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ORIGINAL ARTICLE

Selective extraction of dimethoate from cucumber samples by use of molecularly imprinted microspheres

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KEYWORDS

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Abstract Molecularly imprinted polymers for dimethoate recognition were synthesized by the precipitation polymerization technique using methyl methacrylate (MMA) as the functional monomer and ethylene glycol dimethacrylate (EGDMA) as the cross-linker. The morphology, adsorption and recognition properties were investigated by scanning electron microscopy (SEM), static adsorption test, and competitive adsorption test. To obtain the best selectivity and binding performance, the synthesis and adsorption conditions of MIPs were optimized through single factor experiments. Under the optimized conditions, the resultant polymers exhibited uniform size, satisfactory binding capacity and significant selectivity. Furthermore, the imprinted polymers were successfully applied as a specific solid-phase extractants combined with high performance liquid chromatography (HPLC) for determination of dimethoate residues in the cucumber samples. The average recoveries of three spiked samples ranged from 78.5% to 87.9% with the relative standard deviations (RSDs) less than 4.4% and the limit of detection (LOD) obtained for dimethoate as low as 2.3 μg/mL.

1. Introduction

Dimethoate, as one of the major classes of organophosphorous pesticides, is widely used in the fruit, ornamentals, and field crops to promote the development of farming and satisfy the need for agricultural products [1] owing to its low persistence and biodegradation. However, excessive use of dimethoate could lead to superfluous residues of agricultural products accumulating in the human body through the food chain, which could disrupt cholinesterase enzyme and cause cholinergic dysfunction or even death [2]. Therefore, accurate and reliable analysis of dimethoate residual concentration in agricultural products is of importance to human health. Up to now, the most commonly used methods for detecting organophosphorous pesticide residues mainly include gas chromatography (GC), gas chromatography–mass spectrometry (GC–MS), gas chromatography–tandem mass spectrometry

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(GC–MS/MS), high performance liquid chromatography (HPLC), liquid chromatography–mass spectrometry (LC–MS), and liquid chromatography–tandem mass spectrometry (LC–MS/MS) [3,4]. However, the sample pretreatment process is an extremely necessary step before instrumental analysis [5,6] due to the complexity of the sample matrix. And the routine sample extraction methods, such as liquid–liquid extraction, require a large amount of solvent and multiple consequent steps, and solid-phase extraction usually results in co-extraction of interfering compounds on account of the nonspecific interaction between the analyte and the adsorbent. Thus, the development of new adsorbents with high affinity and specific recognition is greatly desired.

Molecularly imprinted polymers (MIPs), artificial ones, possess tailor-made binding sites complementary to the shapes, sizes and functional groups of the templates. MIPs have numerous merits, including low cost, easy synthesis, high stability to harsh chemical and physical conditions, and excellent reusability [7], which have led to their application in a variety of fields such as solid-phase extraction (SPE) [8–10], matrix solid-phase dispersion (MSPD) [11–13], membrane separation [14,15], chromatographic analysis [16–18], sensors [19,20], catalysis [21,22], and drug controlled release [23–25]. Among these applications, MIPs used as efficient alternative adsorbents of SPE for extraction of environmental contaminants from the complex samples appear to be highly promising. To acquire data, a series of synthesis methods for MIPs have been developed, such as bulk polymerization [26], precipitation polymerization [27], suspension polymerization, surface polymerization [28,29] and in-situ polymerization [30]. Among these, precipitation polymerization tends to decrease the guarant viscosity for great improvement of the operability of polymerization and produce a narrow range of particle sizes, which has gained a lot of attention.

In this paper, we prepared dimethoate molecularly imprinted polymers *via* a simple precipitation polymerization process for specific recognition of dimethoate in cucumber samples. The synthesis conditions were optimized in detail through single factor experiments and the morphology of the resulting products was characterized by SEM, the results exhibited spherical morphology and homogeneous distribution. The obtained imprinted polymers manifested satisfactory recognition and favorable selectivity towards the template molecule through binding experiments. Moreover, an effective analytical method combining the resultant imprinted materials which were used as absorbents for the pretreatment process with HPLC for determination of dimethoate in cucumber samples was established.

2. Experiment

2.1. Chemicals and apparatus

Dimethoate, carbaryl, methamidophos and ethylene glycol dimethacrylate (EGDMA) were purchased from Jingchun Scientifical Co., Ltd. (Shanghai, China). Methacrylic acid (MAA), methyl methacrylate (MMA), acrylamide (AM), azobisisobutyronitrile (AIBN), acetonitrile (ACN), toluene (phMe) and acetic acid were provided by Hongxin Chemical Company (Xi'an, China). The structures of carbaral, dimethoate, and methamidophos are shown in Fig. 1. The highly purified water (18.0 MΩ/cm) was obtained from a WaterPro water system (Axlwater Corporation, TY10AXLC1805-2, China) and used throughout the experiments. All the reagents used were of at least analytical grade.

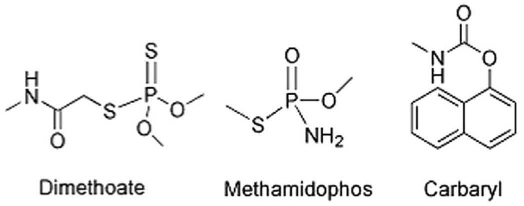

Fig. 1 Molecular structures of dimethoate, methamidophos, and carbaryl.

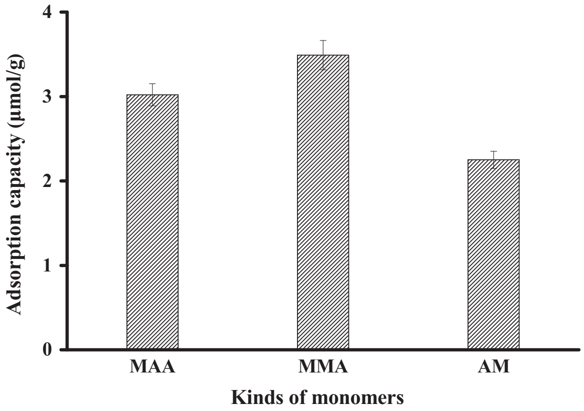

Fig. 2 Adsorption capacities of MIP synthesized using MAA, MMA and AM as functional monomers, respectively. The initial concentration of dimethoate in acetonitrile was 0.30 mM.

The HPLC analyses were performed on a Hitachi L-2130 HPLC system equipped with an L-2130 pump, an L-2400 UV detector, and a Kromosil C_{18} column (150 mm × 4.6 mm, 5 μm). D-2000 software was used to acquire and process the chromatographic data. The mobile phase was methanol-H_2O (40/60, v/v) delivered at a flow rate of 1.0 mL/min. The injection volume was 20 μL, and the column effluent was monitored at 220 nm. Sample solutions were filtered through a 0.22 μm nylon filter before use. The morphology of MIPs was evaluated by a scanning electron microscope (SEM, VEGA TS5136XM).

2.2. Synthesis of MIPs

The dimethoate MIPs were prepared through a precipitation polymerization process. Briefly, template molecule dimethoate (10 mg) was dissolved in acetonitrile (20 mL) in a round-bottom flask, and then mixed with 20, 30 or 60 mg of functional monomer. The mixture was stirred until the solution became homogeneous, and put into the refrigerator for 6 h to gain a prepolymerization solution. After that, the cross-linker EGDMA (200, 250, 300 mg) and the initiator AIBN (100 mg) were added to the prepolymerization solution and the mixture was blended under ultrasonication for 10 min, and then purged with nitrogen for 5 min to degas oxygen. The solution was sealed with a parafilm and reacted on water bath oscillator at 20 °C for 24 h with a certain rotation speed. The resultant products were separated by centrifugation at 4000 rpm for 15 min, and washed with the mixture of methanol and acetic acid (8:2, v/v) until no template molecules were detected in the extraction solvent by HPLC. Then the polymer particles were washed several times with methanol and dried at 80 °C for 24 h under vacuum.