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Analytical Methods

Pyrethroid residue determination in organic and conventional vegetables using liquid-solid extraction coupled with magnetic solid phase extraction based on polystyrene-coated magnetic nanoparticles

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ABSTRACT

A detection method using polystyrene-coated magnetic nanoparticles based extraction technique coupled to HPLC was developed for trace amount of pyrethroids residue detection in vegetable matrixes. The recoveries for five kinds of commonly used pyrethroids were in the range of 91.6%–116.2%. The sensitivity and precision of the method were satisfactory with the limits of detection and limits of quantification in the range of 0.0200–0.0392 ng g^{-1} and 0.072–0.128 ng g^{-1}, respectively. The intra-day and inter-day relative standard deviations for the recoveries of the analytes were lower than 6.8% and 10.7%, respectively. The nanoparticles can be washed and recycled after use. The results indicate that the developed method was efficient, fast, economical and environmentally friendly. The method was successfully applied to detect the pyrethroids residue in ten pairs of commonly consumed organic and conventional fresh vegetables in Singapore. Pyrethroids residue was detected in four kinds of conventional vegetables and one kind of organic vegetable.

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1. Introduction

Vegetables are a very important category of food materials due to their high contents of dietary fiber, vitamins, antioxidants, minerals and diverse beneficial phytochemicals (Demmig-Adams & Adams, 2002; Ren et al., 2014). Regular consumption of vegetables brings great health beneficial effect for human beings by enhancing human immunity and preventing diseases such as diabetes, constipation, cardiovascular diseases, and even colon cancer (Fu et al., 2015; Murphy et al., 2012; Ren, Perera, & Hemar, 2012). However, pesticides residue in vegetables, especially leafy vegetables has been a concern due to the high reliance on the synthetic pesticides in order to boost crop yields (Wilkowska & Biziuk, 2011). Long term over dose exposure to synthetic pesticides can lead to severe health problems since most of these chemicals are teratogenetic or even carcinogenic (Walorczyk et al., 2013). Even worse, they usually cannot be metabolised thoroughly in short term in human body and will thus be accumulated in the form of prototype or metabolite to a dangerous level (Bøhn et al., 2014).

Pyrethroids are widely applied synthetic pesticides derived from naturally occurred chrysanthemum esters (Radford, Panuwet, Hunter, Barr, & Ryan, 2014). Although pyrethroids are mainly applied to crops, they can be accumulated in soil and spread to every link of food production and every part of our daily diet via contamination (Bayen, Zhang, Desai, Ooi, & Kelly, 2013; Farajzadeh, Khoshmaram, & Nabil, 2014; Yu, Sun, Jiang, Gao et al., 2012). Moreover, according to vast research, the contamination of pyrethroids can diffuse to the environment through water circulation such as irrigation and rainfall (Bayen, Yi, Segovia, Zhou, & Kelly, 2014; Bayen et al., 2014; Fernández-Ramos, Šatíns ký, & Solich, 2014). Therefore, it is important to develop accurate and effective technique to detect pyrethroids residue in various matrixes, especially vegetables (Zhu et al., 2014).

Many efforts have been paid to determine pyrethroids in food matrixes since they started to be widely used (Ling & Huang, 1995; Watanabe & Baba, 2015). Due to the complexity of the food matrixes, in the determination the most affective step is the preconcentration since it is decisive in achieving high accuracy and low limit of detection (Bidari, Ganjali, Norouzi, Hosseini, & Assadi, 2011). A competitive enzyme-linked immunosorbent method was developed to extract pyrethroids residue from lettuce and peach (Park et al., 2004) then a clean-up routine using solid phase extraction cartridges to facilitate analysis of pyrethroids

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residue in grape, orange, tomato, carrot and green mustard was developed (Sharif, Man, Hamid, & Keat, 2006). However, all these traditional methods had limitations including long operation hours with multi steps, high cost and large consumption of organic solvent, which make them hard to be used on a large scale for batch detection (Bayen, 2012; Zainudin, Salleh, Mohamed, Yap, & Muhamad, 2015). Most recently, magnetic solid phase extraction (MSPE) has drawn much attention due to its unique advantages of high efficiency, low cost and environmental friendliness (Cao et al., 2012). With the introduction of magnetic adsorbents, some tedious filtration and centrifugation steps are not needed (Wei et al., 2013). In addition, various coatings of different affinities on the magnetic core for targeted analytes greatly improved the selectivity of the extraction and enhanced signal-to-noise ratio while analysing complex samples (Yu, Sun, Jiang, Sun et al., 2012). Recently, nanoparticles were applied for pyrethroids extraction from tea drinks and other beverages (Wang, Sun, Gao et al., 2014; Zhao, Lu, & Feng, 2013). Although these recent methods have advantages, they are mostly confined to liquid samples (Jiang et al., 2014; Wang, Sun, Xu, et al., 2014). There is a need to broaden the applicability of magnetic solid phase extraction thus it can be used for detecting pesticides residue in vegetables, where pesticides were most accumulated (Xie, Guo, Zhang, & Shi, 2014).

In the present work, we successfully developed polystyrene-coated magnetic nanoparticles (PSt/MNPs) based extraction technique for the preconcentration of trace amount of pyrethroids residue in vegetable matrixes. In this method, magnetic solid phase extraction was coupled to solid–liquid phase extraction for the high efficiency preconcentration of pyrethroids residue in vegetables. The polystyrene coating of the MNPs showed strong affinity for beta-cyhalothrin, bifenthrin, fenvalerate, permethrin and decamethrin, which was inspired by the unique separating power for conjugated compounds of chromatographic columns with polystyrene as functional groups of packing material. The present method was proved to be highly efficient, fast, low cost and environmentally friendly for the detection of trace amount of pyrethroids residue in various vegetable matrixes.

2. Materials and methods

2.1. Organic and conventional vegetable samples

Ten pairs of organic and conventional vegetables were purchased from local supermarkets in Singapore, which included cabbage (*Brassica oleraceacapitata*), pakchoi (*Brassica rapachinensis*), Chinese kale (*Brassica oleraceaalboglabra*), rape (*Brassica napus*), Chinese chive (*Allium schoenoprasum*), lettuce (*Lactuca sativa*), amaranth (*Amaranthuscruentus*), broccoli (*Brassica aleraceaitalica*), cauliflower (*Brassica oleracea botrytis*) and Chinese cabbage (*Brassica rapapekinensis*). One batch of organic Chinese cabbage was checked to be free of any targeted pyrethroids residue using the "Quick, Easy, Cheap, Effective, Rugged, and Safe" (QuEChERS) method coupled with HPLC analysis and was used for investigative tests as well as optimisation and validation experiments (Wang, Chow, Leung, & Chang, 2012). The vegetables were first homogenised using an electric juicer. The spiked samples were prepared via adding certain amount of pyrethroids standard solution into the homogenised vegetable paste followed by shaking it vigorously for 1 min and equilibrating for 3 h in dark at 4 °C in refrigerator.

2.2. Chemicals and standards

Standards of beta-cyfluthrin (purity 96.0%), bifenthrin (purity 97.2%), fenvalerate (purity 98.6%), permethrin (purity 99.9%) and decamethrin (98.0%) were obtained from Aoke biology research Co. Ltd (Beijing, China). HPLC-grade acetonitrile, methanol and acetic acid were obtained from Macron Fine Chemicals, USA. Other chemicals were analytical grade if not specified. Sodium dodecylbenzenesulfonate (SDBS), potassium persulfate (KPS), AR grade potassium bromide (KBr), $FeCl_2{\cdot}4H_2O$, oleic acid, methacrylic acid and styrene were obtained from Sigma Aldrich, USA. Sodium hydroxide pearl was purchased form Dickson Instrument & Reagent Store, Singapore. $FeCl_3{\cdot}6H_2O$ was obtained from Merck, Germany. Deionised water was prepared by a Mill-Q purification system.

2.3. Preparation of PSt/MNPs

The PSt/MNPs were prepared following a modified coprecipitation coupled with emulsion polymerisation method: Firstly, 25 mL of 0.4 mol L^{-1} $FeCl_2$ and 0.8 mol L^{-1} $FeCl_3$ were added dropwise into 250 mL of 1.5 mol L^{-1} NaOH. The mixture was stirred vigorously under nitrogen gas at 80 °C for 2 h. The obtained Fe_3O_4 was separated with a permanent magnet, washed with deionised water twice and redispersed in 50 mL water. Oleic acid (1 mL) was added into this magnetofluid and stirred for 30 min at 80 °C under nitrogen gas protection. After that, 0.27 g of SDBS was added and the mixture was stirred at room temperature for 30 min.

In order to prepare the polystyrene coated MNPs, 24 mL of the prepared magnetofluid was first dispersed in 276 mL of deionised water. Then 18 mL of styrene and 1.8 mL of methacrylic acid were added and the mixture was stirred vigorously at 70 °C under nitrogen gas protection. KPS (0.3 g) was added to initiate the polymerisation reaction which was kept running for 6 h. The obtained black brownish product was separated with a permanent magnet and washed with deionised water three times. The final product was dried in convectional oven overnight and kept in glass vials before use.

2.4. PSt/MNPs based extraction procedure for the preconcentration of pyrethroids residue in vegetable matrix

As shown in Fig. S1, the liquid-solid phase extraction coupled with MSPE using the PSt/MNPs was carried out as follows: First, 10 g of homogenised vegetable paste was extracted with 20 mL of acetonitrile in centrifugation tube by vortexing for 3 min and the mixture was then subjected to filtration. The filtrate was transferred to 80 mL deionised water in conical flask, which was added PSt/MNPs (50 mg) and agitated vigorously for 20 min on a magnetic stirrer. The PSt/MNPs absorbing the targeted analytes were separated and transferred to a centrifugation tube with the assistance of a permanent magnet. Acidified acetonitrile of 5 mL (3% acetic acid in acetonitrile, v/v) was added subsequently and the mixture was vortexed for 60 s to elute the analytes from the PSt/MNPs. The PSt/MNPs were separated with permanent magnet and the supernatant was dried at 45 °C with mild nitrogen gas stream. The residue was reconstituted in 200 μL acetonitrile for HPLC analysis.

2.5. HPLC analysis

Chromatographic analysis of the obtained extract was carried out on a Waters 2695 Alliance system equipped with a photodiode array detector, an autosampler and a quaternary pump. Separation was performed on a Luna 5u C18 column (150 mm length, 4.6 mm id, 100 A pore size, Phenomenex, CA, USA). With mobile phase A as 100% water, mobile phase B as 100% acetonitrile and total flow rate set at 1 mL min^{-1}, a gradient program was developed to conduct the HPLC analysis: 0–16 min, 75% B; 16–25 min 85% B. The column oven was kept at 25 °C during analysis and the injection volume of

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