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Preparation of magnetic carbon nanotubes for separation of pyrethroids from tea samples

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Abstract Magnetic carbon nanotubes (MCNTs) have been synthesized by chemical deposition of Fe_3O_4 nanoparticles onto carbon nanotubes. They were characterized by Fourier transform infrared spectroscopy, scanning electron microscope, X-ray diffraction and physical property measurement system. The MCNTs were used as the sorbents for the extraction of pyrethroids including beta-cyfluthrin, cyhalothrin and cyphenothrin from tea samples. The extraction conditions, such as the amount of magnetic sorbent, shaking time and rate, washing and eluting solution have been fully investigated. The analytes desorbed from MCNTs were determined by HPLC with UV detection. Under the optimal conditions, the linearity of the method is in the range of 0.05–25 $\mu g\,g^{-1}$. The limits of detection of the three pyrethroids are 0.017, 0.010 and 0.018 $\mu g\,g^{-1}$, respectively. The relative standard deviations of within- and between-day range from 3.5 % to 6.4 %, and from 4.5 % to 29 7.3 %, respectively. In all three spiked levels (0.05, 0.5 and 5 $\mu g\,g^{-1}$), the recoveries of pyrethroids are in the range of 82.2 %–94.4 %. This method is much faster and more effective than traditional methods, and it is promising for the analysis of pesticides residues.

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Introduction

It is well known that tea is a kind of traditional and popular beverages consumed worldwide due to its specific aroma and flavor as well health-promoting properties [1]. However, tea is easily attacked by several pests and diseases. Some pyrethroid pesticides such as beta-cyfluthrin, cyhalothrin and cyphenothrin have been used in tea production to prevent and control mites, leafhoppers, plant bugs and aphids [2, 3].

Numerous determination methods, such as gas chromatography-electron capture detection[4], gas chromatography–mass spectrometry [5], high performance liquid chromatography-UV detection [6] and high performance liquid chromatography–mass spectrometry [7], have been reported to determine pyrethroid residues. Lots of methods for the extraction of pyrethroid residues in tea have also been reported, including solid phase extraction [8], solid-phase microextraction [9], accelerated solvent extraction, stir bar sorptive extraction [10], microwave-assisted steam distillation [11], ultrasound-assisted extraction [12], liquid–liquid microextraction [13]. Each method has its advantages. However, most of these analytical methods suffer from several disadvantages, such as matrix interference owing to pigments, alkaloids and polyphenols contained in tea samples, large consumption of organic solvents, tedious procedure, and low recoveries.

Carbon nanotubes were first found by Iijima in 1991 [14]. They can be divided into single-walled and multi-walled, according to whether the walls comprise one or more carbon-atom layers. Carbon nanotubes have been applied in different fields (chemical, electronic and biomedical) because of the numerous unique properties of this kind of material [15]. For example, they have been used for extraction of pyrethroid residues in environmental water [16] and tea samples [9], and good results were obtained.

In recent years, magnetic materials have been proved as efficient absorbents for removing low concentration of analytes from sample solution [17]. In this field, magnetic sorbents were added to the solution or suspension containing the target analytes. The analytes were adsorbed onto the magnetic sorbents whether under stirring or standing. The sorbents with captured analytes were then recovered from the suspension using an appropriate magnetic separator. Compared with traditional adsorbents, magnetic materials can make separation process easier and faster without the need of additional centrifugation or filtration procedures and also can avoid the time-consuming column passing operations encountered in traditional solid phase extraction [18].

Carbon nanotubes decorated with magnetic nanoparticles on their external surface will combine the high adsorption capacity of carbon nanotubes with the convenient separation of magnetic materials. The magnetic carbon nanotubes have been studied in various fields such as cancer diagnostic and treatment [19], electrodes [20], reinforcing materials [21], wastewater treatment [22], environmental analysis [23] etc. However, the extraction of pyrethroids from complex sample matrix using magnetic carbon nanotubes as adsorbent has never been reported.

In this study, magnetic carbon nanotubes were synthesized by chemical deposition of Fe_3O_4 nanoparticles onto multiwalled carbon nanotubes. The magnetic carbon nanotubes were characterized by Fourier transformed infrared spectroscopy (FT-IR), scanning electron microscope, X-ray diffraction and physical property measurement system, and their binding properties including adsorption isotherm and adsorption kinetics were investigated. The magnetic carbon nanotubes were then used as sorbents for the extraction of pyrethroids from tea samples, followed by liquid chromatography-UV detection. Under the optimal conditions, good recoveries and precisions were obtained.

Experimental

Chemicals and apparatus

The carbon nanotubes used in this study were purchased from Nanoport (Shenzhen, China, http://www.nanotubes.com.cn/). The standards of beta-cyfluthrin, cyhalothrin and cyphenothrin were purchased from Sigma–Aldrich (St. Louis, MO, USA, http://www.sigmaaldrich.com/ united-states.html). Chromatographic grade acetonitrile was obtained from Fisher (Pittsburgh, PA, USA, http://www.fishersci.com.cn/cn/). Methanol, ethanol, n-hexane, sulfuric acid, nitric acid and acetic acid were of analytical grade and obtained from Kermel (Tianjin, China, http://www.chemreagent.com/). High purity water was obtained from a Milli-Q Water System (Millipore, Billerica, MA, USA, http://www.millipore.com/).

Three kinds of Chinese teas, green tea, scented tea and black tea were purchased from local supermarket (Harbin, China). One sample was checked to be free of the studied pyrethroid pesticides by National standard method used in China [24], and it was used as blank tea for calibration and validation purposes. The spiked tea samples were prepared by adding three pyrethroids standard solution into 1.0 g of tea sample. Then the mixture was incubated uniformly and nitrogen gas was continuously purged until the solvent was evaporated to dryness completely.

Chromatographic analysis was performed on a LC-15C high performance liquid chromatograph with a UV detector. (Shimadzu, Kyoto, Japan, http://www.shimadzu.com.cn/). A Zorbax SB-C18 column (250 mm×4.6 mm I.D., 5 μm) was used as an analytical column (Agilent, Palo Alto, CA, USA, http://www.home.agilent.com/agilent/home.jspx?cc=CN&lc=chi). A KQ5200E ultrasonic apparatus (Kunshan Instrument, Kunshan, China, http://www.ks-csyq.com/), DZKW-C thermostatic bath (Shanghai, China, http://shuliyiqi.cn.china.cn/), TG 16-WS centrifuge (Xiangyi, Changsha, China, http://xylxj.testmart.cn/), SHA-B shaking table (Shengtang, Jintan, China, http://www.jtstyq.com/), FT-IR 360 Fourier transform infrared spectroscopy (Nicolet, Madison, WI, USA, http://www.artisan-scientific.com/69062.htm), FEI Sirion 200 scanning electron microscope (Philips, Eindhoven, Netherlands, http://www.philips.com.cn/) and physical property measurement system (Quantum Design Instrument, San Diego, CA, USA, http://www.qdusa.com/) were used.

Standard solution preparation

The standard stock solutions of pyrethroids (beta-cyfluthrin, cyhalothrin and cyphenothrin) were prepared in acetonitrile with the concentration of 1.0 mgmL^{-1}. All the stock solutions were stored in a refrigerator at 4 °C. Standard solutions of pyrethroids at the concentration of interest were prepared daily by diluting the stock solution.

Preparation of magnetic carbon nanotubes

Firstly, carbon nanotubes were purified with 3 molL^{-1} HNO$_3$ for 6 h under stirring. The purified carbon nanotubes were chemically shortened by sonication in a mixture of concentrated sulfuric acid and nitric acid (3:1) for 3 h. Then the carbon nanotubes were washed with water and dried. Subsequently, 2 g of shortened carbon nanotubes was suspended in 100 mL of mixed solution containing FeCl$_3$·6H$_2$O (17.4 mmol) and FeCl$_2$·4H$_2$O (8.7 mmol). When the temperature reached to 80 °C, 10 mL ammonia was added into the solution with stirring. The reaction was allowed to be continued for 60 min. The magnetic carbon nanotubes were magnetically separated and washed repeatedly with deionized water until pH was 7. The product was then dried at 60 °C for further use.

The Fe_3O_4 magnetite was also prepared for comparison in this work. The preparation process was similar to the synthesis of magnetic carbon nanotubes without adding carbon nanotubes.

Binding experiment

In this work, beta-cyfluthrin was selected as a representative of three pyrethroids for studying of isothermal and kinetics adsorption experiment.

The adsorption experiment was carried out by adding 10.0 mg magnetic carbon nanotubes in a centrifuge tube containing 5.0 mL of beta-cyfluthrin solution. The solution was shaken for some time, and then the suspension was separated and analyzed by HPLC. The amount of beta-cyfluthrin bound to the magnetic carbon nanotubes was obtained by subtracting the free concentration from initial concentration of beta-cyfluthrin added to the mixture.

The concentration of beta-cyfluthrin solution used for studying of isothermal and kinetics adsorption experiment were 1–800 $\mu g\,mL^{-1}$ and 50 $\mu g\,mL^{-1}$, respectively.

Extraction of pyrethroids by magnetic carbon nanotubes

Tea sample (1.0 g) was extracted using ultrasonic method with 10 mL of n-hexane for 10 min, and then the mixture was centrifuged for 5 min. The supernatant was transferred to a 50 mL centrifuge tube, and 40 mg magnetic carbon nanotubes were added. The mixture was then shaken (200 rpm) at room temperature for 15 min. Subsequently, the magnetic carbon nanotubes with absorbed pyrethroids were separated rapidly from the solution under strong external magnetic field. The magnetic sorbents were washed with 2.0 mL of 5 % aqueous methanol. Finally, the pyrethroids were eluted from the magnetic carbon nanotubes with 3×1.0 mL 5 % acetic acid acetonitrile. In order to improve the recoveries, the magnetic carbon nanotubes captured pyrethroids were subjected to ultrasound for 30 s during each elution process. The eluent was combined and evaporated to dryness under nitrogen gas at 40 °C, and the residue was reconstituted with 0.5 mL of 85 % aqueous acetonitrile for further liquid chromatography analysis. The extraction process was shown in Fig. S1 in the Supporting Information.

Liquid chromatography analysis

Liquid chromatography analysis was used for quantification of pyrethroids after filtered through a 0.22 μm membrane. The detection wavelength was recorded at 243 nm. The mobile phase was acetonitrile-water (85:15 v/v). The elution is based on an isocratic protocol. The flow rate was 1.0 mL min^{-1}. The column temperature was set at room temperature and the injection volume was 20 μL.

Results and discussion

Characterization results

FT-IR spectra of Fe_3O_4, carbon nanotubes and magnetic carbon nanotubes were compared in Fig. 1a. As illustrated, the absorption band of Fe-O bond from Fe_3O_4 and magnetic carbon nanotubes are at 574.7 and 570.5 cm^{-1}, respectively, proving that Fe_3O_4 was combined with carbon nanotubes. The peaks at 3451.9 cm^{-1} in Fig. 1a(b) and 3444.1 cm^{-1} in Fig. 1a(c) are both due to OH group. As found from Fig. 1a(c), the peaks at 1384.1, 2854.3 and 2924.2 cm^{-1} are attributed to the in-plane bending vibration of methyl ($-CH_3$) and the symmetric and asymmetric vibration of methylene ($-CH_2-$), respectively.

The morphologies of the synthesized magnetic carbon nanotubes were studied by a scanning electron microscope (Fig. 1b). It was observed that iron oxide nanoparticles were successfully attached onto the surface of carbon nanotubes.

The physical property measurement system was applied to characterize the magnetic properties of the prepared materials (Fig. 1c). The saturation magnetization of magnetic carbon nanotubes decreased to 24.9 emu g^{-1} from 59.8 emu g^{-1} of Fe_3O_4. As shown in Fig. 1c (inset), in the presence of an external magnetic field, the magnetic carbon nanotubes were attracted to the wall of vial, in comparison with a black homogeneous dispersion existed without an external magnetic field.

In Fig. 1d(a), the typical peaks of Fe_3O_4 at $2\theta=30.3°$, 35.4°, 43.1°, 57.4° and 62.4°. Fig. 1d(b) also shows the typical peak of carbon nanotubes at $2\theta=25.8°$. Figure 1d(c) shows the X-Ray diffraction of magnetic carbon nanotubes which includes all the carbon nanotubes and Fe_3O_4 peaks. The results have a good agreement with other reports [25].

Adsorption isotherm

As can be seen from Fig. S2A in the Supporting Information, the amount of beta-cyfluthrin bound to magnetic carbon nanotubes at equilibrium increased with the increase of initial concentration of beta-cyfluthrin. Equilibrium data in this study were analyzed with two common isotherm models: Langmuir and Freundlich isotherm models [26].

The Langmuir equation is given in the following equation:

$$q_e = \frac{K_L q_m c_e}{1 + K_L c_e} \tag{1}$$

it can be rearranged to a linear form:

$$\frac{1}{q_e} = \frac{1}{K_L c_e q_m} + \frac{1}{q_m} \tag{2}$$

where c_e is the concentration of beta-cyfluthrin at equilibrium ($mg\,L^{-1}$), q_m is the maximum adsorption capacity

Fig. 1 **a** Fourier transformed infrared spectra of Fe_3O_4 (a), carbon nanotubes (b) and magnetic carbon nanotubes(c); **b** The scanning electron microscope images of magnetic carbon nanotubes; **c** Magnetization curves of Fe_3O_4 and magnetic carbon nanotubes; **d** The X-Ray diffraction of Fe_3O_4 (a), carbon nanotubes (b) and magnetic carbon nanotubes (c)
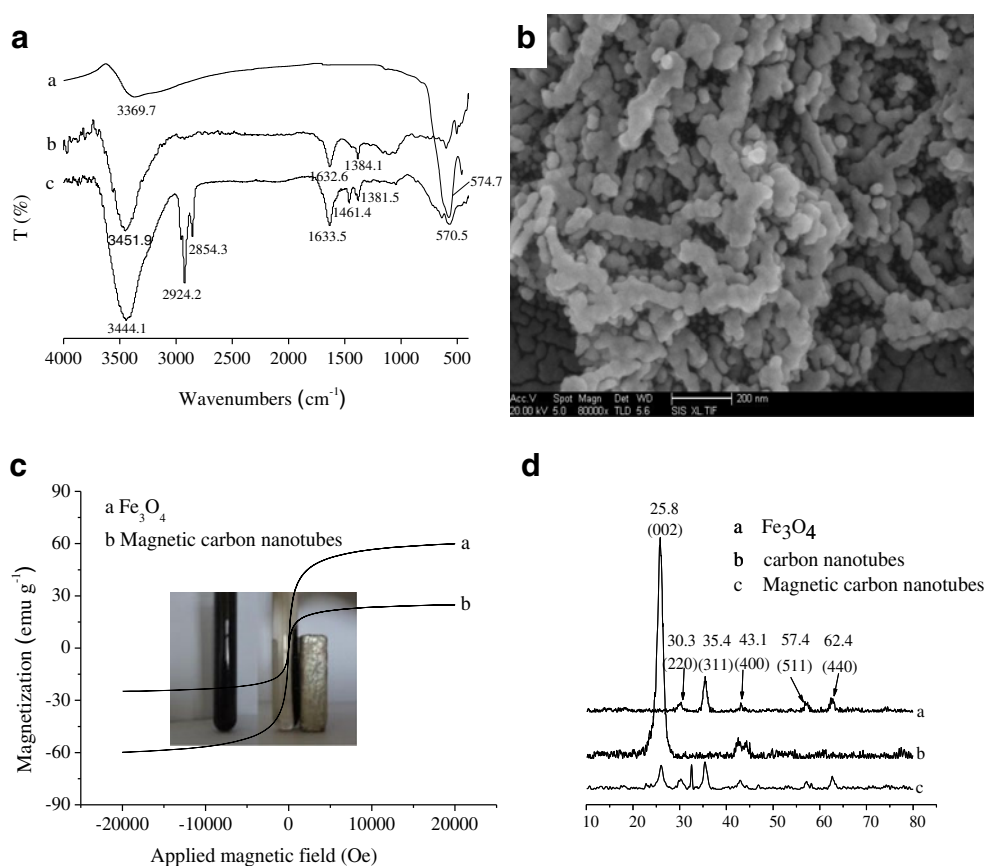
corresponding to complete monolayer coverage on the surface ($mg\,g^{-1}$), q_e is the adsorbate concentration in equilibrium ($mg\,g^{-1}$) and K_L is the Langmuir constant ($L\,mg^{-1}$). Langmuir isotherm analysis curve is shown in Fig. S2B in the Supporting Information. By calculating, the results are as follows:

$$y = 0.296x + 0.0397 \qquad R^2 = 0.9989$$

$$q_m = 25.210 \text{ mg g}^{-1} \qquad K_L = 0.134 \text{ L mg}^{-1}.$$

The Freundlich equation is given in the following equation:

$$q_e = K_F c_e^{1/n} \tag{3}$$

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln c_e \tag{4}$$

where c_e is the concentration of beta-cyfluthrin at equilibrium ($mg\,L^{-1}$), q_e the adsorbate concentration in equilibrium ($mg\,g^{-1}$) and K_F ($mg\,g^{-1}$) is an indicative constant for adsorption capacity of the adsorbent and $1/n$, ranging between 0 and 1, measures the adsorption intensity or

surface heterogeneity [27]. Freundlich isotherm analysis curve is shown in Fig. S2C in the Supporting Information. By calculating, the results are as follows:

$$y = 0.556x + 0.882 \qquad R^2 = 0.956$$

$$1/n = 0.556 \qquad K_f = 2.416 \text{ mg g}^{-1}.$$

It can be observed that the Langmuir isotherm model yielded a better fit than that of the Freundlich isotherm model, for the correlation coefficients (R^2) is above 0.99. The adsorption capacity of magnetic carbon nanotubes was 25.210 mgg^{-1}.

Adsorption kinetics

In order to investigate the mechanism of adsorption, kinetic study which controls the process efficiency is generally used to test experimental data [28]. The effect of contact time on the adsorption of beta-cyfluthrin by magnetic carbon nanotubes is described in Fig. S3 in the Supporting Information. The beta-cyfluthrin reached adsorption equilibrium in a short time. It provided the possibility of a rapid adsorption of pyrethroids in tea sample solution. In this study, the pseudo-first-order and pseudo-second-order were applied to investigate the controlling mechanism of the adsorption of beta-cyfluthrin [28].

The pseudo-first-order model is expressed as follows:

$$\log(q_{e1} - q_t) = \log q_{e1} - k_1 t \qquad (5)$$

where q_{e1} ($mg\,g^{-1}$) and q_t ($mg\,g^{-1}$) refer to the amount of beta-cyfluthrin adsorbed at equilibrium and any time t (min), respectively. k_1 (min^{-1}) is the rate constant of pseudo-first order which can be calculated from the plot of $\log(q_{e1} - q_t)$ versus t.

The pseudo- second -order model is expressed as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q^2_{e2}} + \frac{t}{q_{e2}} \qquad (6)$$

where q_{e2} is the theoretic adsorption capacity. k_2 ($g\,mg^{-1}\,min^{-1}$) is the rate constant of pseudo-second-order which can be calculated from the plot of t/q_t versus t.

As shown in the Table S1 in the Supporting Information, the correlation coefficient (R^2) for the pseudo-second-order adsorption model (0.9999) is higher than that of pseudo-first-order (0.9430), which demonstrated that the adsorption data are well represented by pseudo-second-order kinetic model.

Optimization of the conditions

The parameters affecting the performance of the extraction were investigated. When one factor was changed, the other factors were fixed at their optimal values. Recovery was used as criteria for optimization of the extraction conditions. The recovery was calculated as follows: recovery=(extracted amount of pyrethroids in tea/spiked amount of pyrethroids in tea)×100 %.

(a) The extraction solution: In this work, n-hexane, acetone, n-hexane-acetone (97.5: 2.5 v/v), n-hexane-acetone (50: 50 v/v) [3] were used as the extraction solution to extract the pyrethroids from the tea samples (Fig. S4A in the supporting information). Acetone led to the similar recoveries to n-hexane, but a lot of pigment contained in tea samples will be extracted at the same time with acetone. So in this work, n-hexane was selected as the extraction solution.

(b) The amount of magnetic carbon nanotubes: During the extraction procedure, the magnetic carbon nanotubes were dispersed in n-hexane to rebind analytes. The necessary minimum amount of sorbent getting efficient recovery was investigated. Different amounts of magnetic sorbent ranging from 10 to 50 mg were applied to 10 mL tea sample (Fig. S4B in the supporting information). It was found that 40 mg of sorbent enabled satisfied recovery of the pyrethroids.

After each extraction, the sorbent was easily recovered by the magnetic separation. Recycling experiments showed the performance of the magnetic carbon nanotubes was good. Recoveries of three pyrethroids were almost always greater than 81.4 % even when the magnetic carbon nanotubes had been used up to five binding–removal cycles. No obvious decrease in adsorption capacity was observed, suggesting that adsorbability of the magnetic carbon nanotubes for three pyrethroids was specific and stable for complex samples.

(c) Shaking rate: The effect of shaking rate on pyrethroids adsorption is shown in Fig. S4C in the supporting information. The pyrethroids adsorption percent was noticed to increase with increasing shaking rate from 0 to 200 rpm, the maximum recoveries were obtained at 200 rpm. Thus, 200 rpm was selected as the optimum rate for the subsequent adsorption experiment.

(d) Shaking time: The experimental results indicated that the shaking time had an effect on the target analytes adsorption. The adsorption of pyrethroids must have enough time to approach equilibrium to obtain satisfactory recoveries. Fifteen minutes was sufficient to achieve satisfactory adsorption with the pyrethroids recoveries in the range of 88.4–94.3 % (Fig. S4D in the supporting information).

(e) Washing solution: Due to the tea samples contain complex matrix components, a washing step is required to remove the interfering compounds from sample matrixes without desorbing the target analytes. Different

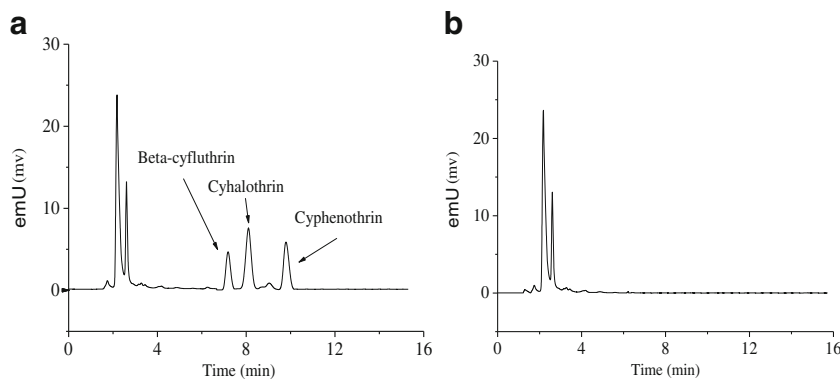Fig. 2 Liquid chromatograms of spiked tea (a) and blank tea (b)

Table 1 The Linearity range, limit of detection and limit of quantification of pyrethroids

Pyrethroids	Linearity range ($\mu g g^{-1}$)	R^2	LOD ($\mu g g^{-1}$)	LOQ ($\mu g g^{-1}$)	Within-day precision RSD (%)	Between-day precision RSD (%)
Beta-cyfluthrin	0.050–25	0.999	0.017	0.056	5.6	4.9
Cyhalothrin	0.050–25	0.999	0.010	0.033	3.5	4.5
Cyphenothrin	0.050–25	0.999	0.018	0.059	6.4	7.3

percentages of methanol aqueous solutions were used as the washing solutions. There was little difference in the pyrethroids recoveries after washing when the percentage of methanol in the washing solutions was in the range of 1 %–5 %. The recoveries of pyrethroids decreased with further increased methanol in the washing solution. In this study, 2 mL 5 % aqueous methanol was used as washing solution.

(f) Eluting solution: In order to obtain the highest recoveries of pyrethroids, a series of eluting solutions, including methanol, acetonitrile, acidified methanol and acidified acetonitrile were used to optimize eluting solution (Fig. S4E in the supporting information). The lower recoveries (65.6 %–69.9 %) and (80.4 %–85.8 %) were found by using methanol and acetonitrile, respectively. The best recoveries (88.0 %–94.4 %) were obtained using 3×1.0 mL of acetonitrile-acetic acid (95:5, v/v) as eluting solution.

Method validation

The chromatographic identification of the pyrethroids was realized by their relative retention time. No interfering peaks and false positive results were observed in the blank chromatogram (Fig. 2). Calibration curves were obtained by plotting the peak-area of the studied analytes versus the theoretical concentration of the analytes added into tea samples. The linearity obtained was in the range of 0.05–25 $\mu g g^{-1}$ (Table 1).

The sensitivity of the method was expressed by the limit of detection (LOD) and limit of quantification (LOQ) [29]. LOD and LOQ are considered as the minimum concentrations of analytes that can be confidently identified and quantified by the method, respectively. The LODs defined as the concentration providing a signal-to-noise of three

were 0.017, 0.010 and 0.018 $\mu g g^{-1}$ for beta-cyfluthrin, cyhalothrin and cyphenothrin, respectively. The LOQs defined as the concentration providing a signal-to-noise of ten were 0.056, 0.033 and 0.059 $\mu g g^{-1}$ for beta-cyfluthrin, cyhalothrin and cyphenothrin, respectively. The maximum residue limit (MRL) of 0.5 $\mu g g^{-1}$ pyrethroids was established by the European Union Commission [30]. As the LOQs were lower than the MRL, this method was suitable for the analysis of pyrethroid residues in tea samples.

The within- and between-day precisions and accuracies of the assay were analyzed. For the within-day assay precision and accuracy, six replicates of quality control samples were analyzed in the same day at three different fortified concentrations of 0.05, 0.5, and 5 $\mu g g^{-1}$. For the between-day assay precision and accuracy, control samples were analyzed once a day for six sequence days at three different fortified concentrations of 0.05, 0.5, and 5 $\mu g g^{-1}$. RSDs of within- and between-day ranging from 3.5 % to 6.4 % and from 4.5 % to 7.3 % were obtained, respectively. In all three fortified levels, recoveries of pyrethroids were in the range of 82.2 %–94.4 %.

This method was compared with other methods used in the literatures [2, 31, 32] for the analysis of pyrethroids in tea sample. The results were presented in Table 2 and indicated that this method provided similar recovery, RSD and LOD. The magnetic separation technique was applied in our method, and the experimental time and consumption of solvent was decreased.

Application to real samples

Three tea samples were detected by this method. In one sample (the green tea), beta-cyfluthrin was found at the concentration of 0.507 $\mu g g^{-1}$. The recoveries of pyrethroids studied with the standard addition in the real sample by

Table 2 Comparison of this method with other methods used in the literatures

Sample preparation	Detection	LOD ($\mu g g^{-1}$)	Recovery (%)	RSD (%)	Reference
Solid-phase extraction with cleanert TPT colum	UPLC-MS	0.009	76.1–96.4	2.7–12.9	[2]
Gel permeation chromatography clean-up	GC-MS	0.012–2.45	59.7–120.9	3.0–20.8	[31]
Matrix solid-phase dispersion	GC-MS	0.005–0.06	83±3	<7	[32]
Magnetic carbon nanotubes separation	HPLC-UV	0.010–0.018	82.2–94.4	3.5–6.4	This method

analyzing the spiked samples under the optimal conditions. The level of pyrethroids added into the samples was 0.5 $\mu g\,g^{-1}$. The following steps were according to the procedure described in experimental. The recoveries of pyrethroids obtained were 86.2 %±3.9 %, which indicated good accuracy of the method.

Conclusion

Magnetic carbon nanotubes were obtained and characterized by FT-IR, scanning electron microscope, X-Ray diffraction and physical property measurement system. The magnetic material was used for adsorbing pyrethroids. The adsorption equilibrium data was described by the Langmuir isotherm well and the adsorption kinetics followed the mechanism of the pseudo-second-order. The pyrethroids extracted from tea sample solution were analyzed by liquid chromatography. This method presented significant advantages such as low cost of organic solvents and simple handling. This work improved the knowledge about the relationships between magnetic carbon nanotubes and pyrethroids. Additionally, the magnetic carbon nanotubes which were endowed with high magnetic properties, large adsorption surfaces, and well adsorption capacities are ideal vehicle for loading pyrethroids and could be extended to the adsorption of other pesticides from complex sample matrix.

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