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Original article

Detection of parathion methyl using a surface plasmon resonance sensor combined with molecularly imprinted films

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ABSTRACT

An ultra-sensitive and highly selective parathion methyl (PM) detection method by surface plasmon resonance (SPR) combined with molecularly imprinted films (MIF) was developed. The PM-imprinted film was prepared by thermo initiated polymerization on the bare Au surface of an SPR sensor chip. Template PM molecules were quickly removed by an organic solution of acetonitrile/acetic acid (9:1, *v*/*v*), causing a shift of 0.5° in SPR angle. In the concentrations range of 10^{-13}–10^{-10} mol/L, the refractive index showed a gradual increase with higher concentrations of template PM and the changes of SPR angles were linear with the negative logarithm of PM concentrations. In the experiment, the minimum detectable concentration was 10^{-13} mol/L. The selectivity of the thin PM-imprinted film against diuron, tetrachlorvinphose and fenitrothion was examined, but no observable binding was detected. The results in the experiment suggested that the MIF had the advantages of high sensitivity and selectivity.

1. Introduction

Parathion methyl (PM), a type of organophosphate pesticides (OPPs), is widely used for the control of a broad range of pests in agricultural domain over the last several decades. Thus, OPPs played an important role in the increased agricultural productivity [1]. However, OPPs are very toxic to organisms, and their residues have always been one of the most important problems in food security [2,3]. Consequently, highly sensitive methods for the determination of OPPs in environmental and biological samples are highly desirable. Currently, several analytical methods for the OPPs detection including gas chromatography (GC) [4], high performance liquid chromatography (HPLC) [5], gas chromatography–mass spectroscopy (GC–MS) [6] and HPLC–mass spectroscopy [7], have achieved low detection levels. However, these methods consume large amount of time and solvent, and require one or more cleanup steps involving liquid–liquid partition or solid-phase extraction [5–7].

Recently, various biosensors have been reported for the determination of OPPs [8–10]. Surface plasmon resonance (SPR) sensors have attracted attention in last two decades [11,12]. SPR is an optical technique that measures changes in the refractive index occurring within approximately several hundred nanometers from the sensor surface [13]. SPR was introduced in the early 1990s as the underlying technology in affinity biosensors for biomolecular interaction analysis [14]. SPR sensors have important applications in the determination of affinity-binding constants [15,16], monitoring [17] and diagnostic devices [12], and genotype analysis [18].

Although many methods are used in sensitive SPR sensors, the most effective method is the molecular imprinting technique. The method relies on the principles of molecular recognition. It is a polymerization reaction that occurs around a template molecule. Molecularly imprinted polymers (MIPs), containing specific recognition sites with selectivity for analytes of interest, have various applications such as artificial enzymes [19], solid-phase extraction [20], bioseparation [21,22], affinity detoxification [23] and sensor devices [24–27].

In this study, we prepared a novel PM-imprinted film on gold surface of SPR chips. To date, although a number of approaches are utilized to prepare the MIF [28–30], few studies can achieve the low detectable concentration of PM (10^{-13} mol/L) that is performed using the thermally initiated polymerization reactions. Thus, this method has some important advantages compared to the traditional analytical methods. In addition, the developed SPR shows high sensitivity and high selectivity for the determination of PM. Furthermore, the MIF exhibits good reproducibility in the later experiments.

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2. Experimental

2.1. Material

Parathion methyl (PM), diuron, tetrachlorvinphose, fenitrothion, ethylene glycol dimethacrylate (EGDMA) were purchased from Aladdin Regent Company (Shanghai, China). Methacrylic acid (MAA) and 2,2-azobis-isobutyronitrile (AIBN) were purchased from J & K Scientific Ltd. (China). Acetonitrile, ethanol and acetic acid were of analytical grades and purchased from Beijing Tongguang Fine Chemicals Company. MAA and EGDMA were distilled under reduced pressure before use. All other reagents except MAA and EGDMA were used as received.

2.2. Preparation of MIF

The MIF was prepared by thermo-polymerization on bare gold surface of the SPR substrate. Firstly, parathion methyl (0.025 mol/L) and MAA (0.1 mol/L) monomer were mixed in acetonitrile (3 mL) at room temperature for 2 h. The cross-linker ethylene glycol dimethacrylate (EGDMA, 0.1 mol/L) and initiator 2,2-azobis-isobutyronitrile (AIBN, 0.013 g/mL) were then added to the pre-polymerization solution, followed by ultra-sonication for 10 min. The SPR substrate was immediately placed on the glass slide with the Au surface facing downwards and fastened tightly with chips. A piece of parafilm was sandwiched between the two glass slides as a spacer. Polymerization was carried out at 60 °C for 6 h in a water bath under nitrogen. The NIF was synthesized as a reference under identical conditions except for the absence of the template. After polymerization, the film coated on an SPR chip was washed with acetonitrile and ethanol (9:1, *v*/*v*) several times and dried under a stream of nitrogen gas.

2.3. Detection of PM

The MIF with recognition cavities was immersed in acetonitrile to monitor the template PM. A peristaltic pump was used to pump the analyte or washing solution from a reservoir into the flow cell. Samples were prepared by spiking in acetonitrile with PM at concentrations ranging from 10^{-13} mol/L to 10^{-10} mol/L. Afterwards, each sample was pumped through the sensor surface for 20 min for the specific detection of PM, followed by rinsing of the sensor surface with acetonitrile for 10 min. For unspecific binding testing, diuron, tetrachlorvinphose and fenitrothion (at the concentrations of 10^{-9}, 10^{-8}, 10^{-7} mol/L) were employed using the same method.

3. Results and discussion

3.1. Characterization of MIF

In order to create recognition cavities in the MIF, the template molecule removal experiments were carried out after polymerization. The imprinted parathion methyl molecules were removed from the imprinted polymer films by injecting 5 mL of acetonitrile/acetic acid solutions in a volume ratio of 9:1. The SPR angular reflectivity spectra were measured independently before and after the MIF rinse. Typical SPR curves obtained in acetonitrile are shown in Fig. 1. Because the release of parathion methyl templates in the MIF generated a decrease of refractive index, a shift of the coupling angle of the MIF decreased by 0.5° (from 63.1° to 62.6°), suggesting that the parathion methyl molecules from MIF were removed.

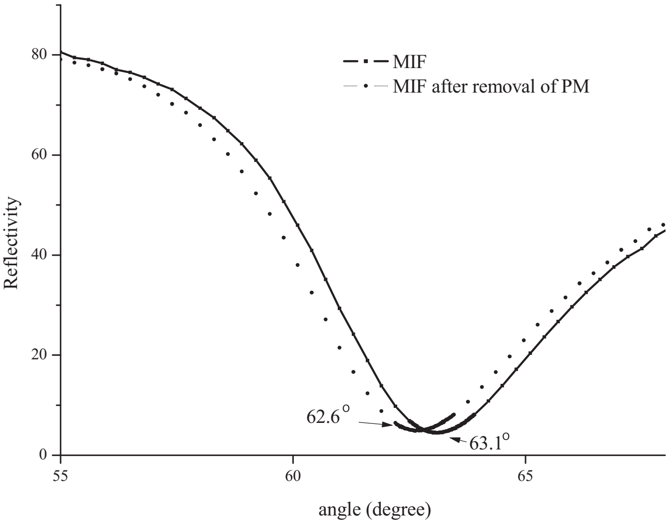

Fig. 1. Angular reflectivity of before and after removal of the template PM.

3.2. Effect of molecular imprinting on SPR sensor sensitivity

The adsorption properties of the sensor chip were characterized by SPR spectroscopy. Fig. 2 shows the SPR angular reflectivity spectra after rebinding the PM molecules with various concentrations of MIF (the inset graph is the enlarged range around coupling angles). Solutions of parathion methyl in acetonitrile with a range of concentrations from 10^{-13} mol/L to 10^{-10} mol/L were successively injected into the flow cell. The injection of each PM sample lasted for 20 min to reach equilibrium adsorption, and the MIF was rinsed with acetonitrile for 10 min. It can be clearly observed that the angles shifted towards higher values after the adsorption of higher concentrations of PM. It should be noticed that the cavities formed by departure of template PM in the MIF were gradually taken by the PM molecules.

As seen in Fig. 3, a plot of the change in resonance angle ($\Delta\theta$) versus the negative logarithmic concentration of PM exhibited a good linear relationship ($R^2 = 0.996$) in the concentration range of 10^{-13}–10^{-10} mol/L, which further suggested that the sensor chip based on grafted imprinted polymer possessed good adsorption to the template molecules. The error bar in the calibration curve indicated a good reproducibility of the MIF for the recognition of PM. In the experiment, the minimum detectable concentration was 10^{-13} mol/L.

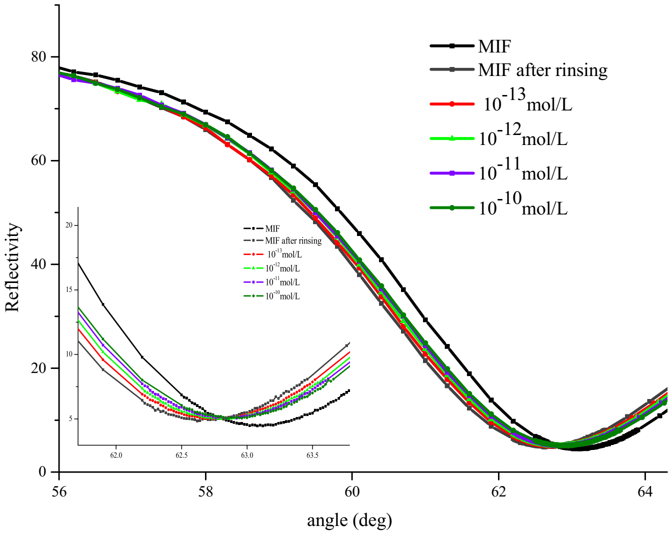

Fig. 2. SPR angular reflectivity spectra measured after rebinding with various concentrations of PM. The inset graph is the enlarged spectra around the coupling angles.