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Determination of five pyrethroids in tea drinks by dispersive solid phase extraction with polyaniline-coated magnetic particles

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ABSTRACT

The polyaniline-coated magnetic particles with bowl-shaped morphology (Fe_3O_4/C/PANI microbowls) were successfully prepared and characterized by scanning electron microscopy, transmission electron microscopy and vibrating sample magnetometry. The prepared microbowls were used as the magnetic adsorbent in dispersive solid phase extraction of five pyrethroids, including cyhalothrin, beta-cypermethrin, esfenvalerate, permethrin and bifenthrin in plain tea drinks. The effects of experiment factors, including amount of Fe_3O_4/C/PANI microbowls, pH value, ultrasound extraction time and desorption conditions, were investigated. The extraction recoveries obtained with 8 mg of magnetic microbowls were satisfactory, and the microbowls can be reused after easy washing. Thus, a simple, selective and effective method for the determination of the pyrethroids was established successfully. The results showed that the method had good linearity (r=0.9992–0.9998), and the limits of detections (LODs) were from 0.025 to 0.032 ng mL^{-1}. The intra-day and inter-day relative standard deviations (RSDs) were in the range of 2.4–6.1% and 3.5–8.8%, respectively. Recoveries obtained by analyzing the real tea drinks were in the range of 72.1–118.4%.

1. Introduction

Pyrethroids are a class of synthetic analogs of the natural insecticide pyrethrum found in chrysanthemum flowers [1]. They are the result of modifying the chemical structures of the natural compounds to achieve stability while retaining effective insecticidal activity [2]. Pyrethroids are used worldwide as pest control agents in agriculture and household applications [3]. They are effective against a wide spectrum of pests at low dosages and are stable under field conditions. Because of the prolonged and widespread use, the pyrethroid residues have been found in a lot of agricultural products [4]. Although pyrethroids are thought to be of low toxicity to humans, studies have concluded that some pyrethroids are neurological toxins, causing prolonged nervous system hyperexcitation and depolarization [5]. The U.S. Environmental Protection Agency (EPA) has approved 18 pyrethroids for use in the United States (Linda Arrington, EPA, 2003, personal communication) [6]. Therefore, fast, reliable and accurate determination of pyrethroids is particularly important in order to guarantee public health and safety.

Tea is one of the most favorite drinks all over the world. However, pyrethroid residues in tea have caused an increasing public concern as drinking tea is an important part of the daily routine for many people. However, tea matrix is very complex, including organic acids, pigments, caffeine, sugars, tea polyphenols and other compounds [7]. Additionally, the low concentrations of pesticide residues in tea drink samples also increase the difficulty in determining them directly. Therefore, there is a need to employ an exhaustive sample preparation technique for the extraction and preconcentration of the insecticide residues from tea drinks before determination.

Different extraction methods have been developed to extract pyrethroids from tea. Liquid–liquid extraction (LLE) [8] is a conventional method to separate and concentrate pyrethroids. However, LLE has the disadvantages of being time-consuming and requiring large amount of organic solvents. Research efforts have been directed towards simplifying the extraction procedure and greatly reducing the consumption of organic solvents, leading to the development of directly suspended droplet microextraction (DSDME) [9], cloud point extraction (CPE) [10] and subcritical water extraction (SCWE) [11]. Compared with LLE, the obvious advantages of dispersive solid-phase extraction (dSPE) [12] are lower consumption of organic solvents and higher enrichment factor. However, routine dSPE still suffers from an inherent limitation of being time-consuming. Nowadays, the magnetic or magnetizable adsorbents are used as specific adsorbents to take the place of the routine nonmagnetic adsorbents in dSPE [13]. In dSPE the magnetic adsorbent is uniformly dispersed in the sample

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solution and can be quickly isolated from the solution by means of an external magnetic field. This extraction method avoids the high consumption of organic solvents in conventional LLE. Moreover, some magnetic adsorbents can be easily recycled after a simple washing operation. The studies on the preparation of novel magnetic materials were reported recently [14,15].

Different magnetic oxides have been prepared and used as magnetic cores, including Fe_3O_4, Fe_2O_3, $CoFe_2O_4$, $NiFe_2O_4$, $CuFe_2O_4$ and $ZnFe_2O_4$ [16]. Among these magnetic oxides, Fe_3O_4 is most widely used and most of these magnetic cores are spherical particles. However, novel magnetic oxides with special morphologies have rarely been used as magnetic cores. Nowadays Fe_3O_4 particles with hollow interiors are receiving immense attention owing to their unique hollow structure and high specific surface area [17]. Modification using compounds and functional groups on inner and outside surface for improving their capabilities will be very interesting. Numerous synthetic and natural polymers have been used to modify magnetic cores, such as polystyrene [18], polyester [19], polyurethane [20], humic acid [21], etc. Polyaniline (PANI) is found to be an attractive polymer because of its ease of synthesis, low cost monomer, tunable properties, and greater stability than other polymers [22]. As PANI contains a good deal of π-conjugated structures, synthesis of a novel adsorbent modified with PANI will be valuable.

Various techniques have been developed for determining pyrethroids such as gas chromatography (GC) [23,24], gas chromatography–mass spectrometry (GC–MS) [25], high performance liquid chromatography (HPLC) [26,27] and liquid chromatography–tandem mass spectrometry (LC–MS) [28]. In this work, Fe_3O_4/C/PANI microbowls with superparamagnetic properties, high specific surface area and high proportion of π-conjugated structures were prepared successfully. Based on Fe_3O_4/C/PANI microbowls, a novel extraction procedure coupled with UFLC was reported for determining pyrethroids in tea drinks. Although there are many kinds of pyrethroids, the five pyrethroids were selected as the analytes because the five pyrethroids are widely used in agriculture and can be an expression of pyrethroids.

2. Experimental

2.1. Reagents and chemicals

Cyhalothrin, beta-cypermethrin, esfenvalerate, permethrin and bifenthrin were obtained from National Institute of Metrology (NIM, China). Stock solution of each standard was prepared by dissolving the pure substance in chromatographic grade acetonitrile at a concentration level of 200 μg mL^{-1} and stored at 4 °C in darkness. The working solutions at desirable concentration levels were prepared by diluting the stock solutions with HPLC-grade acetonitrile.

Chromatographic grade methanol and acetonitrile were purchased from Fisher Scientific Company (UK). Analytical-grade methanol, acetonitrile, ethyl acetate, n-hexane, petroleum ether, ammonia and ethylene glycol (EG) were obtained from Beijing Chemical Works (Beijing, China). Iron(III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) and copper(II) acetate monohydrate ($CuAc_2 \cdot H_2O$) were supplied by Guangfu Fine Chemical Research Institute (Tianjin, China). Analytical-grade polyvinylpyrrolidone (PVP-K40) was purchased from Sigma-Aldrich Co. (Shanghai, China). Analytical-grade urea and D-(+) glucose was obtained from Sinopharm Chemical Reagent Co. (Shanghai, China). Analytical-grade aniline was supplied by Aladdin Reagent Co. (Shanghai, China).

Deionized water was obtained with a Milli-Q water purification system (Millipore, USA).

2.2. Instruments

A UFLC–UV system (Shimadzu, Japan) equipped with two pumps (LC-20AD), an autosampler (SIL-20A), a column oven (CTO-20A) and a UV–vis detector (SPD-20A) was used. A shim-pack XR-ODS column (75 mm × 2 mm, with 2.2 μm particle size) was employed for the UFLC separation of the pyrethroids. Relevant data acquisition and processing were performed with the LC-solution software (Shimadzu, Japan).

An electric constant temperature drying oven (DGG-9070BD, Shanghai, China) was used to prepare magnetic particles. A scanning electron microscope (SEM, JEOL JSM-6700F, Japan) was used to obtain scanning electron microscopic images. A transmission electron microscope (TEM, Hitachi H-800, Japan) was used to obtain transmission electron microscopic images. A magnetic property measurement system (SQUID-VSM, Quantum Design, USA) was used to study the magnetic properties. A pH meter (DELTA 320, METTLER-TOLEDO, Shanghai, China) was used to measure the pH value of solution. An ultrasonic wave cleaning machine (KQ-100, 40KHz, 100 W, Kunshan China) was used to increase extraction rate of analytes.

2.3. Sample preparation

In the study, two kinds of tea drinks (green tea, sample 1 and jasmine tea, sample 2) and two kinds of dry tea (green tea, sample 3 and red tea, sample 4) were purchased from Wal-Mart supermarket (Changchun, China). The tea infusions were prepared by immersing 100 mg of dry tea in boiling water for 10 min. The boiling water was obtained by heating 150 mL of deionized water. Before experiment, all these samples were filtered through 0.45 μm micropore membranes and stored at 4 °C in darkness. Except for the experiments mentioned in Section 3.5, which were performed with sample 1, sample 2 and sample 4, all other experiments were performed with sample 3. The spiked samples containing pyrethroids were prepared by spiking the working solutions into tea drinks.

2.4. Synthesis of Fe_3O_4 microbowls

The synthetic method for Fe_3O_4 microbowls is similar to a previous synthesis of hollow Fe_3O_4 particles [29]. 8.0 g of $FeCl_3 \cdot 6H_2O$ was dissolved in 60 mL EG under vigorous stirring for 30 min. 3.75 g of urea and 0.3 g of PVP were added into the solution and stirred continuously to form a homogeneous solution. Then the resulting solution was transferred into a Teflon-lined stainless-steel autoclave for heating at 180 °C for 20 h. After the autoclave was cooled to room temperature, the obtained black magnetite microspheres were thoroughly washed with ethanol and deionized water several times, and then dried in vacuum at 50 °C overnight.

2.5. Synthesis of Fe_3O_4/C/PANI microbowls

The synthetic method of Fe_3O_4/C/PANI microbowls is conducted according to the previously reported hydrothermal methods with some modification [30–32]. The carbon layer could protect the magnetic core from etching in harsh application occasions.

Briefly, 0.3 g of Fe_3O_4 microbowls were dispersed in 20 mL of deionized water under ultrasonication for 10 min. 5.4 g of glucose was dissolved in 40 mL of deionized water, then the former suspension was added to the solution under vigorous stirring. The mixture was transferred into a Teflon-lined stainless-steel autoclave for heating at 180 °C for 6 h. When the autoclave was cooled to room temperature, the Fe_3O_4/C microbowls were

washed with ethanol and deionized water several times, and then dried in vacuum at 50 °C overnight.

In the following step, 0.18 g of $CuAc_2 \cdot H_2O$ and 64 μL of aniline were dissolved in 10 mL and 38 mL of deionized water, respectively. 30 mg of Fe_3O_4/C microbowls were dispersed in 12 mL of deionized water under ultrasonication. All deionized water is needed to be bubbled with N_2 for at least 30 min in advance. Then the two solutions were transferred into an autoclave, and Fe_3O_4/C microbowls were added in the autoclave at the same time. The mixture was then heated at 180 °C for 4.5 h. The obtained microspheres were washed with ethanol and deionized water several times, and then dried in vacuum at 50 °C overnight.

2.6. Procedure of dSPE

150 mL of tea drink sample was added into a beaker. 8 mg of Fe_3O_4/C/PANI microbowls prepared above were added. The mixture was sonicated for 12 min. Then the microbowls were subsequently settled down with a strong magnet on the wall of the beaker, and the supernatant was decanted. Pyrethroids were eluted from the microbowls with 3 mL of methanol under ultrasonication for 30 s. After magnetic separation again, the eluate was evaporated to dryness under mild nitrogen stream at 40 °C, and the residues were dissolved in 150 μL of acetonitrile. Then the solution was filtered through a 0.22 μm syringe filter and injected into the UFLC system for analysis. After the dSPE, the microbowls were dried and recycled after ultrasonic cleaning with deionized water and methanol in turn. Illustration of the whole procedure of dSPE is shown in Fig. 1.

2.7. UFLC–UV analysis

The mobile phase consisted of acetonitrile (A) and water (B). The gradient program is as follows: 0–20 min, 60% A; 20–22 min, 60–70% A; 22–25 min, 70% A; and 25–33 min, 70–80% A. The flow rate of the mobile phase was set at 0.3 mL min^{-1} and column temperature was kept at 30 °C throughout the run. Injection volume was set at 10 μL. Monitoring wavelength was 210 nm for all the target compounds [33].

3. Results and discussion

3.1. Characterization of Fe_3O_4/C/PANI microbowls

Fe_3O_4/C/PANI microbowls were synthesized by a facile hydrothermal method. In this approach, aniline was polymerized on magnetic Fe_3O_4/C cores using $CuAc_2 \cdot H_2O$ as an initiator. In the following work, characterizations of the synthesized microbowls were carried out by SEM, TEM and a magnetic property measurement system.

Fig. 2 shows SEM and TEM images of Fe_3O_4, Fe_3O_4/C and Fe_3O_4/C/PANI microbowls. The SEM image (Fig. 2a_1) shows that the Fe_3O_4 microbowls with a bowl-shaped morphology are well monodispersed. These microbowls are well-distributed with an average diameter of about 120 nm. After stepwise coating with layers of carbon and PANI, the obtained Fe_3O_4/C microbowls (Fig. 2a_2) and Fe_3O_4/C/PANI microbowls (Fig. 2a_3) are slightly larger than Fe_3O_4 microbowls and have the similar structure as naked Fe_3O_4 microbowls. Additionally, TEM images (Fig. 2b_1–b_3) further prove the above result. The distinguished core–shell structure was formed successfully. The gray layers of carbon and PANI were coated on the dark core of magnetite Fe_3O_4 microbowls, and the final thin coating layer had a thickness of about 10 nm. A typical sandwich structure with a bowl-shaped magnetite core, a carbon layer in the middle layer, and a PANI layer in the outer layer was formed.

Magnetic characterization using a magnetometer at 300 K indicates that the Fe_3O_4, Fe_3O_4/C and Fe_3O_4/C/PANI microbowls have magnetization saturation values of 95.5, 85.0, and 51.3 emu g^{-1}, respectively. Fig. 3 shows the hysteresis loops of the three samples, and it is apparent that all of the samples show

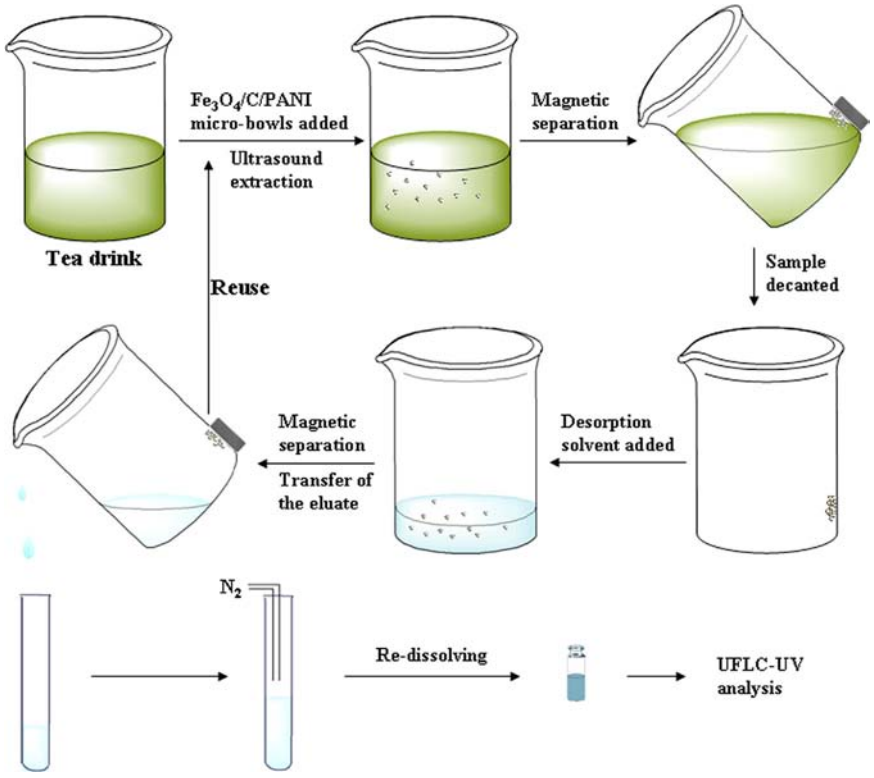

Fig. 1. Procedure of dSPE based on Fe_3O_4/C/PANI microbowls.

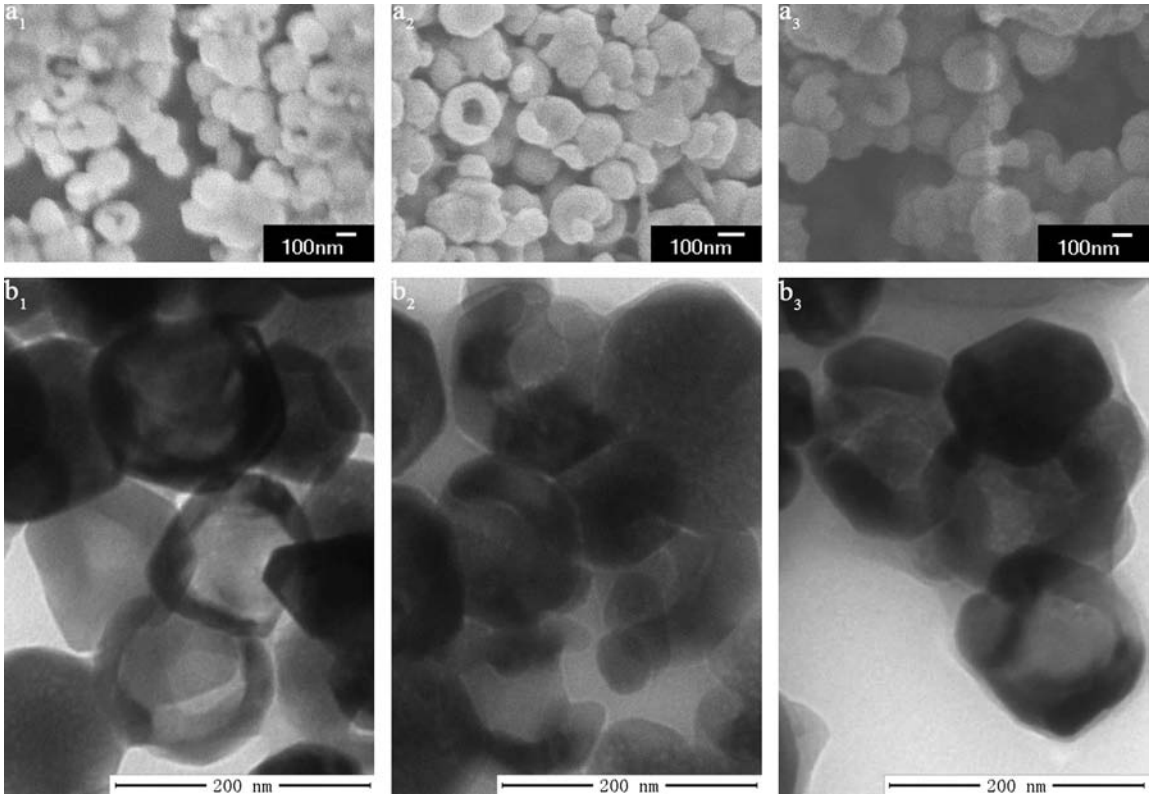

Fig. 2. SEM (a) and TEM (b) images of Fe_3O_4 microbowls ((a_1) and (b_1)), Fe_3O_4/C microbowls ((a_2) and (b_2)), and Fe_3O_4/C/PANI microbowls ((a_3) and (b_3)).

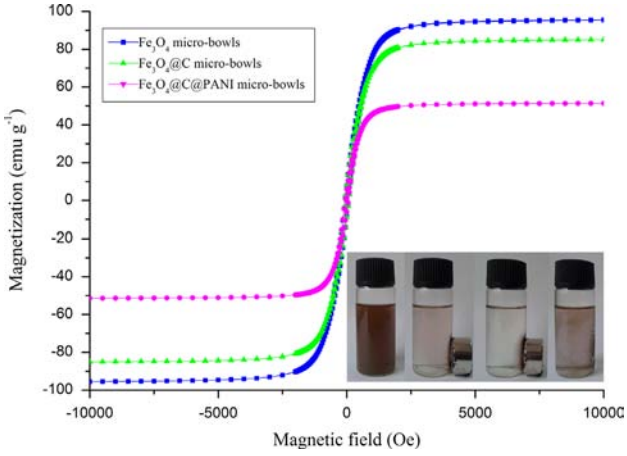

Fig. 3. Hysteresis loops of (a) Fe_3O_4 microbowls, (b) Fe_3O_4/C microbowls and (c) Fe_3O_4/C/PANI microbowls. The inset shows the separation–redispersion process of Fe_3O_4/C/PANI microbowls.

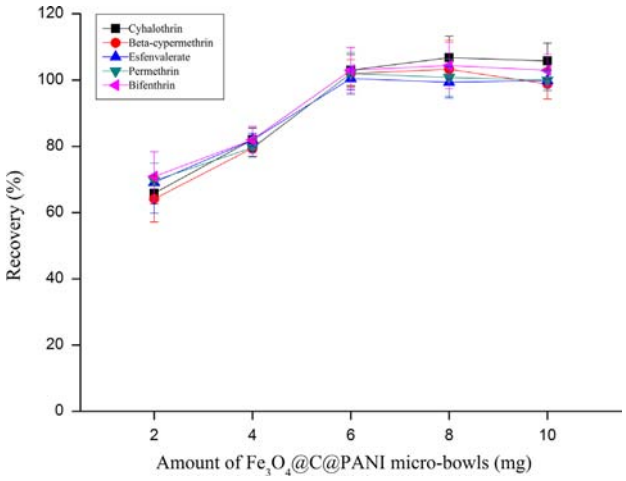

Fig. 4. Effect of the amount of Fe_3O_4/C/PANI microbowls on the recoveries of pyrethroids. Ultrasound extraction time, 14 min; desorption solvent, 3 mL methanol; desorption time, 30 s; and spiked concentration, 2 ng mL^{-1}.

superparamagnetic properties in the presence of magnetite particles in the core. As a result, the Fe_3O_4/C/PANI microbowls in their homogeneous dispersion show fast movement to the applied magnetic field and redisperse quickly with a slight shake once the magnetic field is removed (inset in Fig. 3). It suggests that the microbowls possess excellent magnetic responsivity and redispersibility, which is an advantage to their applications.

3.2. Optimization of dSPE conditions

In order to obtain high extraction efficiency, the influence of experimental parameters, such as amount of Fe_3O_4/C/PANI microbowls, pH value, ultrasound extraction time and desorption conditions, was investigated. All of the experiments were performed in triplicate.

3.2.1. Amount of Fe_3O_4/C/PANI microbowls

The effect of the amount of synthesized adsorbent on the extraction efficiency was investigated. In order to achieve good recovery, different amounts of adsorbent ranging from 2 mg to 10 mg were used. As can be concluded from Fig. 4, the effect of the amount of adsorbent on the recoveries is significant and the recoveries achieved with 6 mg of Fe_3O_4/C/PANI microbowls are the highest. In order to ensure satisfactory recoveries, 8 mg was

employed as the amount of synthesized adsorbent in the following experiments.

3.2.2. pH value of the samples

The pH value of the samples is a significant parameter affecting adsorption and recoveries of the analytes. It always influences the interactions between the analytes and the adsorbent. The stability of pyrethroids is also related to pH value because most pyrethroids tend to hydrolyze in alkaline environment. Therefore, the effect of pH value of the samples in the range of 3.0–11.0 on the extraction recoveries was studied. It can be seen from Fig. 5 that the recoveries of pyrethroids increase with the increase of pH value from 3.0 to 7.0 because hydrolysis of pyrethroids occurs at acidic pH. The optimal extraction recoveries are obtained at pH 7.0. Furthermore, the pH of tea solution samples is about 6.7, which is close to 7.0, so the samples can be directly analyzed without adjusting the pH values in the following procedures.

3.2.3. Ultrasound extraction time

Ultrasound irradiation was applied to increase extraction rate and improve extraction yields of analytes. The effect of ultrasonic extraction time was investigated by increasing the time from 2 to 16 min. It can be seen from Fig. 6 that the extraction equilibrium could be achieved within 14 min and longer extraction time would not affect the extraction efficiency. Therefore, in a further work, extraction time of 14 min was selected.

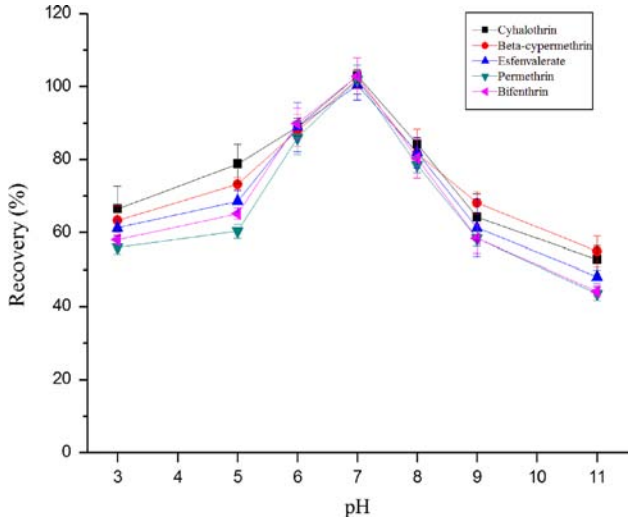

Fig. 5. Effect of pH value of the samples on the recoveries of pyrethroids. Amount of Fe_3O_4/C/PANI microbowls, 8 mg; ultrasound extraction time, 14 min; desorption solvent, 3 mL methanol; desorption time, 30 s; and spiked concentration, 2 ng mL^{-1}.

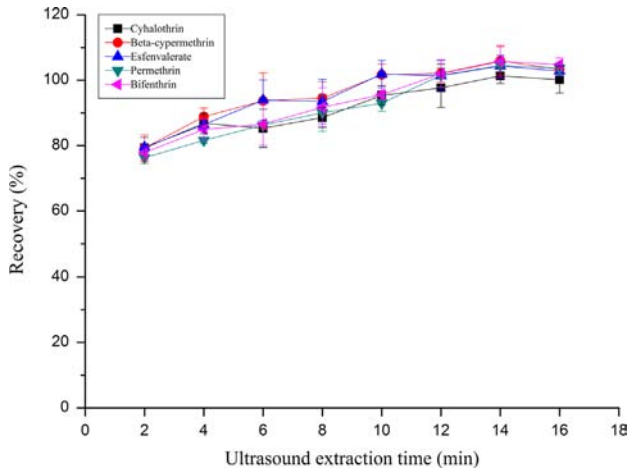

Fig. 6. Effect of the ultrasound extraction time on the recoveries of pyrethroids. Amount of Fe_3O_4/C/PANI microbowls, 8 mg; desorption solvent, 3 mL methanol; desorption time, 30 s; and spiked concentration, 2 ng mL^{-1}.

3.2.4. Optimization of desorption conditions

The type of desorption solvent directly influences desorption efficiency of target analytes. Different kinds of organic solvents were considered as desorption solvents, including methanol, acetonitrile, ethyl acetate, n-hexane, and petroleum ether. Because the synthesized adsorbent could not be dispersed well in ethyl acetate, n-hexane and petroleum ether, poor desorption efficiency was obtained when the desorption solvents were used. Methanol and acetonitrile were selected and employed for desorption of pyrethroids from the adsorbent, and the effect of the volume of the desorption solvents was also studied. The results shown in Fig. 7 indicate that the effect of methanol and acetonitrile on the recoveries of pyrethroids is very significant and recoveries obtained with methanol are higher than those obtained with acetonitrile. Thus, methanol was chosen as the desorption solvent. The recoveries of pyrethroids increase with the increase of the volume of desorption solvent from 1 mL to 3 mL and arrived to the maximum at 3 mL, and no obvious change is observed when the volume is larger than 3 mL. Consequently, 3 mL methanol was selected for desorption of pyrethroids in the following procedures.

The effect of desorption time was conducted by increasing the ultrasonic desorption time from 5 s to 90 s. As shown in Fig. 8, a desorption time of 5 s is valid for beta-cypermethrin. Recoveries of the analytes increase with the increase of desorption time shorter than 30 s, and slightly changed when desorption time is longer than 30 s. Hence, desorption time was fixed at 30 s in subsequent experiments.

3.3. Reusability of the adsorbent

In order to investigate the reusability of the adsorbent, 8 mg of Fe_3O_4/C/PANI microbowls were repeatedly used 15 times in dSPE. The magnetite microbowls were washed with 10 mL methanol and 10 mL deionized water in turn, and dried in vacuum at 50 °C each

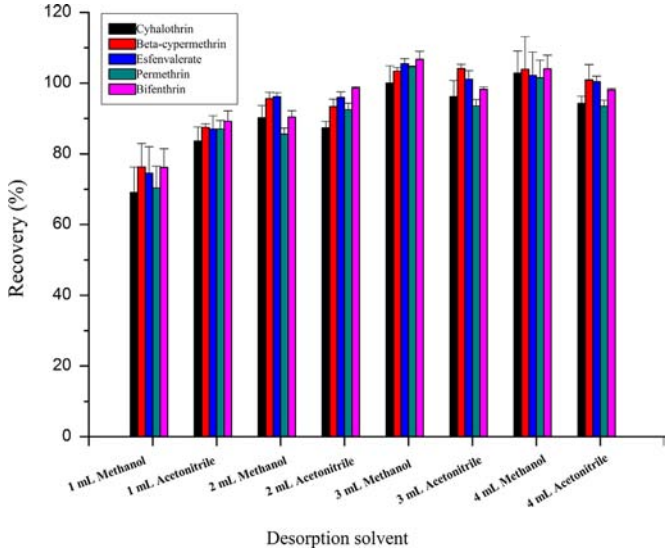

Fig. 7. Effect of the desorption solvent on the recoveries of pyrethroids. Amount of Fe_3O_4/C/PANI microbowls, 8 mg; ultrasound extraction time, 14 min; desorption time, 30 s; and spiked concentration, 2 ng mL^{-1}.

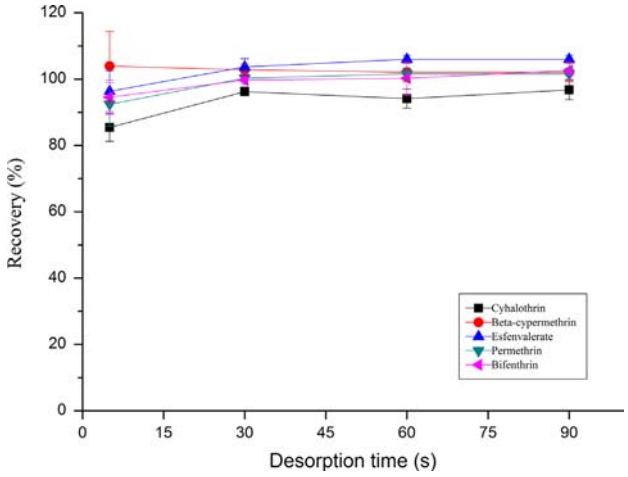

Fig. 8. Effect of the desorption time on the recoveries of pyrethroids. Amount of Fe_3O_4/C/PANI microbowls, 8 mg; ultrasound extraction time, 14 min; desorption solvent, 3 mL methanol; and spiked concentration, 2 ng mL^{-1}.

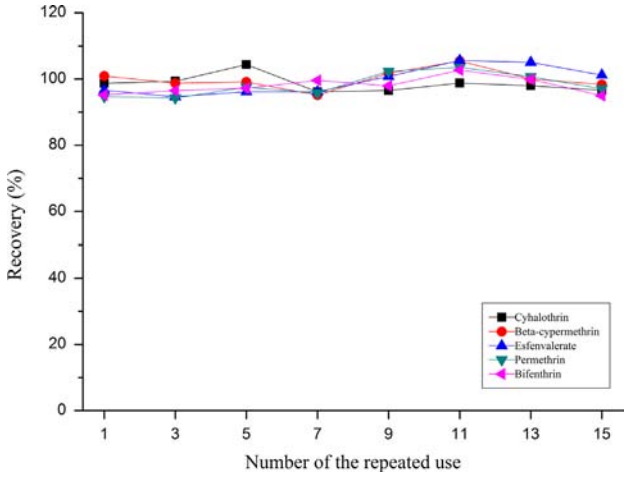

Fig. 9. Reusability of the Fe_3O_4/C/PANI microbowls. Spiked concentration, 2 ng mL^{-1}.

time before reusing. The experimental results shown in Figs. 9 and 10 indicate that there is no significant change in the recoveries of pyrethroids and there is no strange peak from the adsorbent when the adsorbent was reused 15 times.

3.4. Evaluation of the method

3.4.1. Linearity

In order to evaluate the performances of the present method for quantitative determination of the five kinds of pyrethroids in tea drinks, a series of spiked samples were used for constructing working curves and obtaining other analytical performances. As can be seen in Table 1, the linear range is 0.100–20.000 ng mL^{-1} with the correlation coefficients (r) between 0.9992 and 0.9998, suggesting that the linearity is satisfactory in the linear range of the analytes.

Table 2
The recoveries of the analytes and inter- and intra-day precisions (n=5).

Analyte	Concentration (ng mL^{-1})	Intra-day		Inter-day	
		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Cyhalothrin	0.50	94.5	2.8	92.5	3.5
	2.00	94.9	2.4	96.3	4.7
	10.00	108.5	4.5	107.2	4.8
	0.50	118.1	5.6	116.3	6.1
Beta-cypermethrin	2.00	102.4	2.6	101.0	3.6
	10.00	99.3	3.7	99.9	6.0
	0.50	108.4	4.9	106.1	6.1
Esfenvalerate	2.00	102.7	3.3	102.2	4.5
	10.00	101.9	4.0	103.2	5.8
	0.50	113.7	2.5	111.4	5.7
Permethrin	2.00	97.2	6.1	99.4	4.8
	10.00	101.0	3.8	102.0	5.5
	0.50	96.6	3.5	93.3	3.7
Bifenthrin	2.00	99.0	5.0	101.1	5.2
	10.00	109.5	5.3	112.4	8.8

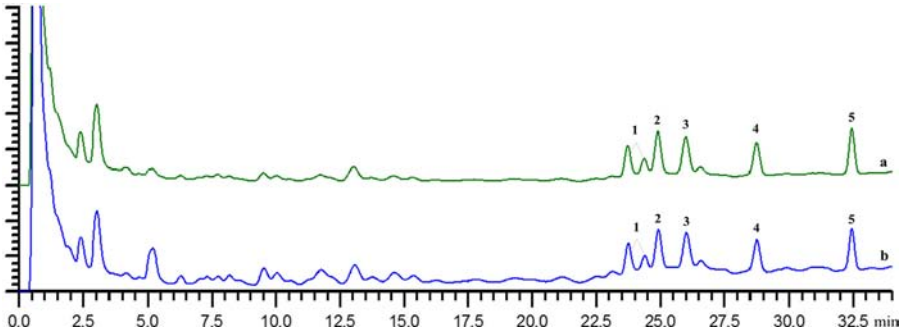

Fig. 10. The chromatograms of extracts obtained with (a) initial and (b) 15th reusable Fe_3O_4/C/PANI microbowls. 1 – Cyhalothrin; 2 – Beta-cypermethrin; 3 – Esfenvalerate; 4 – Permethrin; and 5 – bifenthrin. Spiked concentration, 2 ng mL^{-1}.

Table 1
Analytical performances of the present method.

Analyte	Linear range (ng mL^{-1})	Regression equation	Correlation coefficient (r)	LOD (ng mL^{-1})	LOQ (ng mL^{-1})
Cyhalothrin	0.100–20.000	$y=79816x+5358.3$	0.9992	0.027	0.090
Beta-cypermethrin	0.100–20.000	$y=94338x-12723$	0.9993	0.031	0.104
Esfenvalerate	0.100–20.000	$y=79690x-1513.7$	0.9998	0.027	0.090
Permethrin	0.100–20.000	$y=67944x+2823.6$	0.9994	0.032	0.106
Bifenthrin	0.100–20.000	$y=75825x+20411$	0.9996	0.025	0.083

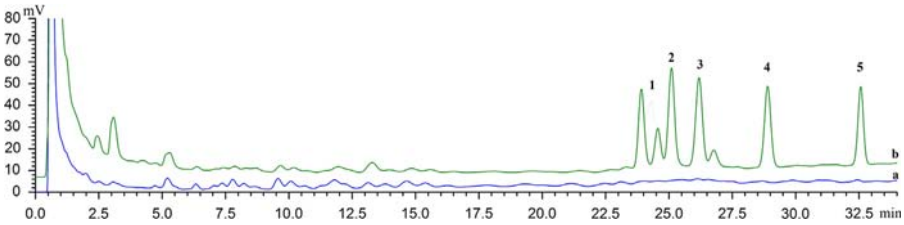

Fig. 11. The chromatograms of (a) tea drink and (b) spiked sample 3. 1 – cyhalothrin; 2 – beta-cypermethrin; 3 – esfenvalerate; 4 – permethrin; and 5 – bifenthrin. Spiked concentration, 5 ng mL^{-1}.

Table 3
Analytical results of real tea drinks.

Sample	Spiked (ng mL^{-1})	Cyhalothrin		Beta-cypermethrin		Esfenvalerate		Permethrin		Permethrin	
		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Sample 1	2.00	104.2	3.9	99.3	3.4	116.1	2.3	116.8	2.5	106.6	8.0
	10.00	108.9	3.0	82.3	5.9	95.0	1.7	97.0	1.3	72.1	0.5
Sample 2	2.00	107.1	4.6	103.7	8.0	104.5	5.6	107.3	7.7	104.3	8.1
	10.00	116.5	4.1	89.6	5.0	103.3	5.5	103.8	5.0	76.3	4.2
Sample 4	2.00	111.6	5.3	104.4	3.0	109.9	5.0	112.6	3.6	118.4	1.1
	10.00	102.2	2.1	80.9	1.3	87.2	1.3	93.6	3.5	74.7	1.8

3.4.2. *Limit of detection and quantification*

The limits of detections (LODs) and quantifications (LOQs) were determined based on the signal to noise (S/N) ratio of 3 and 10, respectively. The results obtained are given in Table 1, the LODs and LOQs are in the range of 0.027–0.032 ng mL^{-1} and 0.083–0.106 ng mL^{-1}, respectively.

3.4.3. *Recovery and precision*

Precision was evaluated by measuring intra-day and inter-day relative standard deviations (RSDs). The intra-day and inter-day precisions of the method were evaluated by analyzing the spiked sample 3 at three concentrations levels (0.50, 2.00 and 10.00 ng mL^{-1}) on the same day and the five consecutive days, respectively. The detailed results obtained are listed in Table 2. The intra- and inter-day precisions are in the range of 2.4–6.1% and 3.5–8.8%, respectively.

3.5. *Analysis of real tea drinks*

To evaluate the applicability of the present method, three kinds of samples were analyzed. The typical chromatograms of the blank and spiked samples are shown in Fig. 11. As can be seen, pyrehroids in the samples were not detectable. The spiked samples were analyzed and the analytical results are shown in Table 3. The recoveries and relative standard deviations (RSDs) are in the range of 72.1–118.4% and 0.5–8.1%, respectively.

4. Conclusion

In this work, the Fe_3O_4/C/PANI microbowls were successfully prepared via hydrothermal reaction and solvothermal reduction, and used as reusable adsorbent for dSPE of pyrethroids in plain tea drinks. All the reactions were simple, low cost and easy to realize. Combined with UFLC, a simple, selective and effective method with high enrichment factor for the determination of the pyrethroids was established successfully. The analytical performances were satisfactory.

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