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Analytical Methods

One-pot preparation of an acryloyled β-cyclodextrin-silica hybrid monolithic column and its application for determination of carbendazim and carbaryl

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Carbaryl (PubChem CID: 6129)
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β-CD (PubChem CID: 4440410)
Acrylyl chloride (PubChem CID: 13528)
Methyltrimethoxysilane (PubChem CID: 14456)
2,2-Azobisisobutyronitrile (PubChem CID: 6547)
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ABSTRACT

This work describes, for the first time, an acryloyled β-cyclodextrin hybrid monolith column was synthesized, under aqueous-phase conditions, and used for solid-phase microextraction of carbendazim and carbaryl. The monolithic column was characterized using scanning electron microscopy, nitrogen adsorption–desorption, thermogravimetric analysis and Fourier transform infrared spectroscopy, and used as the adsorbent for solid phase microextraction (SPME) of carbendazim and carbaryl. After optimization of the SPME conditions, a simple and sensitive SPME-HPLC method was developed for the determination of carbendazim and carbaryl in leafy vegetables. The method exhibited a good liner response in the range 5–400 μg/kg (R^2 = 0.9994) for carbendazim and 10–400 μg/kg (R^2 = 0.9996) for carbaryl, respectively. The limits of detection were 1.0 and 1.5 μg/kg for carbendazim and carbaryl, respectively, in leafy vegetables. Recoveries ranged from 92.6% to 110.1%, and the relative standard deviations were less than 6.1%.

1. Introduction

Pesticides are important for controlling plant food diseases, protecting crops and increasing food production, but their use can lead to residues in foods. Toxicology studies suggest that many pesticides have the potential for acute and chronic effects on human health as well as contamination of groundwater (Pardío et al., 2012; Zentai, Szabo, Kerekes, & Ambrus, 2006; Park et al., 2016). Thus, determination of pesticides is important for food safety.

Usually, pesticide residues are present in foods at low concentrations, and food matrices are very complex, meaning effective pretreatment is essential for accurate determination. Liquid-liquid extraction (LLE) and solid-phase extraction (SPE) are common pretreatment techniques. However, these methods require large volumes of organic solvents and are time-consuming (Duan, Shen, Wu, & Guan, 2011; Płotka-Wasylka et al., 2015). To overcome these drawbacks, solid phase microextraction (SPME) was introduced to analytical practice by Pawliszyn in 1990 (Arthur, & Pawliszyn, 1990). SPME has the advantages of simplicity, less sample and lower consumption of solvent as well as easy coupling with chromatographic instruments (Erica, Silva, Risticevic, & Pawliszyn, 2013; Wen, Chen, Li, Liu, & Chen, 2014). Monolithic columns, used as SPME adsorbents, have received a lot of attention for their desirable porous structure, which provides good permeability and separation efficiency (Hu, Wang, Chen, Hu, & Li, 2010; Quinto, Spadaccino, Palermo, & Centonze, 2009; Zhou et al. 2010). There are three types of monolithic columns: inorganic silica-based monolithic column, organic polymer monolithic column and organic-inorganic hybrid monolithic column (Liu, Oua, & Zoua, 2016; Svec, & Lv, 2015; Jandera, 2013). In recent years, organic-inorganic hybrid silica monolith columns have received attention for their good chemical and

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mechanical stability, relatively high surface area, and sufficient numbers of active sites (Wu, Liang, & Yang, 2016).

Cyclodextrins are torus-shaped cyclic oligosaccharides containing six to twelve glucose units. The individual glucose units are joined by α-1,4 glycosidic links forming a cyclic structure (Duchêne, & Bochot, 2016). Among the different types of cyclodextrins, β-cyclodextrin (β-CD) has been used widely in food, cosmetics, pharmaceuticals (Martin Del Valle, 2004). β-CD-based materials have also been used as adsorbents because of the cavity in β-CD (internal diameter 6.5 Å, depth of 8 Å, Limaa et al., 2016), which recognizes organic molecules with molecular weights between 200 and 800 $g \cdot mol^{-1}$, based on host-guest interactions (Saz, & Marina, 2016; Morin-Crini, & Crini, 2013) and the formation of hydrogen bonds. Sinha and his coworkers synthesized magnetic nanocomposites, based on graphene and porous silica, which were functionalized with cyclodextrin to separate microcystin-LR from contaminated water (Sinha, & Jana, 2015). In Kyzas et al. (Kyzas, Lazaridis, & Bikiaris, 2012), β-CD was used as a monomer in molecularly imprinted polymer to separate dye. β-CD-based materials, used as sorbents, have high adsorption capacities and excellent selectivity from poly-contaminated mixtures, even at low concentrations (Zhang, Qin, He, Li, & Zhang, 2009; Alsbaiee et al., 2016). Unfortunately, no research on the preparation and application of β-CD-based hybrid polymer monolith columns, as SPME adsorbents, has been reported.

In this work, an acryloyled β-CD (A-β-CD) functional monomer was first synthesized using an improved method with less organic solvent and high productivity. The A-β-CD monomer retained the β-CD molecular recognition capacity and a double bond to form polymers. For the first time, a novel hybrid monolithic column was prepared in a pipette tip, using the acryloyled β-CD as the monomer, and a mixture of MeOH and H_2O as the porogenic solvent. The resulting A-β-CD-silica hybrid monolithic column had β-CD molecular recognition and the advantageous of a hybrid monolithic column. The A-β-CD-silica hybrid monolithic column was used as the adsorbent for SPME of carbendazim and carbaryl. After optimization, a novel SPME-HPLC method for the determination of carbendazim and carbaryl in vegetables was developed. The results showed that the SPME-HPLC method was simple and sensitive for analysis of carbendazim and carbaryl in complex food samples.

2. Experimental

2.1. Chemicals and materials

Carbendazim (99%) and carbaryl (99.5%) were purchased from Dikma Technologies Inc. (Beijing, China). β-CD (96%) was purchased from Aladdin Chemistry Co.Ltd., (Shanghai, China) and used following further purification by recrystallization. *N,N*-dimethylformamide (AR) and acetone (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd (Beijing, China). Acrylyl chloride (98%) was purchased from Zahn Chemical Technology Co., Ltd. (Shanghai, China). Methyltrimethoxysilane (MTMS) and 3-methacryloxypropyltrimethoxysilane (γ-MAPS) were obtained from Aladdin Reagent Inc. (Shanghai, China). Triethylamine (AR) was purchased from Tianjin Bodie Chemical Co., Ltd (Tianjin, China). 2,2-azobisisobutyronitrile (AIBN) was purchased from Shanghai Haoshen Chemical Reagent Corp. (Shanghai, China) and purified by recrystallization. Ethylene glycol dimethacrylate (EGDMA) purchased from Acros (New Jersey, USA) was extracted with 5% aqueous sodium hydroxide and water, and dried over anhydrous magnesium sulfate. Methanol and acetonitrile (HPLC grade) were obtained from Tedia Company Inc. (Ohio, USA). Ultrapure water, used in all experiments, was obtained using an Ultrapure Water System (Beijing, China).

2.2. Apparatus

A RE-52AA rotary evaporator (Ya Rong Biochemical Instrument Factory, China) was used to evaporate some solvents. The microscopic morphology of the materials was examined using a Modal X-650 scanning electron microscope (SEM) (Hitachi, Japan). Surface area and pore size distribution in the A-β-CD-silica hybrid monolithic column were measured on a QDS-MP-30 surface area and pore size analyzer (Quantachrome, USA) at 120 °C. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA-7 thermal gravimetric analyzer (Perkin Elmer, USA). The material was also examined using a Fourier transform infrared spectrometer (Perkin Elmer, USA). A HX-24 nitrogen blowing instrument (Wuhan Hanson Century Technology Co. Ltd., China) was used to evaporate the solvent. 0.22 μm membrane was obtained from Xingya Scavenging Material Company (Tianjin jinteng laboratory equipment Co. Ltd., China). The LSP10-1B multi-channel syringe pump (Baoding Longer Precision Pump Co. Ltd., China) was employed for the delivery of samples and the washing solution. Sample pH was determined using a LE438 digital pH meter (mettle toledo Co. Ltd. China).

2.3. HPLC conditions

A Dionex Summit U3000 HPLC system equipped with a manual injector and a Photodiode Array Detector (PAD) (Dionex Technologies, USA) was used for chromatographic analysis. The column was An amethyst-C18 column (4.6 mm × 250 mm, 5 μm) from Sepax Technologies Inc. (Newark, USA) was used for separation. A personal computer equipped with a Chromeleon ChemStation program for LC was used to process chromatographic data. The mobile phase was a mixture of methanol-water solution (70:30, v/v) and the flow rate was 1.0 mL/min. The detection wavelength was set at 275 nm and the column temperature was 30 °C. All injections were performed manually with a 20.0 μL sample loop.

2.4. Preparation of A-β-CD silica hybrid monolithic column

2.4.1. Synthesis of A-β-CD

The synthesis of A-β-CD is shown in Fig. 1(a). Purified β-CD (1 mmol) was dissolved in 30 mL of DMF. Then, 1.17 mL of triethylamine was added, sonicated for 10 min and the mixture cooled in ice-water. A mixed solution consisting of 760 μL of acryloyl chloride and 1.5 mL of DMF was added slowly. After incubation in ice-water bath for 30 min, the solution was left to equilibrate at room temperature for 30 min before being filtered, and a large volume of acetone added to precipitate the products, which were filtered and dried under vacuum at 80 °C for 12 h.

2.4.2. Preparation of A-β-CD-silica hybrid monolithic column

In order to reduce the use of organic solvents, A-β-CD was produced under aqueous-phase synthesis conditions (Fig. 1b).

Preparation of inorganic solution: MeOH (300 μL), 0.1 mol/L HNO_3 (200 μL) and MTMS (800 μL) were mixed and degassed in an ultrasonic

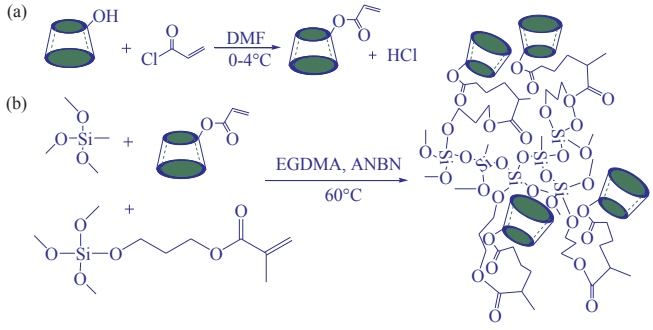

Fig. 1. Scheme for the synthesis of A-β-CD (a) and A-β-CD-silica hybrid monolithic column (b).