Chemical Company, China.

The stock solution of PMT (5×10^{-3} mol L⁻¹) was prepared by dissolving 100.2 mg PMT in a 100 mL amber volumetric flask with ethanol. The standard stock solutions of PMT were diluted successively to the required concentration in the experiment. All the solutions were kept in the dark at 4 °C when they were not used.

2.2. Apparatus

A CHI660D electrochemical workstation (Shanghai ChenHua Instruments Co., China) coupled with a conventional three-electrode cell including a platinum wire auxiliary electrode, a saturated calomel reference electrode (SCE) and a working electrode was used for electrochemical measurements. A S-3C Model pH meter (Shanghai Precision Scientific Instrument Co., China) was used for measuring the pH of solutions. Fourier transform infrared spectra (FT-IR) were recorded at room temperature on a IR Prestige-21. Deionized water used throughout experiments was purified using a Sartorius Arium 611 system (Sartorius, Göttingen, Germany). Transmission electron microscopy (TEM) image was obtained from a JEM-2010HR microscope (JEOL, Japan) at an accelerating voltage of 200 kV.

2.3. Preparation of the modified glassy carbon electrode

MWCNTs and [BMIM][PF₆] composites were synthesized by a simple physical method. 100 mg MWCNTs and 100 µL IL were added into a 50 mL beaker. MWCNTs and IL were thoroughly mixed and dispersed with acetone under ultrasonic assistance for 15 min. Then, the acetone was evaporated in the fume hood.

Prior to surface modification, the bare GCE (3 mm in diameter) was carefully polished with three grades of α -Al₂O₃ slurries (1.0, 0.3 and 0.05 µm) respectively, followed by sonicated in anhydrous ethanol and ultrapure water after each stage of polishing successively and dried at room temperature.

For preparation of the modified electrode, 1 mg mL⁻¹ MWCNTs-IL homogeneously solution was first prepared with deionized water by ultrasonication for 30 min. Then, 8.0 µL suspension were dropped on the surface of the GCE and dried under the infrared lamp to obtain the MWCNTs-IL/GCE.

2.4. Procedure for PMT analysis

The electrochemical behavior and the determination of PMT were performed by CV and DPV at room temperature. All the electrochemical measurements were carried out in 5.0 mL 0.2 mol L⁻¹ phosphate buffer solutions (pH 6.0), which were deoxygenated with high pure nitrogen for 10 min prior to a series of experiments and maintained in a nitrogen atmosphere during the procedures.

After accumulating for 60 s on open-circuit, the CV was recorded from 0.6 to 1.1 V at a scan rate of 0.1 V s⁻¹; the DPV was recorded from 0.6 to 1.1 V with an amplitude of 50 mV and a pulse period of 0.5 s.

2.5. Real sample pretreatment

Fruit samples such as orange and apple were bought from a local store. The pericarps were immersed into 30 mL ethanol to extract PMT for 30 min by ultrasonic. Then sample solutions were filtrated and diluted to 50.00 mL amber volumetric flask.

The water sample was collected from a stream in Shenyang City and adjusted the pH with Na₂HPO₄ and NaH₂PO₄. All above sample solutions were stored at 4 °C in a refrigerator. The content of PMT in real samples were determined by DPV according to the standard additions method.

3. Results and discussion

3.1. Characterization of MWCNTs-IL

The morphology of MWCNTs-IL was first characterized by TEM. Fig. 1A and B showed the typical TEM image of MWCNTs and MWCNTs-IL, which were dispersed in deionized water by sonication, respectively. It could be seen that MWCNTs were highly entangled with the diameter of several tens of nanometers. As a comparison, MWCNTs were much unfolded and a little widened after being treated with IL, indicating that IL could untangle MWCNTs and increase the effective surface area of MWCNTs. This is consistent with a previous report (Zhao et al., 2005).

The evidence for the successful adsorption of IL onto the surface of MWCNTs was also provided by FT-IR spectra. The infrared spectra of MWCNTs (a) and MWCNTs-IL (b) were presented in Fig. 1C. Many absorption signals were matched between the two spectra. However, the stretching vibration of C-H band at 2972 cm⁻¹, 3140 cm⁻¹ and the vibration of N-H in imidazole ring at 1470 cm⁻¹ appeared in the spectrum of the MWCNTs-IL, suggesting that IL was successfully coated on the surface of MWCNTs.

3.2. Effect of the ration of IL in the modifier mixture

The effect of the ratio of IL in 100 mg MWCNTs on the oxidation peak current of PMT has been investigated. It was found that the oxidation peak current of PMT was enhanced with the amount of IL in the composite material increasing from 20 to 100 µL. However, when the amount exceeded 100 µL, the oxidation peak current leveled off. So a modifier that contained 100 µL IL was selected for further study.

3.3. Investigation of electrochemical behavior of PMT at MWCNTs-IL/GCE

Electrochemical behaviors of 5.0×10^{-5} mol L⁻¹ PMT on different electrodes were investigated in PBS (pH = 6.0) by CV. As can be seen in Fig. 2, only an oxidation peak was visible, but no reduction peak was observed in the reverse scan, indicating PMT underwent totally irreversible oxidation at these electrodes. Compared with bare GCE and MWCNTs/GCE, the oxidation current of PMT at MWCNTs-IL/GCE was much higher. The introduction of IL improved the current response of PMT obviously which could be attributed to the synergistic effect of MWCNTs and IL, leading to an increase in sensitivity and decrease in the limit. This kind of synergistic effect could enhance the electron transfer rate because of the high conductivity of both MWCNTs and IL. In addition, there existed a favorable electrostatic interaction between the electron-

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