



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 teratogenic 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, Šatínský, & 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 pre-concentration 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), FeCl₂·4H₂O, oleic acid, methacrylic acid and styrene were obtained from Sigma Aldrich, USA. Sodium hydroxide pearl was purchased from Dickson Instrument & Reagent Store, Singapore. FeCl₃·6H₂O 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 FeCl₂ and 0.8 mol L⁻¹ FeCl₃ 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 Fe₃O₄ 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 Å 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

sample was set at 10 μL per run. The detection wavelength was set at 220 nm.

2.6. Characterisation of the MNPs/PSt

Fourier transform-infrared (FT-IR) spectra, transmission electron microscope (TEM) images, as well as magnetisation curves were collected respectively in order to characterise the chemical composition, particle morphology and magnetism of the self-prepared MNPs/PSt. The FT-IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer using KBr pellet pressing method. The room temperature magnetisation curves were collected with a vibrating sample magnetometer VSM (MPMS, SQUID). A JEOL 3010 microscope was employed for collecting TEM images with the acceleration voltage set at 200 kV.

2.7. Statistical analysis

The optimisation experiments, validation tests as well as actual sample analysis were performed in triplicates in order to achieve reliable and accurate results. For the optimisation experiments and reusability tests, significance of difference was determined by analysis of variance (ANOVA) test at a confidence level of $P < 0.05$ using SAS software (version 9.2, Cary, NC, USA). For the optimisation experiments, the results were displayed in bar charts to achieve intuitive perception while for the reusability test,

the results were displayed as mean \pm RSD (Relative Standard Deviation).

3. Results and discussion

3.1. Characterising PSt/MNPs

The FT-IR spectra of the magnetic nanoparticles (MNPs) and the PSt/MNPs are shown in Fig. 1a. In the spectra of the MNPs, there is a strong absorption band at around 580 cm^{-1} which can be accounted by the vibration of Fe–O bond of Fe_3O_4 MNPs. The adsorption bands that were clearly observed at 3100 , $2900\text{--}2800$, 1600 , $1500\text{--}1400$ and 1000 cm^{-1} correspond to typical absorption bands for polystyrene, with first two representing C–H and C–H stretching vibrations of the aromatic hydrogen and the last two representing C=C stretching of the aromatic ring and C–H bending, respectively. The out plane vibration of benzene ring monosubstitution is represented by the 700 cm^{-1} absorption band. On the other hand, the relatively weak absorption bands at around 1700 cm^{-1} can be attributed to the stretching vibration of carboxyl group introduced by the surfactant, methacrylic acid, which also existed at low amount in the nanoparticles. And the absorption bands at 580 cm^{-1} ascertained the existence of Fe_3O_4 . Therefore, it can be inferred that the PSt/MNPs consisting of polystyrene, methacrylic acid and Fe_3O_4 were successfully prepared.

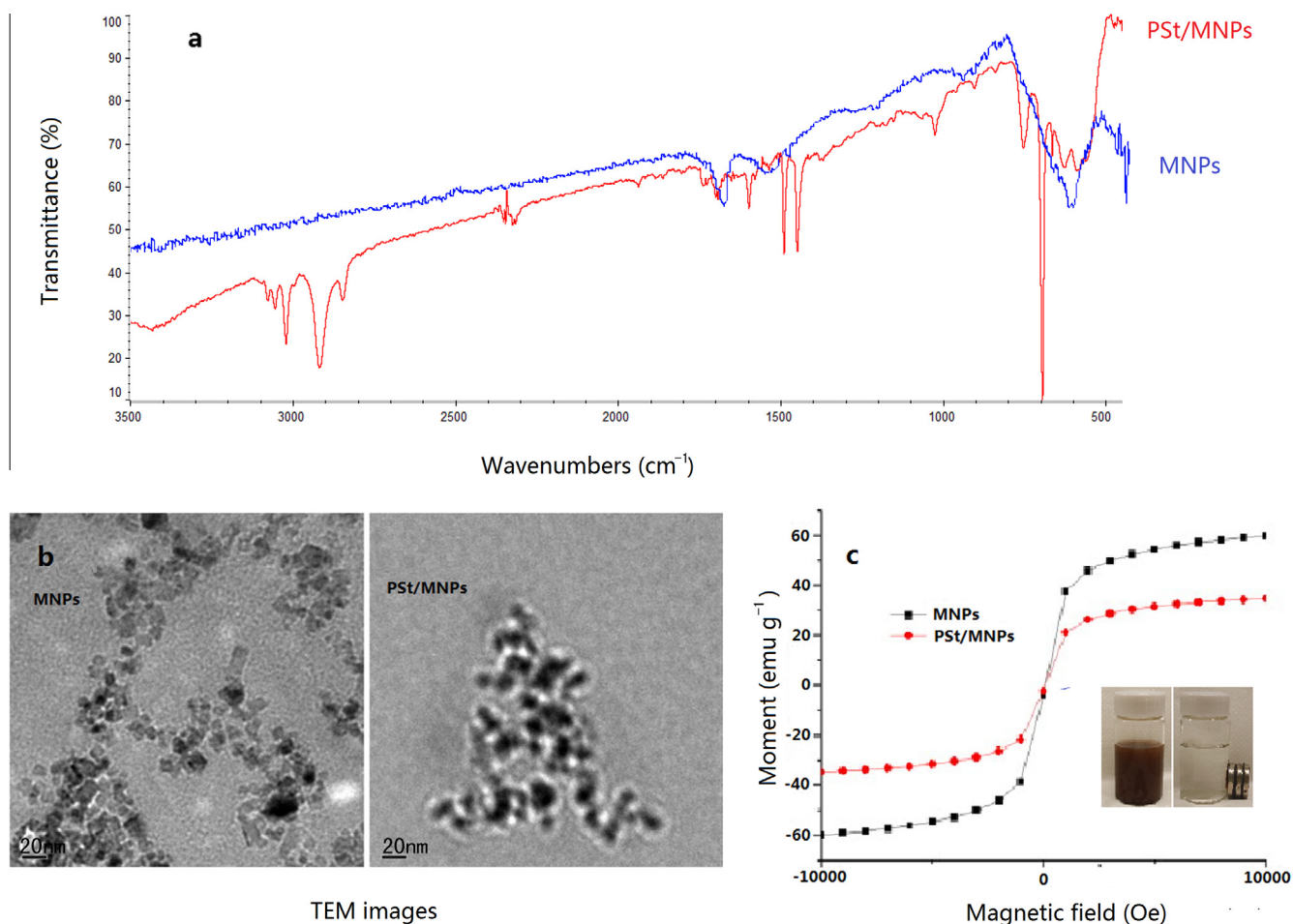


Fig. 1. Characterisation of the MNPs/PSt: (a) FT-IR spectra of the MNPs and PSt/MNPs, (b) TEM images of the MNPs and PSt/MNPs and (c) Room temperature magnetism curves of the MNPs and PSt/MNPs and dispersion and magnetic separation of the PSt/MNPs in water (inset of Fig. 3c).

From the TEM images displayed in Fig. 1b, the MNPs and PSt/MNPs were in the diameter range of around 10 nm and 20 nm, respectively, suggesting that polystyrene existed as a quite thin coating layer outside the magnetic nanoparticles. Based on this result, the final product was promising to have good magnetic properties as well as high surface ratio, preferred adsorbent material for magnetic solid phase extraction.

As was shown in the VSM graph in Fig. 1c, the MNPs and PSt/MNPs are both supermagnetic since their magnetic curves show no hysteresis loop. Additionally, the prepared MNPs showed quite strong magnetic properties with saturation magnetisation of 63.79 emu g^{-1} , while the PSt/MNPs displayed a significant drop in magnetism with the saturation magnetisation of 37.17 emu g^{-1} . This drop of magnetism was obviously caused by the existence of polystyrene, which once again proved the successful combination of the polystyrene and magnetic nanoparticles. The prepared PSt/MNPs could be easily dispersed and magnetically separated in water. The dispersion and magnetic separation of the PSt/MNPs in water are shown in the inset of Fig. 1c. The whole separation process took only 30 s.

3.2. Optimisation of the conditions for MSPE

In order to improve the extraction efficiency of the magnetic solid phase extraction process, several impact factors including the amount of adsorbents, extraction time, elution time, type and volume of desorption solvent were optimised successively. Each optimisation experiment was performed in triplicate and the obtained average was used for plotting the histograms.

As seen from Fig. 2a, the extraction efficiency increased with the increased amount of adsorbents till it reached 50 mg. After that, the extraction efficiency plateaued and stopped increasing anymore. This can be accounted by a combined effect of the total surface ratio of the PSt/MNPs and the degree of saturated adsorption.

Investigative experiments showed that extraction time had significant effect on extraction efficiency. Thus, the time of extraction was optimised in the range of 5–30 min. According to the results displayed in Fig. 2b, the recoveries of the five pyrethroids increased with increased extraction time till 20 min. After 20 min, it reached a plateau, which suggested that 20 min was sufficient to reach

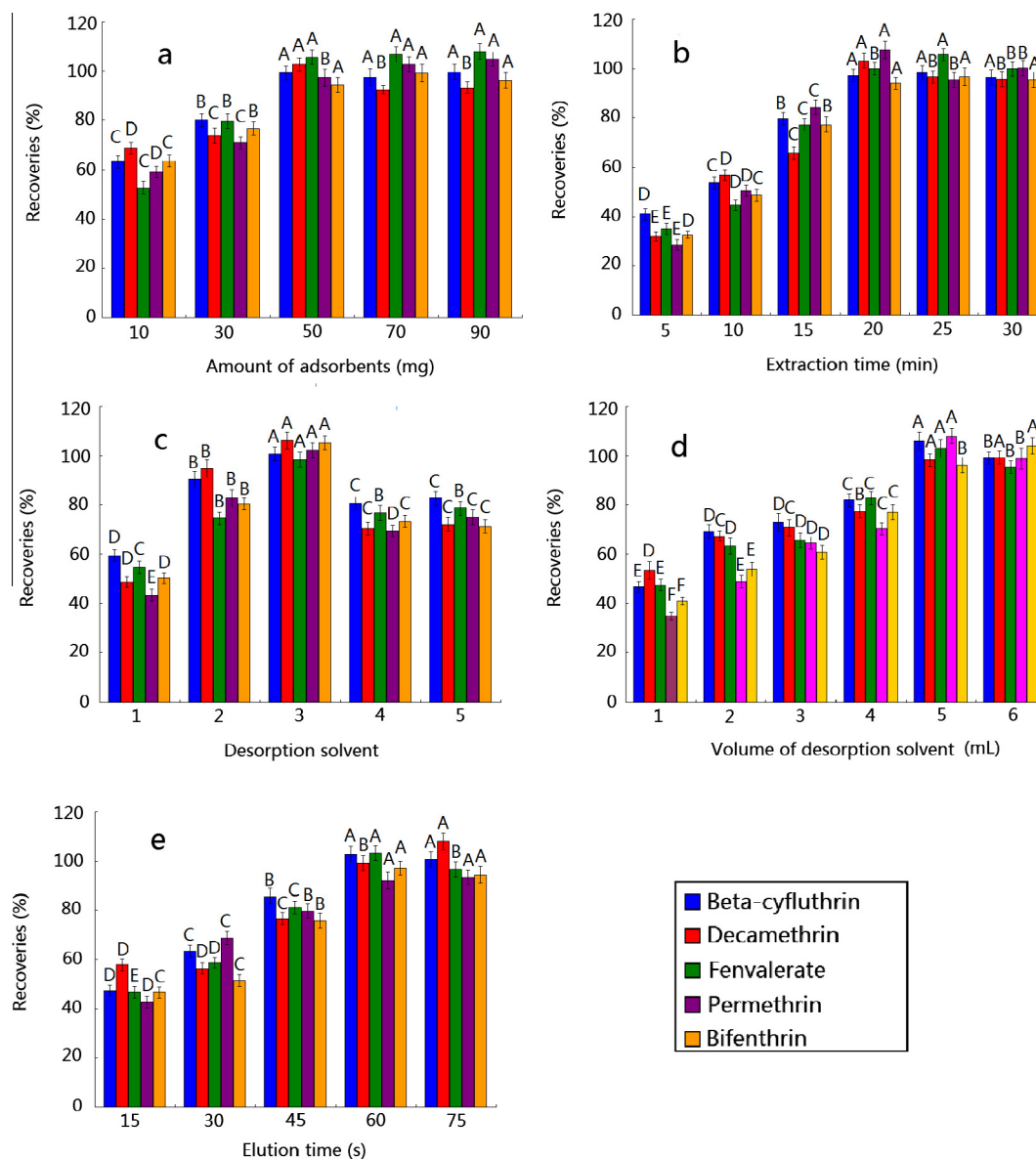


Fig. 2. Optimisation of the extraction conditions: (a) Amount of adsorbents, (b) Extraction time, (c) Type of desorption solvent (1, methanol; 2, acetonitrile; 3, acidified acetonitrile; 4, 75% acetonitrile; 5, acidified 75% acetonitrile.), (d) Volume of desorption solvent, (e) Elution time.

equilibration for the adsorption reaction. Therefore, the optimum extraction time was set at 20 min.

Type of desorption solvent is a critical impact factor which influences the recoveries of the analytes. Since methanol and acetonitrile are the two kinds of commonly used solvent for pyrethroids analysis, the type of desorption solvent was selected among several suitable candidates including methanol, 75% acetonitrile, acidified 75% acetonitrile (3% acetic acid, v/v), acetonitrile and acidified acetonitrile (3% acetic acid, v/v) for the present study. The results are plotted as histogram in Fig. 2. As can be clearly seen from the results, acidified acetonitrile was the most suitable desorption solvent for this experiment.

Volume of desorption solvent was optimised as well. In a series optimisation experiments, 1–6 mL of acidified acetonitrile was used to elute the analytes from the PSt/MNPs. According to the results obtained in Fig. 2d, 5 mL of desorption solvent was sufficient to fully elute the pyrethroids from the adsorbents. Therefore, 5 mL was selected as the optimum volume of desorption solvent.

Elution time was studied as well in order to achieve higher extraction efficiency. As can be obviously seen from Fig. 2e, 60 s was sufficient for the analytes to be fully eluted from the PSt/MNPs. Therefore, the elution time was set at 60 s for the following experiments.

3.3. Reusability of the MNPs/PSt

In order to validate recyclability of the PSt/MNPs as adsorbents for pyrethroids in vegetables, the same batch of 50 mg of PSt/MNPs were repeatedly used to conduct the extraction experiments for 25 times. After each use, the PSt/MNPs were washed for three times with 10 mL of methanol per time and another three times with 10 mL of water per time successively. As can be seen from the results plotted in Table 1, no significant change in recoveries was observed. Therefore, it is proved that the PSt/MNPs can be recycled, which suggests that the material is both economical and environmentally friendly.

3.4. Evaluation of the method performance

The chromatograms of the mixed standard solution of the pyrethroids, the extract of spiked sample as well as the extract of blank sample are shown in Fig. S2. Under optimum conditions, calibration curves of the five targeted pyrethroids were obtained

Table 3
Intra- and inter-day method precisions at three different concentration levels.

Analytes	Spiked level (ng g ⁻¹)	Intra-day (n = 6)		Inter-day (n = 6)	
		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Beta-cyfluthrin	0.5	106.5	5.2	114.3	7.6
	5.0	102.4	3.5	108.5	5.6
	10.0	103.3	2.4	97.3	5.0
Decamethrin	0.5	100.0	6.1	99.5	6.9
	5.0	98.6	4.1	104.3	5.9
	10.0	92.5	3.5	102.4	4.3
Fenvalerate	0.5	98.7	6.8	110.4	10.7
	5.0	94.3	4.2	91.6	6.4
	10.0	93.7	2.9	95.3	3.9
Permethrin	0.5	105.8	6.2	94.5	6.2
	5.0	106.6	4.5	104.4	4.2
	10.0	94.6	2.8	97.3	4.6
Bifenthrin	0.5	103.1	5.4	98.6	7.4
	5.0	106.4	5.6	116.2	6.0
	10.0	112.0	2.8	113.6	5.4

via plotting the theoretical concentration against corresponding area under curve. The results were summarised in Table 2 and the correlation coefficients were all above 0.9971 within the linear range of the analytes, which indicates satisfactory linearity. The limits of detection (LODs) and limits of quantification (LOQs), known to be the lowest concentration for the targeted analyte to be identified or quantified with sufficient confidence, were also studied. The LODs were obtained as the lowest concentration of the analyte with detectable signal response with a signal to noise ratio of over 3 whereas the LOQs were obtained as the lower limit for quantifiable signal with the signal to noise ratio to be at least 10. As can be seen from Table 2, the LODs and LOQs of the pyrethroids were in the range of 0.0200–0.0392 ng g⁻¹ and 0.072–0.128 ng g⁻¹, respectively.

The reproductivity of the method was evaluated via determining the intra-day and inter-day precision at three concentration levels. The experiments for intra-day precision determination were conducted within the same day and were consisted of six replicates at each concentration level. As for the determination of inter-day precision, six replicates of the experiment at each concentration level were conducted in six successive days. As can be concluded from the results displayed in Table 3, the recoveries of the

Table 1
Reusability of the MNPs/PSt.

Time of recycle	Recoveries ± RSD				
	Beta-cyfluthrin	Decamethrin	Fenvalerate	Permethrin	Bifenthrin
5	93.9 ± 3.3 ^B	100.2 ± 3.0 ^A	99.6 ± 4.2 ^A	91.8 ± 5.2 ^B	110.3 ± 3.0 ^A
10	104.6 ± 3.2 ^A	103.2 ± 4.2 ^A	106.8 ± 3.1 ^A	102.3 ± 4.5 ^A	103.7 ± 4.1 ^B
15	101.3 ± 3.7 ^A	97.6 ± 4.6 ^A	102.9 ± 4.1 ^A	101.1 ± 3.2 ^A	101.2 ± 3.1 ^B
20	103.6 ± 4.9 ^A	102.3 ± 4.3 ^A	92.4 ± 4.7 ^B	105.8 ± 3.3 ^A	94.6 ± 3.5 ^C
25	98.1 ± 3.6 ^A	102.5 ± 4.2 ^A	95.1 ± 4.4 ^B	93.4 ± 4.5 ^B	103.4 ± 3.6 ^B

Table 2
Analytical performances: Linearity, linear range, limit of detection and limit of quantification.

Analytes	Regression Equation	R ²	Linearity (ng g ⁻¹)	LOD (ng g ⁻¹)	LOQ (ng g ⁻¹)
Beta-cyfluthrin	y = 461274x + 2656	0.9992	0.200–20.0000	0.0324	0.101
Decamethrin	y = 726818x + 5545	0.9996	0.200–20.0000	0.0200	0.072
Fenvalerate	y = 711276x + 4156	0.9990	0.200–20.0000	0.0392	0.128
Permethrin	y = 444759x + 9029	0.9971	0.200–20.0000	0.0384	0.123
Bifenthrin	y = 1165535x + 9077	0.9993	0.200–20.0000	0.0288	0.101

*Note: LOD: Limit of detection; LOQ: Limit of quantification.

pyrethroids were in the range of 91.6–116.2%. Meanwhile, the precision of the present method was quite desirable with the relative standard deviation (RSD) for intra-day and inter-day experiment lower than 6.8% and 10.7%, respectively.

3.5. Method comparison

In order to obtain objective and comprehensive evaluation of the present detection technique, a comparison between this technique and several other classic or newly reported methods for pyrethroids residue detection in agricultural products was made. Important aspects such as complexity of extraction procedures, amount of organic solvent and adsorbent used per test, the reusability of adsorbent analytical instruments needed, LODs and recoveries were taken into account. The results were summarised in Table S1. As can be obviously seen from the table, compared with both traditional and newly reported methods, our present method is able to achieve desirable recoveries and deviations with reusable adsorbents and easily accessible instruments at relative low cost of toxic organic solvents. Moreover, the fast and convenient magnetic separation technique can save us much time and effort cost by tedious operation processes such as filtration and centrifugation. Besides, since most of other reported methods utilise the solid phase extraction as a cleanup step, the adsorbents used directly or packed in cartridges can bring in an additional part of expense and extra risk of pollution to the environment. Therefore, it can be concluded that our present method has the

advantages of low cost, high accuracy and sensitivity, low demand on instrument as well as environmentally friendliness.

3.6. Real sample analysis of organic and conventional vegetables

The validated PST/MNPs based extraction coupled with HPLC analysis was applied to detect pyrethroids residue in ten pairs of conventional vegetables and corresponding organic products, respectively. In order to achieve reliable results, each of the experiments was carried out in triplicates and spiked sample at concentration level of 5 ng g⁻¹ was tested as well. The results obtained for each conventional vegetable and corresponding organic product are listed in Table 4.

According to the regulations set by Agri-Food and Veterinary Authority of Singapore, the maximum limit for total pyrethroids residue in vegetables is 1000 ng·g⁻¹ ("<http://www.ava.gov.sg/>," 2015). As can be seen from Table 4, out of ten kinds of vegetables commonly consumed in Singapore, four kinds of conventional products were detected with pyrethroids residue, including cauliflower, Chinese chive, lettuce and cabbage. However, none of these products was detected with any violation since the highest amount of total pyrethroids residue detected was lower than 5 ng g⁻¹. Noticeably, among these, Chinese chive and cauliflower were detected with multi residue, which suggested that they might be subject to combination usage of different pyrethroids or the produce might be grown on soil with pyrethroids residue due to past crops. As for the corresponding organic products, one out of

Table 4
Real sample analysis of conventional and organic vegetables.

Analytes	Conventional Broccoli		Conventional Chinese Kale		Conventional Amaranth		Conventional Pak choi		Conventional Lettuce	
	Detected (ng g ⁻¹)	Recovery (%)	Detected (ng g ⁻¹)	Recovery (%)	Detected (ng g ⁻¹)	Recovery (%)	Detected (ng g ⁻¹)	Recovery (%)	Detected (ng g ⁻¹)	Recovery (%)
Beta-cyfluthrin	ND	103.8 ± 2.9	ND	93.2 ± 6.0	ND	108.2 ± 5.8	ND	112.7 ± 6.3	ND	107.2 ± 4.5
Decamethrin	ND	101.4 ± 3.7	ND	99.8 ± 4.3	ND	95.8 ± 4.9	ND	93.7 ± 4.5	ND	99.3 ± 5.1
Fenvalerate	ND	93.6 ± 4.5	ND	105.6 ± 6.8	ND	97.2 ± 5.4	ND	98.6 ± 5.2	ND	97.6 ± 2.9
Permethrin	ND	100.2 ± 3.8	ND	112.9 ± 5.9	ND	107.8 ± 4.6	ND	110.3 ± 3.4	0.22 ± 0.02	115.3 ± 6.1
Bifenthrin	ND	112.9 ± 5.7	ND	106.9 ± 3.9	ND	104.2 ± 3.7	ND	104.6 ± 3.5	ND	108.1 ± 4.9
Analytes	Conventional Rape		Conventional Cauliflower		Conventional Chinese Chive		Conventional Chinese Cabbage		Conventional Cabbage	
	Detected (ng g ⁻¹)	Recovery (%)	Detected (ng g ⁻¹)	Recovery (%)	Detected (ng g ⁻¹)	Recovery (%)	Detected (ng g ⁻¹)	Recovery (%)	Detected (ng g ⁻¹)	Recovery (%)
Beta-cyfluthrin	ND	98.7 ± 3.5	1.55 ± 0.14	128.6 ± 6.2	0.28 ± 0.01	109.6 ± 2.9	ND	92.7 ± 2.6	0.34 ± 0.02	106.8 ± 4.1
Decamethrin	ND	94.3 ± 5.9	ND	103.6 ± 3.6	ND	98.4 ± 3.6	ND	101.3 ± 3.1	ND	100.2 ± 2.5
Fenvalerate	ND	100.8 ± 4.7	ND	95.7 ± 4.3	4.17 ± 0.26	183.7 ± 5.5	ND	101.6 ± 4.5	ND	101.3 ± 4.3
Permethrin	ND	103.9 ± 3.8	ND	91.8 ± 5.2	ND	105.3 ± 4.7	ND	104.2 ± 5.6	ND	103.3 ± 3.6
Bifenthrin	ND	101.2 ± 4.0	0.42 ± 0.03	113.6 ± 3.7	0.23 ± 0.01	99.4 ± 4.5	ND	97.6 ± 3.7	ND	95.3 ± 4.1
Analytes	Organic Broccoli		Organic Chinese Kale		Organic Amaranth		Organic Pak choi		Organic Lettuce	
	Detected (mg kg ⁻¹)	Recovery (%)	Detected (mg kg ⁻¹)	Recovery (%)	Detected (mg kg ⁻¹)	Recovery (%)	Detected (mg kg ⁻¹)	Recovery (%)	Detected (mg kg ⁻¹)	Recovery (%)
Beta-cyfluthrin	ND	93.9 ± 2.9	ND	100.2 ± 3.7	ND	99.6 ± 6.1	ND	91.8 ± 6.3	0.32 ± 0.02	110.3 ± 6.0
Decamethrin	ND	104.6 ± 4.1	ND	103.2 ± 5.1	ND	106.8 ± 5.2	ND	102.3 ± 4.0	ND	103.7 ± 5.9
Fenvalerate	ND	101.3 ± 5.0	ND	97.6 ± 3.1	ND	102.9 ± 3.7	ND	101.1 ± 3.9	ND	101.2 ± 3.4
Permethrin	ND	103.6 ± 6.2	ND	102.3 ± 3.4	ND	92.4 ± 3.4	ND	105.8 ± 3.5	ND	94.6 ± 2.7
Bifenthrin	ND	98.1 ± 2.9	ND	102.5 ± 4.6	ND	95.1 ± 3.2	ND	93.4 ± 2.8	ND	103.4 ± 4.2
Analytes	Organic Rape		Organic Cauliflower		Organic Chinese Chive		Organic Chinese Cabbage		Organic Cabbage	
	Detected (mg kg ⁻¹)	Recovery (%)	Detected (mg kg ⁻¹)	Recovery (%)	Detected (mg kg ⁻¹)	Recovery (%)	Detected (mg kg ⁻¹)	Recovery (%)	Detected (mg kg ⁻¹)	Recovery (%)
Beta-cyfluthrin	ND	100.6 ± 5.1	ND	106.3 ± 4.6	ND	100.6 ± 4.5	ND	92.8 ± 6.1	ND	105.0 ± 3.7
Decamethrin	ND	103.3 ± 2.9	ND	91.9 ± 2.8	ND	93.8 ± 5.2	ND	93.2 ± 3.9	ND	104.8 ± 2.9
Fenvalerate	ND	106.3 ± 2.7	ND	99.6 ± 3.9	ND	98.8 ± 3.6	ND	99.6 ± 5.6	ND	100.2 ± 4.1
Permethrin	ND	104.1 ± 4.9	ND	106.6 ± 4.8	ND	106.7 ± 3.9	ND	102.5 ± 3.5	ND	97.4 ± 6.2
Bifenthrin	ND	107.5 ± 4.8	ND	101.2 ± 3.1	ND	102.9 ± 4.7	ND	94.8 ± 3.7	ND	92.7 ± 4.9

*ND: not detected. Spiked level: 5 ng g⁻¹.

ten kinds of the vegetables was detected with trace amount of beta-cyfluthrin residue as well. Based on these results, it can be seen that pyrethroids residue exist in both conventional and organic vegetables, although organic products tend to show much lower amount of residue than their conventional counterparts. Luckily, the amount of pyrethroids residue detected in both organic and conventional vegetables were notably lower than the limitations set by authorities, which means that common dietary consumption of these vegetables is safe and should not cause any harm to our health.

4. Conclusions

The present method using PSt/MNPs based extraction technique for pyrethroids residue detection in vegetable matrix was proved to be highly efficient, low cost and environmentally friendly. The recoveries for five kinds of commonly used pyrethroids were in the range of 91.6%–116.2%. The accuracy and precision of the method was desirable with the LODs and LOQs in the range of 0.0200–0.0392 ng g⁻¹ and 0.072–0.128 ng g⁻¹, respectively and the intra-day and inter-day RSDs for recoveries lower than 6.8% and 10.7%, respectively. The method was successfully applied to the detection of pyrethroids residue in ten pairs of commonly consumed organic and conventional vegetables in Singapore. Four kinds of conventional vegetables and two kinds of organic products were detected with trace amount of pyrethroids residue while no violation was observed. According to the results, common dietary consumption of both organic and conventional vegetables is safe and should not cause any harm to our health since the amount of pyrethroids residue detected in both kinds of the products were far more lower than the limitations set by Singapore authorities. By exploring the way less traveled in using the recyclable polymer-coated magnetic nano-adsorbents in food analysis, the present method helped us obtain lower detection limits and shorter analysis time in solving the problem of trace amount hazard analysis in complex vegetable matrix, thus offering us a better chance to guarantee food safety to the largest extent.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.foodchem.2016.08.115>.

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