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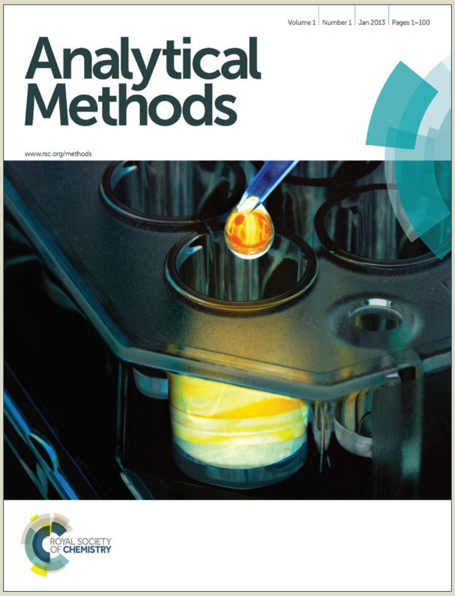

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Microwave-assisted synthesis of poly (ionic liquid)-coated magnetic nanoparticles for the extraction of sulfonylurea herbicides from soil for HPLC

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Abstract

Poly(ionic liquid) (PIL) was synthesized and immobilized onto prepared silica-coated magnetic nanoparticles, which was used as magnetic solid-phase (MSPE) sorbent and applied to the extraction of sulfonylurea herbicides (SUHs) in soil samples prior to high-performance liquid chromatography analysis. The type and volume of desorption solvent and quantity of the sorbent were optimized for the extraction process. Under the optimized conditions, the matrix matched calibrations curves were linear (R^2>0.999) for sulfonylurea herbicide concentrations in the range of 10-1500 ng/mL. The relative standard deviation range for repeat determinations of the analytes was 3.2-4.5%. The ranges for the limits of detection and quantification were 1.62-2.94 and 5.4-9.8 ng/mL, respectively. These results demonstrate that the Fe_3O_4@SiO_2@PIL provide efficient extraction of sulfonylurea herbicides from soil samples.

Keyword: sulfonylurea herbicides, magnetic solid-phase extraction, high-performance liquid chromatography, Fe_3O_4@SiO_2@PIL, extraction

1. Introduction

Sulfonylurea herbicides (SUHs) are broad-spectrum herbicides that are widely used for the control of broadleaf weeds and annual grasses in numerous crops [1]. SUHs are effective inhibitors of the synthesis of acetolactate, which is a key enzyme in the biosynthesis of branched-chain amino acids. This inhibition leads to termination of plant cell division and growth [3]. SUHs contain an aliphatic, aromatic, or heterocyclic group and a sulfonylurea bridge (Fig.1). They are weak acids and highly water-soluble (log Kow < 1) with pKa ranging from 3.3 to 5.2 [2]. These compounds degrade slowly in the environment [4-5]. Their half-lives in soil vary from 5 to 70 d depending on soil pH and other soil characteristics [6]. The SUH residues are phytotoxic and may affect the growth of numerous crops. Sensitive, robust and reliable methods for the detection of multiple SUH residues in soil are being developed.

Different techniques for the separation and preconcentration of SUHs from environmental samples involving solid-phase extraction (SPE) [7-11], supercritical fluid extraction (SFE) [12], and molecularly imprinted SPE [13] have been reported. The extraction methods mentioned above are time-consuming and complex for preparation. As an alternative to conventional extraction methods, magnetic solid-phase extraction (MSPE) has many unique features. Magnetic nanoparticles (MNPs) can be fully dispersed in a matrix and adsorb the target analytes more efficiently because of their high specific surface area. The sorbent can be easily separated from the matrix solution by applying an external magnetic field, which avoids the time-consuming column or filtration operations encountered in SPE [14]. MNPs have been applied to extraction of polycyclic aromatic hydrocarbons [15], organophosphorus pesticides [16] and triazine herbicides [17].

Poly (ionic liquid) (PIL) is a new kind of polyelectrolytes with structural and properties characteristics of both polymers and ionic liquids (ILs), including negligible vapor pressure, high thermal stability, reusability, and variable viscosity [18]. PIL display enhanced performance compared to ILs [19]. MNPs coated with PIL have potential applications in the fields of separation and preconcentration. Zheng synthesized PIL coated MNPs and used them to extract organophosphorus pesticides[20]. Zhang reported the extraction of triazines herbicides using poly ionic liquid-modified magnetic nanoparticles [21]. Absalan used PIL coated MNPs to remove reactive red-120 and 4-(2-pyridylazo) resorcinol from water matrix [22].

Conventional synthesis of MNPs coated with PIL involves heating under reflux, which is time-consuming and has high energy requirements. Microwave-assisted synthesis is promising for the synthesis of MNPs coated with PIL because it can not only reduce the time and energy requirements, but also reduce side reactions, increase yields and improve reproducibility [23]. Moreover, it provides uniformity and selectivity because of the unique polarization effect of microwaves [24].

In this study, poly (ionic liquid) (PIL) was synthesized and immobilized onto prepared silica-coated magnetic nanoparticles by a microwave-assisted synthesis method. The coated MNPs were served as MSPE sorbent for multiple-herbicide residues extraction from soil samples prior to HPLC analysis. The SUHs metsulfuron-methyl, sulfometuron-methyl and thifensulfuron were selected as target analytes because of their widespread use in agriculture and forestry. The influence of different factors on the extraction efficiency was investigated. A notable finding of MNPs was good dispersion, stability, reutilization and extraction efficiency to the target.

2. Experimental

2.1 Reagents and materials

Ferric chloride hexahydrate ($FeCl_3·6H_2O$), ammonium hydroxide ($NH_3·H_2O$, mass fraction 28%), triethylamine, and concentrated hydrochloric acid (HCl, 37.5%) were acquired from Beijing Chemical Reagent Co. Ltd (Beijing, China). Tetraethyl orthosilicate (TEOS), 3-chloropropyltriethoxysilane, methanol, acetonitrile and hexane (HPLC-grade) were purchased from J&K Scientific Ltd (Beijing, China). Standard solutions (100 μg mL^{-1}) of the herbicides metsulfuron-methyl, sulfometuron-methyl and thifensulfuron were purchased from the Ministry of Agriculture Scientific Monitoring and Environmental Protection (Tianjin, China). 1-Vinylimidazolium and bis (trifluoromethane) sulfonimide lithium salt ($LiNTf_2$) were purchased from Lanzhou Greenchem ILs, LICP, CAS (Lanzhou, China). Soil samples were obtained from a garden at Beijing University of Chemical Technology (Beijing, China). All other chemical reagents were of analytical grade. All HPLC solvents were filtered through a 0.22-μm membrane before use.

2.2 Instrumentation and analytical conditions

A microwave synthesis system (Discover® SP, CEM, Matthews, NC) was used in this study. Analysis for SUHs was conducted using an Agilent 1100 Series HPLC (Agilent, Santa Clara, CA) equipped with an Agilent ODS-SP C18 column (4.6 mm × 150 mm i.d., particle size 5μm, Agilent Technologies) and an UV-Vis detector operating at 230 nm. The mobile phase components were acetonitrile (A) and water (B) (40:60, v/v). The injection volume was 10 μL, and the mobile phase flow rate was 1.0 mL min^{-1}.

2.3. Sample preparation and extraction

Soil samples were obtained by quincunx sampling from a garden at the Beijing University of Chemical and Technology. Plants, roots and stones were removed from the soil samples. The soil samples were air dried at room temperature, crushed in a mortar and passed through a 160 mesh sieve. 100 mL of deionized water was added to 30 g of sieved soil sample, extracted ultrasonically (100W, 25°C) for 20 min. The suspension was centrifuged and the supernatant filtered through a 0.45 μm membrane. This procedure was repeated twice with another two portions of deionized water (100 mL) and the extracted solutions were combined for the MSPE extraction procedure. The spiked soil samples were prepared by adding accurately volumes of the stock solution into the soil extracts.

The MSPE extraction procedure was conducted by Fig. 2. 60 mg of sorbent was added to 10 mL prepared soil extracts solution and mixed for 25 min. The sorbent was collected by using an external magnetic field. The SUHs bound to the sorbent were eluted with 8 mL acetonitrile. The eluate was concentrated to dry under a stream of N_2 and redissolved in 0.5 mL acetonitrile for HPLC analysis. All samples were filtered through a 0.22-μm membrane before injection.

2.4 Preparation of core–shell $Fe_3O_4@SiO_2$ MNPs

Magnetic iron oxide nanoparticles (Fe_3O_4) were prepared using a standard solvothermal reduction method [25]. Briefly, $FeCl_3 \cdot 6H_2O$ (1.35 g) was added to ethylene glycol (40 mL), and stirred for 10 min to obtain a homogeneous solution. Anhydrous sodium acetate (3.60 g) was then added with vigorous stirring for 30 min to give a homogeneous yellow solution, which was transferred into a polytetrafluoroethylene-lined stainless-steel autoclave. The autoclave was sealed, and heated at 200 °C for 8 h. The resulting black magnetic precipitate was then cooled and washed several times before being dried under vacuum.

Next, silica-coated Fe_3O_4 was synthesized according to a previously reported sol-gel method [26-27]. In brief, Fe_3O_4 (1 g) were dispersed in a solution of deionized water (50 mL), ethanol (150 mL), and $NH_3 \cdot H_2O$ (5 mL), and subjected to ultrasonication for 10 min. Then, a solution of 50 mL of ethanol and 2 mL of TEOS was added dropwise with stirring for 8 h at room temperature. The product was washed sequentially with 1 mol L^{-1} HCl, deionized water, and ethanol, and dried under vacuum.

2.5 Synthesis of MNPs coated with PIL

The MNPs coated with PIL were synthesized following a reported method with some modifications [28]. Briefly, a mixture of 1-vinylimidazole (6 mL) and 3-chloropropyltriethoxysilane (12 mL) was suspended in toluene and placed in a microwave reactor for 4 h at 80 W and 100 °C under N_2 with magnetic stirring. The mixture was then cooled to ambient temperature and followed by the addition of 2 % (mass fraction) 2, 2-azobisisobutyronitrile (157.3 mg). Thereafter the mixture was carrying out the polymerization in the microwave reactor for 4 h at 80 W and 80 °C. Next, triethylamine (0.6 mL) and Fe_3O_4@SiO_2 (0.5 g) were added, and the mixture was heated for 2 h at 80 W and 100 °C. The hydrophilic MNPs coated with PIL were obtained by magnetic separation and washed sequentially with acetonitrile, methanol and deionized water before being dried under vacuum.

To obtain hydrophobic MNPs coated with PIL (Fe_3O_4@SiO_2@PIL), $LiNTf_2$ (2.8 g) was dissolved in 50 mL of acetonitrile, followed by adding 0.5 g of the hydrophilic MNPs coated with PIL. The mixture was stirred vigorously in the microwave for 2 h at 60 W and 60 °C. The resulting product was separated using a magnet and washed sequentially with acetonitrile, methanol and deionized water before being dried under vacuum.

2.6. Characterization

The prepared MNPs were observed by scanning electronic microscopy (SEM; SUPRA55, Zeiss, Oberkochen, Germany) and transmission electron microscopy (TEM; Tecnai 20, FEI, Hillsboro, OR) to evaluate their size and morphology. Fourier transform-infrared spectra (4000–400 cm^{-1}) were recorded on a Nicolet spectrometer (Thermo Fisher Scientific, Waltham, MA) using KBr pellets. Elemental analysis (Vario EL cube, Elementar, Hanau, Germany) was used to obtain the C, H and N contents of the samples. The magnetic properties of the prepared materials were determined on a Lake Shore 7410 vibrating sample magnetometer (VSM, Westerville, OH, USA).

3. Results and discussion

3.1 Characterization of Fe_3O_4@SiO_2@PIL prepared by microwave irradiation

The size and shape of the MNPs were investigated by TEM, and SEM was used to determine their morphology. The Fe_3O_4 magnetic nanoparticles had an average diameter of about 500 nm and were spherical with good dispersibility and uniform surface morphology (Fig. 3(A-C)). After stepwise coating with layers of PILs, the obtained Fe_3O_4@SiO_2@PIL were slightly larger than the Fe_3O_4@SiO_2 nanoparticles because of the additional shell covers the surface of the silica layer. In addition, the SEM images validated the conclusion above. The MNPs appeared to be three-dimensional with core-shell structures. The surface of Fe_3O_4@SiO_2@PIL appeared to be rougher than the layer of silica, which could be attributed to surface modification of the PIL.

FTIR spectroscopy and elemental analysis were used to further evaluate the successful immobilization of the PILs on the surface of the MNPs. Characteristic absorption bands at 2945 cm^{-1} and 2858 cm^{-1} could be assigned to the symmetric and asymmetric stretching vibrations of $–CH_2–$, respectively. These bands verify the existence of organic compounds on the surface of the Fe_3O_4 particles. Peaks at 3108 cm^{-1}, 1497 cm^{-1}, 1415 cm^{-1}, 1084 cm^{-1} correlated to imidazolium ring n(C–H) stretching, imidazolium H–C–C bending, H–C–N bending, and $C_2–N_1–C_5$ bending, respectively. Deformation and rocking vibrations of –CH– were observed at 1283 cm^{-1}, 912 cm^{-1}, 1229 cm^{-1}, and 819 cm^{-1}, and at 743 $cm^{-1}$and 663 cm^{-1} for $–CH_2–$. These results are similar to those in the literature, which suggested that the PILs were successfully attached to the MNPs (Fig. S1)

The elemental analysis of the MNPs showed the N content increased after modification with the PIL (Table 1), which indicated that the PIL were successfully immobilized on the MNPs. The C/N ratio in the Fe_3O_4@SiO_2@PILs was about 5.67, which further confirmed that the PILs were bound to the MNPs.

The magnetic properties of the prepared nanomaterials were determined at room temperature by VSM. No obviously coercivity or remanence for all the magnetic samples was detected after the applied magnetic field was removed, indicating that the synthesized magnetic materials were superparamagnetic. The magnetization saturation (Ms) values of the Fe_3O_4, Fe_3O_4@SiO_2 and Fe_3O_4@SiO_2@PIL were 86, 61 and 48 emu g^{-1}, respectively. The magnetic responsiveness significantly reduced after modification because of the non-magnetic coatings, including silica and PIL. Besides, the Ms of Fe_3O_4@SiO_2@PIL is adequate for its fast collection and separation in solution (Fig. S2).

3.2. Optimization of MSPE conditions

To achieve the highest extraction efficiency, optimization of the elution steps and extraction steps was performed. All experiments were performed in triplicate.

3.2.1. Type of desorption solvent

The proper choice of solvent is crucial for obtaining high desorption efficiency of the SUHs. Various solvents, including hexane, dichloromethane, ethyl acetate, acetonitrile and methanol were investigated. As shown in Fig. 4(A), the largest peak areas were obtained when using acetonitrile or methanol as the desorption solvent. However, there was less interference observed in the HPLC chromatograms when acetonitrile was used compared with methanol. This was likely because of the weaker polarity of acetonitrile. Therefore, acetonitrile was selected as the desorption solvent.

3.2.2. Quantity of sorbent

In order to obtain efficient extraction of the SUHs from the adsorbent, differing amounts of adsorbent from 15 to 90 mg were investigated. As can be concluded from Fig. 4(B), the peak areas of the SUHs increased along as the quantity of sorbent was increased from 15 to 45 mg. The peak areas then increased slowly and tended to be stabilization with 45 to 90 mg of sorbent. Consequently, 60 mg of the sorbent was selected as the optimum quantity.

3.2.3 Extraction time

To examine the effect of extraction time on extraction efficiency, extraction times of 10-35 min were studied. As displayed in Fig. 4(C), the peak areas of the three analytes increased with the extraction time from 10 min to 20 min, and the extraction equilibrium was reached at times of 25 min. Therefore, 25 min was chosen as the optimum extraction time.

3.2.4. Volume of eluent

To investigate the influence of eluent volume on desorption efficiency, various volumes of acetonitrile from 2 to 14 mL were tested. As shown in Fig. 4(D), the peak areas of the SUHs increased with the eluent volume from 1 to 6 mL. For volumes greater than 8 mL, there was no significant increase in peak area response. Consequently, 8 mL of acetonitrile was selected for desorption of the SUHs.

3.2.5 Optimization of the elution time

To examine the effect of elution time on the desorption efficiency, elution times between 2 and 16 min were studied. The peak areas of the analytes increased with the elution time from 1 to 6 min. For elution times greater than 8 min, the peak area response remained unchanging. Therefore, an elution time of 8 min was used (Fig. S3).

3.2.6 Optimization of ionic strength

The influence of ionic strength on the extraction efficiency was examined by increasing NaCl concentration in the matrix solution, ranging from 0 to 7% (w/v). As shown in the Fig. S4, the peak area of SUHs all decreased after the addition of NaCl, which means salt addition had a negative effect on the extraction efficiency. The addition of salt might change the physical properties of the Nernst diffusion film, reduce the diffusion rates of solutes from water to the adsorbent surface, and ultimately affect the extraction efficiency [29].Thus, no NaCl was added.

3.3 Reusability of the sorbent

To examine the reusability of the nanoparticle adsorbent, the modified MNPs were washed twice by ultrasonication with 5 mL of methanol and dried in vacuum before re-using in repeat cycles.

After 19 cycles of reuse, there was no significant decrease in the extraction efficiency. These results indicate that the modified MNPs are stable and robust in terms of reusability (Fig. S5).

3.4 Analytical performance

To evaluate the analytical performance of the proposed method, the matrix matched calibrations curves were made. The spiked matrix solutions with concentration of 0.5μg mL^{-1}, 1μg mL^{-1}, 2.5μg mL^{-1}, 5μg mL^{-1}, 10μg $mL^{-1}$and 15μg mL^{-1} were obtained by adding stock solutions of accurately measured volumes into the soil extracts (obtained in section 2.3). The spiked matrix solutions were filtered through a 0.22-μm membrane before HPLC analysis.

The linear range for the three analytes was 10-1500 ng/mL with correlation coefficients (R^2) between 0.9996 and 0.9999 (Table 2). The ranges for the limit of detection (LOD) and limit of quantification (LOQ), which were determined based on signal to noise ratios of 3 and 10, were 1.62-2.94 and 5.4-9.8 ng/mL, respectively. The precision was evaluated based on six repeat extractions of a sample. The range for the relative standard deviation (RSD, n = 6) was 3.2-4.5%.

3.5 Application to real soil samples

The application and accuracy of the present method was evaluated using real soil samples. Typical chromatograms of blank and spiked samples after extraction by the MNPs coated with PILs are shown in Fig. 5. No herbicides was detected in the soil samples. As shown in Table 3, a recovery study was carried out by spiking the samples at three different concentration levels, with each sample treatment performed in triplicate.

The present method is compared with previously reported methods for the three herbicides in Table 4. Compared with the methods in the literatures, the PIL-modified MNPs gave a lower LOD and better sensitivity, perhaps because of their high surface area and specific functional groups. The proposed method is rapid, simple, and gives satisfactory recoveries. The PIL-modified MNPs can be reused at least 19 times without an obvious decrease in extraction efficiency. Therefore, the results indicate that the proposed method is highly suitable for the determination of SUHs, such as thifensulfuron, metsulfuron-methyl, and sulfometuron-methyl, in soil samples.

4 Concluding remarks

A new PIL immobilized magnetic nanoparticle-based MSPE method combined with HPLC-ultraviolet detection has been developed for SUHs in soil samples. Compared with conventional synthesis, the microwave synthesis was time-saving, environmentally friendly, and simple. The PIL-modified MNPs had a large effective contact area, high viscosity and good interaction with the target compounds, which can provide rapid separation of SUHs from the sample solution with the aid of an external magnetic field, offers an environment-friendly and inexpensive method for sample extraction. The separation process by HPLC was complete within 10 min. The adsorbent could be reused at least 19 times without an obvious decrease in the extraction efficiency. All of the experimental results clearly demonstrate that Fe_3O_4@SiO_2@PIL (NTf_2) is an attractive adsorbent for MSPE of herbicides in soil samples.

Acknowledgments

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Notes

The authors have no competing financial interests to declare

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Figure captions

Fig. 1 The structures of the SUHs

Fig. 2 MSPE using the MNPs coated with PILs

Fig. 3 TEM images of Fe_3O_4 (A), Fe_3O_4@SiO_2 (B), Fe_3O_4@SiO_2@PILs (C), and SEM image of Fe_3O_4@SiO_2 (D), Fe_3O_4@SiO_2@PILs (E).

Fig. 4(A) Comparison of eluent type. Amount of Fe_3O_4@SiO_2@PILs 60 mg, vortex time, 30 min; volume of eluent, 10 mL; desorption time, 10 min; concentration of SUHs, 80ng/mL. (B) Effect of sorbent quantity. Vortex time, 30 min; eluent type, acetonitrile; volume of eluent, 10 mL; desorption time, 10 min; concentration of SUHs, 80ng/mL. (C) Effect of vortex time. Quantity of Fe_3O_4@SiO_2@PILs, 60 mg; eluent type, acetonitrile; volume of eluent, 10 mL; desorption time, 10 min; concentration of SUHs, 80ng/mL. (D) Effect of elution volume. Quantity of Fe_3O_4@SiO_2@PILs, 60 mg; eluent type, acetonitrile; vortex time, 25 min; elution time, 10 min; concentration of SUHs, 80ng/mL.

Fig. 5 HPLC chromatograms for blank and spiked soil samples. (a) Soil sample extracted without Fe_3O_4@SiO_2@PILs, (b) Soil sample extracted with Fe_3O_4@SiO_2@PILs.

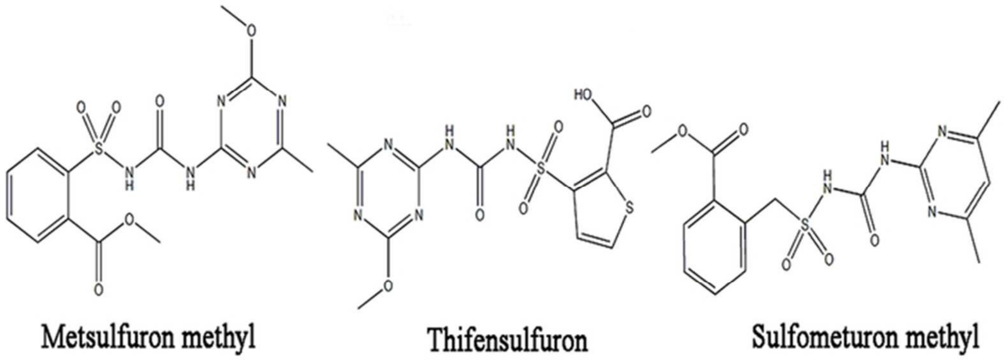

Fig.1 the structures of SUHs
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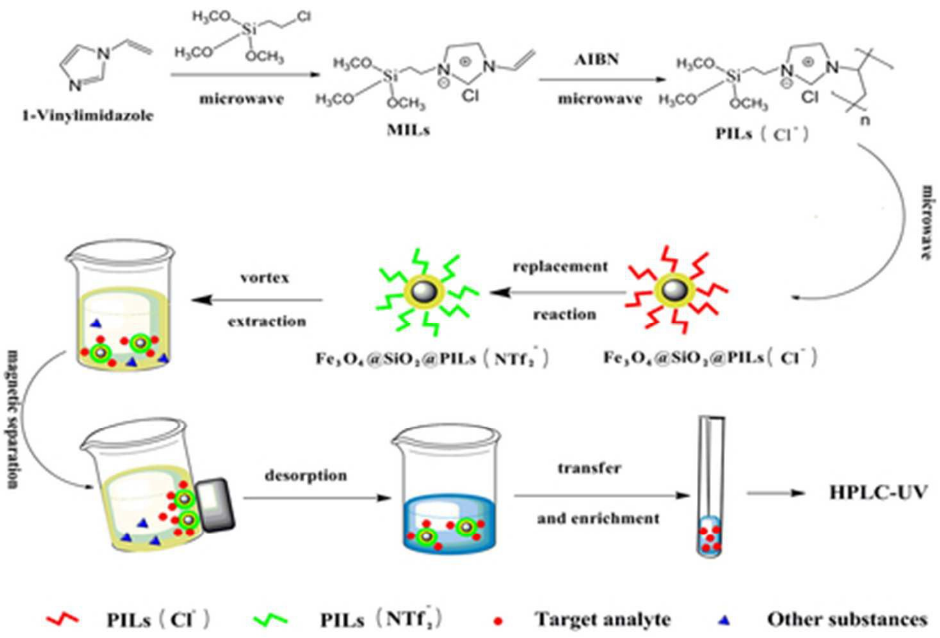

Fig.2 MSPE using the MNPs coated with PILs
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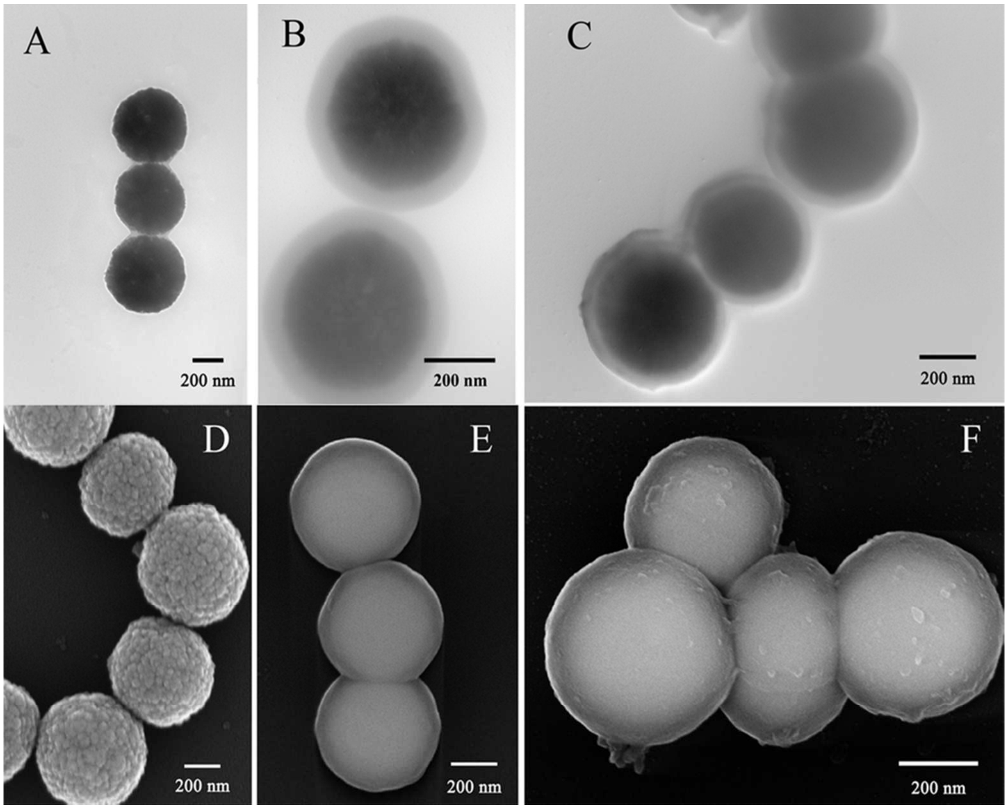

Fig.3 TEM images of Fe3O4 (A), Fe3O4@SiO2 (B), Fe3O4@SiO2@PILs (C), and SEM image of Fe3O4@SiO2 (D), Fe3O4@SiO2@PILs (E).
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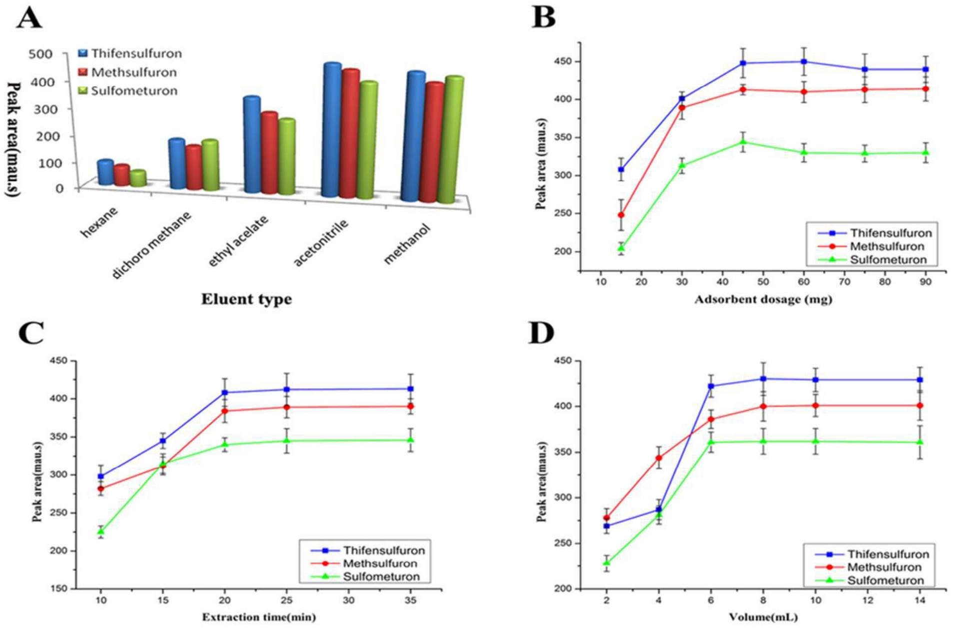

Fig. 4 (A) Comparison of eluent type. Amount of Fe3O4@SiO2@PILs 60 mg, vortex time, 30 min, volume of eluent, 10 mL, desorption time, 10 min, concentration of SUHs, 80ng/mL. (B) Effect of sorbent quantity. Vortex time, 30 min, eluent type, acetonitrile, volume of eluent, 10 mL, desorption time, 10 min, concentration of SUHs, 80ng/mL. (C) Effect of vortex time. Quantity of Fe3O4@SiO2@PILs, 60 mg, eluent type, acetonitrile, volume of eluent, 10 mL, desorption time, 10 min, concentration of SUHs, 80ng/mL. (D) Effect of elution volume. Quantity of Fe3O4@SiO2@PILs, 60 mg, eluent type, acetonitrile, vortex time, 25 min, elution time, 10 min, concentration of SUHs, 80ng/mL.
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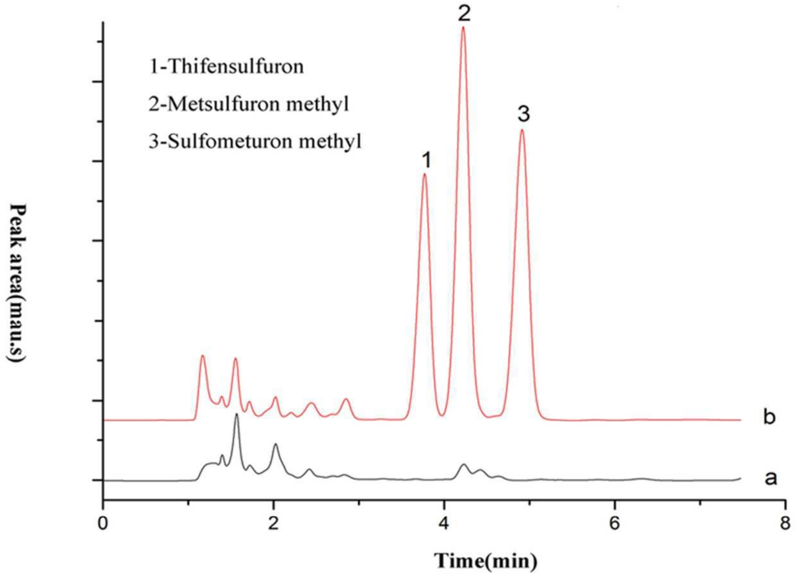

Fig. 5 HPLC chromatograms for blank and spiked soil samples. (a) Soil sample extracted without Fe3O4@SiO2@PILs, (b) soil sample extracted with Fe3O4@SiO2@PILs.
40x26mm (600 x 600 DPI)

Table 1 Elemental analysis data

Name	N%	C%	H%
Fe_3O_4	0.016	2.06	0.670
Fe_3O_4@SiO_2	0.062	1.91	1.211
Fe_3O_4@SiO_2 @PILs	3.177	18.01	0.092

Table 2 Quality parameters of the calibration method for the SUHs (*n*=6)

SUHs	**Linearity equation**	**Linearity ($ng\ mL^{-1}$)**	**Correlation coefficient (R^2)**	**LOD ($ng\ mL^{-1}$)**	**LOQ ($ng\ mL^{-1}$)**	**RSDs (%) (n=6)**
Thifensulfuron	y=4.664x+0.1978	10-1500	0.9999	1.95	6.5	3.8
Methsulfuron	y=5.819x+1.0617	10-1500	0.9997	2.94	9.8	3.2
Sulfometuron	y=4.110x+1.6000	10-1500	0.9996	1.62	5.4	4.5

Table 3 Recoveries and RSDs of soil samples after extraction with Fe_3O_4@SiO_2@ PILs (n = 3).

Samples	**Spiked (ng mL^{-1})**	**Mean recovery ± SD (%)**		
		Thifensulfuron	**Methsulfuron**	**Sulfometuron**
Soil	11	81.8±4.5	91.2±4.8	97.6±4.9
	110	80.2±5.5	92.6±4.8	89.4±3.8
	1110	77.4±5.1	93.4±3.2	86.7±5.2

Table 4 Comparison of proposed method with other methods for determination of SUHs

Analytes	Method	Recovery	LOD(ng mL^{-1})	RSDs (%) (n=6)	Time(min)	Ref
Thifensulfuron	SPE-CZE-UV	65.71	50	3.01	20	[29]
Methsulfuron		86.4	50	4.89		
Sulfometuron		95.83	75	3.15		
Thifensulfuron	MISPE-HPLC-DAD	78	3.00	7.1	24	[30]
Thifensulfuron	SPE-HPLC-UV	60	13.5	-	>60	[31]
Methsulfuron	SPE-CLC-DAD	72.9	6.00	3.9	25	[32]
Thifensulfuron	MSPE-HPLC-UV	81.8	4.93	3.8	25	This work
Methsulfuron		93.4	8.36	3.2		
Sulfometuron		97.6	2.28	4.5		