



Analytical Methods

A dispersive magnetic solid phase microextraction based on ionic liquid-coated and cyclodextrin-functionalized magnetic core dendrimer nanocomposites for the determination of pyrethroids in juice samples



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ABSTRACT

A novel dispersive magnetic solid phase microextraction method based on ionic liquid-coated and cyclodextrin-functionalized magnetic core dendrimer nanocomposites has been developed for the determination of pyrethroids in juice samples. The different generation magnetic core dendrimer nanocomposites were successfully synthesized and the nanocomposites possess both the selective retention of guest dendrimer and cyclodextrin molecules and high adsorption capacities of ionic liquids. The extraction efficiencies of different generation magnetic core dendrimer nanocomposites were compared, and the type of nanocomposite with the highest recovery was obtained. Under the optimized experimental conditions, the method showed good linearity in the range of 3.5–500 $\mu\text{g L}^{-1}$. The LODs and LOQs were in the ranges of 0.36–1.3 $\mu\text{g L}^{-1}$ and 1.2–4.3 $\mu\text{g L}^{-1}$, respectively. The method also showed acceptable accuracies ranging from 98.2% to 99.4%. The proposed method was demonstrated to broaden the potential applications of dendrimer for the detection of pyrethroid residues in various juice samples.

1. Introduction

Pyrethroids have been applied for worldwide commercial and retail use to control insect pests in agriculture and public health because of their broad spectrum and high activity since the 1970s (Li, Morgan, Graham, & Starr, 2016). However, the association of acute pyrethroid intoxication with altered nerve function has been confirmed by physiological and neurochemical studies of animals intoxicated with pyrethroids. (Soderlund et al., 2002) Additionally, pyrethroid residues are an important source of pollution in agriculture and a potential public health threat (Kolaczinski & Curtis, 2004). The maximum residue limits (MRLs) of pyrethroids established by the European Union in fruits is in the range of 0.02–0.3 mg/kg. (Regulation, xxxx) Thus, there is an urgent need for the development of a novel adsorbent and pretreatment method for the determination of pesticide residues.

Dendrimers are a class of monodisperse, highly branched, and symmetrical polymers with a high density of functional groups, and they have been widely applied in various fields, including biology, materials science, catalysis, surface modification, electronics, electro-

optics, chemical or biological sensors, and coatings. (Tomalia et al., 1985) Typically, poly (amide amine) dendrimers (PAMAM), which are the first members of the dendrimer family synthesized, characterized and completely commercialized (Tomalia & Esfand, 1997), are usually synthesized by a two-step iterative reaction using a divergent method. The concentric branch was grafted with the central initiator core continuously according to Michael addition and amidation reactions to grow linearly in diameter (Tomalia, 1996). Higher generation dendrimers can be used as hosts for a range of molecules and ions due to their three-dimensional structure and multiple internal and external functional groups (Jansen, Debrabandervandenberg, & Meijer, 1994). Simultaneously, the high density of external surface groups allows attachment of targeted molecules or functional modification to meet our needs. The target molecules may be encapsulated into the interior of the dendrimers or chemically attached/physically adsorbed onto the dendrimer surface due to the multivalent surface containing a large number of potentially reactive/passive sites (Svenson & Tomalia, 2005). Consequently, dendrimers have been reported to be applied in environmental analysis for the adsorption of metal ions (Wu, Luo, Chen, &

Abbreviations: MNP@PAMAM@CD@IL, ionic liquid-coated and cyclodextrin-functionalized magnetic core dendrimer nanocomposites; PAMAM, poly (amide amine) dendrimers; β -CD, β -cyclodextrin; MNPs, magnetic nanoparticles; IL, ionic liquid; CD-O-Ts, mono-6-deoxy-(p-tolylsulfonyl)- β -cyclodextrin; G, generation; d-MSPE, dispersive magnetic solid phase microextraction; APTES, 3-aminopropyltrimethoxysilane; HPLC, High performance liquid chromatography

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Liang, 2016), removal of toxic trace elements (Xiao, Yan, Zeng, & Liu, 2016); detection of organic carcinogens such as nitrosamines (Sanagi, Chong, Endud, Ibrahim, & Ali, 2015), and determination of drugs (Li et al., 2015; Pan et al., 2015). However, it's rare for PAMAM to be used for the extraction of pesticides, and the above findings make PAMAM particularly promising as an adsorbent for the determination of pesticides. Hence, it's necessary for us to broaden their application and develop a fast and efficient extraction method using PAMAM as the adsorbent for the determination of pyrethroids.

The procedure of sample preparation is usually the most tedious step in chemical analysis, and on average, it requires 61% of the time required to perform analytical tasks (Fritz, Dumont, & Schmidt, 1995). Up until now, various sample preparation techniques have been reported to have been applied for the determination of pyrethroids from different matrices, including solid phase extraction (SPE) (Fernandez-Ramos, Satinsky, & Solich, 2014; Hildmann, Gottert, Frenzel, Kempe, & Speer, 2015), dispersive liquid–liquid micro-extraction (DLLME) (Rego et al., 2015) and stir bar sorptive extraction (SBSE) (Noronha, Neves, Queiroz, & Oliveira, 2015). Among these above-mentioned methods, SPE is considered superior to the other procedures because of its low cost, high efficiency, high reproducibility and applicability in different formats for various organic or inorganic analytes. In addition, SPE even can be automated in offline or online modes (Pintado-Herrera, Gonzalez-Mazo, & Lara-Martin, 2014). Despite its advantages, SPE can still be boring, time consuming, and relatively expensive (Carnizello et al., 2009). A new type of SPE called dispersive magnetic solid phase microextraction (d-MSPE), which is considered an advanced technique, has been proposed since it offers important benefits in the separation and preconcentration of analytes from large volumes of solution (Wu et al., 2012). Accordingly, choosing a d-MSPE method is especially suitable for the determination of pyrethroid compounds from complicated matrices.

In the present study, we successfully synthesized an ionic liquid-coated and cyclodextrin-functionalized magnetic core dendrimer nanocomposite (MNP@PAMAM@CD@IL). The nanocomposites were composed of inorganic magnetic nanoparticles, cyclodextrin-functionalized PAMAM with the ability for the selective retention of guest molecules and ionic liquids with high adsorption capacities. From this purpose, we herein focus on preparing dendrimer nanocomposites and broadening the potential for their use as a novel adsorbent to determine trace amounts of pyrethroids. A novel dispersive magnetic solid phase microextraction method based on the MNP@PAMAM@CD@IL was developed for the separation and preconcentration of pyrethroid residues in complex juice samples. The proposed method proved to be highly efficient, fast, and convenient for the detection of pyrethroid residues in various juice samples.

2. Materials and methods

2.1. Reagents and materials

Three pesticides standards (permethrin, phenothrin, and bifenthrin), monodispersed magnetite microspheres, 3-aminopropyltrimethoxysilane ($\text{NH}_2\text{-(CH}_2\text{)}_3\text{-Si-(OCH}_3\text{)}_3$, APTES) and methyl acrylate were purchased from the Aladdin Reagent Corporation (Shanghai). Ethylene diamine, methanol, ethyl alcohol, sodium chloride (NaCl), ammonium hydroxide, β -CD, and hydrochloric acid were all obtained from the Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). Lithium bis(trifluoromethanesulfonimide) was purchased from the Zhejiang Jiuzhou Pharmaceutical Co., Ltd. (Zhejiang, China). 1-Octyl-3-methylimidazolium chlorides ([OMIM] Cl) were purchased from the Center for Green Chemistry and Catalysis, LICP, CAS (Lanzhou, China). The deionized water was purified on a Milli-Q SP Reagent Water System (Millipore, Bedford, MA, USA). Acetonitrile (HPLC grade) was obtained from Dikma Limited (Beijing, China). All the above analytical grade reagents were used without further purification. All stock standards of

studied pesticides (500 mg L^{-1}) were prepared in acetonitrile and stored in the dark at $4\text{ }^\circ\text{C}$. The working standard solutions were prepared by diluting the stock standard solutions.

2.2. Preparation of real samples

Three real juice samples, including peach juice, pear juice and grape juice, were used as the fruit juice models. All of the juices were purchased from a local supermarket (Beijing, China). The fruit juice samples were stored in the dark at $4\text{ }^\circ\text{C}$ and filtered through $0.22\text{ }\mu\text{m}$ membranes before being used as the sample matrix.

2.3. Instrumentation

Chromatographic analyses were performed with an Agilent 1100 HPLC system (CA, USA) equipped with a diode array detection (DAD) system and an automatic sample injector. Agilent ChemStation software was used to control the HPLC–UV system and to carry out data analysis. Separations were performed on Spursil C18 columns ($5\text{ }\mu\text{m}$, $4.6 \times 250\text{ mm}$, Dikma Limited) with Spursil C18 guard cartridges ($5\text{ }\mu\text{m}$, $2.1 \times 10\text{ mm}$, Dikma Limited) using an acetonitrile–water (82:18, v/v) solution as the mobile phase. The UV wavelength for detection was 230 nm , and the sample injection volume was $10\text{ }\mu\text{L}$. The flow rate was 1 mL min^{-1} , and the column temperature was maintained at $25\text{ }^\circ\text{C}$.

The morphologies of the materials were studied using an S-3400N (Hitachi, Japan) scanning electron microscope and a JSM-2100F (Jeol, Japan) transmission electron microscope. X-ray diffraction (XRD) measurements were performed with a D8 Advance diffractometer (Bruker, Germany). The Fourier-transform infrared spectra of the compounds were recorded using a Spectrum 100 spectrometer (PerkinElmer, USA).

2.4. Synthesis of the MNP@PAMAM@CD@IL

2.4.1. Preparation of MNP@PAMAM

Magnetic core dendrimer nanoparticles were synthesized by grafting the PAMAM onto the surface of the MNPs according to the following procedures (Safarikova & Safarik, 1999). A 200 mL ethanol mixture containing 2 g of MNPs was sonicated for 30 min to suspend the particles. Ten milliliters of APTES were added to the mixture, and it was stirred vigorously at $60\text{ }^\circ\text{C}$ for 7 h with condensing. The mixture was then washed by methanol three times and collected by an external magnetic field, followed by drying at $60\text{ }^\circ\text{C}$ under vacuum. The amino-modified nanoparticles, described as MNP-G₀, were conjugated to PAMAM through repeating Michael addition and amidation reactions. Two grams of MNP-G₀ were redispersed in 50 mL of methanol and sonicated for 30 min. Twenty milliliters of methyl acrylate were added dropwise into the solution in an ice bath. After 15 h of continuous stirring at $35\text{ }^\circ\text{C}$, the reaction mixture was washed with methanol five times. Then, the resulting particles were immersed in 20 mL of methanol and sonicated for 30 min. Four milliliters of ethylene diamine were added dropwise into the solution in an ice bath. After 3 h of continuous stirring at room temperature, the reaction mixture was washed with methanol five times. The newly prepared nanoparticles were termed the first generation magnetic core dendrimer nanoparticles (MNP -G1). The higher generation dendrimer nanoparticles were obtained by repeating the Michael addition and amidation reactions described above.

2.4.2. Preparation of mono-6-deoxy-(p-tolylsulfonyl)- β -cyclodextrin (CD-O-Ts)

Mono [6-O-(p-toluenesulfonyl)]- β -CD was synthesized based on the previously reported work (Chou & Lien, 2011). β -CD (6.3 g) was immersed in 50 mL of water with magnetic stirring at room temperature, and 2 mL of a sodium hydroxide solution (8.2 mol L^{-1}) were added

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