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Hydrophilic–lipophilic balanced magnetic nanoparticles: Preparation and application in magnetic solid-phase extraction of organochlorine pesticides and triazine herbicides in environmental water samples

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ABSTRACT

In this study, a novel hydrophilic–lipophilic balanced magnetic nanoparticle, magnetic poly(divinylbenzene-co-N-vinylpyrrolidone) (HLB-MPNP) was successfully synthesized and applied for the extraction and determination of triazine and organochlorine pesticides in environmental water samples. The specific ratio of two monomers, hydrophilic N-vinylpyrrolidone and lipophilic divinylbenzene, endowed the magnetic nanoparticles with hydrophilic–lipophilic balanced character, which made it capable of extracting both polar and nonpolar analytes. The experimental parameters affecting extraction efficiency, including desorption conditions, sample pH, sample volume and extraction time were investigated and optimized. Under the optimum conditions, good linearity was obtained in the range of 0.20–10 $\mu g\,L^{-1}$ for triazine herbicides and 5.0–100 $ng\,L^{-1}$ for organochlorine pesticides, with correlation coefficients ranging from 0.994 to 0.999. The limits of determination were between 0.048 and 0.081 $\mu g\,L^{-1}$ for triazine herbicides and 0.39 and 3.26 $ng\,L^{-1}$ for organochlorine pesticides. The proposed method was successfully applied in the analysis of triazine and organochlorine pesticides in environmental water samples (ground, river and reservoir).

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1. Introduction

Magnetic solid-phase extraction (MSPE) based on functionalized magnetic materials has received considerable attention in recent years, especially as a promising sample preparation technique. In MSPE, magnetic adsorbent is added to the solution for the adsorption of the analytes. The adsorbent with the adsorbed analyte is then separated from the solution using a magnet. The analyte is consequently eluted and analyzed. Compared with traditional SPE, the phase separation process in MSPE is easier and faster without the need of additional filtration procedure in SPE, because of the use of magnetic field. Adsorbent material is the most important component of the MSPE technique.

To date, many different types of magnetic adsorbents have been developed for MSPE, such as surfactant [1], C18 [2], carbon nanotubes [3], graphene [4], and polymer materials [5–7]. Recently, polymer coated magnetic nanoparticles (MNPs) have gained considerable attention. Polymer coating endows the MNPs with a diversity of adsorption selectivity. Besides, the polymer coating provides the MNPs with protection from aggregation and oxidization. But, for most of the polymer coated MNPs, polystyrene is main component [8,9].

All the magnetic adsorbents mentioned above present an undiversified structure, either hydrophobic or hydrophilic. Their interactions with the analytes are basically hydrophobic and π–π interactions. For this reason, these magnetic adsorbents present low recoveries for the polar compounds or are too specific to a particular analyte [10].

To overcome this drawback, a hydrophilic–lipophilic balanced magnetic material is needed, and polymer coated magnetic material is a good candidate. There are plenty of monomers of interest to choose. In this work, we introduced a hydrophilic monomer N-vinylpyrrolidone into the polymer preparation inspired by the Waters Oasis® HLB SPE sorbent. A certain ratio of hydrophilic N-vinylpyrrolidone and lipophilic divinylbenzene made the polymer hydrophilic–lipophilic balanced. The prepared magnetic polymer nanoparticles present good extraction performance for both polar and non-polar compounds.

Organochlorine pesticides (OCPs) were the first synthetic pesticides used for agricultural and industrial purposes [11]. However, OCPs have been included in the class of persistent organic pollutants (POPs) due to their potential risk for human

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health, persistence and tendency to bio-accumulate. OCPs are still widely detected in a broad range of natural samples including ground water and surface water, even the use of these compounds has been banned in many countries since the 1970s.

Triazine herbicides are widely used as selective herbicides for the control of broadleaf and grassy weeds in many agricultural crops [12]. They have achieved considerable attention in recent years due to their toxicity and high resistance. Moreover, atrazine is suspected as one of the endocrine disrupters and human carcinogens [13,14]. The triazine herbicides have a wide range of solubility in aqueous media and high mobility through the soils according to their structure [15]. And because of their widespread use, they are frequently detected in surface and ground water [16].

In order to protect the water system, the OCPs and triazine herbicides need to be more heavily monitored due to their toxicity, persistence and accumulation. The European Union Directive 98/83/EC has set a maximum level for each individual herbicide at 0.1 $\mu g\,L^{-1}$ and 0.5 $\mu g\,L^{-1}$ for mixtures of pesticides. And the concentration levels of OCPs and triazine herbicides found in drinking and natural water samples are typically in the order of ppt ($ng\,L^{-1}$) [17,18]and ppb ($\mu g\,L^{-1}$) [19,20], respectively. These levels are too low for direct GC and HPLC analysis. As a result, a fast and compatible preconcentration step is necessary prior to the analysis. The most commonly used preconcentration methods are liquid–liquid microextraction (LLME) [12,21], solid-phase extraction (SPE) [22,23], solid-phase microextraction (SPME) [24,25] and stir bar sorptive extraction (SBSE) [26,27]. All these traditional preconcentration methods have some drawbacks such as time and solvent consuming, expensive and so on. Compared to these methods, MSPE is environment friendly, labor saving and low cost.

In this work, a novel hydrophilic–lipophilic balanced polymer magnetic nanoparticle was prepared. This adsorbent was successfully used in MSPE for the preconcentration of both lipophilic OCPs and hydrophilic triazine herbicides from environmental water samples.

2. Experimental

2.1. Reagents and materials

The chemicals, including $FeCl_3 \cdot 6H_2O$, $FeCl_2 \cdot 4H_2O$, sodium dodecyl sulfate (SDS), n-hexadecane (HD), hydroxyethylcellulose (HEC), 2,2′-azobisisobutyronitrile (AIBN), polyvinyl pyrrolidone (PVP) and oleic acid (OA), were of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). N-vinylpyrrolidone (99%) and divinylbenzene (DVB) (80%) were purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China). OCP standards (α-BHC, hexachlorobenzene, γ-BHC, quintozene, heptachlor, heptachlor epoxide, α-endosulfan, dieldrin, β-endosulfan, p,p′-DDD, and aldrin) 200 $mg\,L^{-1}$ in n-hexane and triazine herbicide standards (atrazine (99.9%), ametryn (98.8%), terbuthylazine (99.0%), prometryn (99.5%), and terbutryn (99.0%)) were from Agricultural Environmental Protection Institution (Tianjin, China). Acetonitrile, methanol, acetone and n-hexane were of HPLC grade and purchased from Dima Technology (Richmond Hill, VA, USA). Ultrapure water used in all experiments was purified by a Milli-Q (Millipore, Billerica, MA, USA) system.

2.2. Apparatus

Triazine herbicides were analyzed on an Agilent-1200 HPLC system configured with an quaternary pump system, mobile phase vacuum degasser, autosampler, thermostated column compartment, and diode array detector (Agilent Technologies, Inc., Wilmington, DE, USA). The chromatographic separation of the analytes was performed using an Agilent TC-C18 column (250 mm × 4.6 mm i.d., 5 μm; Agilent) at 15 °C. The detection wavelength was 220 nm and the injection volume was 20 μL. The mobile phase was a mixture of water, acetonitrile, and methanol (50:40:10, v/v/v), and the flow rate was 1 $mL\,min^{-1}$.

OCPs were analyzed on an Agilent-7890 GC equipped with a μ-63Ni electron capture detector (GC–μECD) and an HP-5 fused silica capillary column (30 m × 0.32 mm × 0.25 μm; Agilent). The carrier gas was ultrapure nitrogen with a flow rate of 1 $mL\,min^{-1}$. The temperatures of the injector and detector were kept at 270 °C and 320 °C, respectively. The oven temperature was programmed from 90 (1 min hold) to 180 °C (5 min hold) at the rate of 15 $°C\,min^{-1}$, to 185 °C (11.5 min hold) at the rate of 5 $°C\,min^{-1}$, to 218 °C (6 min hold) at the rate of 35 $°C\,min^{-1}$, and finally to 270 °C (3 min hold) at the rate of 20 $°C\,min^{-1}$. The injection volume was 1.0 μL splitlessly.

Characterization of OA–MNPs and HLB-MPNPs was carried out using a Fourier Infrared Spectrometer (Perkin-Elmer, Inc. CA, USA) and a Transmission Electron Microscope (Hitachi H800 Transmission electron microscopy, Japan).

2.3. Preparation of hydrophilic–lipophilic balanced magnetic polymer nanoparticles

2.3.1. Synthesis of oleic acid-coated magnetite nanoparticles (OA–MNPs)

Oleic acid-coated magnetite nanoparticles were prepared by a co-precipitation method [28]. The procedure was as follows. $FeCl_3 \cdot 6H_2O$ (10.8 g) and $FeCl_2 \cdot 4H_2O$ (3.98 g) were dissolved in 300 mL of deionized water (deoxygenated by nitrogen bubbling) and then 4.0 g OA was dissolved in 30 mL acetone and added under stirring. After 30 min, 30 mL of 25% NH_4OH solution was added, over a period of 10–15 min. The resulting suspension was stirred for 1 h and then heated at 85 °C for 1 h. Then, the suspension was allowed to cool to 70 °C and pH was adjusted to 2 by adding 1 M HCl solution to ensure that oleate was converted to OA. The black pasty product was washed several times with water and dried in an oven at 60 °C for 12 h. In this way, the OA–MNPs were obtained.

2.3.2. Preparation of hydrophilic–lipophilic balanced magnetic polymer nanoparticles (HLB-MPNPs)

Magnetic polymer nanoparticles were prepared by miniemulsion polymerization based on the method reported by Lu and Forcada [28], with some modification. The water phase was prepared by dissolving 0.14 g SDS, 0.7 g PVP and 0.14 g HEC in 63 mL water; the oil phase was prepared by mixing 0.7 g OA–MNPs, 4.48 g DVB, 2.82 g N-vinylpyrrolidone and 0.5 g AIBN to a homogeneous solution. Two phases were mixed together and stirred under a mechanical stirrer for 10 min in an ice-cooled bath. During the stirring, the mixture was sonicated using an ultrasonic cleaner to produce a miniemulsion. Then, the miniemulsion was transferred to a water bath at 70 °C under moderate stirring for polymerization. After 21 h, the resulting HLB-MPNPs were collected by magnet and washed with methanol and acetone for several times. The resulting adsorbent was vacuum dried for 24 h.

2.4. Extraction procedure

The MSPE procedure was carried out as follows. HLB-MPNPs (60 mg) were first activated by adding 100 μL of methanol, and then dispersed in 200 mL water samples by ultrasonic irradiation. After adsorption equilibrium (20 min for triazine herbicides; 5 min for OCPs), the magnetic adsorbent was isolated from the suspension with an Nd–Fe–B strong magnet (100 mm × 100 mm × 20 mm,

Ningbo jiangbei sky magnetic materials Co., Ltd, China). The supernatant was decanted and the residue solution and magnetic adsorbent were transferred to a 10 mL plastic centrifuge tube. The magnetic adsorbent was again aggregated by a magnet to remove the residue solution completely by a syringe. The analytes were eluted from the magnetic adsorbent with suitable solvent. Subsequently, the desorption solutions were mixed into a 5 mL centrifuge tube and evaporated to dryness at 30 °C under a stream of nitrogen. The residue was redissolved in 200 μL of solvent (methanol for triazine herbicides; n-hexane for OCPs) and filtered through a PTEE filter (0.22 μm) before chromatographic analysis.

2.5. Analysis of real water samples

Three kinds of environmental water samples were collected and analyzed, including ground water, river water and reservoir water. Ground water was collected in our laboratory in Haidian district, Beijing. River water was collected from Xiaoqinghe River which was polluted by municipal sewage (Haidian district, Beijing). Reservoir water was collected from the Miyun reservoir (Miyun district, Beijing). No previous treatment was conducted for ground water, whereas the other water samples were filtered through medium-speed qualitative filter papers. All samples were stored in dark containers at 4 °C until analysis.

3. Results and discussion

3.1. Characterization of OA–MNPs and HLB-MPNPs

The functional groups of OA–MNPs and HLB-MPNPs were identified by FT-IR. The FT-IR spectra of OA–MNPs and HLB-MPNPs are shown in Fig. 1. The spectrum of OA–NMPs (Fig. 1a) exhibited strong bands at 599 and 3427 cm^{-1} due to Fe–O–Fe and O–H stretching vibrations of magnetic Fe_3O_4 nanoparticles. The peaks at 2927 and 2853 cm^{-1} were attributed to the C–H stretching vibrations of OA, and the peak at 1711 cm^{-1} contributed to the C=O stretching vibration of OA. All these adsorption peaks confirmed the successful coating of Fe_3O_4 nanoparticles by OA. The spectrum of HLB-MPNPs (Fig. 1b) showed the characteristic absorption peaks of Fe_3O_4, N-vinylpyrrolidone and DVB. The peak at 585 cm^{-1} was from the Fe_3O_4 nanoparticles. The peaks in the ranges of 1400–1650, 3000–3100 and 2800–3000 cm^{-1} were related to the stretching vibrations of aromatic rings (C=C), the aromatic C–H stretching vibrations and stretching vibrations of methylene C–H, respectively. The peaks at 795 and 707 cm^{-1} were from the aromatic C–H bending vibrations. The peak at 1689 cm^{-1} was contributed to the C=O stretching vibration of N-vinylpyrrolidone. These adsorption peaks confirmed the formation of magnetite/poly (N-vinylpyrrolidone-divinylbenzene) composite.

The size and morphological features of OA–MNPs and HLB-MPNPs were visualized with TEM. As can be seen in Fig. 2a, the OA–MNPs has an average size of about 7 nm. Fig. 2b shows the TEM micrograph of HLB-MPNPs. Magnetic nanoparticles containing magnetite (the dark spots inside) of around 200 nm were found.

3.2. Optimization of extraction conditions

To evaluate the applicability of HLB-MPNPs for the enrichment of different kinds of pesticides, the parameters that might affect the extraction efficiency, such as eluting solvent, sample pH, sample volume and extraction time were optimized. In all optimization experiments, 1.0 μg of each analyte was added for triazine herbicides and 10 ng of each analyte for OCPs. Recovery was used to assess the extraction efficiency.

3.2.1. Desorption conditions

Desorption of the analytes from adsorbent is an important parameter which determines their overall recoveries. For triazine herbicides, different solvents (methanol, acetonitrile, and acetone), extraction time (vortexing for 0.5, 1.0, and 2.0 min) and solvent volumes (1, 2, and 3 mL) were studied. It was found that vortexing

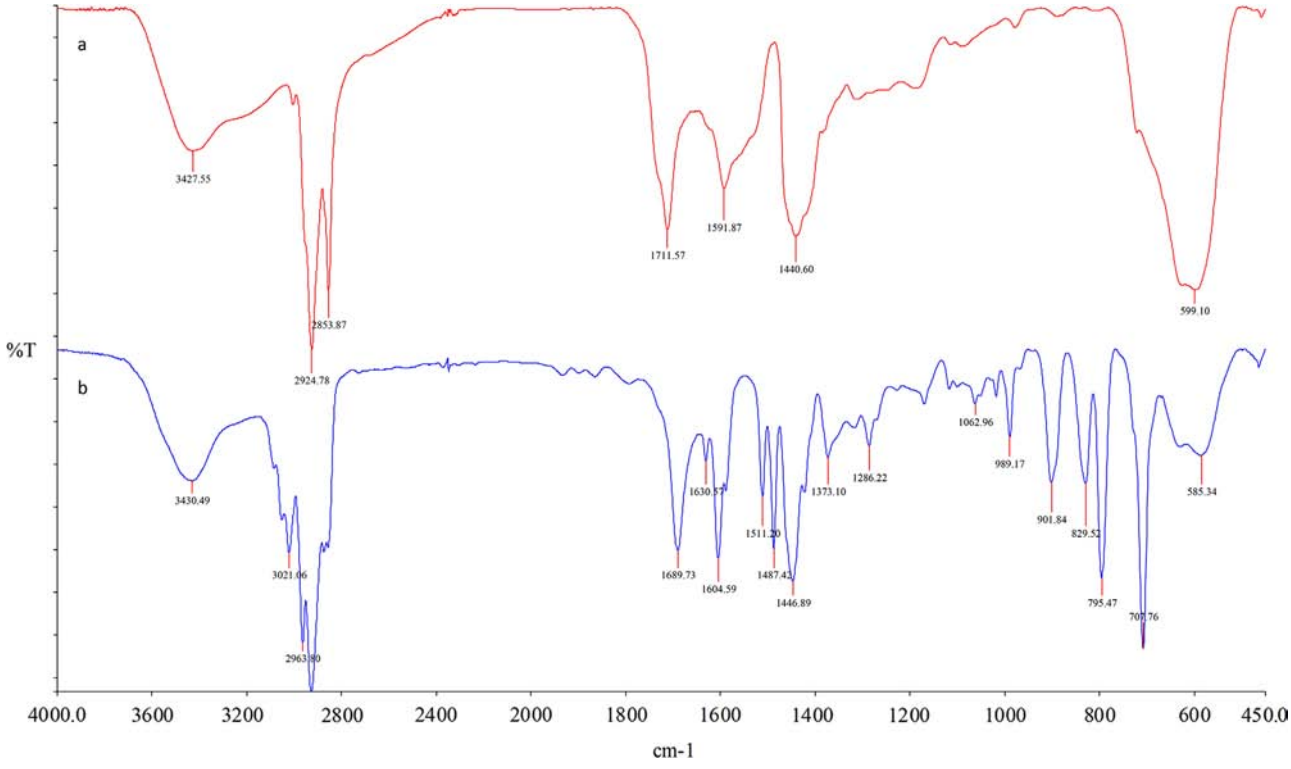

Fig. 1. The FT-IR spectra of (a) OA–MNPs and (b) HLB-MPNPs.

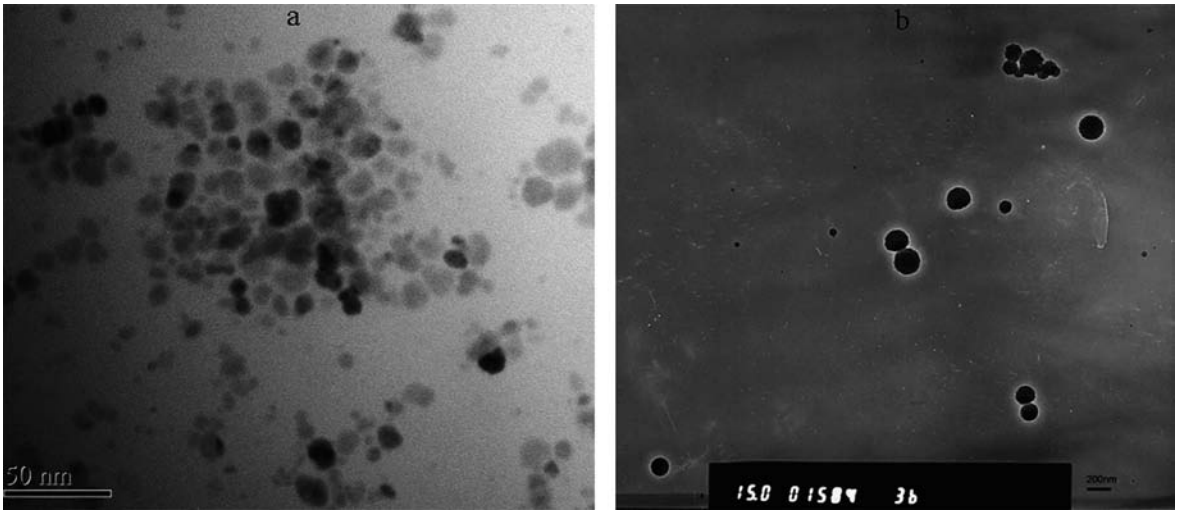

Fig. 2. TEM images of (a) OA–MNPs and (b) HLB-MPNPs.

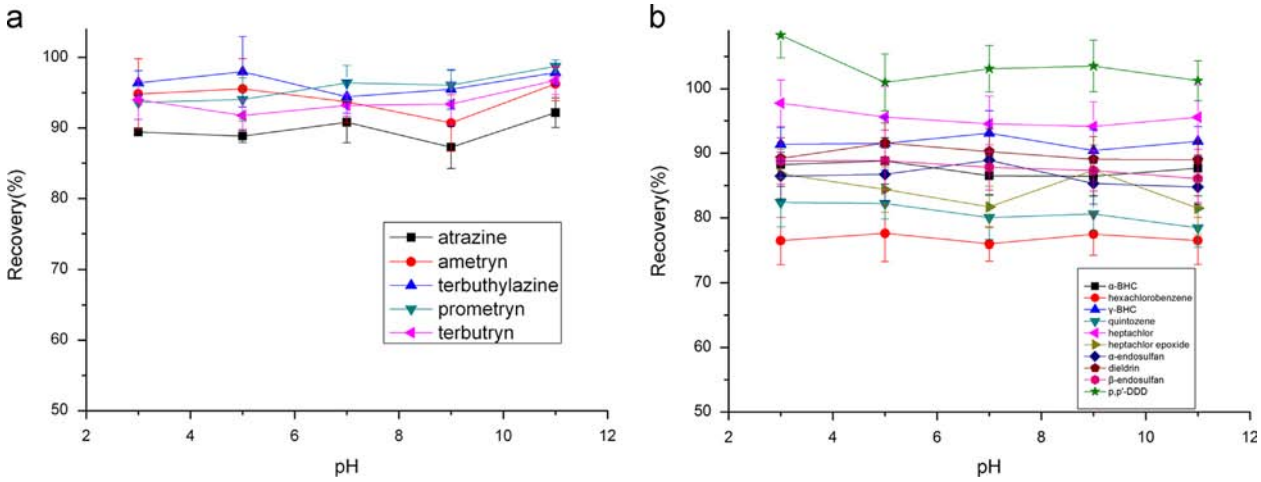

Fig. 3. Effect of sample pH on the extraction efficiency of (a) triazine herbicides and (b) OCPs.

time had no significant influence on the eluting efficiency; therefore, 0.5 min was chosen. The desorption solvent was optimized to achieve accurate quantification of the analytes. The results indicated that 2 mL of acetone (1 mL every time) can completely elute the extracted triazine herbicides.

For OCPs, n-hexane was selected to be the desorption solvent since there was significant loss of analytes during the nitrogen concentration process when using polar solvent as desorption solvent because of the little water co-extracted into the desorption solution. The extraction and solvent volumes were studied. It was found that, 3 mL of n-hexane (1 mL every time, vortexing for 3 min) was sufficient for the quantitative desorption of OCPs.

3.2.2. *Effect of sample pH*

The influence of pH ranging between 3.0 and 11.0 was investigated by adjusting the sample solution with hydrochloric acid or sodium hydroxide solution. As shown in Fig. 3, the results showed no obvious change in extraction efficiency both for triazine herbicides and OCPs. The polymer did not possess ionized group and was stable throughout the full pH range. For OCPs, it is reasonable that sample pH did not affect the extraction efficiency; for triazine herbicides, the pKa values of the five analytes ranged from 1.7 to 4.3. The fact that sample pH (3.0–11.0) did not affect the extraction efficiency demonstrated that dipole–dipole and hydrogen-bond interaction between analyte and hydrophilic component may play an important role as well as hydrophobic interactions. As a result, it is unnecessary to adjust the pH of the sample solution.

3.2.3. *Effect of sample volume*

The sample volume is an important factor affecting the extraction efficiency. Volumes of water between 100 and 400 mL were studied in order to reach the maximum enrichment factors. As shown in Fig. 4, the recoveries remained nearly constant with the sample volume for up to 200 mL for triazine herbicides, and the recoveries for OCPs declined gradually as the volume increased, but still acceptable when the volume was 200 mL. Thus, 200 mL of solution volume was selected for both triazine herbicides and OCPs.

3.2.4. *Effect of extraction time*

In the MSPE process, the extraction time is one of the prime factors that influence the extraction efficiency. A sufficient extraction time is required after the HLB-MPNPs are dispersed into the sample solution. Fig. 5 shows the recoveries values as function of the extraction time (0–40 min) for each analyte. As can be seen, only 5 min was sufficient for the OCPs to reach the adsorption

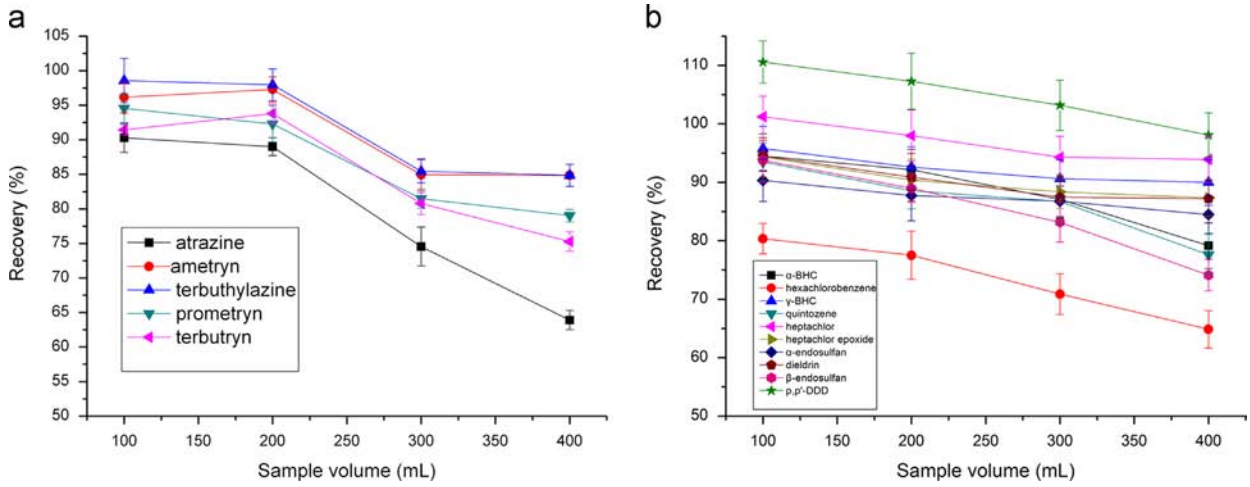

Fig. 4. Effect of sample volume on the extraction efficiency of (a) triazine herbicides and (b) OCPs.

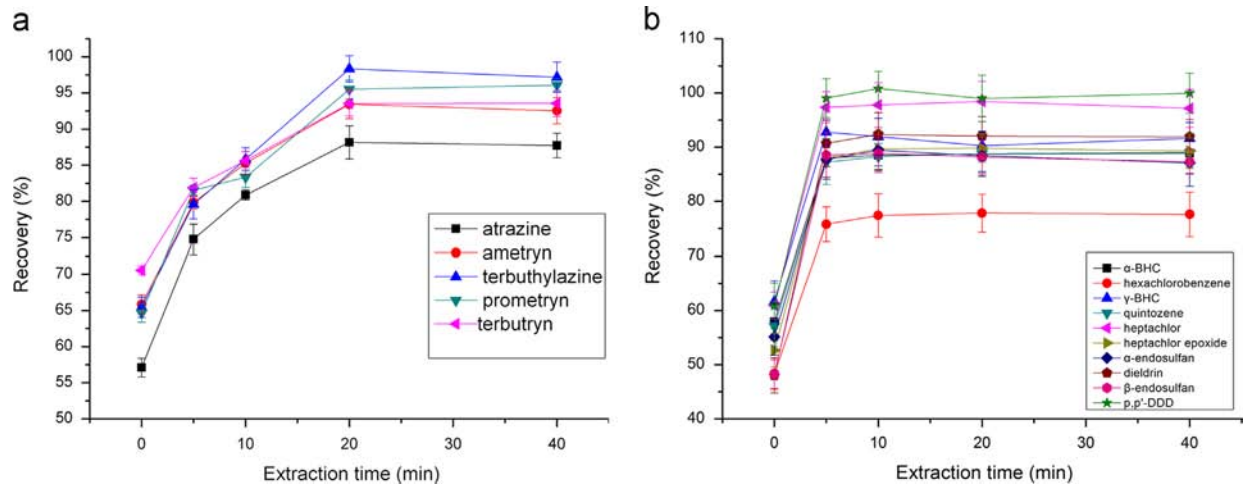

Fig. 5. Effect of extraction time on the extraction efficiency of (a) triazine herbicides and (b) OCPs.

Table 1
Linear range, correlation, LOD, and precision of the MSPE method for trazine herbicides.

Triazine herbicides	Linear equation	Correlation coefficient (r^2)	LR (μg L^{-1})	LOD (μg L^{-1})	RSD (%)	EF[a]
Atrazine	$Y=271.7X-18.88$	0.998	0.2–10	0.048	2.7	883
Ametryn	$Y=197.5X-16.05$	0.997	0.2–10	0.081	3.8	841
Terbuthylazine	$Y=177.5X-11.09$	0.998	0.2–10	0.063	4.6	876
Prometryn	$Y=213.4X-16.54$	0.999	0.2–10	0.057	1.5	868
Terbutryn	$Y=179.3X-0.816$	0.999	0.2–10	0.075	2.5	863

[a] EF is enrichment factor, the ratio of the analyte concentration in redissolving solvent to the initial concentration in the water samples.

equilibrium, but for triazine herbicides, 20 min was needed to reach extraction platform.

3.3. Method validation

To investigate the applicability of the method for the determination of the triazine herbicides and OCPs, several factors in the term of linearity, repeatability, limits of detection (LODs), and recoveries were studied under the optimum working conditions (triazine herbicides: 2 mL of acetone for desorption, 20 min of extraction time; OCPs: 3 mL of n-hexane for desorption, 5 min of extraction time), respectively.

The results of triazine herbicides are summarized in Table 1. Calibration curves were established for all the analytes in the concentration range of 0.2–10 μg L^{-1} at five different levels (0.2, 0.5, 1, 5 and 10 μg L^{-1}). Good linearity was obtained with the correlation coefficients ranging from 0.997 to 0.999. The LODs for the triazine herbicides, calculated at a signal-to-noise ratio of 3, ranged from 0.048 to 0.081 μg L^{-1}. The repeatability was studied by five parallel experiments at concentration of 5.0 μg L^{-1} for each analyte under the optimal conditions. The relative standard deviations ranged from 1.5% to 4.6%, illustrating the satisfactory repeatability achieved in the MSPE procedure for triazine herbicides.

The results of OCPs are listed in Table 2. Calibration curves were established for all the analytes in the concentration range of 5.0–100 ng L^{-1} at five different levels (5, 10, 20, 50 and 100 ng L^{-1}). Good linearity was obtained with the correlation coefficients ranging from 0.994 to 0.999. The LODs for the triazine

Table 2
Linear range, correlation, LOD, and precision of the MSPE method for OCPs.

OCPs	Linear equation	Correlation coefficient (r^2)	LR (ng L^{-1})	LOD (ng L^{-1})	RSD (%)	EF[a]
α-BHC	$Y=0.038X-0.119$	0.997	5–100	1.07	3.2	805
Hexachlorobenzene	$Y=0.039X-0.174$	0.998	5–100	1.06	3.6	724
γ-BHC	$Y=0.032X-0.099$	0.998	5–100	1.40	2.9	897
Quintozene	$Y=0.028X-0.050$	0.999	5–100	1.74	4.1	853
Heptachlor	$Y=0.033X-0.121$	0.997	5–100	0.39	2.7	925
Heptachlor epoxide	$Y=0.029X-0.038$	0.996	5–100	3.26	3.5	813
α-endosulfan	$Y=0.027X-0.059$	0.997	5–100	1.40	3.1	825
Dieldrin	$Y=0.024X+0.001$	0.996	5–100	3.00	2.4	834
β-endosulfan	$Y=0.018X-0.004$	0.999	5–100	2.34	4.5	790
p,p′-DDD	$Y=0.018X+0.090$	0.994	5–100	0.63	3.0	785

[a] EF is enrichment factor, the ratio of the analyte concentration in redissolving solvent to the initial concentration in the water samples.

Table 3
Matrix effects and determination coefficients obtained for the target pesticides in environmental water samples.

Pesticide	Underground water		Reservoir water		River water	
	Matrix effect	R^2	Matrix effect	R^2	Matrix effect	R^2
Atrazine	1.03	0.998	1.04	0.999	1.00	0.998
Ametryn	1.10	0.999	1.07	0.997	1.04	0.997
Terbuthylazine	0.97	0.999	1.02	0.998	1.00	0.999
Prometryn	1.03	0.999	1.07	0.998	1.05	0.997
Terbutryn	0.88	0.998	1.00	0.999	0.90	0.999
α-BHC	1.04	0.996	1.19	0.997	1.21	0.997
Hexachlorobenzene	1.01	0.999	1.12	0.999	1.12	0.998
γ-BHC	1.02	0.997	1.23	0.998	1.22	0.999
Quintozene	0.97	0.998	1.08	0.997	1.07	0.996
Heptachlor	0.96	0.998	1.01	0.999	1.08	0.995
Heptachlor epoxide	1.02	0.999	1.11	0.996	1.11	0.998
α-endosulfan	1.08	0.996	1.12	0.998	1.03	0.999
Dieldrin	1.17	0.998	1.16	0.997	1.00	0.996
β-endosulfan	1.05	0.999	1.15	0.998	1.16	0.999
p,p′-DDD	1.23	0.996	1.13	0.995	1.14	0.996

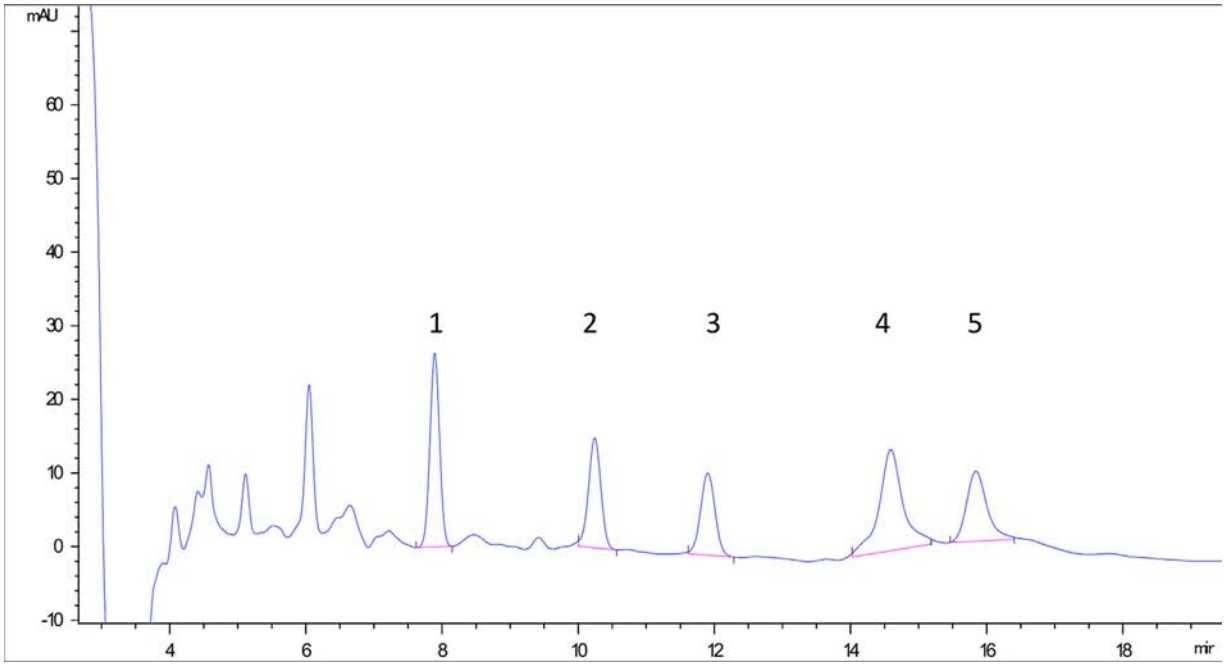

Fig. 6. HPLC chromatograms of ground water sample spiked at 1 μg L^{-1}. Chromatographic peaks: (1) atrazine, (2) ametryn, (3) terbuthylazine, (4) prometryn, and (5) terbutryn.

herbicides, calculated at a signal-to-noise ratio of 3, ranged from 0.39 to 3.26 ng L^{-1}. The repeatability was studied by five parallel experiments at concentration of 50 ng L^{-1} for each analyte under the optimal conditions. The relative standard deviations ranged from 2.4% to 4.5%. The results suggested that the method has a high repeatability for OCPs.

3.4. Analysis of environmental water samples

In order to validate the applicability of the proposed method in genuine samples, the method was applied to analyze the analytes in ground, river and reservoir water samples. Before real sample spiking experiment, matrix effect was determined since it played an important role in the quality of the quantitative data. The slopes obtained in the calibration with matrix-matched standards were compared with those obtained with solvent-based standards. The slope ratio matrix/solvent (matrix effect) was calculated for each of the target analyte in the three environmental samples. Table 3 summarizes the results. It can be seen that for most of the analytes in the three environmental water samples, the matrix effects were in the range of 0.9–1.1, meaning that the matrix effects were almost negligible by using the present methodology.

Initial analysis confirmed that no analyte was found in the water samples. So the recoveries and RSDs of the triazine herbicides were studied by spiking at two concentrations (0.5 and 5.0 μg L^{-1}). The recoveries for triazine herbicides in ground, river and reservoir water samples were in the range from 76.0% to 105.8% with relative standard deviations between 0.13% and 8.22% ($n=3$). The chromatogram of spiked ground water sample is shown in Fig. 6. The recoveries and RSDs of the OCPs were studied by spiking at two concentrations (5 and 50 ng L^{-1}). The recoveries for OCPs in ground, river and reservoir water samples were in the range from 63.0% to 97.4% with relative standard deviations between 0.30% and 10.5% ($n=3$). The chromatogram of spiked ground water sample is shown in Fig. 7. The results demonstrated that this method was reliable for trace level analysis of both triazine herbicides and OCPs in environmental water samples.

3.5. Comparison to other extraction methods

The analytical method concerning the preconcentration of triazine herbicides and OCPs in water samples has been extensively studied including liquid–liquid extraction, liquid–liquid microextraction, solid-phase extraction, solid-phase microextraction and liquid-phase microextraction. But, all these methods were developed for specific analytes; usually analytes belonged to the same class with similar polarity. This presented MSPE method can

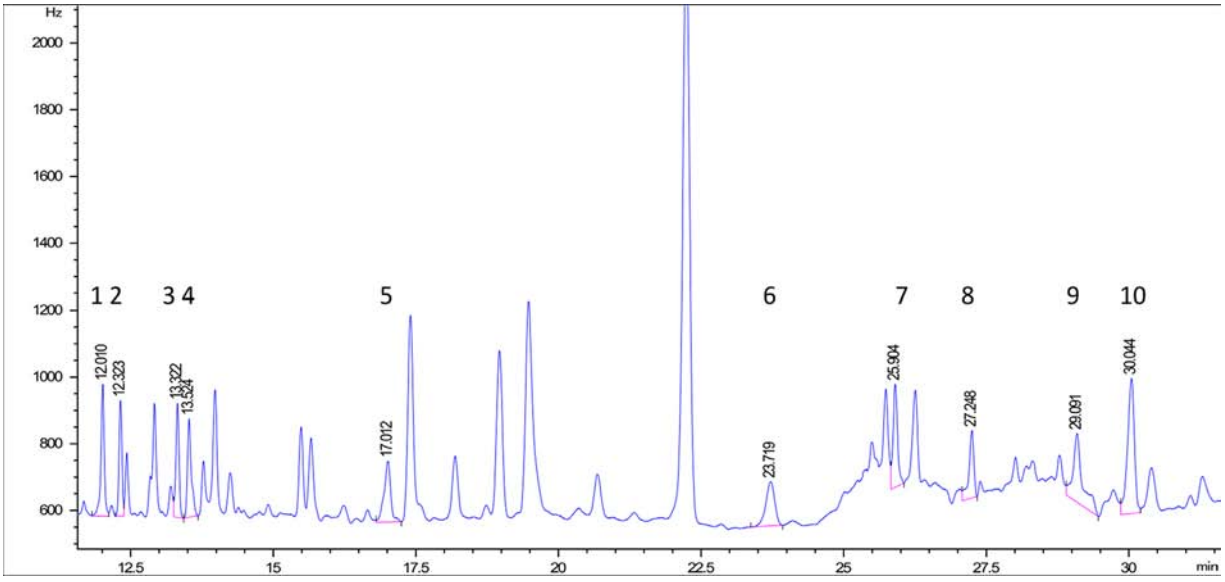

Fig. 7. GC–ECD chromatograms of ground water sample spiked at 10 ng L^{-1}. Chromatographic peaks: (1) α-BHC, (2) hexachlorobenzene, (3) γ-BHC, (4) quintozene, (5) heptachlor, (6) heptachlor epoxide, (7) α-endosulfan, (8) dieldrin, (9) β-endosulfan and (10) p,p′-DDD.

Table 4
Comparison of this work with other methods for the determination of triazine herbicides and OCPs in environmental water samples.

Analyte	Method	LOD (μg L^{-1})	EF[a]	Extraction time (min)	Solvent used (mL)	References
Triazine Herbicides	LLME[c]	0.05–0.1	3000[b]	5	1.1	[11]
	SPE	20–50	50[b]	–	30	[22]
	SPME[d]	0.05–0.2	200[b]	30	50	[24]
	MSPE	0.02–0.04	474–868	20	3.5	[4]
	SBSE[e]	0.1–0.5	250	360	10	[26]
	This work	0.05–0.08	809–878	20	2	This work
	Method	LOD (ng L^{-1})	EF[a]	Extraction time (min)	Solvent used (mL)	References
OCPs	LLME[c]	1.81–3	883–1137	2	1.1	[21]
	SPE	200	100[b]	33	15	[23]
	SPME[d]	0.2–6.6	–	45	–	[25]
	MSPE	6–48	50[b]	60	6	[29]
	SBSE[e]	2.3–25.2	–	120	–	[27]
	This work	0.4–3.2	729–881	5	3	This work

[a] EF is the ratio of the analyte concentration in 200 μL of redissolving solvent to the initial concentration in the water samples.
[b] EF in the reference papers is calculated based on the experiment data without taking recoveries into consideration.
[c] LLME: liquid–liquid microextraction.
[d] SPME: solid-phase microextraction.
[e] SBSE: stir bar sorptive extraction.

extract both polar and nonpolar analytes, which was the greatest advantage compared to other methods. Besides, this presented method was comparable or superior to other methods in terms of LOD, enrichment factors (EFs), extraction time and organic solvent used (see Table 4).

3.6. Conclusions

Novel hydrophilic–lipophilic balanced polymer magnetic nanoparticles were prepared for the first time. This adsorbent can be used for the preconcentration of pesticides with different polarities; nevertheless, other magnetic adsorbents can only adsorb specific analytes with similar polarity. This merit made the magnetic nanoparticle a versatile adsorbent for the magnetic solid phase extraction of a broad range of analytes from environmental water samples. Good repeatability and recoveries and high enrichment factors were obtained for the extraction of triazine herbicides and OCPs. The results indicated that the extraction procedure was also simple and rapid, which made this method an efficient preconcentration technique for the trace pollutants in water samples before chromatographic analysis.

References

[1] Y. Moliner-Martínez, A. Ribera, E. Coronado, P. Campins-Falco, J. Chromatogr. A 1218 (2011) 2276.
[2] B. Maddah, J. Shamsi, J. Chromatogr. A 1256 (2012) 40.
[3] D. Pardasani, P.K. Kanaujia, A.K. Purohit, A.R. Shrivastava, D. Dubey, Talanta 80 (2011) 248.
[4] G. Zhao, S. Song, C. Wang, Q. Wu, Z. Wang, Anal. Chim. Acta 708 (2011) 155.
[5] J. Meng, J. Bu, C. Deng, X. Zhang, J. Chromatogr. A 1218 (2011) 1585.
[6] J. Meng, C. Shi, B. Wei, W. Yu, C. Deng, X. Zhang, J. Chromatogr. A 1218 (2011) 2841.
[7] E. Tahmasebi, Y. Yamini, A. Mehdinia, F. Rouhi, J. Sep. Sci. 35 (2012) 2256.
[8] X. Yu, Y. Sun, C. Jiang, X. Sun, Y. Gao, Y. Wang, H. Zhang, D. Song, Talanta 98 (2012) 257.
[9] H. Eskandari, A. Naderi-Darehshori, Anal. Chim. Acta 743 (2012) 137.
[10] N. Fontanals, R. Marce, F. Borrull, Trends Anal. Chem. 24 (2005) 394.
[11] Z. Zhao, L. Zhang, J. Wu, M. Jin, C. Fan, Anal. Sci. 27 (2011) 547.
[12] C. Wang, S. Ji, Q. Wu, C. Wu, Z. Wang, J. Chromatogr. Sci. 49 (2011) 689.
[13] Q. Zhou, J. Xiao, W. Wang, G. Liu, Q. Shi, J. Wang, Talanta 68 (2006) 1309.
[14] H. Jiang, C. Adams, N. Graziano, A. Roberson, M. McGuire, D. Khiari, Environ. Sci. Technol. 40 (2006) 3609.
[15] J.M. Jiménez–Soto, S. Cárdenas, M. Valcárcel, J. Chromatogr. A 1245 (2012) 17.
[16] D. Djozan, M.A. Farajzadeh, S.M. Sorouraddin, T. Baheri, J. Norouzi, Chromatographia 75 (2012) 139.
[17] A. Derouiche, M.R. Driss, J.P. Morizur, M.H. Taphanel, J. Chromatogr. A 1138 (2007) 231.
[18] C. Gonçalves, M. Alpendurada, J. Chromatogr. A 968 (2002) 177.
[19] M. Kuster, S. Díaz-Cruz, M. Rosell, M. López de Alda, D. Barceló, Chemosphere 79 (2010) 880.
[20] R. Loos, G. Locoro, S. Comero, S. Contini, D. Schwesig, F. Werres, P. Balsaa, O. Gans, S. Weiss, L. Blaha, Water Res. 44 (2010) 4115.
[21] M. Zuo, J. Cheng, G. Matsadiq, L. Liu, M.L. Li, M. Zhang, CLEAN—Soil Air Water 40 (2012) 1326.
[22] L.T.D. Cappelini, D. Cordeiro, S.H.G. Brondi, K.R. Prieto, E.M. Vieira, Environ. Technol. 33 (2012) 2299.
[23] G. Fang, W. Chen, Y. Yao, J. Wang, J. Qin, S. Wang, J. Sep. Sci. 35 (2012) 534.
[24] Q. Wu, C. Feng, G. Zhao, C. Wang, Z. Wang, J. Sep. Sci. 35 (2012) 193.
[25] A. Lara-Gonzalo, J.E. Sánchez-Uría, E. Segovia-García, A. Sanz-Medel, Int. J. Environ. Anal. Chem. 92 (2012) 856.
[26] F. Portugal, M.L. Pinto, J. Nogueira, Talanta 77 (2008) 765.
[27] P. Tolgyessy, B. Vrana, Z. Krascsenits, Talanta 87 (2011) 152.
[28] S. Lu, J. Forcada, J. Polym. Sci.: Polym. Chem. 44 (2006) 4187.
[29] S. Ozcan, A. Tor, M.M. Aydin, J. AOAC Int. 95 (2012) 1343.