



Comparative study of pyrethroids residue in fruit peels and fleshes using polystyrene-coated magnetic nanoparticles based clean-up techniques

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ABSTRACT

An efficient and rapid method for quantifying pyrethroids pesticide residue in fruits samples was developed in the present study. The application of lab prepared polystyrene magnetic nanoparticles based magnetic solid phase extraction technique combined with liquid-solid extraction helped clean-up the sample and preconcentrate the targeted analytes prior to HPLC quantification. The lab prepared nanoparticles were characterised with Fourier transform infrared spectroscopy, atomic force microscopy, X-ray diffraction spectroscopy, as well as vibrating sample magnetometer to study their size, morphology, crystal structure, functional groups and magnetism properties, respectively. Afterwards, optimisation of the parameters affecting extraction efficiency was carried out in order to achieve optimum conditions for extracting pyrethroids residue from fruit samples. Analytical performances were evaluated by carrying out experiments at optimum conditions. Results showed that the limit of detection and limit of quantification were below 0.1445 and 0.5116 ng g⁻¹, respectively for the six pyrethroids tested. The recovery rates were within the range of 73.6%–123.1% with intra-day and inter-day relative standard deviation being less than 16.5% and 15.4%, respectively, suggesting satisfactory reproducibility of the proposed method. Real sample analysis was performed using 6 kinds of commonly consumed fruits obtained from local supermarkets in Singapore, including apples, pears, oranges, lemons, grapes and nectarines. The peel and flesh were tested separately to study the difference of pyrethroids residue in different parts of fruits. The grape sample tested was detected with permethrin residue on its peel. There was no violation since the permethrin amount detected was way much lower than the maximum residue limit set by local government.

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1. Introduction

Fruits play an inseparable part in our daily diet as they are known to contain various nutrients, which can help us lead a

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healthy and energetic life (Pertuzatti, Sganzerla, Jacques, Barcia, & Zambiasi, 2015). They are also versatile in the recipes for many popular processed food products, including flavoured soft drinks, fruit wines, puddings, cakes, pies, salads etc. Being abundant in dietary fibres, oligosaccharides, minerals as well as multiple natural antioxidants, the consumption of fruits reduces health risks such as cancer, stroke and coronary heart diseases and meanwhile slows down our ageing process and preserves the youth (Fu et al., 2015; Wang et al., 2012). Noticeably, many fruits show a greater amount of nutrients such as the dark coloured proanthocyanidins, polyphenols and flavonoids on their peels as compared to flesh and thus are recommended by nutrition specialists to be consumed as a whole rather than peeled (Cao et al., 2016).

Synthetic pesticides, such as pyrethroids, are widely used to protect the crops in modern agriculture due to their enhanced performances compared to traditional pest control approaches (Yu, Ang, Yang, Zheng, & Zhang, 2017). However, these effective chemicals in agricultural can be detrimental to our health (Liu, Nayigiziki, Kong, Mustapha, & Lin, 2017; Yu & Yang, 2017), which is one key factor that organic foods now get popular (Li et al., 2015; Liu, Tan, Yang, & Wang, 2017; Sow et al., 2017; Zhang & Yang, 2017; Zhao, Zhang, & Yang, 2017). The chemical structures of several commonly applied pyrethroids in agriculture, including bifenthrin, cypermethrin, decamethrin, fenvalerate, fenpropathrin and permethrin are shown in Fig. 1. According to existing studies, most of the pesticide residues are found on fruit peels rather than the flesh part (Yang et al., 2016; Yang et al., 2016; Yang, Zhao, Kinchla, Clark, & He, 2017). Fernández-Cruz et al. reported that 88% of the fenitrothion residue exist on kaki fruit peels (Fernández-Cruz, Villaroya, Llanos, Alonso-Prados, & García-Baudín, 2004). Li et al. found that majority of the tomato clothianidin residues are detected on their peels (Li et al., 2012). While the peeling of fruits before consumption is a common practice to reduce pyrethroid exposure, much of the nutrients are found on fruit peels, thus decreasing its nutritional value.

After recognising the usage of pyrethroids as a potential health threat, strict regulations have been set up around the world and

maximum residue limits (MRLs) for pyrethroids residue in fruits have been drawn up by authorities such as World Health Organisation (WHO), Food and Drug Association (FDA) and the Agri-Food & Veterinary Authority of Singapore (AVA) (AVA, 2017; FDA, 2017; WHO, 2017). In Singapore, more than 90% of food products are imported as it is a country with limited natural resources and the fruits have to be tested to be within the MRLs before it can be released to the market (Isabelle et al., 2010). Although the standards may vary between different countries and regions, the MRLs for different pyrethroids in various fruits and fruit related products are usually set at part per million levels, which are trace amount, in order to safeguard our health when we consume these fruits (Radišić, Vasiljević, Dujaković, & Laušević, 2013). Unfortunately, it is hardly possible for us to make an exhaustive list for MRLs, which means that these regulations are not stringent enough and may have loopholes. Fruits and fruits related products with over amount of pyrethroids residue which might harm our health are still frequently reported (Quijano, Yusà, Font, & Pardo, 2016). And we need not only more elaborated regulation system, but also sensitive, rapid and convenient detection techniques to help us determine the actual amount of pyrethroids in fruit samples (Nguyen, Zhang, Mustapha, Li, & Lin, 2014).

Association of analytical chemists (AOAC) had come up with a series of standard analytical methods for determination of chemical hazards in food materials, which are generally acknowledged as authoritative and reliable (Zarzycki, 2017). The AOAC method for determination of pyrethroids in fruits is liquid-solid extraction combined with solid phase extraction clean-up (Zhang, Zhang, & Jiao, 2014). However, this method suffers from drawbacks such as long analysis time and high cost per test. Scientists also came up with ways to improve the method, including matrix solid-phase dispersion, molecularly imprinted polymers based solid phase extraction and ultrasonic assisted extraction techniques etc. (Gao, Piao, & Chen, 2015; Ling et al., 2016; Ma & Chen, 2014). However, each method has its respective disadvantages such as non-recyclable expensive adsorbents, tedious packing and elution procedures, low selectivity and application limitation for specific

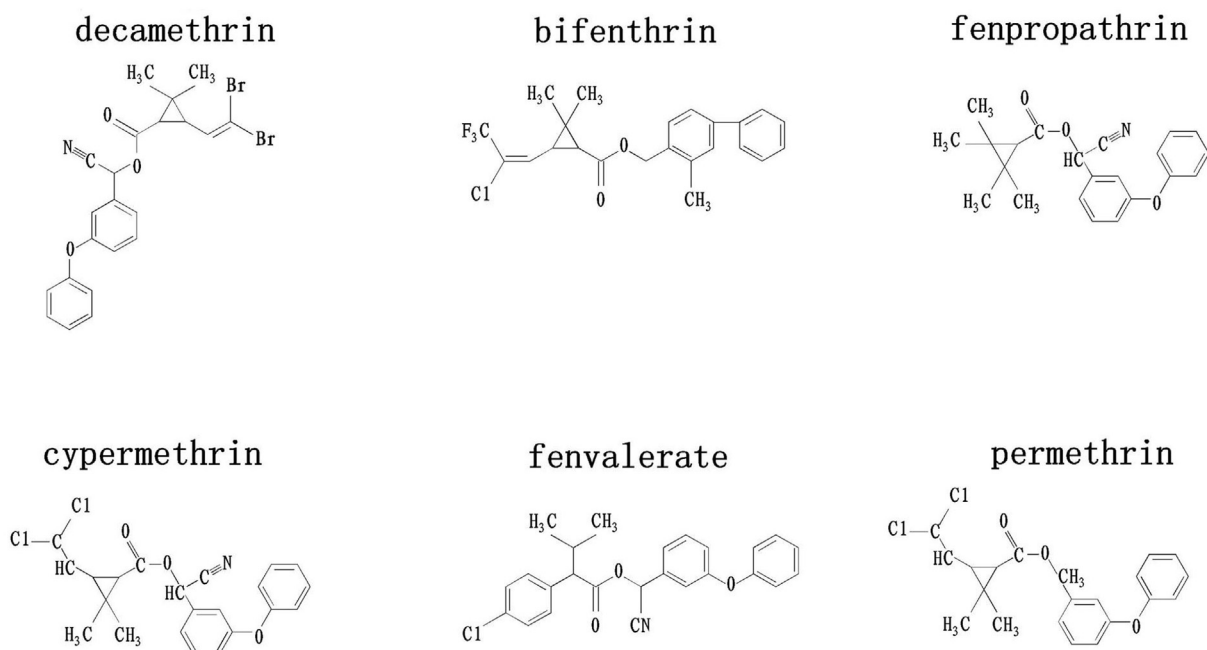


Fig. 1. Chemical structures of six kinds of commonly applied pyrethroids.

sample types etc.

Recently, various magnetic solid phase extraction techniques have been developed and showed great promise in preconcentrating trace analytes in bulk sample matrixes (Chen, Pang, He, & Nugen, 2016). Their great easiness and relatively high selectivity have promoted the popularity of such techniques. Moreover, the development and application of different nanoparticles with unique properties contributed much to the capacity and versatility of such techniques (Dong et al., 2016; Nguyen, Vardhanabhuti, Lin, & Mustapha, 2017; Wang, Su, Schulmerich, & Padua, 2013). However, according to vast scientific reports, such techniques are limited to the application on liquid samples, which greatly restricts their development.

In the present research, extraction method based on polystyrene coated magnetic nanoparticles (PSt@MNPs) was developed for the pretreatment of fruit samples. Polystyrene was selected as the coating layer of the magnetic nano adsorbents since it was proved to be effective in capturing compounds with highly conjugated chemical structure by acting as the surface functional group of the packaging material of commercial benzene HPLC columns. As was shown in Fig. 1, all of the pyrethroids of interest possess multiple benzene rings, which means that they are highly conjugated and have strong affinity for polystyrene. The usage of these recyclable magnetic nanoparticles during extraction ensures that the proposed method is fast, cost efficient, selective, environmentally-friendly and highly sensitive. Since the MRLs for pyrethroids in fruits are set at trace amounts, the proposed method is a desirable choice for the preconcentration of targeted analytes.

2. Materials and methods

2.1. Samples

Fruit samples including apple (*Malus domestica*), pear (*Pyrus*), oranges (*Citrus sinensis*), nectarines (*Prunus persica* var. *nucipersica*), lemon (*Citrus limon*) and grapes (*Vitis labrusca*) were selected as samples due to a history of having high amounts of pesticides residue or a high consumption rate (Chen et al., 2011). Additionally, the peels of these fruits are edible since orange peels, lemon peels and nectarine peels are consumed in fruit teas or used in fruit jam while grapes are usually treated as whole to produce rasins or wines. The fruits used for optimisation and real sample tests were purchased from various supermarkets around Singapore. The peel and flesh were separated using a store-bought peeler and knife before being homogenised into paste in a food processor. One specific brand of oranges was tested to be free of any pyrethroids using a modified AOAC method and used for preliminary tests as well as the optimisation and method evaluation experiments (Lehotay, Kok, Hiemstra, & Bodegraven, 2005).

2.2. Reagents

A mixed standard consisting of six pyrethroids (bifenthrin, cypermethrin, decamethrin, fenvalerate, fenpropathrin and permethrin) was used for preparing spiked samples at different concentration levels. Among the pyrethroid standards, bifenthrin, decamethrin, fenvalerate and permethrin were procured from Aoke biology research Co. Ltd (Shanghai, Jiangsu Province) in China while fenpropathrin, and cypermethrin were purchased from Supelco and Fluka from Sigma Aldrich (St. Louis, MA, USA).

Majority of the chemicals used for synthesis of the adsorbents were also acquired from Sigma Aldrich such as sodium dodecylbenzenesulfonate (SDBS, technical grade), oleic acid, concentrated hydrochloric acid, methacrylic acid, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, and potassium persulfate (KPS, analytical grade) and styrene. The other iron salt of

ACS reagent grade, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was obtained from Merck Germany and sodium hydroxide peal was from Dickson Instrument & Reagent Store in Singapore.

HPLC grade acetonitrile was obtained from Fulltime, China. Phosphate buffer was made with sodium phosphate dibasic dihydrate and sodium phosphate monobasic monohydrate, both of analytical quality from Sigma Aldrich.

2.3. Instrumental analysis

The images from atomic force microscope (AFM) were generated from MultiMode V, Veeco AFM (Plainview, NY, USA) using ScanAsyst mode. Perkin Elmer Spectrum One Fourier transform-infrared (FT-IR) spectrometer (Waltham, MA, USA) was used to obtain FT-IR spectra while the KBr pellet pressing method was employed for preparing samples for test. The X-Ray diffraction (XRD) patterns of nanoparticles were collected with a Bruker D5005 instrument (Billerica, MA, USA). A QuantumDesign vibrating sample magnetometer (VSM), MPMS, SQUID (San Diego, CA, USA) was used to determine the magnetisation of the nanoparticles (Xin et al., 2010; Yu & Yang, 2017).

The chromatograms were collected using Waters 2695 Alliance system (Milford, Massachusetts, USA) equipped with a photo diode assay (PDA) detector, an autosampler and a quaternary pump. A Luna 5 μ C18 column (150 mm length, 4.6 mm id, 100 Å pore size, Phenomenex, CA, USA) was used for sample separation. 100% deionised water and 100% acetonitrile were used as mobile phases A and B for elution, respectively. Gradient elution was employed as follows: 0–20 min, 68% B, 32% A; 20–45 min, 75% B, 25% A; 45–50 min, 80% B, 20% A.

2.4. Preparation of PSt@MNPs

An alkaline solution containing NaOH in 250 mL of deionised water (1.5 mol L^{-1}) was made up in a four-necked round bottom flask connected with a stirrer, a condenser and a dropping funnel. The set-up was kept in a heated water bath at 70 °C under N_2 atmosphere protection. Next, 2.2 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and 5.4 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were dissolved in 25 mL of acidic aqueous solution containing 0.85 mL of concentrated hydrochloric acid. The homogenous solution was added dropwise into the round bottom flask, causing the solution to turn black, and left to stir vigorously under reflux for 2 h.

The raw Fe_3O_4 synthesised via chemical precipitation was rinsed with deionised water twice to remove the impurities before being transferred to another flask containing 250 mL of deionised water. With the same experimental conditions, 5 mL of oleic acid was added and the solution was stirred for 0.5 h. The solution was then cooled to room temperature before being stirred for another 0.5 h after 1.35 g of SDDBS dissolved in 5 mL of deionised water was added.

After grafting the bilayer surfactants onto the nanoparticles, 40 mL of the bulk colloidal solution was added to 260 mL of deionised water. Thereafter, 18 mL of styrene and 1.8 mL of methacrylic acid were added. 0.3 g of KPS dissolved in 5 mL of water was added to the mixture to initiate the emulsion polymerization chain reaction. The as-prepared PSt@MNPs were washed thrice with water and methanol in turn before drying in convection oven for overnight to be used for extraction (Yu et al., 2017).

2.5. Extraction of pyrethroids residue from fruit samples

The extraction procedures of pyrethroids from fruit samples are clearly illustrated in Fig. 2. With the aid of a food processor, 10 g of fruit sample (peel or flesh) was measured out and homogenised into paste in a food processor. Acetonitrile (20 mL) was then added

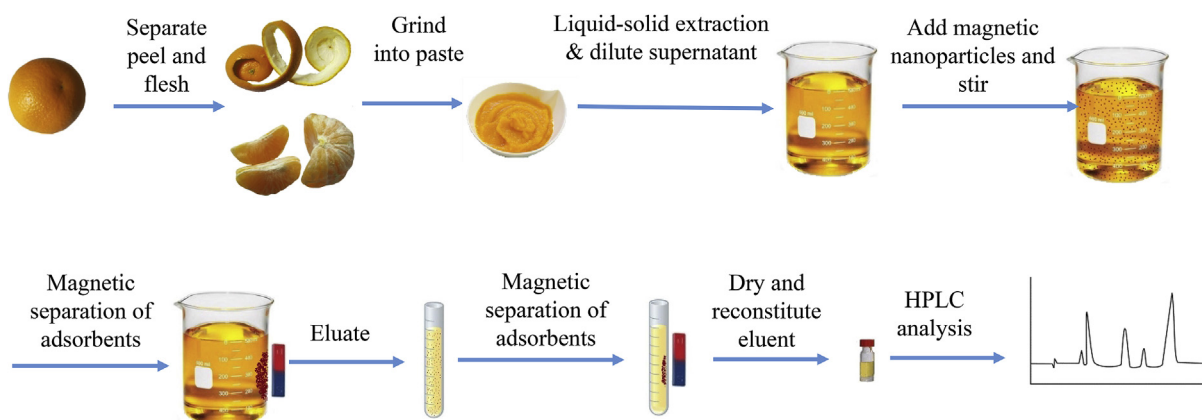


Fig. 2. Protocol for the extraction of pyrethroids from fruit peel and flesh samples followed by HPLC quantitative analysis.

to carry out liquid-solid extraction for 0.5 h via vigorous stirring. The filtrate was recovered via reduced pressure filtration and 80 mL of phosphate buffer (0.1 M, pH 7) was added to the solution, after which 50 mg of PSt@MNPs were added. The mixture was stirred at high speed for 25 min. Using a permanent magnet, the PSt@MNPs were collected and transferred to a 15 mL centrifuge tube. Acetonitrile (2 mL) was added to the tube and vortex was carried out for 30 s to allow for the desorption of pyrethroids attached on the PSt@MNPs. The eluent was dried with N_2 gas in 40 °C water bath. The residue was reconstituted with 300 μ L of acetonitrile. Finally, the solution was filtered with 0.22 μ m filter prior to HPLC analysis.

2.6. Statistical analysis

In order to evaluate reliability between sample sets, triplicate experiments were carried out for each set and Relative Standard Deviation (RSD) was shown to be below 15%. The sample data was analysed using IBM SPSS Statistics. A one-way ANOVA test (Analysis

of Variance) at $P < 0.05$ was carried out for each pyrethroid during optimisation to ensure that the triplicates were reliable.

3. Results and discussion

3.1. Characterisation of adsorbents

3.1.1. FT-IR spectroscopy

In order to understand the functional groups of the obtained nanoparticles and make sure the polystyrene coating layer was successfully grafted, FT-IR spectroscopy was carried out for PSt@MNPs. From Fig. 3a, the FT-IR spectrum of the nanoparticles showed a peak at 581 cm^{-1} that was unique to the Fe-O bond. The absorption peaks found at 3059 and 3024 cm^{-1} represented the =CH stretching vibration on benzene rings while the adsorption peak at 2850 cm^{-1} corresponded to the -CH₂- symmetrical stretching vibration. The monosubstitution of the benzene ring was proved by the peak at 700 cm^{-1} and the peak at 1452, 1492 and

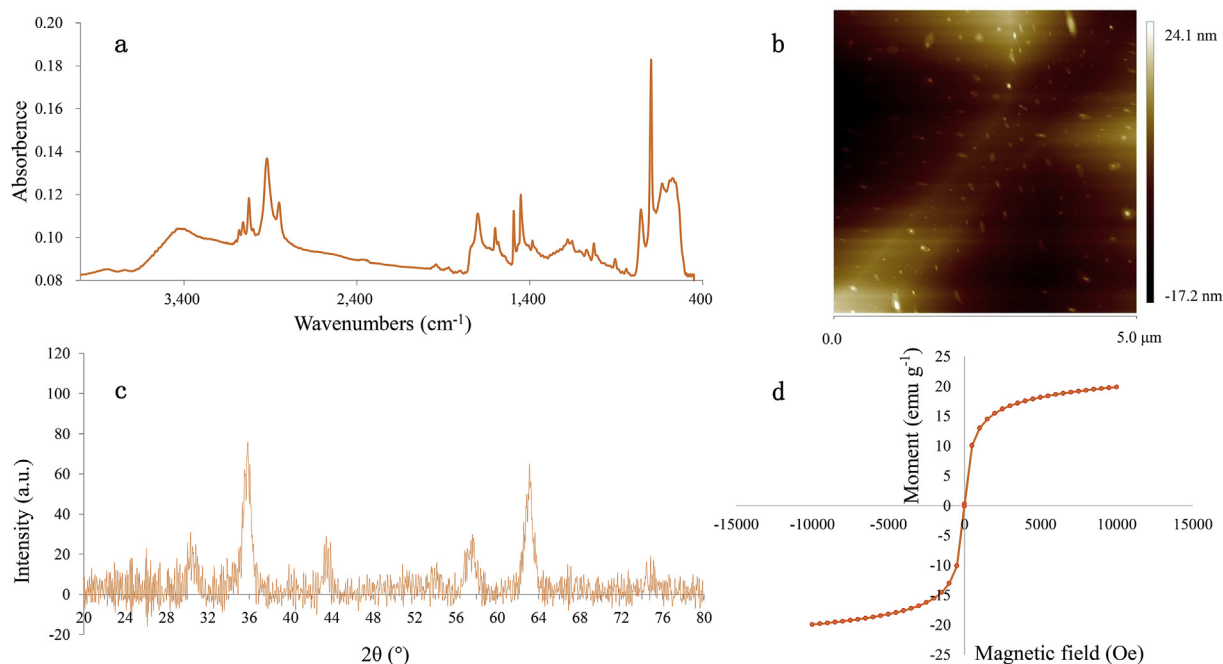


Fig. 3. Characterisation results of the nano adsorbents: (a) FT-IR spectrum, (b) Atomic force microscopy (AFM) image, (c) XRD spectrum, (d) Vibrating Sample Magnetometer (VSM) curve.

1600 cm^{-1} was caused by the bending vibration of $-\text{C}=\text{C}-$ on benzene rings. A peak at 1700 cm^{-1} corresponds to the $\text{C}=\text{O}$ bond from methacrylic acid, which proved that the surfactant still existed after the synthesis was completed. Hence, the peaks of the polystyrene coating along with the presence of the $\text{Fe}-\text{O}$ bond indicate that the synthesis of the PSt@MNPs was successful (Wu, Wu, Wu, & Chang, 2001).

3.1.2. AFM imaging

Characterisation of the size and shape of the PSt@MNPs was carried out using ScanAsyst mode of AFM. The sample was first dispersed in ethanol with the assistance of 30 min of ultrasonic. After that, the sample turbid was dropped onto freshly prepared mica sheet with clean surface and dried under nitrogen gas flow before being sent for scanning. According to the image obtained in Fig. 3b, despite the coagulated bulks caused by magnetism in between the particles, most of the PSt@MNPs were successfully dispersed showing sphere like shape. The diameter of the nanoparticles was within the range of 50–100 nm (Sow & Yang, 2015).

3.1.3. XRD

According to Fig. 3c, the XRD spectrum of the PSt@MNPs showed clear peaks at 30.02° , 35.52° , 43.22° , 53.58° , 56.98° and 63.08° , respectively, corresponding to the 220, 311, 400, 422, 511

and 440 crystal planes of typical Fe_3O_4 crystal, indicating that the lab prepared PSt@MNPs had the typical crystal structure same as Fe_3O_4 crystal, which was trans spinel (Fu & Qutubuddin, 2001).

3.1.4. VSM

From Fig. 3d, the magnetisation of PSt@MNPs was proved to be quite strong with saturated magnetism being calculated to be at 0.248 emu g^{-1} . Such magnetism well assists their application by making the accumulation and dispersion of the nanoparticles quick and neat (Wang et al., 2014).

3.2. Optimisation of extraction conditions

After the synthesis of the PSt@MNPs , they were then utilised in the extraction of pyrethroid residues in fruits. Each extraction parameter leading up to the change of extraction efficiency of the sample was optimised via single variable optimisation. The optimisation experiment sets were performed in triplicates and were shown to have recovery rates with relative standard deviation (RSD) value being less than 15%, indicating that the methodology is precise. Curve graphs showing the optimisation parameters can be found in Fig. 4.

The effect of the amount of adsorbents on extraction efficiency is obvious. As the amount of adsorbents were added in 20 g

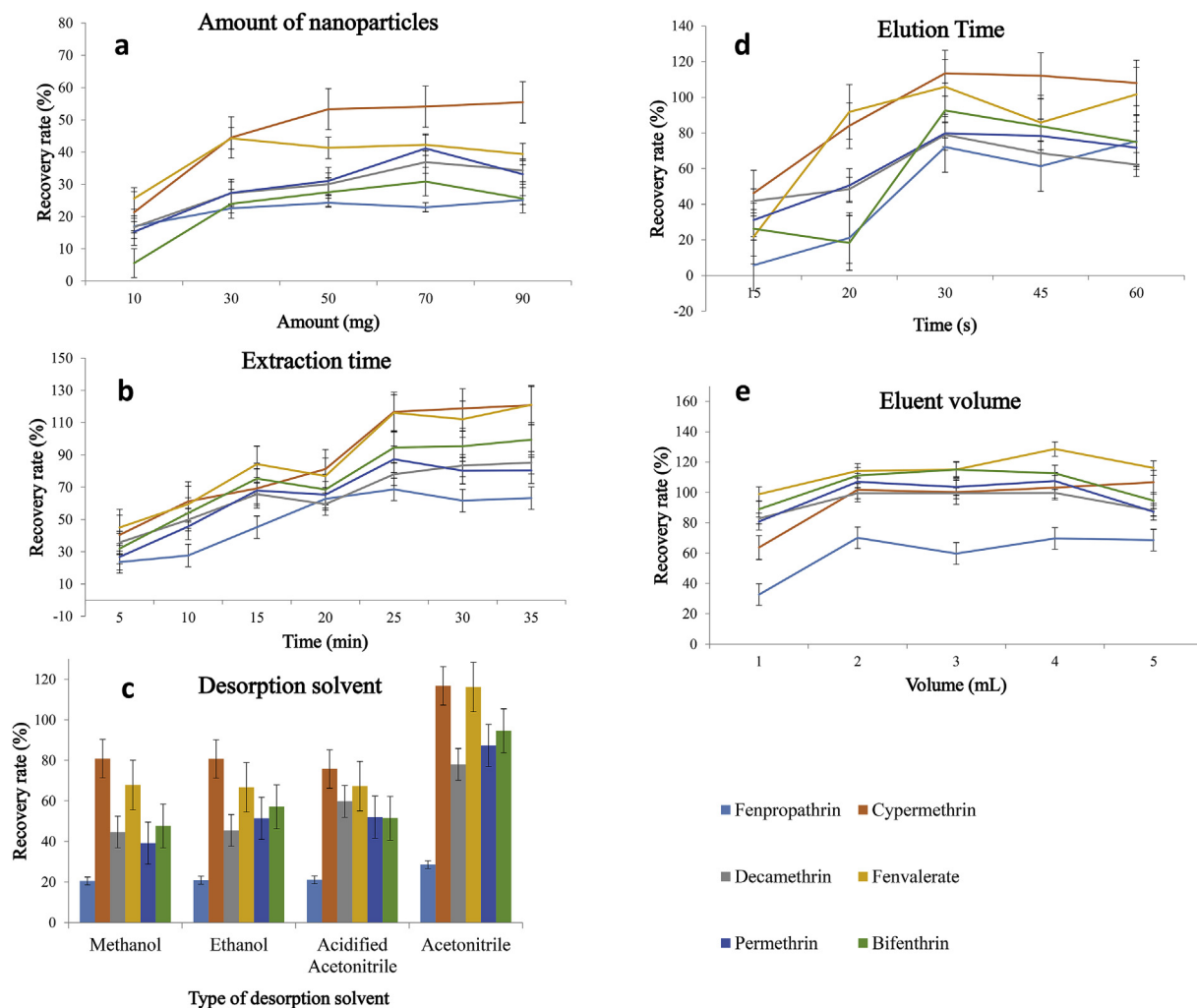


Fig. 4. Optimisation of factors affecting extraction efficiency: (a) Amount of nanoparticles, (b) Time of extraction, (c) Desorption solvent, (d) Time of elution, (e) Volume of eluent.

increments, the extraction efficiency increased. With reference from Fig. 4a, excluding bifenthrin which has an optimal amount at 70 mg, the other pyrethroids reached a plateau at 50 mg. Hence, the optimal amount of PSt@MNPs to be added was 50 mg.

Besides the amount of adsorbents, extraction time also affects the recovery rates dramatically. After the adding 50 mg of PSt@MNPs into the solution, the extraction time was then optimised using 5 min intervals. From Fig. 4b, there was an increasing trend until a plateau was reached at 25 min, which was then determined to be the optimal extraction time.

Five types of desorption solvent were tested including methanol, ethanol, hexane, 0.3% acidified acetonitrile (with acetic acid) and acetonitrile. The addition of adsorbents in hexane caused them to clump up and lose their extraction ability while the other solvents except for acetonitrile did not show satisfactory elution efficiency. Looking at Fig. 4c, acetonitrile was shown to have the best elution capacity. Therefore, acetonitrile was picked as elution solvent for the proposed method.

With acetonitrile having the strongest desorption ability, the elution time was then identified to be 30 s since it was the point observed at Fig. 4d before leveling off. Next, eluent amount ranging between 1 and 5 mL were added and vortexed to eluate the pyrethroids from the adsorbents after the extraction procedure. With reference to Fig. 4e and 2 mL of extraction solvent was sufficient to eluate the targeted analytes from the nanoparticles thoroughly.

The above optimised factors were quite consistent with our previous report on developing clean-up method for determination of pyrethroids residue in vegetable oils, slight difference on the extraction time, amount of adsorbent might be caused by the usage of phosphate buffer instead of deionized water, which assisted in balancing the pH variation of different fruit samples (Yu et al., 2017). The other factors which might affect the optimisation results include the nature of the sample itself, sample size and type of targeted analytes and etc.

Compared with other solid phase extraction methods using conventional non-magnetic adsorbents, the ease of separation of the lab-prepared magnetic adsorbents from complex fruit samples using a simple permanent magnet helped save much time and effort during the whole detection process (Sun et al., 2017). There was no need of any tedious centrifugation and filtration procedures and the waiting time in between each step decreased significantly due to the highly efficient magnetic separation. After an easy wash process, the adsorbents can be recycled and used again, which largely reduced the cost of the proposed detection method. More importantly, such recyclable property of the magnetic nano adsorbents helped prevent the release of large amount of nano materials into the environment, which is deemed as a severe and dangerous pollution source (Wang et al., 2017). Since only little amount of organic solvent was used during the extraction compared to traditional preconcentration techniques based multiple liquid-liquid extraction, the method was environmentally-friendly and economical as well.

Table 1
Correlation analysis, linearity, LODs and LOQs.

Analyte	Regression Equation	R ²	Linearity (ng g ⁻¹)	LOD (ng g ⁻¹)	LOQ (ng g ⁻¹)
Fenpropathrin	y = 97983x + 2000000	0.9976	0.2–50.0	0.0475	0.1788
Cypermethrin	y = 193650x + 26312	0.9999	0.2–50.0	0.1445	0.5116
Decamethrin	y = 484862x + 69184	0.9983	0.2–50.0	0.0920	0.3325
Fenvalerate	y = 75333x + 538603	0.9996	0.2–50.0	0.1290	0.4582
Permethrin	y = 359781x + 122453	0.9930	0.2–50.0	0.1008	0.3156
Bifenthrin	Y = 796915x + 335710	0.9949	0.2–50.0	0.0675	0.2258

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

3.3. Evaluation of the proposed method

3.3.1. Analytical performances

As shown by the results in Table 1, the linearity of the pyrethroids were desirable with majority of the pyrethroids having a R² value of at least 0.9930 which indicated a strong correlation between the peak area and the concentration. The limit of detection (LOD) and limit of quantification (LOQ) were determined as the analyte concentration which was detected with signal-to-noise ratio being 3:1 and 10:1, respectively. As shown in Table 1, the LODs of the pyrethroids detected using the proposed method were determined to be below 0.1445 ng g⁻¹ while of LOQs were no more than 0.5116 ng g⁻¹. Since the MRLs set by AVA in Singapore for pyrethroids in fruits are at µg g⁻¹ levels, such as that the MRLs for cypermethrin in nectarins and grapes are 2 and 1 µg g⁻¹, respectively while the MRL for permethrin in citrus fruits is 0.5 µg g⁻¹, the proposed method is more than qualified for the detection of the safety of fruits (AVA, 2017).

3.3.2. Reproducibility

The reproducibility of the proposed method at different concentrations within one day and over a period of a few days were tested using the optimised parameters. The results are shown in Table 2. It revealed that the recovery rates were fair and intra and inter day RSDs were below 16.5% and 15.4%, respectively. The Inter-day RSD values were generally higher than that of intra-day. One possible reason that might have caused this could be the higher systematic error.

To sum up, the proposed method showed high sensitivity as was proved by the much lower LODs and LOQs compared with the standard AOAC method as well as other traditional and recently reported methods for the detection of pesticides residue in fruits. The accuracy and reproducibility of the method was quite satisfactory as evidenced by the high linear correlation coefficient, low intra-day and inter-day RSDs. Moreover, compared with the

Table 2
Intra-day and inter-day reproducibility tests.

Analyte	Spiked concentration (ng g ⁻¹)	Intra-day (n=6)		Inter-day (n=6)	
		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Fenpropathrin	0.5	73.8	10.6	84.6	13.6
	5.0	82.6	16.5	96.5	10.5
Cypermethrin	0.5	106.3	11.0	106.5	9.3
	5.0	116.8	10.8	112.9	8.4
Decamethrin	0.5	78.6	11.3	73.6	11.8
	5.0	105.7	9.3	82.4	15.4
Fenvalerate	0.5	77.2	8.2	114.8	9.6
	5.0	96.3	11.2	84.7	8.9
Permethrin	0.5	113.4	5.3	88.4	12.8
	5.0	123.1	7.8	94.3	11.2
Bifenthrin	0.5	89.2	10.3	106.8	10.0
	5.0	84.9	12.6	117.4	9.7

Table 3
Real fruit sample analyses of six pairs of fruit fleshs and peels.

Analytes	Apple peel		Apple flesh		Pear peel		Pear flesh	
	Detected (ng g ⁻¹)	Recovery (%)	Detected (ng g ⁻¹)	Recovery (%)	Detected (ng g ⁻¹)	Recovery (%)	Detected (ng g ⁻¹)	Recovery (%)
Fenpropathrin	ND	113.2 ± 8.5	ND	88.9 ± 7.1	ND	105.65 ± 5.4	ND	108.3 ± 9.4
Cypermethrin	ND	81.7 ± 7.3	ND	84.6 ± 10.3	ND	103.28 ± 3.7	ND	96.5 ± 5.4
Decamethrin	ND	96.9 ± 6.9	ND	96.3 ± 8.1	ND	93.26 ± 4.6	ND	93.2 ± 5.1
Fenvalerate	ND	104.2 ± 11.6	ND	113.8 ± 6.1	ND	112.87 ± 8.1	ND	97.3 ± 6.9
Permethrin	ND	83.3 ± 9.3	ND	84.8 ± 10.3	ND	102.87 ± 6.3	ND	104.6 ± 10.1
Bifenthrin	ND	86.5 ± 9.4	ND	106.9 ± 5.8	ND	110.21 ± 3.9	ND	102.9 ± 8.4
Analytes	Orange peel		Orange flesh		Lemon peel		Lemon flesh	
	Detected (ng g ⁻¹)	Recovery (%)	Detected (ng g ⁻¹)	Recovery (%)	Detected (ng g ⁻¹)	Recovery (%)	Detected (ng g ⁻¹)	Recovery (%)
Fenpropathrin	ND	117.8 ± 13.2	ND	98.6 ± 8.9	ND	103.6 ± 4.9	ND	108.6 ± 6.7
Cypermethrin	ND	108.3 ± 6.1	ND	78.7 ± 11.3	ND	107.2 ± 7.8	ND	96.4 ± 7.9
Decamethrin	ND	98.7 ± 9.6	ND	77.4 ± 6.9	ND	92.1 ± 5.7	ND	91.6 ± 10.8
Fenvalerate	ND	101.5 ± 11.6	ND	113.8 ± 6.1	ND	115.2 ± 14.1	ND	93.2 ± 8.1
Permethrin	ND	108.4 ± 9.9	ND	74.8 ± 10.7	ND	110.0 ± 9.3	ND	99.6 ± 12.1
Bifenthrin	ND	112.7 ± 4.9	ND	85.3 ± 11.2	ND	112.1 ± 7.8	ND	105.5 ± 9.2
Analytes	Grape peel		Grape flesh		Nectarine peel		Nectarine flesh	
	Detected (ng g ⁻¹)	Recovery (%)	Detected (ng g ⁻¹)	Recovery (%)	Detected (ng g ⁻¹)	Recovery (%)	Detected (ng g ⁻¹)	Recovery (%)
Fenpropathrin	ND	115.4 ± 8.5	ND	109.4 ± 8.8	ND	93.6 ± 11.4	ND	105.2 ± 4.6
Cypermethrin	ND	83.2 ± 7.3	ND	73.9 ± 11.3	ND	84.2 ± 11.7	ND	96.4 ± 10.2
Decamethrin	ND	97.8 ± 6.9	ND	76.4 ± 6.9	ND	79.1 ± 12.8	ND	84.4 ± 4.9
Fenvalerate	ND	107.5 ± 10.6	ND	114.3 ± 14.1	ND	102.8 ± 3.4	ND	95.1 ± 3.1
Permethrin	23.8	84.2 ± 9.3	ND	85.8 ± 10.3	ND	82.7 ± 4.6	ND	83.5 ± 4.1
Bifenthrin	ND	88.6 ± 11.4	ND	107.7 ± 9.8	ND	106.1 ± 9.9	ND	111.5 ± 8.1

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

standard AOAC method and other traditional and recently reported methods, the proposed method is much more rapid since it doesn't require the tedious filtration and centrifugation procedures. Instead, the easy and fast magnetic separation helps us separate the adsorbents from the complex samples within seconds. The proposed method is environmentally friendly as well because the magnetic adsorbents can be recycled after wash, thus leaving no nano waste to the environment. Last but not least, the cost of the adsorbents of our proposed method was greatly reduced by using the recyclable magnetic nano adsorbents instead of the disposable SPE cartridges of the standard AOAC method and other traditional techniques (Lehotay et al., 2005; Luo, Huang, Lai, Rasco, & Fan, 2016; Yu, Liu, Liu, Wang, & Wang, 2016; Zhang et al., 2014).

3.4. Real sample analysis

The chosen fruits were subject to the same extraction procedures without spiking. From the results showed in Table 3, 23.8 ng g⁻¹ of permethrin was found on the peel of grape sample. The amount of pyrethroid found was within the MRLs set by the authorities such as WHO and AVA (both are 2 µg g⁻¹ for permethrin in grapes). Despite the limited sample size, these results were consistent with previous findings on the point that the residue has higher possibility to exist on fruit peels rather than flesh (Li et al., 2012; Fernández-Cruz et al., 2004). Considering that the experiments were conducted with fruits obtained from local supermarkets without any further cleaning process and consumers tend to clean the fruits with tap water before eating them, which will help reduce the residue amount, generally speaking, it is safe to consume fruit peels in Singapore.

4. Conclusion

In the present work, PSt@MNPs were successfully synthesised

and employed for the extraction of pyrethroids from both fruit peel and flesh. The conditions which might affect the extraction efficiency were optimised via single variable method. Under the optimum conditions, the method was evaluated and the results showed that the proposed method has satisfactory linearity, sensitivity and reproducibility. The peel and flesh of six different kinds of fruits were tested separately using the proposed method. While grapes contained one of our pyrethroids of interest, they were below the MRLs set by FDA, WHO and AVA.

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