



Preparation of parathion imprinted polymer beads and its applications in electrochemical sensing

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ABSTRACT

Parathion imprinted polymer beads were prepared by free radical polymerization using parathion as template, methacrylic acid as functional monomer, divinyl benzene as cross-linking reagent and 2,2'-azobis(isobutyronitrile) as initiator. The obtained molecularly imprinted beads were characterized with transmission electron micrograph. The rebinding properties of these imprinted beads towards parathion were studied by saturation binding experiments using ultraviolet/visible spectroscopy. Effects of the template, functional monomer, cross-linking reagent and initiator on selective adsorption of parathion were investigated. The high selectivity of the imprinted beads was successfully demonstrated by their selective adsorption of free parathion from an ethanol–water ($v/v = 1:5$) solution. In addition, the parathion imprinted beads were dispersed into dihexadecyl hydrogen phosphate solution at the concentration of 1.0 mg mL^{-1} . By coating this solution onto a glassy carbon electrode surface, a molecularly imprinted electrochemical sensor for parathion was obtained. The electrochemical sensor exhibited good selectivity and fast response to parathion. Under optimized experimental conditions, the peak currents were found linearly proportional to the parathion concentration in the range of $1.0 \times 10^{-7} \text{ mol L}^{-1}$ to $1.0 \times 10^{-5} \text{ mol L}^{-1}$ with a detection limit of $5.4 \times 10^{-8} \text{ mol L}^{-1}$ ($S/N = 3$). The developed sensor was successfully employed for the determination of parathion in pear juice samples.

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1. Introduction

The highly neurotoxic organophosphorus (Ops) compounds are often used as chemical war agents, pesticides and insecticides [1–3]. Parathion is a typical organophosphorus pesticide, which is widely used in modern agriculture to increase productivity. Recently, it was prohibited for use in agriculture in many countries due to its high toxicity. However, it was still used stealthily by some farmers and thus created high-risk of health hazards to people and animals [4,5]. Therefore, environmental and food pollutions from parathion are still important issues that attract widespread public concerns [6–8]. Many analytical methods have been developed for the selective and sensitive determination of parathion residues in water, plants, soils and foodstuff, etc. [9–11]. Among the reported methods, chromatography is the most popular [11–13]. However, this technique is time consuming and requires expensive instrumentation together with highly qualified personnel. Moreover, it is difficult to meet the requirements of high sensitive and fast

measurement for parathion determination. Electrochemical techniques based on chemically modified electrodes have been proved to be highly sensitive and advantageous methods for the determination of parathion but usually suffer from the poor selectivity [14–17]. A novel disposable amperometric proton selective sensor specifically and simultaneously targeting parathion and methyl parathion was developed with a microhole-liquid/gel interface. A wide dynamic range of detection for parathion and methyl parathion with an excellent linearity was achieved via the specific catalysis of OPH followed by the assisted transfer of released protons from the hydrolysis across the polarized microhole-water/organic gel interface. A discriminative detection of both parathion and methyl parathion down to 0.5 mM was achieved when using the time-resolved DPSV method based on the different catalytic kinetics of OPH towards the different OP agents [18]. Although biosensors based on antigen/antibody and enzymes have high selectivity towards parathion, the readily loss of activity limits their practical applications [19,20]. In recent years, the use of molecularly imprinted polymers (MIPs) for electrochemical sensing has been developed and provided promising platforms for selective and sensitive analysis of parathion [21–25]. Molecular imprinting is a technique for the fabrication of functional

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materials that have the ability to recognize the template molecules from a mixture of closely related compounds [26–28]. These materials have high selectivity for the target molecule due to the formation of unique binding sites in the synthetic procedures. In a typical preparation, the template molecule is linked by covalent or non-covalent forces to suitable monomer(s) containing functional groups. After the templates are removed, the imprinted sites of the template molecules remain in the polymer structure and these imprinted sites are responsible for the recognition properties of the MIPs. In a conventional procedure, MIPs are often crushed and ground in a mortar to obtain particles in different sizes for utilization. This process often destroys the imprinted sites and decreases the specific binding properties. Thus, many methods, such as emulsion polymerization [29], surface imprinting [30,31], suspension polymerization [32], seed swelling and polymerization [33], and precipitation polymerization [34] have been developed in order to prepare the MIP beads.

In this paper, parathion imprinted polymer beads were prepared in nanometer size via the free-radical polymerization in ethanol solution using methacrylic acid as monomer and functional monomer, parathion as template, divinyl benzene as cross-linking reagent and 2,2'-azobis-(isobutyronitrile) as initiator. Free radical polymerization is a key synthesis route for obtaining a wide variety of different polymers and material composites. The relatively non-specific nature of free radical chemical interactions makes this one of the most versatile forms of polymerization available and allows facile reactions of polymeric free radical chain ends and other chemicals or substrates. Up to now, it has been widely used in the molecularly imprinted polymers preparation [35–38]. The selective rebinding of parathion to the molecularly imprinted beads was investigated with UV/Vis spectroscopy. The molecularly imprinted beads homogeneously dispersed in dihexadecyl hydrogen phosphate (DHP) solution were coated to a glassy carbon electrode surface and used as an electrochemical sensor for the selective determination of parathion. The results of high selectivity and fast response towards parathion obtained with this sensor demonstrated the potential application of the molecularly imprinted polymer beads.

2. Experimental

2.1. Apparatus and reagents

Electrochemical measurements were performed on an EC 550 electrochemical workstation (GaossUnion Technology Co., Ltd, Wuhan, China) with a three-electrode system consisting of a 3 mm imprinted sensor as working electrode, a saturated calomel electrode (SCE) as reference electrode and a platinum wire as auxiliary electrode in a 10 mL voltammetric cell at room temperature (about 25 °C). For UV/Vis measurements, a Perkin-Elmer LAMBOA-35 spectrometer (Perkin-Elmer, USA) equipped with 1 cm quartz cell was used. Transmission electron microscopy (TEM) measurements were conducted on a FEI Tecnai G² 20 instrument (FEI Company, Netherlands). The pH values of phosphate buffer solutions were adjusted by pHs-2 meter (Leici instrument factory, Shanghai, China).

Parathion and methyl parathion were bought from Shanonda Corporation (Shashi, China) and were dissolved in ethanol and stored at ~4 °C until used. Then, it was diluted to a desired concentration using an ethanol–water (v/v=1:5) solution. 2,2'-Azobis-(isobutyronitrile) (AIBN) was obtained from Shanghai Chemical Plant (Shanghai, China) and was recrystallized from methanol. Methacrylic acid (MAA) and divinyl benzene (DVB) were purchased from Shanghai Medicinal Company (Shanghai, China) and Tianjing Guangfu Institute of Fine Chemicals (Tianjing,

China), respectively. They were distilled under vacuum to remove the inhibitor before use. Dihexadecyl hydrogen phosphate was purchased from Sinopharm Chemical reagent Co., Ltd (Shanghai, China). Other chemicals were of analytical grade, and used without further purification. Chemical structures for the selected substrates in this study were presented in Fig. S1.

2.2. Preparation of parathion molecularly imprinted polymer beads

In a typical molecularly imprinted beads synthesis, pre-polymerization solution was prepared by mixing 2.0 mL of ethanol, 200 μL of 0.1 mol L⁻¹ parathion, 50 μL of methacrylic acid, 250 μL of divinyl benzene and 2.0 mg AIBN with ultrasonic agitation for 10 min. The pre-polymerization solution was purged with a stream of nitrogen gas for 10 min, sealed and allowed to polymerize for 48 h at 60 °C. Other MIP beads were synthesized according to the above procedures with a few modifications. A reference non-imprinted polymer (NIP) beads was similarly made by omitting the parathion template.

Both the MIP and NIP beads were washed 5 times with ethanol under ultrasonic agitation. After centrifugation (10 min, 4000 rpm), the separated MIP and NIP beads were rinsed twice with water and twice more with ethanol. The MIP and NIP beads were then dried under an infrared lamp in air and stored in sealed plastic tubes.

2.3. Rebinding experiments

Equilibrium binding experiments were conducted to evaluate the selective rebinding properties of the MIP and NIP beads. The MIP and NIP beads (2.0 mg) were separately placed in microcentrifuge tubes containing 10 mL of the selected substrate solution in the concentration range from 2.5 × 10⁻⁵ mol L⁻¹ to 1.25 × 10⁻⁴ mol L⁻¹ and shaken for 5.0 h at room temperature. After centrifugation (10 min, 4000 rpm), the concentration of the solution was determined with UV/Vis spectrometer. The rebinding amount of parathion to the beads (Q , mol g⁻¹) was calculated according to Eq. (1):

$$Q = \frac{V(C_0 - C_1)}{Q_1} \quad (1)$$

where V , C_0 , C_1 and Q_1 represent the volume of the solution (L), initial solution concentration (mol L⁻¹), the solution concentration after rebinding (mol L⁻¹), and the mass of beads (g) respectively.

2.4. Preparation of MIP beads modified electrode

1.0 mg of DHP was dissolved into 2.5 mL of ethanol–water (v/v=1:4) solution. 2.0 mg of MIP beads were dispersed into the produced DHP solution with ultrasonic agitation to obtain a well dispersed mixture. Prior to the modification, the bare glassy carbon electrode (GCE) was polished to a mirror-like surface with 0.05–0.30 mm alumina slurries. After rinsing with water, the GCE was ultrasonicated in HNO₃ solution, ethanol and ultrapure water for 5 min, sequentially. Finally, the cleaned GCE was coated with 10 μL of the obtained MIP beads/DHP suspension and the solvent evaporated to obtain a film modified electrode, referred as MIP/GCE. A NIP beads/DHP film modified glassy carbon electrode was prepared by the same procedure presented above using NIP beads instead of MIP beads.

2.5. Electrochemical measurements

Electrochemical investigations of parathion were carried out in an electrochemical cell containing 10 mL of phosphate buffer solution at pH 4.49. After accumulation with open-circuit potential for

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