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Paper

Development of field sampling method based on magnetic nanoparticles for enrichment of pesticides in aqueous sample

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A field sampling method based on magnetic core-shell silica nanoparticles was developed for field sampling and enrichment of low concentration pesticides in aqueous sample. The magnetic nanoparticles (MNP) could be easily collected from water sample by the homemade MNPs collector to achieve field sampling and enrichment. For 500 mL water sample, recovery of 15 mg magnetic particles was 90.8 %. Mixture of seven pesticides spiked in pure water and pond water was used as the marker sample to evaluate the field sampling method. Average recoveries at three spiked levels were in the range of 60.0-104.7 % with relative standard deviations below 7.1 %. The proposed method shows good linearity with correlation coefficient over 0.9990 in the concentration range of 0.5-15 μg L^{-1}. Analysis results of poisoned pond water indicate that this method is fast, convenient and efficient for field sampling and enrichment of pesticides in aqueous samples.

Introduction

For low concentration target components in aqueous sample, pre-concentration step is necessary before determination to achieve higher sensitivity. Various sample pretreatment methods such as liquid-liquid extraction (LLE),[1-3] solid-phase extraction (SPE),[4-8] solid-phase micro-extraction (SPME)[9-13] and stir-bar sorptive extraction (SBSE)[14-16] over the years have revealed the existence of trace levels of pollutant in natural surface water. SPE is currently the most widely used analytical method for measuring a wide variety of pollutant from water sample. Selman et al. prepared filter-free HILIC SPE micro-tips with cotton wool for micro-scale purification of tryptic IgG Fc N-glycopeptides.[8] SPME is another attractive alternative technique, which combined sample extraction and pre-concentration in a single step.[10] Although the sample matrix and target compounds dictate the complexity level of sample extraction, it has been widely used in analysis of food products, pharmaceuticals, environmental and biological samples. Automated SPE and SPME devices and their on-line coupling with chromatography techniques are ideal for high throughput analysis.[5, 6, 9] However, transportation and storage of large volume sample trouble its analysis. For low concentration sample with large volume, even automated SPE device couldn't accomplish extraction and enrichment in short time. Insoluble purities in real sample may cause blocking of SPE column too. Then, a field sampling method is needed for pretreatment of large volume aqueous sample in a short span of time.

Dispersive solid phase extraction (DSPE) is a simple and straightforward sample preparation technique suitable for a wide variety of products.[17-19] The combination of traditional extraction techniques, such as ultrasound-assisted leaching (USAL) with DSPE, has been successfully applied for sample preparation prior to gas chromatography- mass spectrometry (GC-MS) analysis.[20] However, centrifugation or filtration step was necessary to isolate sorbent from liquid phase. Nanoparticle is a good candidate of SPE and DSPE stationary phase. The involvement of nanoparticle improves the extraction ability because of its large surface-to-volume ratio and unique physical and chemical properties. But extremely high back pressure or difficult filtering process resulted from small particle size limits its application in SPE or DSPE. Magnetic solid-phase extraction based on the use of magnetic materials,[17, 21] such as magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3), overcomes difficulty of solid-liquid separation. Magnetic adsorbents are added to aqueous sample. Then the target analyte is adsorbed onto the magnetic adsorbent, which can be quickly isolated from the suspension by an external magnet. Giokas et al. combined cloud point extraction with dispersive micro solid phase extraction.[17] The target analytes were extracted by cloud point extraction in the micelles of a non-ionic surfactant medium; then highly hydrophobic polysiloxane-coated core–shell Fe_2O_3@C magnetic nanoparticles (MNPs) were used to retrieve the micellar phase. Li et al. used C_{18}-functionalized interior pore-walls magnetic mesoporous microspheres with an average diameter of 300 nm to extract and analyze phthalates.[22] In our previous work, we proposed a new solid-phase extraction method based on magnetic core-shell silica nanoparticles for the determination of low concentration pesticides in aqueous samples.[23] In addition, some other specific techniques involving magnetic nanoparticles were also developed for sample preparation[24] and separation[25]. Short dense bed or open-tube column were prepared in capillary by immobilizing nanoparticles with magnets. Unfortunately, even magnet with strong magnetic field can only immobilize nanoparticles in small size channel; these columns are just suitable for small volume samples because of low velocity of flow (e.g. μL min^{-1}).

Pesticide residue is one of main problems in water pollution.[26] In additional, criminal cases of poisoning fish pond has often occurred.[27-29] The characteristics of water sample containing

pesticide residue are large volume, low concentration. Then, development of a field sampling method based on great enrichment capacity of MNPs is necessary to meet the need of large volume aqueous sample.

In this paper, we developed a field sampling method based on magnetic core-shell silica nanoparticles to extract and enrich the pesticides residues in large volume water sample. The MNPs were collected with homemade portable MNPs collector. Seven pesticides were selected as model compounds to evaluate the extraction ability of this method and GC-MS were used for qualitative and quantitative analysis.

Materials and methods

Materials and Chemicals

HPLC grade methanol and n-hexane were purchased from Shandong Yuwang Industrial Co., Ltd. (Shandong, China). Water was purified by a Milli-Q system (Milford, MA, USA). All other chemicals were of analytical grade.

Standard pesticides (resmethrin, bifenthrin, fenpropathrin, permethrin, cypermethrin, fenvalerate and deltamethrin) with purity＞99.0% were obtained from Shanghai Pesticide Research Institute (Shanghai, China). Stock solutions of the seven pesticides were dissolved in methanol at concentration of 100 μg L^{-1} and stored at 4 ℃. Standard calibration mixtures were prepared in a concentration range of 0.5-15 μg L^{-1} by adding adequate volumes of each standard solution into pond water.

The C_{18}-modified MNPs (220 nm) were synthesized as described in our previous work.[23] HT208 tesla meter (Shanghai Hengtong Magnetoelectricity, China) was used to characterize the flux density of magnet.

GC-MS analysis

Analyses were carried out on an Agilent 7890A gas chromatograph-5975C mass spectrometric detector combination (Agilent Technologies, Little Falls, DE, USA) equipped with HP-5 capillary column (30 m × 0.25 mm id, 0.25 μm film thickness; Agilent Technologies). Helium (purity 99.999%) was used as carrier gas at a constant flow rate of 1.0 mL min^{-1}. A 2.0 μL sample was injected into the GC using splitless injection mode. The injector and the interface temperatures were 260 ℃and 280 ℃, respectively. The column oven temperature was programmed as follows: the initial temperature was 80 ℃ for 2.0 min, increased to 280 ℃ at a rate of 20 ℃ min^{-1}, and held for 8 min. The instrument was operated in selected ion-monitoring mode (SIM). Ionization was performed by electron ionization in positive mode at an ion source voltage of 70 eV. A temperature of 220 ℃ and a solvent delay of 5.0 min were used. Three characteristic ions for each compound were selected, the most abundant characteristic ion in the spectrum was used for quantification and three qualifier ions were used for compound identification (Table 1).

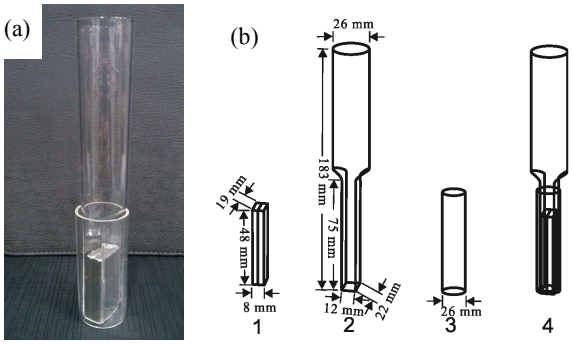

Fig. 1 Schematic illustration of MNPs collector (a) real object photograph (b) 1, Nd-Fe-B magnet; 2, glassy shell; 3, elution tube; 4, composite collector.

Preparation of homemade MNPs collector

The structure of homemade MNPs collector is shown in Fig. 1. The homemade collector is composed of three parts: Nd-Fe-B magnet, glassy shell and elution tube. The magnet measures 48 mm × 19 mm × 8 mm. The cuboids part of the glassy shell measures 75 mm × 22 mm ×12 mm (outside diameters). The length and inner diameter of the cylindrical handles are 183 mm and 26 mm. The thickness of glass wall is about 1.5 mm. The elution tube is a flat-bottomed glass test tube with inner diameter of 26 mm. A piece of rubber was put at the bottom of the glass shell to avoid collision of magnet and glass bottom.

Field sampling using homemade MNPs collector

A typical MSPE process to enrich low-concentration pesticide from aqueous sample with homemade MNPs collector is displayed in Fig. 2. First, 200 mL of water sample containing seven pesticides with a concentration of 0.5 μg L^{-1} was poured to a 500 mL beaker. Then, 15 mg of C_{18}-modified MNPs which had

Table 1. Retention time, quantitative ion, qualitative ions, and time program for SIM mode detection of seven pesticides

Analytes	Retention time (min)	Quantitative ion (m/z)	Qualitative ions (m/z)	Time program (min)
Resmethrin	12.659, 12.729	123	171, 143, 128	12.58-12.90
Bifenthrin	13.058	181	165, 166, 182	12.90-13.60
Fenpropathrin	13.176	97	181, 125, 265	12.90-13.60
Permethrin	14.504, 14.629	183	163, 165, 184	14.00-15.00
Cypermethrin	15.525, 15.634 15.410, 15.793	163	165, 181, 91	15.00-16.00
Fenvalerate	16.962, 17.303	125	167, 225, 419	16.60-17.60
Deltamethrin	17.896, 18.372	181	253, 251, 255	17.60-19.00

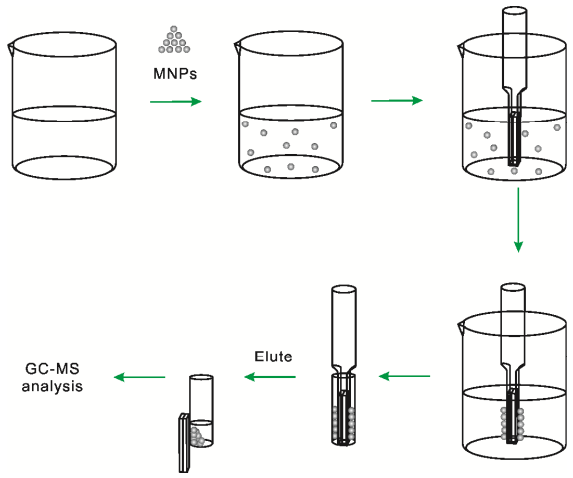

Fig. 2 The workflow of field sampling using C_{18}-modified MNPs and homemade collector.

been activated by methanol and distilled water in sequence were mixed with the sample solution. The mixture was sonicated at room temperature for 20 s and shaken for 20 min to achieve equilibrium. Then homemade MNPs collector with magnet inside was put into water sample and stirred for 10 min to collect MNPs until no particle can be observed by naked eye. Subsequently, the isolated MNPs were washed with pure water (2× 1 mL), then the analytes were eluted with 3×1.7 mL of n-hexane: acetone= (75:25, v/v) and concentrated to 200 μL with a gentle stream of N_2 at room temperature. Finally, 2 μL of eluting solution was injected into GC-MS for qualitative and quantitative analysis.

Results and discussions

Working principle of homemade MNPs collector

When putting magnet outside of the beaker to isolate MNPs from water sample, precipitate in dirty water would mix with magnetic particles and long standing time was needed because of decay of magnetic strength caused by water layer and glass wall. For example, for 200 mL water more than 30 min was needed for complete recovery of MNPs. The homemade MNPs collector can overcome these problems because it can be dipped into sample to collect nanoparticles dispersed in water. Although the existence of glass shell reduced magnetic strengths by 15%, the valid magnetic strength (267 mT) was stronger than putting the magnet under the container (2 cm water layer results in decrease of magnetic strength by 85%). In addition, the precipitate can be easily isolated from adsorbents. We also prepared collector with Teflon shell, but the adsorption of MNPs on Teflon surface interfered elution of target compounds and recycling of MNPs. Although electromagnet can provide stronger magnetic field, higher current supplied by heavy power source is needed.

Taking all these into account, permanent magnet and glassy shell with no need of sealing were adopted to prepare MNPs collector. Comparing with capillary columns prepared by magnetic immobilization [24,25], the proposed MNPs collector are time-saving and suitable for field sampling and pretreatment of large-volume sample.

To investigate the recovery capacity of the collector, different weights of magnetic particles (15 mg, 35mg and 55 mg) were dispersed into water sample with different volumes (100 mL, 200 mL and 500 mL). As shown in Table 2, even for 500 mL water sample, the recovery of MNPs is higher than 90.8% (15 mg, 500 mL) while consuming collecting time of 10 min. This field sampling procedure can be easily accomplished without any other equipment avoiding difficulties of transportation and storage. The small gap between glass shell and elution tube was full of elution solvent to desorb pesticides.

Table 2 The MNPs recovery capacities of the collector

Aqueous sample volume/mL	MNPs/mg	Recoveries/% (n=3)
100	15	92.7
100	35	96.0
100	55	95.3
200	15	96.9
200	35	93.8
200	55	95.5
500	15	90.8
500	35	92.8
500	55	97.2

Evaluation of field sampling method

It is well known that C_{18}-modified MNPs can be used as absorbent for the extraction of pesticides due to its hydrophobic interactions with pesticides in aqueous solution. Therefore, we believed that the proposed field sampling method using homemade MNPs collector would has advantage in extraction of pesticides with simple operation process, high extraction efficiency as well as quick magnetism separation for low-concentration pesticides in aqueous samples. To investigate the efficiency of the field sampling method in pesticide extraction, an aqueous sample containing seven pesticides was employed. The elution conditions were selected as optimized in previous work. [23] Fig. 3 displays the chromatograms of the blank pond water and spiked sample with pesticides concentration of 2.0 μg L^{-1}. After

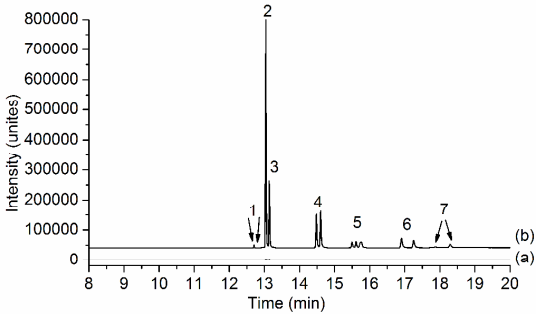

Fig. 3 Chromatograms of the seven pesticides from (a) blank pond water sample and (b) spiked pond water at 2.0 μg L^{-1} level pretreated by field sampling of MNPs. Chromatographic peaks are labeled as followed: 1, resmethrin; 2, bifenthrin; 3, fenpropathrin; 4, permethrin; 5, cypermethrin; 6, fenvalerate; and 7, deltamethrin.

Table 3 Recoveries and RSDs of the developed method

Analytes	Pure water			Pond water		
	Recovery and RSD (%) n=3					
	0.5 μg L^{-1}	2 μg L^{-1}	10 μg L^{-1}	0.5 μg L^{-1}	2 μg L^{-1}	10 μg L^{-1}
Resmethrin	60.1±5.4	63.1±4.4	75.4±6.6	72.0±3.4	60.0±3.6	81.0±6.2
Bifenthrin	63.9±5.5	86.3±4.5	95.6±5.1	90.1±2.4	88.7±5.0	90.5±3.5
Fenpropathrin	65.8±2.6	65.6±2.5	72.3±4.5	72.9±3.9	63.9±1.8	80.1±1.4
Permethrin	65.4±6.1	81.6±4.9	96.7±7.1	91.8±5.5	90.7±5.2	96.3±6.9
Cypermethrin	86.0±6.9	100.3±4.5	91.6±4.9	104.6±1.9	99.0±6.1	100.5±6.7
Fenvalerate	98.0±5.2	99.2±2.4	98.5±4.7	99.9±5.9	98.0±6.7	89.8±5.6
Deltamethrin	87.3±5.4	96.7±3.3	104.7±4.4	94.5±6.0	101.6±6.6	98.2±6.9

sampling, the seven pesticides can be easily detected. The results demonstrated good extraction performance of the proposed method for low concentration pesticides. It's worth noting that resmethrin, permethrin, cypermethrin, fenvalerate and deltamethrin showed two, two, four, two and two peaks respectively because of existence of isomers.

The recoveries of pesticides pretreated by proposed sampling method were listed in Table 3. The repeatability was evaluated by analyzing three replicates at three fortification concentrations in pond water samples, and the recoveries varied from 60.0 % to 104.6 % with RSDs from 1.4 % to 6.9%, indicating a good precision of the method. The recoveries and repeatability are comparable to direct MSPE pretreatment in our previous work [23]. The recyclability of the field sampling method was tested by repeating extraction six times with the same nanoparticles, no significant changes of recoveries were found, indicating the performance is stable and robust.

To investigate the matrix effect of pond water, the extraction was performed to spiked pure water samples too. The recoveries varied from 60.1 % to 104.7 % with RSDs from 2.4 % to 7.1 %. The results were slightly different from pond water, indicating small influence of the matrix effect.

In this paper, C_{18} modified magnetic nanoparticles were employed to exact and enrich pesticides with weak and middle polarities. The recoveries of pesticides were related to their polarities. For pesticides with weak polarity, such as cypermethrin, fenvalerate and deltamethrin, recoveries were higher than 86 %, owing to strong interaction between C_{18} groups and nonpolar groups. When the sample concentration increased from 0.5 μg L^{-1} to 10 μg L^{-1}, no significant recovery changes were found for samples with high distribution coefficients (K). For pesticide with polar groups, the hydrophobic interaction was weakened with lower recovery (as low as 60%). For these pesticides, the fluctuation of recovery for different concentrations was more significant. In our previous work [30], extreme low recoveries (<10%) were found for polar samples, indicating that C_{18} modified nanoparticle was suitable for nonpolar and middle polar samples.

For precise quantification, matrix-matched calibration solutions were prepared at seven different concentration levels by adding certain amount of pesticides into pond water to eliminate the matrix effect. Linear ranges, regression coefficients and limit of detection (LOD) and limit of quantization (LOQ) were summarized in Table 4. Good linearity was obtained with the correlation coefficient (R^2) > 0.9990 in the concentration range of 0.5- 15 μg L^{-1}. The LODs and LOQs for seven pesticides were estimated using the signal-to-noise ratio of 3 and 10, respectively. The LODs were situated between 0.002 and 0.010 μg L^{-1}, whereas the LOQs were between 0.008 and 0.030 μg L^{-1}.

Table 4 Linear ranges, regression coefficients, LODs and LOQs of the developed method

Analytes	Linear range μg L^{-1}	R^2	LOD μg L^{-1}	LOQ μg L^{-1}
Resmethrin	0.5-15	0.9991	0.010	0.030
Bifenthrin	0.5-15	0.9990	0.002	0.008
Fenpropathrin	0.25-15	0.9996	0.003	0.010
Permethrin	0.5-15	0.9995	0.005	0.020
Cypermethrin	0.5-20	0.9994	0.008	0.030
Fenvalerate	0.5-15	0.9990	0.010	0.030
Deltamethrin	0.5-10	0.9998	0.010	0.030

Application in real sample

To evaluate the applicability of the proposed field sampling method for real water samples, we further applied the method for analysis of poisoned pond water sample provided by Shanghai Key Laboratory of Crime Scene Evidence. Cypermethrin was detected and confirmed (as shown in Fig. 4).The result demonstrated that the proposed method could be used for the field sampling and enrichment of the low-concentration pesticide in real aqueous sample.

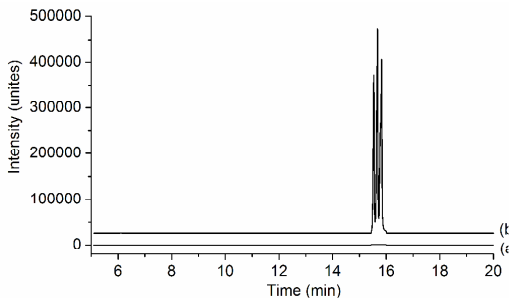

Fig. 4 Chromatogram of the pesticide residue from (a) blank pond water sample and (b) poisoned pond water sample.

Conclusions

In this research, a field sampling method for enrichment of pesticides in water samples has been developed and applied to detection of pesticide residue in poisoned pond water. Small magnetic strength loss of homemade MNPs collector results in faster and convenient recycle of magnetic particles and simple extraction procedure fits for field sampling of large volume sample containing low concentration target compounds. The proposed method has high application potential for the field pretreatment of trace organic pollutants and biological analytes from water samples.

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Note and references

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