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Magnetic solid-phase extraction of five pyrethroids from environmental water samples followed by ultrafast liquid chromatography analysis

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ABSTRACT

In this study, the polystyrene-coated magnetic nanoparticles (MNPs/PSt) were successfully prepared and characterized by Fourier transform infrared spectroscopy, transmission electron microscopy and vibrating sample magnetometry. The as-prepared MNPs/PSt were used as the adsorbent in magnetic solid phase extraction of five pyrethroids, including lambda-cyhalothrin, deltamethrin, esfenvalerate, permethrin, bifenthrin, in environmental water samples. The five pyrethroids were determined by ultra fast liquid chromatography-ultraviolet spectrometry. The influencing factors, including amount of MNPs/Pst, extraction time, pH value, type and volume of desorption solvent and desorption time, were examined and optimized. The extraction recoveries obtained with merely 50 mg of MNPs/Pst were very satisfactory. The whole extraction process could be completed within 0.5 h. The MNPs/PSt can be reused after an easy washing process. Thus, a simple, green, economical, time saving and effective method for pyrethroids analysis in environmental water samples was established. A high enrichment factor of 500 was achieved and the limits of detection for lambda-cyhalothrin, deltamethrin, esfenvalerate, permethrin, bifenthrin were 0.015 ± 0.001 ng mL^{-1}, 0.012 ± 0.001 ng mL^{-1}, 0.026 ± 0.001 ng mL^{-1}, 0.020 ± 0.001 ng mL^{-1}, 0.013 ± 0.001 ng mL^{-1}, respectively. Recoveries obtained by analyzing spiked water samples at three concentration levels (0.100 ± 0.001 ng mL^{-1}, 1.000 ± 0.001 ng mL^{-1}, 10.000 ± 0.001 ng mL^{-1}) were between $78.97 \pm 8.38\%$ and $96.05 \pm 8.38\%$. The standard curves for the five pyrethroids showed good linearity with the correlation coefficients in the range of 0.9994–0.9999. The intra-day and inter-day precision were satisfactory with the RSDs in the range of 2.05–5.52% and 2.73–8.38%, respectively.

1. Introduction

The monitoring and control of environmental water hygiene status is always of great importance to human beings, especially when there are various kinds of pollutants from agriculture, industry and daily activities of people in the modern world [1]. Many permission standards were set up to make sure that human and animals have safe and clean water for themselves as well as their future generations. Effective and sensitive analytical methods play an important role in the implementation of these ruling standards [2,3]. In recent years, scientists have made tremendous efforts to develop various sample pretreatment and analytical methods for environmental waters, including solid-phase extraction combined with capillary liquid chromatography tandem mass spectrometry [4], ionic liquid dispersive liquid–liquid microextraction coupled with high performance liquid chromatography [5], ultrasound-assisted emulsification–extraction coupled with gas chromatography-mass spectrometry [6]. Since the concentration levels of pollutants in environmental waters are usually very low, novel sample pretreatment methods with high enrichment factors are distinctly important.

Pyrethroids are a large group of synthetic insecticides based on the structure and properties of the pyrethrins naturally occurred in *Chrysanthemum cinerariaefolium* [7]. They have some notable advantages such as high killing activity, rapid knock down activity, vapor action at room temperature and photostability [8]. Meanwhile, they successfully retained other desirable qualities of pyrethrins such as low mammal toxicity and quick degradation in environment [9,10]. The U.S. Environmental Protection Agency (EPA) has granted 18 pyrethroid substances for application in the United States (Linda Arrington, EPA, 2003, personal communication) [11]. And pyrethroids are embracing an escalated use for agriculture, public health and household insect control instead of conventional organophosphate and organochlorine pesticides. Nowadays, they are widely used to protect crops and prevent transmission of vector-borne diseases in homes [12]. People are now utilizing various kinds of pyrethroids for treating bed nets, window curtains, military uniforms, recreational clothing and other items for pest and vector control. Considering the above

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reasons, pyrethroids can easily enter environmental water system from irrigation, laundry, rain and many other ways. Since there are still some inevitable adverse effects of pyrethroids, such as inducing teratogenicity, carcinogenicity and mutagenicity, fast and accurate detection of pyrethroids in environmental waters is necessary in order to guarantee our safety and health [13].

As a promising sample pretreatment technique, magnetic solid phase extraction (MSPE) has caught much attention recently [14]. MSPE avoid the high consumption of organic solvents in the conventional liquid-liquid extraction. Moreover, most magnetic nanoparticles (MNPs) can be readily recycled by a simple washing operation, which makes the method environmentally friendly and economical [15,16]. At the same time, with the outstanding advantage of convenient phase separation by an applied magnetic field, MSPE is an excellent alternative of the ordinary time-consuming solid-phase extraction and micro solid-phase extraction. The latter two methods tend to take much more operation time due to limited rate of diffusion and mass transfer of the analytes [17]. Because MSPE has the above advantages, many scientists are working on the preparation of novel MNPs [18–21]. Currently, considerable attentions are paid to the exploitation of various polymer-coated MNPs because they have plentiful functional groups for adsorption [22–25]. Besides, different types of polymer coating endow the MNPs with a diversity of adsorptive selectivity, which makes them become excellent candidates for MSPE. The polymer coating also provides the MNPs with protection from oxidization and coagulation so that the MNPs are stable and will not lose their magnetism easily. The polystyrene-coated magnetic nanoparticles (MNP/PSt) with superparamagnetism were synthesized by An et al. in 2005 [26]. However, relevent studies mainly focused on the surface modification and characterization of the nanoparticles, and few attempts were made for their MSPE application. Considering that polystyrene is the main bonding group of silica packing HPLC phenyl columns, which are known for their exceeding advantages in the separation of various compounds with high proportion of π-conjugated structures, the MNPs/PSt are very likely to be proper adsorbents for the MSPE.

Some other methods have been established for determining pyrethroids such as gas chromatography–mass spectrometry (GC–MS) [27], gas chromatography-electron-capture detection (GC-ECD) [28], gas chromatography–mass spectrometry in negative chemical ionization (GC–NCI–MS) [29], liquid chromatography-heated electrospray ionization tandem mass spectrometry (LC–HESI-MS/MS) and liquid chromatography–electrospray mass spectrometry (LC–ESI-MS) [30,31]. However, there are very few reports on ultra fast liquid chromatography–ultraviolet spectrometry (UFLC–UV) for determining pyrethroids. In this study, the MNPs/PSt were prepared and successfully used as MSPE adsorbents for extracting pyrethroids in water sample. The determination of the pyrethroids was carried out by UFLC–UV.

2. Experimental

2.1. Chemicals

Lambda-cyhalothrin, deltamethrin, and esfenvalerate were purchased from National Research Center for Certified Reference (NRCCR, China), and permethrin, bifenthrin were obtained from National Institute of Metrology (NIM, China). The purity of the pyrethroids is $\geq$99.6% (w/w). Chemical information of the compounds is shown in Table 1. Stock solution of each standard was prepared by dissolving the pure substances in HPLC-grade acetonitrile at a concentration level of 0.500 ± 0.001 mg mL^{-1} and stored at 4 °C in darkness. Results of preliminary experiments indicated that the stock solutions were kept stable for at least three months. The mixed working standard solutions at desirable concentration levels were freshly prepared by diluting the 0.500 ± 0.001 mg mL^{-1} standard stock solutions with HPLC-grade acetonitrile.

Fenuron, chlorotoluron, prometon, sulfadimethoxine, sulfamethoxazole, sulfathiozole and sodium chloride polybenzoxazines standards were obtained from National Institute for the Control of Pharmaceutical and Biological Products (Beijing, China). The purity of these standards is $\geq$99.0% (w/w) and they were used to verify the selectivity of the MNP/PSt.

HPLC-grade methanol and acetonitrile were purchased from Fisher, USA. Analytical-grade ferric chloride ($FeCl_3 \cdot 6H_2O$), ferrous chloride ($FeCl_2 \cdot 4H_2O$) and oleic acid were supplied by Guangfu Fine Chemical Research Institute (Tianjin, China). Chemical pure Styrene (St) was purchased from Xilong Chemical Reagent Works (Shantou, China) and purified through reduced-pressure distillation before used. Analytical-grade potassium peroxydisulfate (KPS) was bought from Huadong Chemical Works (Tianjin, China). Nanjing Chemical Reagent Co. Ltd (Nanjing, China) supplied analytical-grade sodium dodecyl benzene sulfonate (SDBS). Analytical-grade ammonia, hydrochloric acid, methacrylic acid (MA), ethanol, acetone, petroleum ether and methanol were obtained from Beijing Chemical Works (Beijing, China).

Deionized water was prepared with Milli-Q water purification system (Millipore, USA). It was checked to be free of any target compounds and was used to prepare blank and spiked water samples for purposes of optimization, calibration and validation.

2.2. Water samples

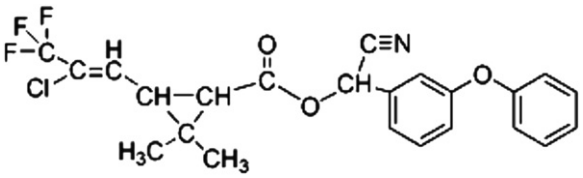
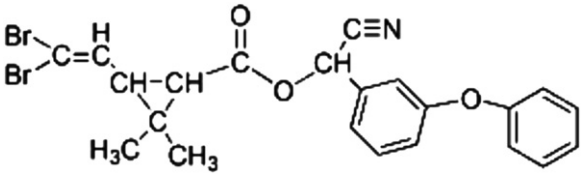
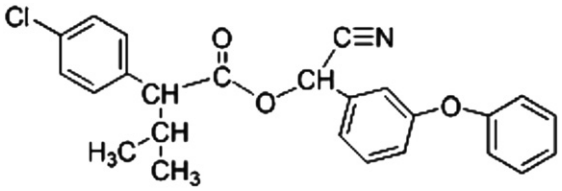
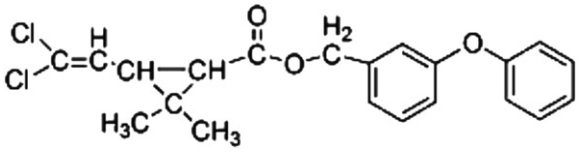
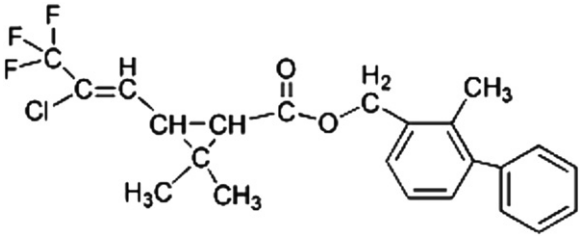
Five kinds of environmental water samples were collected for validating the proposed method, including river water, lake water, tap water, melted snow and reservoir water. River water and reservoir water were acquired from Hun River and Dahuofang Reservoir in Liaoning province, China, respectively. Lake water and melted snow water was obtained from Nanhu Lake and Jilin University in Jilin province, China, respectively. Tap water was taken from our own laboratory. These environmental water samples were filtered through 0.45 μm micro-pore membranes and stored in glass containers at 4 °C in darkness before used.

2.3. Preparation of polystyrene-coated magnetite nanoparticles

The Fe_3O_4 MNPs coated with bilayer surfactants of oleic acid and sodium dodecyl benzene sulfonate (SDBS) were prepared according to a modified coprecipitation method. 1.0 g $FeCl_2 \cdot 4H_2O$, 2.6 g $FeCl_3 \cdot 6H_2O$ and 425 μl of 12 mol L^{-1} HCl were dissolved in 12.5 mL of deionized water. This mixture was added dropwise through a dropping funnel into a four-neck flask containing 125 mL of 1.5 mol L^{-1} NaOH solution and 1 mL oleic acid. The four-neck flask was placed in an 80 °C water bath during the reaction and the solution was kept stirred vigorously with a nitrogen current. After 1 h, the obtained oleic-coated magnetite precipitate was separated from the reaction medium by magnetic decantation and washed with deionized water for several times. Then this magnetite was dispersed in 100 mL of 0.007 mol L^{-1} SDBS solution and stirred for 30 min with nitrogen gas passing through the solution. After that, Fe_3O_4 MNPs coated with bilayer surfactants of oleic acid and sodium dodecyl benzene sulfonate were obtained. These MNPs were separated with a permanent magnet and washed up with deionized water.

The preparation of MNPs/PSt was carried out by emulsion polymerization [26]. Newly prepared Fe_3O_4 MNPs coated with bilayer surfactants were dispersed in 100 mL deionized water. 6 mL styrene (St) and 0.6 mL methacrylic acid (MA) were added and the mixture was stirred continuously with a nitrogen current.

Table 1
Chemical information of the pyrethroids.

Compounds	Structure	Chemical formula	Molecular weight
Lamda-cyhalothrin		$C_{23}H_{19}ClF_3NO_3$	449.85
Deltamethrin		$C_{22}H_{19}Br_2NO_3$	505.20
Esfenvalerate		$C_{25}H_{22}ClNO_3$	419.90
Permethrin		$C_{21}H_{20}Cl_2O_3$	391.29
Bifenthrin		$C_{23}H_{22}ClF_3O_2$	422.87

The reaction system was heated to 70 °C through water bath. Then 0.1 g of KPS was added to initiate the polymerization. The reaction proceeded overnight under continuous stirring with nitrogen current. The resulting MNPs/PSt were washed with deionized water and ethanol in turn and separated by magnetic decantation. Then the MNPs/PSt were dried in a vacuum oven at 60 °C for 24 h.

A Hitachi H-800 transmission electron microscope (Hitachi, Japan) was used to observe the morphology and particle size of the materials. FT-IR was performed on a Nicolet FT-IR 360 spectrometer (Nicolet, USA). A MPMS (SQUID) VSM Vibrating sample magnetometer (Quantum Design, USA) was used to study the magnetic properties of the MNPs/PSt.

2.4. MSPE procedure

Under optimized conditions, real sample analysis was carried out. 100 mL of water sample was adjusted to pH 4 with phosphate buffer, and placed in a 250 mL conical flask. 50 mg of MNPs/PSt were added into the flask. The mixture was stirred for 20 min. Then the solution was decanted with a permanent magnet on the wall of the conical flask. The pyrethroids were eluted with a vortex agitator from the MNPs/PSt with 3 mL acetonitrile. The eluate was evaporated to dryness with mild nitrogen stream at 40 °C, and the residues were dissolved in 200 μL acetonitrile. The resulting solution was placed in a 300 μL-insert, which was inserted in a 1.5 mL-vial for UFLC–UV analysis. After the MSPE, the MNPs/PSt were dried and recycled after ultrasonic cleaning with deionized water and methanol in turn.

2.5. UFLC–UV analysis

A UFLC–UV system (Shimadzu, Japan) equipped with two LC-20AD pumps, a SIL-20A automatic sample injector, a CTO-20A column oven and a SPD-20A UV–vis detector 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 isocratic LC condition was adopted for the separation and determination for the pyrethroids. The mobile phase consisted of acetonitrile/water (75: 25, v/v) and the flow rate was 0.3 mL min^{-1}. The column temperature was kept at 25 °C throughout the run. Injection volume was set at 3 μL. Monitoring wavelength was 210 nm for all the target compounds.

2.6. Validation

LODs and LOQs of the analytes were separately estimated as the lowest concentration generating a signal to noise ratio (S/N) of 3 and 10, respectively. Accuracy of the proposed method was tested by analyzing the spiked samples. The concentrations of the

analytes in the spiked samples are 0.100 ± 0.001, 1.000 ± 0.001 and 10.000 ± 0.001 ng mL^{-1}, respectively. Precision of the method was evaluated by measuring the intra-day and inter-day relative standard deviations (RSDs). The intra-day precision was obtained by analyzing spiked water samples six times in one day and the inter-day precision was determined by analyzing replicate water samples once a day in six successive days. Evaluation of linearty was carried out by calculating the correlation coefficients and plotting the residual values.

3. Results and discussion

3.1. Characterization of MNPs/PSt

The characterization of the MNPs/PSt was carried out based on FT-IR spectra, TEM images and maganetization curves of both the semi-product (MNPs) and the MNPs/PSt.

To ascertain the formation of polystyrene layer on the MNPs, FT-IR spectra of the MNPs/PSt and the MNPs were obtained. Fig. 1 exhibits these spectra. The FT-IR spectrum of the MNPs shows typical Fe–O–Fe absorption bands at 560 cm^{-1} and weak absorption bands around 1600 cm^{-1} and 1400 cm^{-1} owing to the oleic acid and SDBS modification. While in the FT-IR spectrum of the MNPs/PSt, the bands at 3030–2800 cm^{-1}, 1600 cm^{-1}, 1400–1000 cm^{-1} and 700 cm^{-1} are well consistent with the standard FT-IR spectrum of polystyrene, which can be attributed to stretching vibration of C–H in benzene aromatics, C–C ring stretching vibration of the benzene rings and C–H out-plane vibration of monosubstituted benzene, respectively. Meanwhile, the absorption peak at 1700 cm^{-1} is assigned to stretching vibration of C=O in methacrylic acid. The absorption peak at 560 cm^{-1} confirms the existence of Fe_3O_4 in the nanocomposite. The experimental results suggested that a polystyrene layer had been successfully grafted on the Fe_3O_4 nanoparticles through bilayer surfactants.

Fig. 2 displays the TEM images of MNPs and MNPs/PSt. As is shown in Fig. 2a, MNPs consist of monodisperse and sphere-like nanoparticles with a mean size of around 8–10 nm. In Fig. 2b, the MNPs/PSt exhibits no significant changes in diameter compared with MNPs, which implies that the PSt coating is very thin.

Typical room temperature magnetic curves of MNPs and MNPs/PSt are shown in Fig. 3. Neither of the magnetic curves has hysteresis loop, indicating that they are both supermagnetic. Moreover, satisfactory magnetic property of MNPs/PSt is proved with saturation magnetization of 38.82 emu g^{-1}, which is

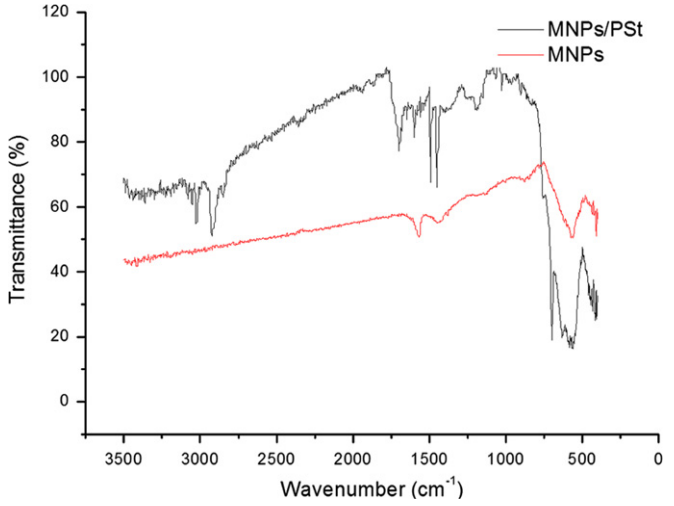


Fig. 1. FT-IR spectra of MNPs and MNPs/PSt.

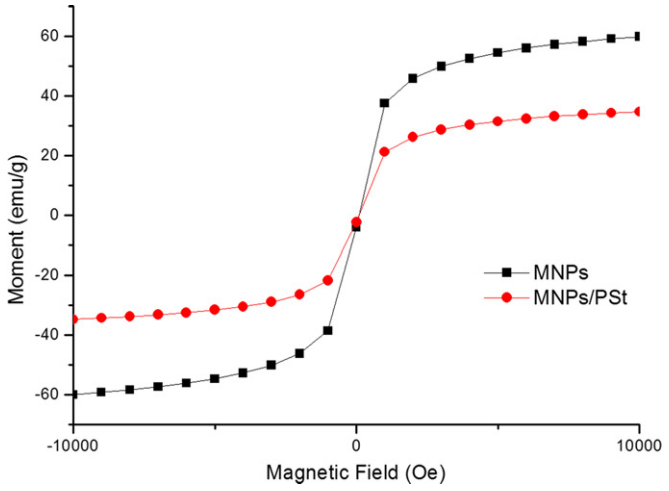


Fig. 3. Magnetization curves of MNPs and MNPs/PSt.

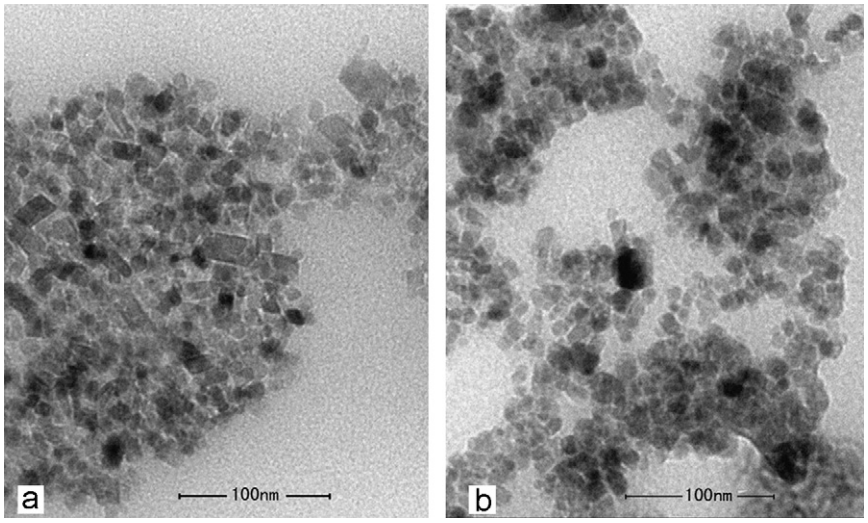


Fig. 2. TEM images of MNPs (a) and MNPs/PSt (b).

obviously lower than that of MNPs (66.81 emu g^{-1}), implying the existence of a significant amount of PSt in MNPs/PSt.

3.2. Optimization of conditions for MSPE

In this study, the following six major influencing parameters were optimized in order to evaluate the feasibility of the method and improve it for further practical application. Spiked water samples at a concentration level of 0.800 ± 0.001 ng mL^{-1} were employed for experimental optimization and each experiment was conducted three times to ensure veracity. Once a parameter was optimized, it was set at its optimal value in subsequent experiments. Analysis of variance (ANOVA) was performed in order to evaluate the statistical significance of the differences among treatment during the optimization process [32]. The results indicated that all the six factors are highly influential in the MSPE procedure.

3.2.1. Amount of MNPs/PSt

In order to achieve good recovery, different amounts of MNPs/PSt ranging from 10 mg to 90 mg were used. As can be concluded from Table 2, the effect of the amount of the MNPs/PSt on the recoveries is significant and the recoveries achieved by 50 mg MNPs/PSt are the highest. This can be attributed to a comprehension influence of the total specific surface area of the MNPs/PSt and their dispersibility in the water sample. Thus, 50 mg was employed as the amount of MNPs/PSt in the following experiments.

3.2.2. Extraction time

The optimization of extraction time was conducted by increasing the stirring time from 5 min to 40 min. It can be seen from Table 3 that extraction time has an obvious effect on the recoveries of the target compounds. The results show that the recoveries increase with the increase of the extraction time shorter than 20 min, and slightly changed when the extraction time is longer than 20 min. Accordingly, the extraction time was fixed at 20 min.

3.2.3. Desorption solvent

The type of solvent is a vital factor that affects desorption efficiency. However, the polystyrene coating of the MNPs/PSt tends to dissolve or swell in certain kinds of organic solvents. MNPs/PSt were immersed in different kinds of organic solvents for 30 min to check their dissolvability before they were used as desorption solvents. Suitable candidates were selected and employed for desorption of pytrthroids from MNPs/PSt, including acetone, methanol, acetonitrile and petroleum ether. As is obviously shown in Table 4, the effect of the nature of desorption solvent on the recoveries is very significant and recoveries obtained with acetonitrile are the highest. Thus, acetonitrile was chosen as the desorption solvent.

3.2.4. Volume of desorption solvent

The influence of the volume of desorption solvent was studied. The results in Table 5 indicate that the recoveries of the pyrethroids increase with the increase of the volume of desorption solvent, and the increase of the recoveries are not significant when the volume is larger than 3 mL. Accordingly, 3 mL was selected as the volume of desorption solvent for subsequent experiments.

3.2.5. pH value of the water samples

The pH value of the samples plays an important role in the analysis of organic compounds, and is a major factor affecting their extraction performance. The stability of pyrethroids is related to pH value. Most pyrethroids tend to hydrolyze in alkaline environment. Since the MNPs/PSt are not stable when pH value is below 4, the effect of pH value was evaluated in the range of 4–9. Table 6 displays the results clearly. It is obvious that the effect of the pH value of the water samples on the recoveries is significant. The recoveries of pyrethroids increase with the

Table 2
Effect of the amount of MNPs/PSt.

Level (mg)	Lambda-cyhalothrin			Deltamethrin			Esfenvalerate			Permethrin			Bifenthrin			Critical value $F_{h-1,\ N-h\ (P=0.05)}$
	Recovery (%)	RSD (%)	F	Recovery (%)	RSD (%)	F	Recovery (%)	RSD (%)	F	Recovery (%)	RSD (%)	F	Recovery (%)	RSD (%)	F	
10	63.48	3.17	71.62	65.30	3.27	63.64	61.29	3.06	96.36	65.79	3.29	106.96	58.24	2.91	134.80	$F_{4,\ 10\ (P=0.05)}=3.478$
30	84.14	4.21		82.84	4.14		78.18	3.91		93.62	4.68		88.24	4.41		
50	88.24	4.41		89.36	4.47		85.68	4.28		95.05	4.75		89.94	4.50		
70	84.99	4.25		85.64	4.28		91.23	4.56		85.38	4.27		90.30	4.52		
90	79.96	4.00		79.80	4.00		79.49	3.97		77.05	3.85		82.52	4.13		

Note: extraction time, 30 min; type of desorption solvent, acetonitrile; volume of desorption solvent, 4.0 mL; sample pH, 4; desorption time, 3.0 min.

Table 3
Effect of the extraction time.

Level (min)	Lambda-cyhalothrin			Deltamethrin			Esfenvalerate			Permethrin			Bifenthrin			Critical value $F_{h-1,\ N-h\ (P=0.05)}$
	Recovery (%)	RSD (%)	F	Recovery (%)	RSD (%)	F	Recovery (%)	RSD (%)	F	Recovery (%)	RSD (%)	F	Recovery (%)	RSD (%)	F	
5	54.40	2.72	222.67	66.08	3.30	144.04	58.27	2.91	115.99	92.22	4.61	1.59	61.26	3.06	120.88	$F_{4,\ 10\ (P=0.05)}=3.478$
10	61.74	3.09		65.21	3.26		72.08	3.60		93.61	4.68		70.06	3.50		
20	84.85	4.24		88.26	4.41		85.84	4.29		95.09	4.75		85.32	4.27		
30	89.22	4.46		90.37	4.51		85.55	4.28		95.20	4.76		88.28	4.14		
40	90.39	4.52		93.74	4.68		85.58	4.28		91.80	4.59		89.30	4.47		

Note: amount of MNPs/PSt, 50 mg; type of desorption solvent, acetonitrile; volume of desorption solvent, 4.0 mL; sample pH, 4; desorption time 3.0 min.

Table 4
Effect of the type of desorption solvent.

Level	Lambda-cyhalothrin			Deltamethrin			Esfenvalerate			Permethrin			Bifenthrin			Critical value
	Recovery (%)	RSD (%)	F	Recovery (%)	RSD (%)	F	Recovery (%)	RSD (%)	F	Recovery (%)	RSD (%)	F	Recovery (%)	RSD (%)	F	$F_{h-1,\ N-h\ (P=0.05)}$
Acetone	84.19	4.21		84.53	4.23		58.23	2.91		67.50	3.38		77.24	3.86		
Methanol	83.38	4.17		85.38	4.27		71.50	3.58		72.48	3.62		98.04	4.90		
Acetonitrile	91.20	3.71	775.03	90.59	4.53	750.62	95.13	4.76	984.18	83.58	4.18	510.84	84.21	4.21	522.08	$F_{3,\ 8\ (P=0.05)=4.066}$
Petroleum ether	27.68	1.38		27.09	1.35		19.48	0.97		30.04	1.50		38.60	1.93		

Note: amount of MNPs/PSt, 50 mg; extraction time, 20 min; volume of desorption solvent, 4.0 mL; sample pH, 4; desorption time, 3.0 min.

Table 5
Effect of the volume of desorption solvent.

Level (mL)	Lambda-cyhalothrin			Deltamethrin			Esfenvalerate			Permethrin			Bifenthrin			Critical value
	Recovery (%)	RSD (%)	F	Recovery (%)	RSD (%)	F	Recovery (%)	RSD (%)	F	Recovery (%)	RSD (%)	F	Recovery (%)	RSD (%)	F	$F_{h-1,\ N-h\ (P=0.05)}$
1.0	79.80	3.99		68.52	3.43		68.42	3.42		58.95	2.95		61.90	3.10		
1.5	86.14	4.31		75.68	3.78		80.27	4.01		77.50	3.88		81.19	4.06		
2.0	87.32	4.37	43.38	84.06	4.20	99.00	87.55	4.38	66.54	84.41	4.22	137.36	82.38	4.01	146.46	$F_{5,\ 12\ (P=0.05)=3.106}$
2.5	98.64	4.93		94.89	4.74		92.23	4.61		83.16	4.16		99.41	4.97		
3.0	99.83	4.99		95.20	4.76		93.75	4.69		93.18	4.66		98.89	4.94		
4.0	96.71	4.84		97.38	4.87		91.71	4.59		98.24	4.91		95.53	4.78		

Note: amount of MNPs/PSt, 50 mg; extraction time, 20 min; type of desorption solvent, acetonitrile; sample pH, 4; desorption time 3.0 min.

Table 6
Effect of the pH value of the water samples.

Level	Lambda-cyhalothrin			Deltamethrin			Esfenvalerate			Permethrin			Bifenthrin			Critical value
	Recovery (%)	RSD (%)	F	Recovery (%)	RSD (%)	F	Recovery (%)	RSD (%)	F	Recovery (%)	RSD (%)	F	Recovery (%)	RSD (%)	F	$F_{h-1,\ N-h\ (P=0.05)}$
3	91.44	4.57		97.92	4.90		70.11	3.51		81.16	3.56		78.61	3.93		
4	81.54	4.08		87.50	4.38		70.52	3.53		82.03	4.10		75.05	3.75		
5	81.03	4.05	739.86	63.51	3.18	630.20	72.56	3.63	373.61	81.03	4.05	14.90	62.13	3.10	113.41	$F_{5,\ 12\ (P=0.05)=3.106}$
6	54.34	2.72		48.03	2.41		54.86	2.74		81.27	4.06		55.99	2.80		
7	32.17	0.61		39.48	1.97		36.92	1.35		70.61	3.53		55.25	2.76		
8	29.72	1.49		36.96	1.85		30.68	1.53		81.25	4.06		52.30	3.12		

Note: amount of MNPs/PSt, 50 mg; extraction time, 20 min; type of desorption solvent, acetonitrile; volume of desorption solvent, 3.0 mL; desorption time, 3.0 min.

Table 7
Effect of the desorption time.

Level (min)	Lambda-cyhalothrin			Deltamethrin			Esfenvalerate			Permethrin			Bifenthrin			Critical value
	Recovery (%)	RSD (%)	F	Recovery (%)	RSD (%)	F	Recovery (%)	RSD (%)	F	Recovery (%)	RSD (%)	F	Recovery (%)	RSD (%)	F	$F_{h-1,\ N-h\ (P=0.05)}$
0.5	83.70	4.69		81.46	4.07		78.40	3.92		90.16	4.51		68.99	3.45		
1.0	94.62	4.73		86.02	4.30		77.66	3.88		96.69	4.83		71.41	3.57		
3.0	94.45	4.72	13.58	92.19	4.61	14.25	96.40	4.82	56.02	97.40	4.87	19.69	76.39	3.82	7.94	$F_{4,\ 10\ (P=0.05)=3.478}$
5.0	93.86	4.69		92.26	4.37		94.02	4.70		84.65	4.23		75.88	3.79		
7.0	91.65	4.58		87.33	4.43		93.12	4.91		88.84	3.94		72.49	3.62		

Note: amount of MNPs/PSt, 50 mg; extraction time, 20 min; type of desorption solvent, acetonitrile; volume of desorption solvent, 3.0 mL; sample pH, 4.

increase of pH value. Accordingly, pH value of sample was set at 4 in the following procedures.

3.2.6. Desorption time

As shown in Table 7, the effect of desorption time in the range of 0.5–7.0 min was investigated to improve extraction efficiency. No significant effect was observed when desorption time was longer than 3.0 min. Therefore, desorption time of 3.0 min was selected in subsequent experiments.

3.3. Reusability of the MNPs/PSt

In order to assess the reusability of the MNPs/PSt, 50 mg of MNPs/PSt were repeatedly used for 30 times. Recoveries obtained were displayed in Table 8. The MNPs/PSt were washed with 20 mL deionized water and 20 mL methanol in turn and thoroughly dried by a stream of nitrogen gas each time before reusing. Based on the results of ANOVA, there was no significant decrease in the recoveries of the analytes when the MNPs/PSt were reused.

Table 8
Reusibility of the MNPs/PSt. ($n=3$, spiked concentration level: 0.800 ± 0.001 ng mL^{-1}).

Number of the repeated use of the MNPs/PSt	Lambda-cyhalothrin			Deltamethrin			Esfenvalerate			Permethrin			Bifenthrin			Critical value
	Recovery (%)	RSD (%)	F	Recovery (%)	RSD (%)	F	Recovery (%)	RSD (%)	F	Recovery (%)	RSD (%)	F	Recovery (%)	RSD (%)	F	$F_{h-1,\ N-h}$ $(P=0.05)$
10	86.01	4.30		87.10	4.36		88.23	4.41		86.77	4.34		77.55	3.88		
15	83.88	4.19		92.90	4.65		89.94	4.50		86.33	4.32		77.64	3.88		
20	90.53	4.53	4.48	89.28	4.31	4.09	86.79	4.34	1.61	80.76	4.04	4.01	78.46	3.92	2.54	$F_{4,\ 10}$
25	86.28	4.31		91.92	4.60		88.51	4.43		84.48	4.22		81.60	4.08		$(P=0.05)=3.478$
30	88.53	4.43		92.51	4.63		90.75	4.54		85.07	4.25		80.60	4.03		

Note: amount of MNPs/PSt, 50 mg; extraction time, 20 min; type of desorption solvent, acetonitrile; volume of desorption solvent, 3.0 mL; sample pH, 4; desorption time, 3 min.

Table 9
Analytical performances.

Analytes	Linear range (ng mL^{-1})	Calibration equations	Correlation coefficient (r)	LOD (ng mL^{-1})	LOQ (ng mL^{-1})
Lamda-cyhalothrin	0.050–20.000	$y=35199x+4671.4$	0.9997	0.015	0.049
Deltamethrin	0.050–20.000	$y=28344x+4086.9$	0.9997	0.012	0.041
Esfenvalerate	0.100–20.000	$y=36576x+6304.4$	0.9994	0.026	0.087
Permethrin	0.050–20.000	$y=29866x+2597.3$	0.9996	0.020	0.068
Bifenthrin	0.050–20.000	$y=46129x-448.02$	0.9999	0.013	0.043

Table 10
The recoveries of the analytes and inter-day and intra-day precision.

Analytes	Added (ng mL^{-1})	Intra-day ($n=6$)		Inter-day ($n=6$)	
		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Lamda-cyhalothrin	0.100 ± 0.001	85.83	4.22	87.93	5.30
	1.000 ± 0.001	86.81	3.40	82.65	6.48
	10.000 ± 0.001	86.06	3.05	84.66	4.01
Deltamethrin	0.100 ± 0.001	86.43	3.03	88.79	2.98
	1.000 ± 0.001	94.03	4.76	88.98	8.38
	10.000 ± 0.001	93.46	5.52	85.91	6.38
Esfenvalerate	0.100 ± 0.001	88.94	2.03	87.94	5.54
	1.000 ± 0.001	90.36	3.05	96.05	3.40
	10.000 ± 0.001	85.85	4.31	85.80	4.56
Permethrin	0.100 ± 0.001	83.29	3.87	84.96	5.98
	1.000 ± 0.001	89.01	3.35	89.92	4.26
	10.000 ± 0.001	80.45	3.62	86.52	4.64
Bifenthrin	0.100 ± 0.001	78.97	3.56	81.02	4.52
	1.000 ± 0.001	86.18	2.57	80.36	4.15
	10.000 ± 0.001	80.60	3.31	86.49	6.92

3.4. Evaluation of the method performances

3.4.1. Linearity

The calibration curves of the five kinds of pyrethroids were constructed by plotting the peak area versus the concentration of standard solutions. Corresponding linear regression equations and correlation coefficients are listed in Table 9. The correlation coefficients are between 0.9996 and 0.9999, suggesting that the linearity is satisfactory in the linear range of the analytes. Residue plots were constructed and the residuals were randomly scattered within a horizontal band around the centre line, which indicates that the linear regression model well fits the data (The detailed information about residual analysis can be found in Suppl. Figs. S1–S5).

3.4.2. Limit of detection and limit of quantification

Limits of detection (LODs) and quantification (LOQs) are considered as the lowest concentration of a certain analyte for its confident identification and quantification, respectively. The results are shown in Table 9. The LODs of the pyrethroids are in the range of 0.012–0.026 ng mL^{-1}, and the LOQs are between 0.041 ng mL^{-1} and 0.087 ng mL^{-1}.

3.4.3. Recovery and precision

The intra-day and inter-day precision obtained are in the range of 2.03–5.52% and 2.98–8.38%, respectively. The detailed results are listed in Table 10.

3.4.4. Selectivity

The MNPs/PSt showed good selectivity for weakly polar compounds such as pyrethroids. As can be seen from the chromatogram of the mixed standard solution of the five target pyrethroids and seven other kinds of pollutants and the chromatogram of the extract of spiked water sample, only the five target pyrethroids were successfully extracted and detected with desirable recoveries, suggesting that the MNPs/PSt have good selectivity for these pyrethroids (Detailed information is shown in Suppl. Fig. S6). The resolutions of the peaks are high and range from 1.679 to 7.782.

3.4.5. Real water sample analysis

Five kinds of environmental water samples, including river water, lake water, tap water, melted snow and reservoir water were analyzed in order to validate the proposed method. Both blank and spiked samples were analyzed at the optimal conditions. No pyrethroids residues were detectable in all these five kinds of real water samples. Related data are listed in Table 11.

4. Conclusions

The MNP/PSt were successfully prepared and used as reusable adsorbent for MSPE of pyrethroids in environmental water samples. The MSPE coupled with UFLC–UV is a simple, selective and effective method for the determination of the pyrethroids. The analytical performances are satisfactory. The present method should be applied to the analysis of other samples by varying the extraction conditions.

Table 11
Real water sample analysis (mean ± SD, $n=3$, spiked concentration level: 0.800 ± 0.001 ng mL^{-1}).

Analytes	Recoveries (%)				
	River water	Lake water	Tap water	Melted snow	Reservoir water
Lamda-cyhalothrin	83.28 ± 1.94	81.11 ± 1.24	82.90 ± 3.90	89.71 ± 4.42	89.90 ± 5.60
Deltamethrin	90.80 ± 1.83	92.63 ± 7.32	84.56 ± 4.72	82.57 ± 4.43	86.90 ± 8.83
Esfenvalerate	91.39 ± 8.23	92.59 ± 8.12	91.84 ± 8.43	93.52 ± 2.72	81.28 ± 5.60
Permethrin	82.72 ± 3.72	81.19 ± 8.53	89.78 ± 5.84	90.48 ± 3.83	85.69 ± 7.72
Bifenthrin	80.94 ± 1.94	81.76 ± 1.21	84.44 ± 4.22	89.96 ± 5.23	87.66 ± 5.21

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2012.07.022.

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