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Colorimetric detection of pyrethroid metabolite by using surface molecularly imprinted polymer

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ABSTRACT

A simple colorimetric method was developed for the detection of 3-Phenoxybenzaldehyde (3-PBD), the metabolite of pyrethroid pesticides, based on surface molecularly imprinted polymer (MIP). In this method, MIP layer was coated on the surface of monodispersed silica nanoparticles via sol-gel process with 3-Aminopropyltriethoxysilane (APTES) and phenyltrimethoxysilane (PTES) as monomers. Compare with single functional monomer, APTES and PTES can interact with 3-PBD mainly by hydrogen bonding and π-π staking interaction, which makes the synthetic MIPs show better affinity and absorption capacity towards target than that of signal functional monomer. After eluted from MIP nanoparticles, the 3- PBD resulted in a distinctive color fading by potassium permanganate reduction. Taking advantage of this phenomenon, the 3- PBD could be detected by recording the absorption of potassium permanganate solution with MIPs as the recognition element. The MIPs, synthesized under various conditions, were characterized by fourier transform infrared spectrometry and scanning electro microscopy. Meanwhile, their absorption performance were also investigated. Under the optimum condition, the proposed method exhibited a linear concentration range of 3-PBD from 0.1 μg mL^{-1} to 1 μg mL^{-1} with a lower detection limit of 0.052 μg mL^{-1} (S/N = 3). Moreover, this method was further used to detect 3-PBD in real samples form river water, fruit juice, and beverage. Satisfactory recovery was achieved in the range of 90.0 ~ 98.9%, which clearly demonstrating the potential value of this strategy in the detection of total pyrethroid pesticides.

1. Introduction

Pyrethroid pesticides are a series of synthetic esters deprived from natural chemical pyrethrins found in chrysanthemum flower. As a commercial insecticide, pyrethroid pesticides have been widely used in agriculture due to their low toxicity, long-term of stability, and broad-spectrum resistance to pests [1]. With increasing abuse of pesticide, the residual of pyrethroid pesticides are accumulated in the fruits and vegetables, which affect the food safety of daily life seriously [2]. Thus, in order to reduce the risk of contaminated food, it is imperative to develop sensitive methods for the detection of pyrethroid pesticides. Up to now, the most popular methods for the detection of pyrethroid pesticides are chromatographic methods, which including gas chromatography, high-performance liquid chromatography (HPLC), and capillary electrophoresis [3–5]. These methods showed satisfactory sensitivity in multi-analysis, but suffered from time-consuming sample preparation and high operation costs which limited these approaches impractical for routine food safety monitoring. Moreover, this method also produces a large amount of toxic organic solvent wastes, making it a less environment-friendly option. Compared with instrumental analysis, colorimetric method showed much more advantages than that in pesticides detection such as cost-effectiveness, easy to use, and the results can be read with naked eye [6–8]. Hammock and co-workers had found that type II pyrethroids, which contain nitrile group, could hydrolysis to yield cyanide ions under alkaline conditions [9]. Based on this principle, several colored products were obtained as the signal for the detection of type II pyrethroids [10,11]. Owing to the differences of molecular formula between two kinds of pyrethroids, this strategy was not available for the detection of type I pyrethroids. In order to develop a versatile method to detect the entire range of pyrethroids,

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the hydrolysis product was selected as a metabolic biomarker to assess the level of pesticide residual contamination [12]. Among the pyrethroids metabolites, 3-phenoxybenzoic acid had attracted the most attention in recent research reports [13]. As a non-specific and frequently detected metabolite of pyrethroids, the detection of 3-phenoxybenzoic acid mainly focus on immunoassays through the interaction between antigen and antibody [14]. McCoy employed hydrogen peroxide as oxidant to convert the type II pyrethroids to 3-phenoxybenzoic acid, which could be detected through enzyme-linked immunosorbent assay [15]. Liu developed a competitive immunoassay by using 3-phenoxybenzoic acid-bovine serum albumin as an immunogen [16]. Nevertheless, the performance of all these immunoassays was subjected to the vulnerable monoclonal antibody, which increasing the cost and manipulation steps in the detection of pyrethroids metabolite.

Molecular imprinted polymers (MIPs), as an artificial antibody, had been selected as an alternative for the enrichment and recognition of target molecule [17,18]. Due to their high specific three dimension recognition cavities, MIPs have been widely used as sorbent in sample preparation and as bio-receptors in biosensors [19]. Recently, hybrid MIPs, which integrate signal transduction and target recognition, were attracted many interest in novel optical sensor construction [20]. Many luminophores, including quantum dots, dyes, and up conversion nanoparticles, were encapsulated in MIPs through in-suit polymerization and surface modification [20–22]. Although high sensitive and selective detection were achieved with these luminescent MIPs, the cumbersome preparation process and unstable fluorescence signal were the key drawbacks in their further application.

Recently, It was found that 3-PBD, an intermediate metabolite of pyrethroid pesticides, could be oxidized to 3-phenoxybenzoic acid, which lead to a color fading of potassium permanganate. Inspired by this phenomenon, we developed a surface imprinted polymer coupled with colorimetric method for the detection of 3-PBD. In this method, monodispersed silica was selected as imprinted matrix for surface imprinting. According to the molecule structure of 3-PBD, 3-aminopropyltriethoxysilane and phenyltrimethoxysilane were chose as functional monomers to form imprinting layer on the surface of silica nanoparticles through sol-gel process. Taking advantage of selective enrichment of MIPs, 3-PBD could be selective detected by a colorimetric method. Moreover, due to the excellent separation capacity of molecular imprinted polymers, the proposed method also showed good performance in real sample detection.

2. Materials and methods

2.1. Reagents and apparatus

All the reagents used in the study were of analytical grade unless otherwise stated. Tetraethyl orthosilicate (99%) (TEOS), 3-Aminopropyl triethoxysilane (98%) (APTES), 3-phenyltrimethoxysilane (PTES), 3-phenoxybenzaldehyde (3-PBD), 3-phenoxybenzenemethanol (3-PBM) and 4-phenylphenol were procured from Sigma-Aldrich (St. Louis, MO, USA). The fenvalerate was purchased from Shanghai Pesticide Research Institute (Shanghai, China). High-purity water was obtained from a Milli-Q water system (Millipore, Billerica, MA, USA). The UV spectrum was recorded on a TU-1901 spectrometer (Persee, Beijing, China). The infrared spectra were recorded on PerkinElmer Frontier FT-IR spectrometer. Morphology observation of molecular imprinted polymers was carried via scanning electron microscopy (SEM; FEI Quanta FEG 250 microscope) at an acceleration voltage of 15 kV. All optical measurements were performed at room temperature under ambient conditions.

2.2. Preparation of monodisperse silica and molecular imprinted polymers

Before prepared the molecular imprinted polymers, monodispersed nano silica were synthesize by following the earlier reported method with slight modification [23]. Briefly, to a three necked flask, 61 mL of ethanol, 5 mL of TEOS, 25 mL of purity water, and 9 mL of ammonium hydroxide were added in sequence and the mixture was stirred at 400 rpm under ambient for 3 h. After centrifuging at 5000 rpm for 10 min, the precipitated particles were washed twice with ethanol and dried in vacuum for the further use.

To a 25 mL flask, 100 mg of 3-PBD, 10 mL of ethanol, 500 μL of PTES and 250 μL of APTES were added and mixed thoroughly. Then, 1 mL of TEOS was added and stirred for 5 min. After that, 400 mg of prepared monodisperse nano silica was added and followed by 2 mL of $NH_3 \cdot H_2O$ (6%, v/v), the mixture was continuously stirred for 16 h. After the polymerization, with the help of centrifugation, the resultant MIPs were washed with acetonitrile to remove the unreacted reagents and then washed with acetonitrile/acetic acid (90:10, v/v) to remove the template molecules until no template was detected. The non-imprinted polymers (NIPs) were prepared using the same procedure but without addition of 3-PBD.

2.3. Colorimetric detection of 3-PBD

Various concentration of 3-PBD were added to PBS buffer which contained 20 mg MIPs in a reaction volume of 20 mL. After 15 min absorption, the precipitation was obtained through centrifuge at 5000 rpm for 5 min. Then, 2 mL acetonitrile-acetic acid mixture was added and sonicated for 8 min to remove the binding target. Followed by centrifugation, the supernatant was obtained for the further experiment.

For the colorimetric detection with acid potassium permanganate, 100 μL of potassium permanganate (0.01 M), 1.2 mL of sulfur acid, and 770 μL of the supernatant were added together. Then the homogenous mixture was placed to record the absorbance intensity at 523 nm.

The adsorption capacity (Q, $\mu g\ mg^{-1}$) was evaluated from the following formula:

$$Q = \frac{(C_0 - C_F)V}{M}$$

Where Q ($\mu g\ mg^{-1}$) is the mass of 3-PBD adsorbed by a unit amount of dry particles, C_0 ($\mu g\ mL^{-1}$) and C_F ($\mu g\ mL^{-1}$) are the initial and final 3-PBD solution concentrations, respectively. V (mL) is the volume of the initial solution, and M (mg) is the mass of MIPs.

2.4. Sample preparation

Fruit juice and Beverage were purchased from the local market. The river water was obtained from Pujiang River. Before recovery assay, all the sample were filtered with 0.2 μm membrane to get rid of insoluble sediment. The filter sample were collected for the further detection.

3. Results and discussions

3.1. Spectrometric detection of 3-PBD

In the proposed method, a simple and effective method for the detection of 3-PBD was the key factor. Considering the molecular structure of 3-PBD, the main challenge was to select the proper oxidant that could convert the aldehyde to the carboxylic acid accompanying with distinctive color change. In order to meet this requirement, acid potassium permanganate was selected as