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Low temperature cleanup combined with magnetic nanoparticle extraction to determine pyrethroids residue in vegetables oils

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ABSTRACT

To quantify trace pesticide residue in vegetable oil rapidly, low temperature cleanup combined with magnetic nanoparticle based solid phase extraction was developed to determine eight pyrethroids in vegetable oils, including tetramethrin, fenpropathrin, cypermethrin, decamethrin, fenvalerate, acrinathrin, permethrin and bifenthrin. Polystyrene coated magnetic nanoparticles were synthesised by a modified chemical coprecipitation combined with emulsion polymerisation method. The nanoparticles were afterwards characterised by Fourier transform-infrared spectroscopy, X-ray diffraction, transmission electron microscopy as well as vibrating sample magnetometer, and successfully employed as adsorbents for the magnetic solid phase extraction of pyrethroids which were cleaned up using low temperature approach in advance. Critical impact factors on the efficiency of the extraction method such as the mass of adsorbents used, volume and type of eluent solvent, extraction time as well as elution time were optimised subsequently. Regression analysis of the calibration curves of the eight pyrethroids yielded satisfactory correlation coefficients within the range of 0.980–0.998. Limit of detection and limit of quantification were calculated to be between 0.0290-0.0658 and 0.0890–0.1994 ng g^{-1}, respectively. Intra-day and inter-day reproducibility at different concentration levels also produced satisfactory recovery rates of 83.18–112.79% with relative standard deviations not exceeding 10.84% and 12.01%, respectively, suggesting desirable stability of the proposed method.

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1. Introduction

Pyrethroids are man-made pesticides, with structures derived from naturally occurred pyrethrins found within *Chrysanthemum*

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cineraraefolum flowers. Pyrethroids are generally carboxylic esters and can be classified into two groups, namely Type I and Type II pyrethroids, differentiated by the absence (Type I) or presence (Type II) of a cyano group on the alcohol moiety (Blankson, Osei-Fosu, Adeendze, & Ashie, 2016). The addition of the cyano substituent greatly improves the capability of pyrethroid as an insect killer, and results in numerous uses of pyrethroids (Esteve-Turrillas, Pastor, & de la Guardia, 2005). Pyrethroids can be found in a multitude of pest control formulations commonly used in households and gardens (Yang, Dey, Buchanan, & Biswas, 2014). In addition, the much better photostability and environmental persistence of pyrethroids over its natural counterparts contribute to their huge popularity for its use in agricultural fields (Kodba & Vončina, 2007).

However, studies have revealed a link between consumption of agricultural produce such as vegetables and fruits and exposure to pyrethroid residues (Chowdhury et al., 2013; Pirsaheb, Fattahi, & Shamsipur, 2013; Yu et al., 2012b), alarming chronic exposure of pyrethroids may have some potential adverse effects on human health. Some biologists even raised concerns that exposure to pyrethroids could have undesirable effects on male reproductive system, resulting in poor quality sperms (Hayward, Wong, & Park, 2015). Other studies also discussed the harmful effects of pyrethroids on the neurological systems of humans (Yu et al., 2012b). As such, many countries have set the maximum residue limits of pyrethroid residues in various foods in order to protect the health of mass population (Yu & Yang, 2017).

Vegetable oils contain pyrethroids due to the transfer from respective oil seeds during extraction process (Lentza-Rizos, Avramides, & Visi, 2001). And since vegetable oil is an essential ingredient in the recipe of many processed food products, it is a major source of exposure to these dangerous compounds. Only trace levels of pyrethroids are deemed acceptable in vegetable oils. Considering that a mixture of pyrethroids could be present in a single oil type and the potential health hazards, developing a sensitive and efficient method of analysing trace amounts of pyrethroids multi residues in vegetable oils is essential and highly important (Wang et al., 2014a).

Compared to the pesticide residues in fruits and vegetables which can be analysed by newly developed nanotechnology (Ling et al., 2016; Yang et al., 2016; Yang, Lv, Yan, Wu, & Li, 2015; Zhang, Yu, Li, Mustapha, & Lin, 2015), in any analysis process of an oil sample, it is crucial that lipids are well separated from the analytes of interest since a slight amount of lipids can lead to severe interference of the analysis results (Oujji et al., 2013; Wei et al., 2012). However, fatty matrices are notorious for being difficult to clean up and remove (Oujji et al., 2014). Conventional methods include liquid-liquid extraction which usually involves multiple liquid-liquid partitioning procedures. Other methods include saponification and Soxhlet extraction (Taghvaee, Piravivanak, Rezaei, & Faraji, 2016). These methods, however, either require large amounts of solvents, rendering them environmentally unfriendly or are essentially too laborious (Farajzadeh, Khoshmaram, & Nabil, 2014). Low-temperature cleanup method, on the other hand, uses very limited amount of organic solvents and minimises the need for lengthy procedures (Chen et al., 2009). To carry out the procedure, a small amount of organic solvent is typically used to extract analytes of interest from the oil sample before the mixture is frozen at between −18 and −25 °C. The difference in melting points of the fat and the organic solvent allows the fat to be frozen out whilst the organic solvent remains in the liquid supernatant. The organic layer can then be simply decanted off for subsequent steps. A previous report introduced this method to determine multiresidues in rapeseed oil (Jiang, Li, Jiang, Li, & Pan, 2012). Later, another group applied this method to determine polycyclic

aromatic hydrocarbons in edible oils successfully (Payanan, Leepipatpiboon, & Varanusupakul, 2013).

For the extraction step, traditional methods such as solid phase extraction and solid phase microextraction have their shortcomings (Wilkowska & Biziuk, 2011; Yang et al., 2015). The former is too time-consuming, tedious and requires vacuum while the latter utilises an expensive fibre that is fragile (Cao et al., 2014). Therefore, over the years, solid phase extraction (SPE) technology was much developed in order to overcome the shortcomings.

Most developments in SPE technology are directly related to the sorbent material. Efforts have been made to make the sorbent material magnetic, which led to magnetic solid phase extraction (MSPE) (Wan Ibrahim, Nodeh, Aboul-Enein, & Sanagi, 2015; Zhao et al., 2011). The magnetic properties ease the removal of the extraction medium from the sample solution by using a strong magnet (Bagheri et al., 2016; Jiang et al., 2012). Further developments incorporated nanoparticles in MSPE (Yu & Yang, 2017). Nanoparticles were shown effective due to the high surface area to volume ratio which allows for rapid adsorption of analytes (Yu et al., 2012a). Furthermore, magnetic nanoparticles can be functionalised and modified with different types of coating with affinity to specific analytes of interest (Wang et al., 2014b). For example, ferrite nanoparticles were used to extract Sudan dyes from food and water samples (Yu et al., 2012a). And polyaniline-coated magnetic particles were able to determine pyrethroids residue concentrations in tea drinks (Wang et al., 2014a). These methods could also be applied for pesticide residue in organic foods due to the trace amount of residue (Li et al., 2015; Liu, Tan, Yang, & Wang, 2017; Zhang & Yang, 2017).

In the present study, a novel approach utilising a low temperature clean-up and subsequent MSPE extraction with polystyrene-coated magnetic nanoparticles (PSt/MNPs) was developed to determine eight different pyrethroids commonly used in agricultural sector in vegetable oils, including tetramethrin, fenpropathrin, cypermethrin, decamethrin, fenvalerate, permethrin, acrinathrin and bifenthrin. The coupling of these two methods successfully removed lipid matrices and efficiently preconcentrated the targeted analytes, indicating affinity between polystyrene coatings and the analytes. The developed method was potentially excellent, efficient, economic and requiring less solvent for detecting pyrethroids residue in oil. It could aid in ensuring that vegetable oils exceeding acceptable threshold of pyrethroids residue can be quickly screened and not consumed by the public.

2. Materials and methods

2.1. Oil samples

Five different oils were purchased from local supermarkets in Singapore. These consisted of soybean oil, canola oil, sunflower oil, corn oil and virgin olive oil. The canola oil was determined to be free of pyrethroid residues using a modified standard recommended by Association of Official Analytical Chemists (AOAC) and was therefore used for the optimisation and method validation experiments (Pang, Cao, Fan, Zhang, & Li, 1998).

2.2. Chemicals and standards

Pyrethroid standards of bifenthrin (97.2%), fenvalerate (98.6%), permethrin (99.9%) and decamethrin (98.0%) were acquired from Aoke Biology Research Co. Ltd, China. Acrinathrin (99.7%), cypermethrin (94.3%), tetramethrin (98.3%) were acquired from Fluka, Sigma Aldrich Co., USA. Fenpropathrin (99.4%) was acquired from Chem Service Inc., USA. HPLC-grade acetonitrile, methanol and acetic acid were sourced from Macron Fine Chemicals, USA.

Remaining chemicals listed were of analytical grade if unspecified. Hydrated iron (II) chloride ($FeCl_2·4H_2O$), sodium dodecylbenzenesulfonate (SDBS), oleic acid, methacrylic acid, styrene, potassium persulfate (KPS) and potassium bromide (KBr) were obtained from Sigma Aldrich Co., USA. Sodium hydroxide was obtained from Dickson Instrument & Reagent Store, Singapore. Hydrated iron (III) chloride ($FeCl_3·6H_2O$) was obtained from Merck, Germany. Deionised water was filtered using a Mill-Q purification system.

2.3. Preparation and characterisation of PSt/MNPs

2.3.1. Synthesis of PSt/MNPs

PSt/MNPs were synthesised using a standard coprecipitation and a modified emulsion polymerisation method. As is shown in Fig. 1a adapted from our previous publication, for the coprecipitation step, 2 g of $FeCl_2·4H_2O$, 5.4 g of $FeCl_3·6H_2O$ and 850 μL of HCl were dissolved in 25 mL of deionised water. The mixture of iron salts was added dropwise to 250 mL of NaOH (1.5 M) and stirred vigorously under nitrogen gas protection for 2 h at 80 °C. Fe_3O_4 formed from this reaction was separated out from the mixture and washed thrice with deionised water before being dispersed in 250 mL of deionised water. Oleic acid (5 mL) was added and stirred vigorously under nitrogen gas for 1 h at 80 °C. Subsequently, 1.35 g of SDBS was added and the mixture was again continuously stirred under nitrogen at room temperature. The obtained solution was a colloidal solution of Fe_3O_4 with a bilayer surfactant. For the emulsion polymerisation step, 40 mL of the colloidal solution was dissolved in 260 mL of deionised water, and 18 mL of styrene, 1.8 mL of methacrylic acid and 0.3 g of potassium persulfate were added to the solution to form the polystyrene coating. This mixture was stirred vigorously under nitrogen gas for 6 h at 80 °C. The formed PSt/MNPs were then separated using a strong permanent magnet and washed thrice with water, thrice with methanol before being dried in an oven (Yu & Yang, 2017).

2.3.2. Characterisation of PSt/MNPs

The chemical composition, morphology and size as well as the magnetism of the synthesised PSt/MNPs were analysed by X-Ray Diffraction (XRD), Fourier Transform Infrared spectroscopy (FT-IR), Transmission Electron Microscopy (TEM) and Vibrating Sample Magnetometer (VSM). For XRD analysis, a Bruker-AXS D5005 instrument was used. For FT-IR, samples were mixed with KBr and pressed into a pellet before analysis on a Perkin Elmer Spectrum One FT-IR spectrometer. For TEM, a JEOL 3010 microscope with acceleration voltage fixed at 200 kV was applied. The magnetism study was conducted on an instrument from MPMS, SQUID technology.

2.4. Determination of pyrethroid residues in oil samples

As illustrated in Fig. 1b, 5 g of vegetable oil was vortexed for 10 min with 20 mL of acetonitrile in a centrifuge tube. This mixture was then frozen in a −20 °C freezer for at least 24 h. The supernatant (acetonitrile layer) was decanted, diluted with 80 mL of deionised water, transferred into a conical flask and stirred with 70 mg PSt/MNPs for 30 min. A strong permanent magnet was used to transfer the PSt/MNPs into a centrifuge tube. 4 mL of acidified acetonitrile (acetic acid/acetonitrile, 3:97, v/v) was added to the PSt/MNPs and vortexed for 70 s for desorption to take place. The eluent solvent was then decanted into a clean centrifuge tube with a strong permanent magnet holding the PSt/MNPs in place. The acidified acetonitrile with the extracted analytes was then blown dry using a nitrogen blower. The sample was reconstituted with 300 μL of acetonitrile and sent for HPLC analysis.

For the optimisation experiment, extracted samples were analysed with HPLC Waters 2965 Alliance system equipped with a photodiode array detector and a detection wavelength at 220 nm was used. A gradient flow programme was optimised to separate the 8 pyrethroid residues: 0–32 min: 68% B, 32–40 min: 75% B and 40–50 min: 85% B (A: deionised water, B: acetonitrile). Sample injection volume was set at 10 μL for each run with a Luna 5u C18 column (Phenomenex, USA, 150 mm length, 4.6 mm internal diameter, 100 Å pore size) kept at 25 °C.

2.5. Statistical analysis

All experiments were carried out in triplicates. For the optimisation tests, significant differences were determined using one-way analysis of variance (ANOVA) at $P < 0.05$ followed by a post-hoc Duncan's multiple range test with a SPSS software (Version 22). Results were presented in histograms and alphabets represented the means belonging to the same group. For linearity tests, regression lines and residual values were determined using regression analysis in SPSS software (Version 22).

3. Results and discussion

3.1. Characterisation of PSt/MNPs

3.1.1. FT-IR

In the FT-IR spectrum obtained for the uncoated Fe_3O_4 nanoparticles (Fig. S1a), there was a strong absorption band at approximately 580 cm^{-1}, which can be attributed to a stretching vibration mode of Fe–O within the Fe_3O_4 lattice, also indicating the successful synthesis of the ferrite nanoparticles. Interestingly, the FT-IR spectrum for PSt/MNPs showed a number of additional peaks aside from the Fe–O absorption band around 3000–3100, 1450–1600 and 700 cm^{-1}. These peaks may represent aromatic C–H stretches, aromatic C–C stretches as well as a C–H group bending respectively, while the peaks of 2800–3000 cm^{-1} arose from an alkyl C–H stretch (Fu et al., 2015a; Fu et al., 2015b; Zhang, Chen, Zhang, Lai, & Yang, 2017). The presence of these peaks indicated that polystyrene was successfully coated onto Fe_3O_4.

3.1.2. TEM

From the TEM images shown in Fig. S1b, the average diameters of the uncoated Fe_3O_4 and PSt/MNPs were 11.7 and 18.6 nm, respectively. Averages were calculated based on 10 particles in each TEM image. The small size of the particles indicated that nanoparticles with high surface area to volume ratios were successfully developed. The high surface area to volume ratio is essential in ensuring highly efficient adsorption of analytes during extraction. A slight increase in the size of PSt/MNPs as compared to uncoated Fe_3O_4 nanoparticles suggested that a thin layer of polystyrene was formed around the ferrite nanoparticles.

3.1.3. XRD

From Fig. S1c, XRD spectra of both the uncoated Fe_3O_4 nanoparticles and the PSt/MNPs show six characteristic peaks: 30.26°, 35,60°, 43.30°, 53.96°, 57.41° and 63.00°, corresponding to the 220, 311, 400, 422, 511 and 440 crystal planes of a Fe_3O_4 crystal, respectively. Therefore, it can be inferred that ferrite nanoparticles were successfully synthesised and retained their integrity even after the emulsion polymerisation step.

3.1.4. VSM

The magnetism curves of both uncoated Fe_3O_4 nanoparticles and PSt/MNPs in Fig. S1d show a low level or almost non-existent hysteresis, implying that both compounds were superparamagnetic. The maximal saturation magnetism of the uncoated
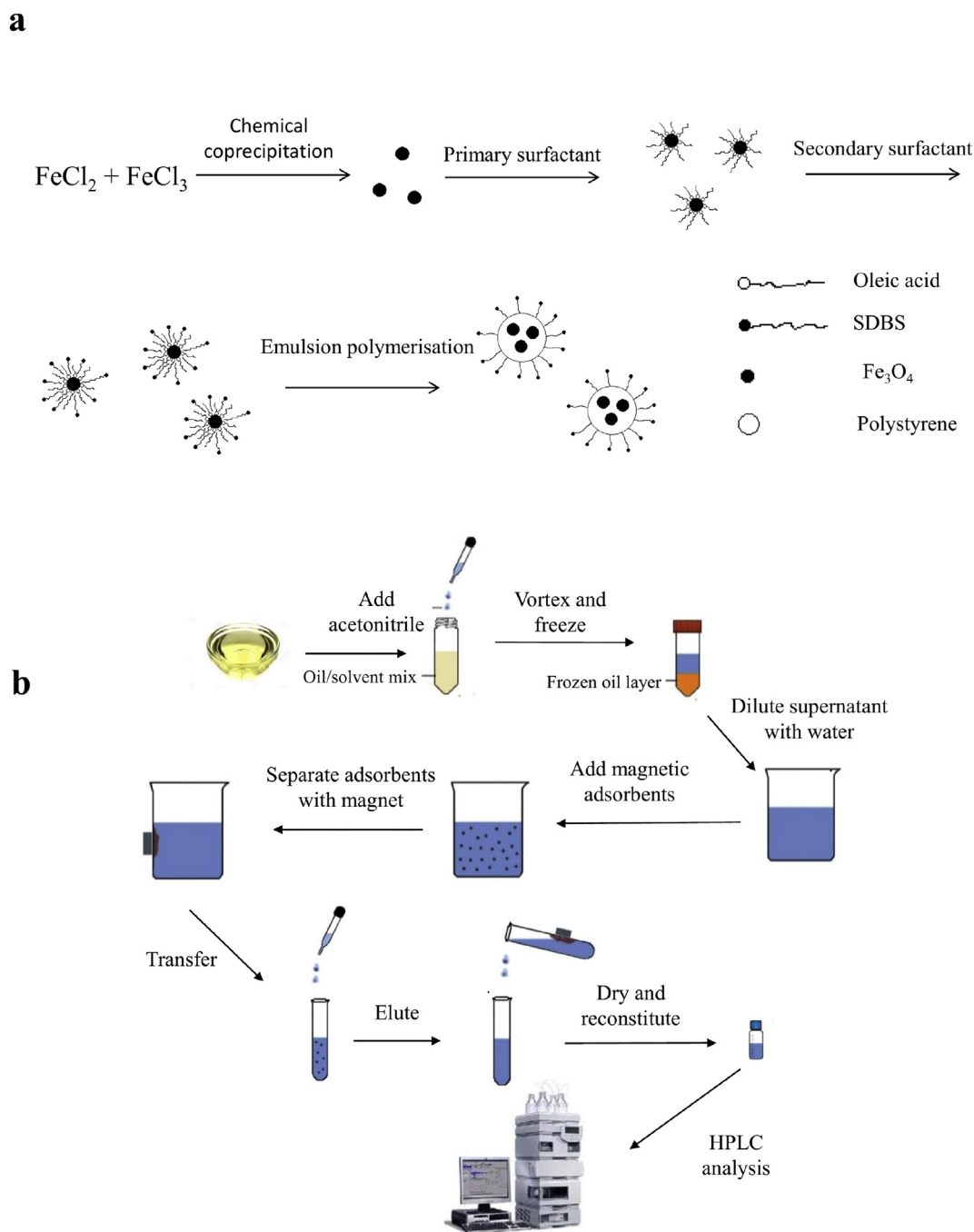
a

b

Fig. 1. (a) Preparation of the magnetic nano adsorbents and (b) Illustrative scheme of the low temperature cleanup combined with magnetic solid phase extraction procedures (Fig. 1a is adapted from Yu et al., 2012a).

Fe$_3$O$_4$ nanoparticles was 48.9137 emu g^{-1} whilst that of the PSt/MNPs was significantly lower with a level of 21.2510 emu g^{-1}. The discrepancy in magnetism could be caused by the polystyrene coating, which formed a barrier around the ferrite nanoparticle, hence reducing the magnetism level. These VSM results also provided evidence that coated PSt/MNPs was successfully synthesised.

3.2. Optimisation of extraction procedures

To maximise the extraction efficiency of the magnetic solid-phase extraction, various factors that typically affect the recovery rates were optimised. These included the mass of the magnetic solid phase nanoparticles, the extraction time, the type of eluent solvent, the amount of eluent solvent used as well as the elution time. Optimisation experiments were performed successively via single variable optimisation. To do this, when one parameter was varied, the other parameters were kept constant. Triplicates were performed for all the tested values and averages obtained were used to plot the graphs. The optimised value obtained was then used in subsequent extractions.

3.2.1. Amount of adsorbents
From Fig. 2a, it can be seen that the peak areas of the pyrethroids recovered increased until 70 mg of the adsorbents were used. The
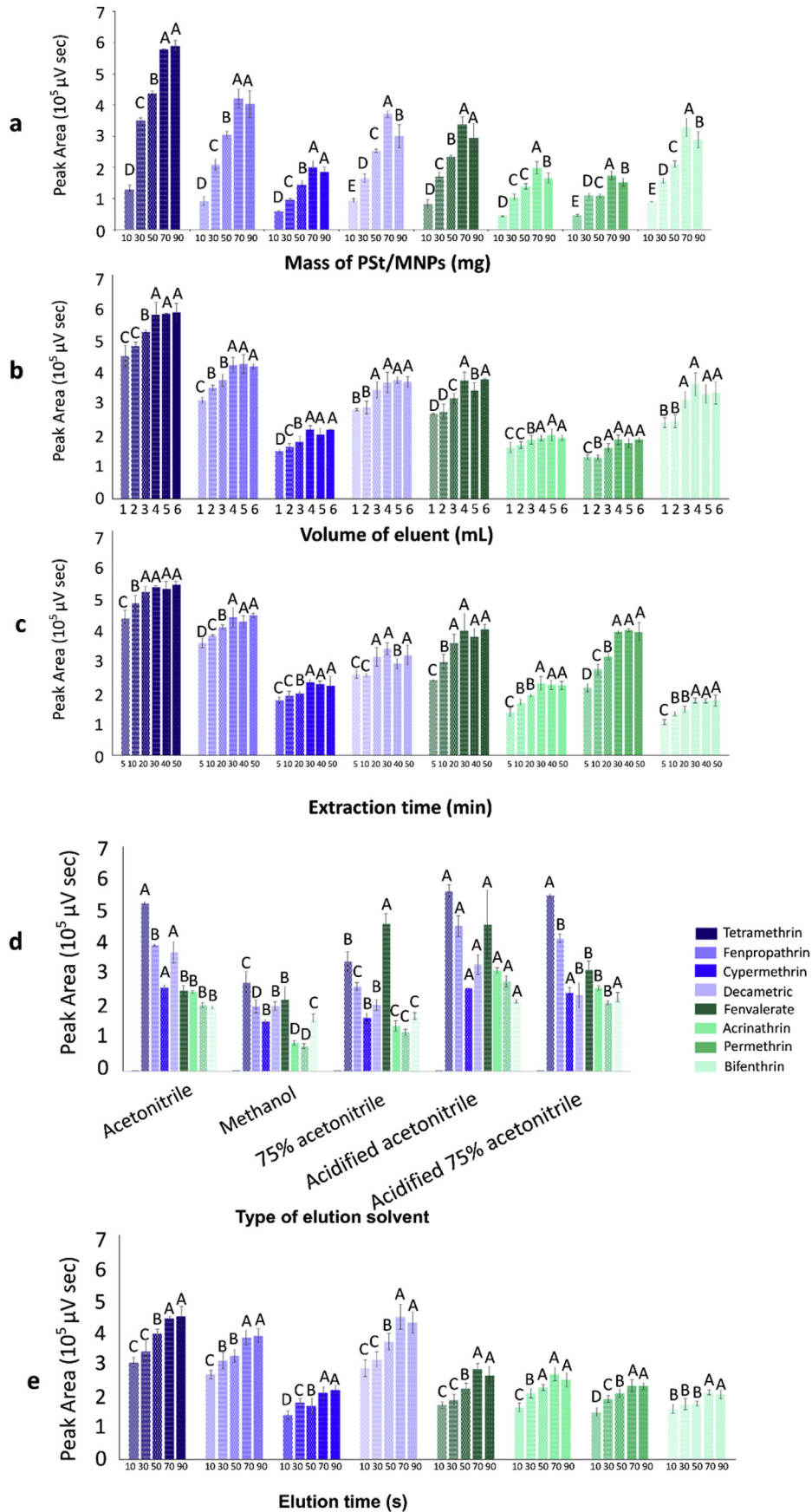
Fig. 2. Optimisation of the extraction conditions: (a) Mass of MNPs, (b) Volume of eluent, (c) Extraction time, (d) Type of elution solvent, (e) Elution time.
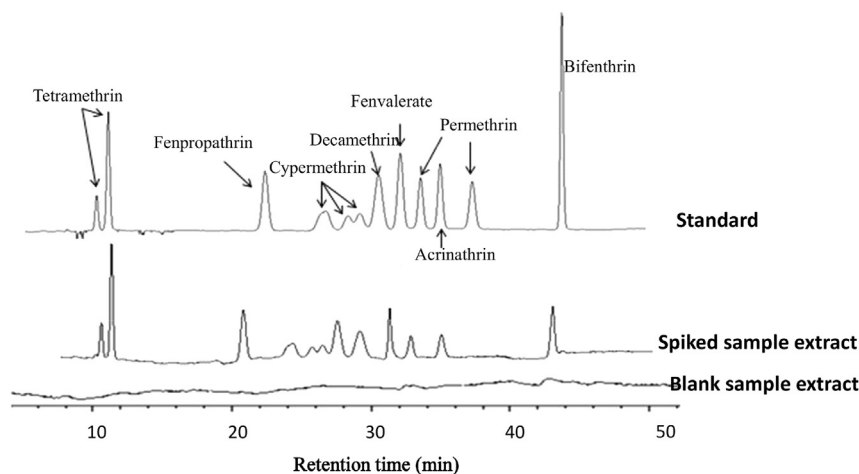
Fig. 3. HPLC chromatograms of the standard solution of pyrethroids, the extract of the spiked sample and the extract of blank sample.

increase was due to the polystyrene coating being saturated with adsorbed analytes. However, any increase further than 70 mg failed to contribute to additional recoveries of pyrethroids as there was a plateau in the curve. Therefore, 70 mg was selected as the optimal amount of PSt/MNPs for subsequent extractions.

3.2.2. Volume of the eluent

The volume of eluent solvent used was also optimised. Actually, the eluent volume affected the peak areas of pyrethroids recovered marginally (Fig. 2b). And there was no significant differences from 4 mL acidified acetonitrile upwards, suggesting that desorption volume of 4 mL of acidified acetonitrile was sufficient to elute the analytes of interests from the PSt/MNPs. Therefore, 4 mL was determined to be the optimal volume of eluent solvent to be used.

3.2.3. Extraction time

From the bar charts plotted in Fig. 2c, it can be seen that there was a considerable impact of extraction time on the peak areas of the pyrethroids recovered. Although peak areas of tetramethrin, decamethrin and fenvalerate recovered plateaued after 20 min, the remaining 5 pyrethroids took at least 30 min to attain maximal peak areas. Therefore, 30 min was selected as the optimal extraction time required for the complete adsorption of analytes.

3.2.4. Type of the eluent

One of the most vital factors that affect the extraction efficiency is the type of elution solvent used to elute analytes of interest. In the current study, five different types of elution solvents were tested, including acetonitrile, methanol, 75% acetonitrile, acidified acetonitrile (3% acetic acid, v/v) and acidified 75% acetonitrile (3%

acetic acid, v/v). Acetonitrile and methanol were chosen since they were the more commonly used eluting solvents in analytical chemistry. Fig. 2d shows that acidified acetonitrile was the most powerful desorption solvent within the 5 tested for all the eight pyrethroids. Therefore, acidified acetonitrile was selected as the most appropriate eluent solvent.

3.2.5. Elution time

Time required for the desorption of analytes from the PSt/MNPs was also determined by a series of experiments. It can be seen that 70 s was ample for the pyrethroids to be eluted from the PSt/MNPs (Fig. 2e). Therefore, 70 s was set as the optimal amount of time required for vortexing the PSt/MNPs with eluting solvent.

3.3. Analytical performances

3.3.1. Linearity and limit of detection

To conduct linearity tests, blank oil samples were spiked with 7 different concentrations of mixed pyrethroid standard solution. Spiking concentrations were selected within the range of 0.2–5.0 ng g^{-1}. Typical chromatograms obtained for blank oil samples, spiked oil samples and mixed pyrethroid standards are shown in Fig. 3. Under the optimal conditions determined from previous section, the peak area against concentration was plotted to study the linearity of the calibration curves. Results of the regression analysis are summarised in Table 1. The minimal correlation coefficient of all the 8 pyrethroids was 0.980, which indicates satisfactory linearity of the proposed method. Analytical limits, the lowest concentrations of an analyte that allow it to be accurately detected or quantified, were also determined. The limit of detection

Table 1
Analytical performances for pyrethroids.

Analyte	Regression equation	R^2	Linearity (ng g^{-1})	LOD (ng g^{-1})	LOQ (ng g^{-1})
Tetramethrin	y = 184108x−48196	0.980	0.2−5.0	0.0294	0.0891
Fenpropathrin	y = 155215x−31415	0.991	0.2−5.0	0.0331	0.1003
Cypermethrin	y = 83827x−13136	0.993	0.2−5.0	0.0290	0.0890
Decamethrin	y = 126041x−16138	0.991	0.2−5.0	0.0475	0.1438
Fenvalerate	y = 131269x−22817	0.994	0.2−5.0	0.0403	0.1221
Acrinathrin	y = 71720x + 1239	0.998	0.2−5.0	0.0303	0.0918
Permethrin	y = 75073x−8711	0.987	0.2−5.0	0.0658	0.1994
Bifenthrin	y = 123357x−21039	0.991	0.2−5.0	0.0400	0.1211

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

Table 2
Inter-day and intra-day reproducibility of pyrethroids.

Analyte	Spiked concentration (ng g^{-1})	Intra-day (n = 6)		Inter-day (n = 6)	
		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Tetramethrin	0.5	98.36	3.25	98.92	3.31
	5	104.01	7.57	100.43	6.45
Fenpropathrin	0.5	98.17	6.33	95.55	9.18
	5	103.15	3.25	103.65	2.87
Cypermethrin	0.5	102.39	10.56	103.53	6.77
	5	100.75	3.03	104.39	3.85
Decamethrin	0.5	100.15	4.78	96.62	10.36
	5	101.45	4.91	102.51	5.25
Fenvalerate	0.5	89.11	10.84	83.18	9.03
	5	102.21	1.75	106.50	2.78
Acrinathrin	0.5	108.24	7.61	110.56	10.82
	5	99.64	2.03	101.63	5.27
Permethrin	0.5	97.83	8.19	97.47	10.04
	5	100.72	5.64	100.74	6.38
Bifenthrin	0.5	104.49	8.70	112.79	12.01
	5	102.57	4.76	104.44	7.29

Table 3
Comparison of methods for pyrethroid residue determination in vegetable oils.

Samples	Major sample pretreatment procedure	Solvent amount (mL)	Adsorbent amount (mg)	Adsorbent reusability	Analytical instrument	LOQ (ng g^{-1})	Recoveries (%)	RSD (%)	Reference
Virgin olive oil	a. Liquid-liquid extraction b. Low temperature cleanup c. Solid phase extraction	12	1000	No	Gas chromatography (GC) and electron capture detection	50 −1000	71−91	17	Lentza-Rizos et al., 2001
Vegetable oils	a. Liquid-liquid extraction b. Solid phase extraction	40.5	500	No	GC-MS/MS	0.3−1.4	91−104	13	Esteve-Turrillas et al., 2005
Vegetable oils	a. Magnetic ionic liquid-based dispersive liquid−liquid microextraction	10	400	No	HPLC-UV	4.33 −4.91	81.8 −114.2	7.7	Wang et al., 2014b
Vegetable oils	a. Liquid-liquid extraction b. MSPE	24	70	Yes	HPLC-PDA	0.0890 −0.1994	83.18 −112.79	12.01	This method

(LOD) and limit of quantification (LOQ) were between 0.0290−0.0658 and 0.0890−0.1994 ng g^{-1}, respectively.

3.3.2. Reproducibility

Reproducibility tests were conducted by analysing intra-day and inter-day precision. For intra-day extractions, six replicates at both concentrations were conducted within the same day. For inter-day experiments, six replicates at both concentrations were conducted over six different days. Table 2 summarises the recovery rates and their relative standard deviations. As shown, the recovery rates of pyrethroids ranged from 83.18% to 112.79% for both concentrations. Relative standard deviations were also satisfactory, being below 10.84% and 12.01% for intra-day and inter-day extractions, respectively. These results demonstrated that the developed approach was highly accurate and reliable.

3.4. Method comparison

Method comparison was presented in Table 3 in order to evaluate the proposed method objectively and comprehensively. Major impacting factors including extraction procedures, usage of organic solvent and adsorbent, reusability of adsorbent as well as instrumental requirements were listed. Analytical performances such as LODs and recoveries rates were also summarised for reference. Compared with other traditional methods as well as recently developed techniques using either low temperature cleanup or magnetic extraction approaches alone, the present method shows more advantages, e.g. low LODs, moderate amount of reusable adsorbents and easily accessible instruments. Most importantly, through the joint application of low temperature cleanup and MSPE, the proposed method not only can help us get rid of the

Table 4
Analysis of pyrethroids in real vegetable oils.

Analytes	Soybean oil		Corn oil		Sunflower oil		Olive oil	
	Detected (ng g^{-1})	Recovery (%)	Detected (ng g^{-1})	Recovery (%)	Detected (ng g^{-1})	Recovery (%)	Detected (ng g^{-1})	Recovery (%)
Tetramethrin	ND	103.52 ± 5.9	ND	100.16 ± 7.0	ND	103.28 ± 7.9	ND	106.23 ± 6.5
Fenpropathrin	ND	109.65 ± 7.3	ND	84.81 ± 9.3	ND	105.65 ± 5.4	ND	107.26 ± 7.3
Cypermethrin	ND	113.74 ± 10.2	ND	87.98 ± 11.1	ND	103.28 ± 3.7	ND	95.64 ± 4.5
Decamethrin	ND	93.61 ± 6.7	ND	98.91 ± 2.2	ND	93.26 ± 4.6	ND	91.26 ± 4.9
Fenvalerate	ND	100.38 ± 7.4	ND	95.18 ± 3.7	ND	112.87 ± 8.1	ND	95.32 ± 3.1
Acrinathrin	ND	107.62 ± 3.5	ND	105.79 ± 8.9	ND	99.12 ± 6.2	ND	91.29 ± 4.5
Permethrin	ND	96.56 ± 8.1	ND	93.87 ± 7.2	ND	102.87 ± 6.3	ND	94.56 ± 2.1
Bifenthrin	ND	87.85 ± 7.2	0.21	91.78 ± 3.5	ND	110.21 ± 3.9	ND	103.45 ± 4.2

*Note: ND: not detected. Spiked level: 5 ng g^{-1}.

notorious fat and lipid interferences conveniently at low cost, but also can reduce the sample pretreatment time to the least. Being different from traditional solid phase extraction techniques which use disposable adsorbents, the magnetic adsorbents can be easily collected using magnet and recycled after use due to its stable properties, thus being environmentally-friendly and help save the cost.

3.5. Real sample analysis

The developed method was employed to detect pyrethroids in four other different types of oil samples (Table 4). Trace amount of bifenthrin that was far below the maximum residue limits set by health authorities was detected in the corn oil sample. This technique will also be applicable for cereal products (Bu et al., 2014; Du, An, Liu, Yang, & Wei, 2014), fruits and vegetables (Chong, Lai, & Yang, 2015; Xin, Zhang, Yang, & Adhikari, 2015), seafood (Deng et al., 2014; Feng, Bansal, & Yang, 2016; Li et al., 2016; Feng, Fu & Yang, 2017a; Feng, Ng, Mikš-Krajnik, & Yang, 2017b;), especially organic food (Zhao, Zhang, & Yang, 2017). Interaction between the nanoparticles and the pesticides can be investigated by atomic force microscopy for improving the extract efficiency (Yang, 2014).

4. Conclusion

Recovery rates of pyrethroids residue in vegetable oils were satisfactory within the range of 83.18—112.79%. Desirable reproducibility was achieved with inter and intra-day RSD lower than 12.01%. Furthermore, it is highly environmentally-friendly since only very limited amount of organic solvent is used for the sample preparation. It suggests that the developed method using low temperature clean up coupled with magnetic solid phase extraction for detecting pyrethroids residue in vegetable oils is efficient and convenient.

Acknowledgements

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.foodcont.2016.11.036.

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