Porous monolith-based magnetism-reinforced in-tube solid phase microextraction of sulfonylurea herbicides in water and soil samples

Jinling Pang, Xiaochong Song, Xiaojia Huang*, Dongxing Yuan

Key Laboratory of the Ministry of Education for Coastal and Wetland Ecosystem, Fujian Provincial Key Laboratory for Coastal Ecology and Environmental Studies, College of the Environment and Ecology, Xiamen University, P.O. Box 1009, Xiamen, Fujian 361005, PR China

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ABSTRACT

In the present study, porous monolith-based magnetism-reinforced in-tube solid phase microextraction (MB-MR/IT-SPME) was first introduced to concentrate sulfonylurea herbicides (SUHs). To realize the effective capture of SUHs, a monolithic capillary microextraction column (MCMC) based on poly (vinylimidazole-*co*-ethylene dimethacrylate) polymer doped with Fe_3O_4 magnetic nanoparticles was *in-situ* synthesized in the first step. After that, the MCMC was twined with a magnetic coil which was employed to carry out variable magnetic field during adsorption and desorption procedure. Various important parameters that affecting the extraction performance were inspected in detailed. Results well indicated that exertion of magnetic field in the whole extraction procedure was in favor of the capture and release of the studied SUHs, with the extraction efficiencies increased from 36.8–58.1% to 82.6–94.5%. At the same time, the proposed MB-MR/IT-SPME was online combined to HPLC with diode array detection (HPLC/DAD) to quantify trace levels of SUHs in water and soil samples. The limits of detection ($S/N = 3$) for water and soil samples were in the ranges of 0.030–0.15 μg/L and 0.30–1.5 μg/kg, respectively. The relative standard deviations (RSDs) for intra- and inter-day variability were both less than 10%. Finally, the introduced approach was successfully applied to monitor the low contents of studied SUHs in environmental water and soil samples. Satisfying fortified recovery and precision were achieved.

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1. Introduction

Sulfonylurea herbicides (SUHs) have been widely applied to control broadleaf weeds and annual grasses due to its low application rates and high herbicidal activity [1,2]. However, with the ever-increasing application in agriculture, several SUHs residues have been found in field soils [3]. Besides, SUHs can be transferred into various environmental waters due to its high mobility [2,4]. Studies have evidenced that SUHs possessed high phytotoxicity, and could produce adverse impacts to human such as the formation of urinary calculus [5]. To protect human health and environment, the maximum concentration levels for herbicides have been regulated by several governments and organizations [6,7]. Therefore, it is crucial to develop sensitive, reliable and robust approach for the monitoring of SUHs residuals in water and soils.

Due to the flexibility, cost-effectiveness, highly qualitative and quantitative performance, HPLC coupled to diode array detector (DAD) or mass spectrometry (MS) has been extensively applied to analyze SUHs [8,9]. However, appropriate sample pretreatment should be performed before HPLC analysis due to the low contents of analytes and the complexity of sample matrix. Until now, various methods which can be divided into adsorbent-based extraction (ABE) [10–12] and solvent-based extraction (SBE) [13,14] have been exploited to capture SUHs in all kinds of samples. In comparison with SBE approach, ABE is more attractive because it consumes less toxic organic solvent. The ABE approaches used for the analysis of SUHs mainly include solid phase extraction (SPE) [15,16], dispersive solid-phase extraction (DSPE) [17], solid phase microextraction (SPME) [11] and magnetic solid-phase extraction (MSPE) [18,19]. However, the above-mentioned technologies are difficult to be online coupled with HPLC, and they still require manual operation between extraction and chromatographic analysis. Herein, developing online couplable sample preparation and minimizing labor are attractive in the analysis of SUHs. In 1997, Eisert and Pawliszyn firstly developed in-tube SPME (IT-SPME) which not only inherited the prominent merits of traditional SPME but also exhibited additional features including easy automation and online coupling with HPLC [20]. Based on the advantages, IT-SPME is an ideal sample preparation method for the determination of SUHs. However,

* Corresponding address at: P.O. Box 1009, Xiamen University, Xiamen 361005, PR China.

E-mail addresses: hxj@xmu.edu.cn, xiaojiahuang@aliyun.com (X. Huang).

to the best of our knowledge, there is no related study that employs IT-SPME to extract SUHs. Herein, developing online IT-SPME technology for the analysis of SUHs is interesting.

According to previous studies [21], unsatisfying extraction efficiency still can be found in IT-SPME. To overcome this problem, magnetic-IT-SPME approach utilizing magnetic microfluidic principle and the diamagnetism of analytes was introduced by Campíns-Falcó and co-workers [22]. In their works, a silica capillary column contained magnetic Fe_3O_4 nanoparticles in the inner surface was employed as microextraction column. The capillary column was twined with a magnetic coil which could be exerted different directions of magnetic field during adsorption and desorption steps. Under the influence of magnetic force, the extraction efficiencies of studied analytes were enhanced obviously. However, the extraction capacity of magnetic-IT-SPME was limited due to open-tubular capillary column (OTCC) was utilized to capture analytes. Recently, an improved extraction format of magnetic-IT-SPME, namely, monolith-based magnetism-reinforced IT-SPME (MB-MR/IT-SPME) was introduced in our group [23]. The MB-MR/IT-SPME can improve the extraction efficiency and enhance extraction capacity for studied analytes because it combines the magnetic microfluidic principles and the prominent features of porous monolith. MB-MR/IT-SPME has been online coupled to HPLC equipped with diode array detection (HPLC-DAD) to successfully quantify several pollutants in environmental waters [24,25].

Considering the attractive merits of MB-MR/IT-SPME and the needs of the monitoring of SUHs, in the present study, we tried to introduce MB-MR/IT-SPME approach and online combine it with HPLC/DAD for the efficient extraction and high sensitive quantification of SUHs. Based on the molecular structure and chemical properties of studied SUHs, a monolithic capillary microextraction column (MCMC) based on poly (vinylimidazole-*co*-ethylene dimethacrylate) polymer (VIED) doped with Fe_3O_4 magnetic nanoparticles was *in-situ* synthesized and employed as the extraction phase of the proposed online MB-MR/IT-SPME-HPLC-DAD system. According to the magnetic microfluidic principles [22], when a magnetic field is applied, the adsorbent doped with the Fe_3O_4 nanoparticles in the MCMC will be magnetized. The diamagnetic SUHs in paramagnetic medium tend to move to the area where the intensity of magnetic field is weakest. Therefore, the extraction performance for SUHs can be enhanced under the help of

magnetic field. Various parameters influencing the extraction performance were inspected in detail. Under the most favorable conditions, the introduced approach was successfully applied to quantify trace levels of studied SUHs in environmental and soil samples.

2. Experimental

2.1. Chemicals and materials

Functional monomer, 1-vinylimidazole (VI, 99%) was purchased from Macklin Biochemical Co. (Shanghai, China). Ethylene dimethacrylate (ED, 98%) and 3-(trimethoxysilyl)propyl methacrylate (γ-MAPS, 95%) were obtained from Tokyo kaseikogyo Co. (TCI, Japan). Azobisisobutyronitrile (AIBN, 97%), PEG 4000, formic acid (FA), sodium hydroxide and hydrochloric acid was supplied by Xilong Chemical (Guangzhou, China). *N,N*-dimethylformamide (DMF, 98%) was bought from Shanghai Chemical Co. (China). Acetonitrile (ACN) and methanol were chromatographic grade and they were got from Tedia (Fairfield, USA). A Milli-Q Reference water-purification system (Merck Millipore, Germany) was employed to prepare ultrapure water used in the whole study. The fused silica capillary (320 μm i.d.) was bought from Ruifeng Instrumental Co. (Hebei, China).

Five studied SUHs, including thifensulfuron methyl (THM), metsulfuron methyl (MEM), chlorsulfuron (CHS), prosulfuron (PRS) and triflulsulfuron methyl (TRM) were all above 99%, and they were supplied by the National Institute for the Control of Pharmaceutical and Biological Products (Beijing, China). Table S1 lists the basic properties of studied SUHs. Individual stock solution of each target analyte was prepared at the concentration of 10.0 mg/L in methanol and stored at 4 °C. The stock solution was diluted with ultrapure water to give the desired concentration.

2.2. Instruments and chromatographic conditions

Fig. 1 displays the diagram of the introduced online MB-MR/IT-SPME-HPLC/DAD system, which including a pretreatment section and a chromatographic separation segment. The pretreatment section includes a high-pressure six-port valve (valve 1) (Rheodyne 7725i, Cotati, CA, USA), two high pressure pumps (pump A and
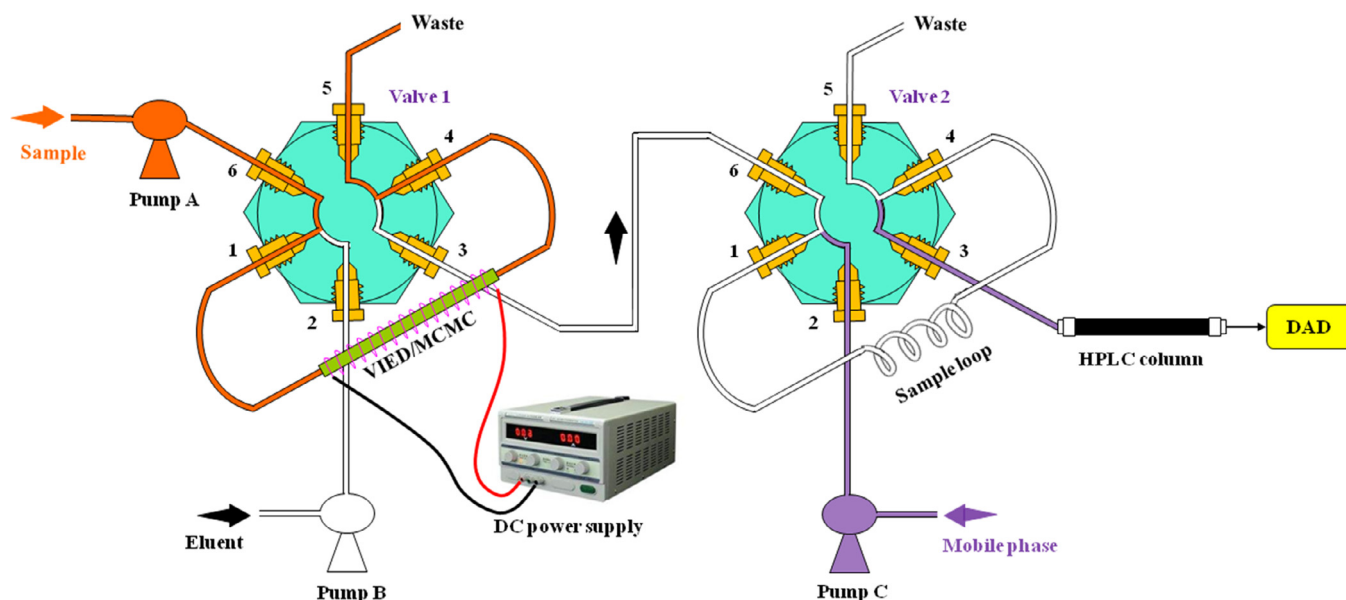

Fig. 1. The introduced MB-MR/IT-SPME-HPLC/DAD system.

pump B) (P230 II, Elite, Dalian, China) and a DC power supply (TPR-6405D, Long Wei, Guangzhou, China). The chromatographic separation and determination section consisted of high-pressure six-port valve (valve 2) (Rheodyne 7725i, Cotati, CA, USA) with sample loop (100 μL, Cotati, CA, USA), and chromatographic system (Agilent 1260 LC, USA) equipped with quaternary pump (pump C) (1260 Quatpump) and DAD.

Various technologies including elemental analysis (EA), Fourier transform infrared (FT-IR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), mercury intrusion porosimeter (MIP) and energy dispersive spectrometer (EDS) were employed to characterize the morphological features and magnetic properties of VIED/MCMC. The specific information about these instruments is shown in Supplementary material.

A Kromasil C18 column (5 μm particle size, 250 mm × 4.6 mm i.d.) was utilized to chromatographic analysis of studied SUHs. The mobile phase was composed of 0.4% (v/v) phosphoric acid aqueous solution (solvent A) and ACN (solvent B). The optimized separation of SUHs was realized by gradient elution and the detailed program was as follows: 0~5.0 min = =30% B; 5.0~10.0 min = =30~55% B; 10.0~13.0 min = =55~60% B; 13.0~15.0 min=60% B; 15.0~18.0 min=60~90% B; 18.0~23.0 min = =90~30% B and kept to 28.0 min. The flow rate and detection wavelength were 1.0 mL/min and 224 nm, respectively.

2.3. Synthesis of VIED/MCMC

In-situ heat-initiated polymerization approach was employed to synthesize VIED/MCMC doped with magnetic nanoparticles. The preparation of Fe_3O_4 and its modification to form $Fe_3O_4@SiO_2@\gamma$-MAPS are based on our previous study [26]. After that, 13.5 mg VI, 16.5 mg ED and 2.0 mg AIBN were mixed with PEG 4000 (70 mg) which was dissolved in 168 μL DMF. To get a homogeneous reaction solution, the mixed solution was sonicated for 15 min, and then 2.5 mg of $Fe_3O_4@SiO_2@\gamma$-MAPS was added and kept ultrasonic continuously until the nanoparticles were dispersed well in the solution. The reaction solution was introduced into a fused silica capillary column (21 cm long), which was pre-modified with γ-MAPS. Subsequently, the ends of the capillary were sealed, and then the capillary was placed into an oven for polymerization at 70 °C for 12 h. After the reaction, 5.0 mm long each part of the capillary ends were cut off, and removing the residue solvent in the monolith by methanol.

2.4. Online MB-MR/IT-SPME-HPLC/DAD procedure

As shown in Fig. 1, two high pressure six-port valves (V1 and V2) were connected with one 18 cm long polyether ether ketone tube (250 μm i.d.). The obtained VIED/MCMC was set at the 1 and 4 position of V1 and wrapped with a magnetic coil which was connected to a DC power supply. A sample loop (100 μL) which was used to receive the studied analytes released from the VIED/MCMC, was located at the 1 and 4 positions of valve 2. In the adsorption procedure, V1 and V2 were set at LOAD position. Five milliliters sample solution (pH value was adjusted to 5.0) was driven through the microextraction column at a flow rate of 0.14 mL/min. At the same time, 40 Gs magnetic field with the same direction as the sample solution passing through the VIED/MCMC was applied. After the adsorption, pump A was turned off and V1 was switched to INJECT position while V2 was still located at LOAD position. The intensity of the magnetic field was adjusted to 30 Gs with its polarity reversed. The pump B was turned on to drive 80 μL eluent (ACN/FA=98/2.0, v/v) through the VIED/MCMC at a flow rate of 20 μL/min to release the adsorptive analytes. After the desorption procedure, pump B and the external power were

turned off. Switching V2 to the INJECT position, the studied analytes were delivered into HPLC/DAD by the mobile phase for analysis. Meanwhile, V1 was kept at INJECT position. The VIED/MCMC was washed with eluent at a flow rate of 0.10 mL/min for 15 min to clean the microextraction column. After that, the VIED/MCMC was applied to extract next sample.

2.5. Preparation of water and soil samples

Farmland water and lake water were gathered in Xiamen city. Tap water was collected in our lab. All water samples were vacuum-filtered through 0.22 μm nylon filters to remove any particles. The pH values of sample solutions were adjusted to 5.0 and the ionic strength of sample matrices did not be changed. After that, the dissolved SUHs in water samples were extracted and analyzed with the introduced *online* MB-MR/IT-SPME-HPLC/DAD system.

Three soil samples were collected from farmland located at Xiang'an in Xiamen city. After removal of sundries, the soil samples were dried at 60 °C until constant weight was obtained, then grinding the soil samples and passed through 100 mesh sieve. Dried soil sample (0.5 g) was mixed with 1.0 mL ACN/FA (98/2.0, v/v) and sonicated for 2 min. The suspension was centrifuged at 3500 rpm/min for 10 min, and then the supernatant was filtered through 0.45 mm membrane. The above procedure was repeated once more. Two milliliters filtrate was evaporated with nitrogen, and the dried residue was dissolved with 5 mL ultrapure water. The pH water was adjusted to 5.0. Subsequently, the online MB-MR/IT-SPME-HPLC/DAD procedure was the same as the pretreatment of water samples.

3. Results and discussion
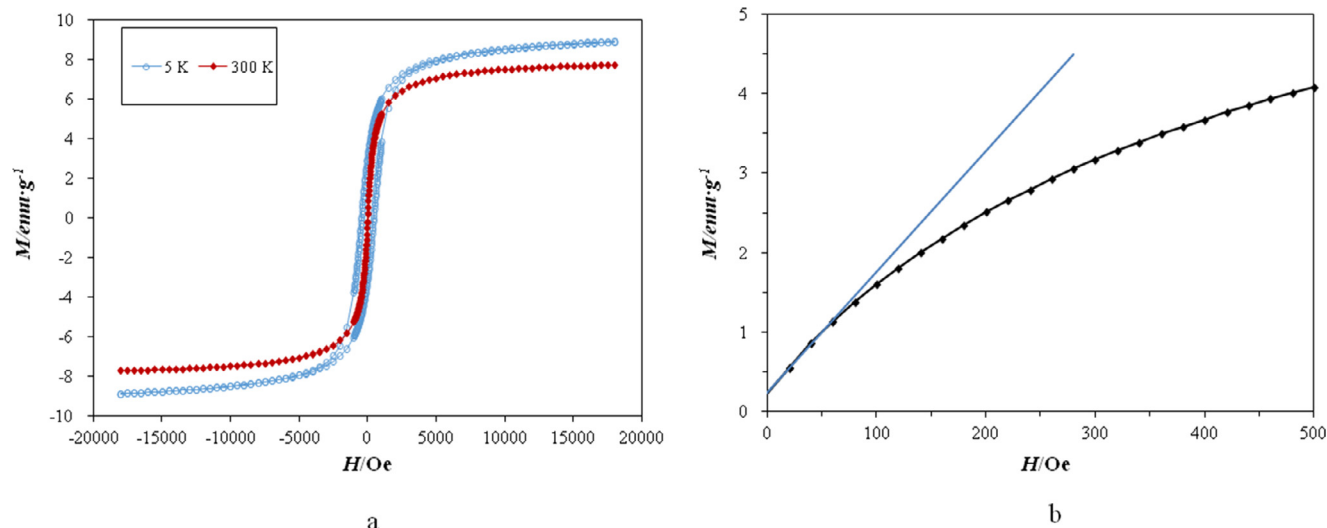
3.1. Synthesis of VIED/MCMC

As other extraction formats based on adsorbents, the extraction phase is the core of the MB-MR/IT-SPME. The extraction performance, permeability, stability and magnetic feature of adsorbent should be considered in MB-MR/IT-SPME. Among the various parameters, the amount of magnetic nanoparticles in the polymerization solution is the first factor needed to be optimized due to it can influence the permeability and magnetic character of VIED/MCMC. The experimental results well indicated that the permeability of the microextraction column was unsatisfactory if too many $Fe_3O_4@SiO_2@\gamma$-MAPS particles were employed. However, the magnetism-enhanced effect was poor if low content of magnetic nanoparticles were used. Studied results evidenced that the optimal amount of magnetic nanoparticles was 25 mg per 1.0 g polymerization solution.

According to the molecular structure and chemical properties of studied SUHs, VI and ED were selected as functional monomer and cross-linker, respectively, to prepare the VIED/MCMC. The contents of VI, ED and porogenic solvent in the polymerization solution can influence the extraction performance, permeability and stability of the microextraction column. As shown in Table 1, when the VI content in monomer mixture enhances from 35% to 55%, the texture of the monolith become more hard and better permeability can be obtained. It also can be found from the data that the monolith become very hard with the decrease of the content of porogenic solvent from 70% to 50%. The column pressure also enhances obviously. Furthermore, the ratios of VI, ED and poroenic solvent also affect the extraction performance obviously. Balancing the concentration performance and life-span of the VIED/MCMC, the optimal ratio of VI to ED in monomer mixture was 45/55 (w/w). The favorable percentage of porogenic solvent in the polymerization solution was kept 70% (w/w) (VIED/MCMC-6). Under

Table 1
Extraction performance of different MCC/MNPs for five SUHs.

No.	Monomer mixture (%, w/w)		Polymerization mixture (%, w/w)		Peak area[a]					Pressure[b]	
	Monomer	Cross-linker	Monomer mixture	Porogen solvent	THM	MEM	CHS	PRS	TRM	(MPa)	Hardness
1	35	65	40	60	205.2	330.2	381.4	189.1	149.7	4.2	very fragile
2	40	60	40	60	184.1	318.2	327.7	167.2	147.8	4.0	fragile
3	45	55	40	60	217.8	376.8	370.0	180.6	159.3	3.9	hard
4	50	50	40	60	208.5	357.1	377.5	183.2	157.7	3.7	hard
5	55	45	40	60	203.6	348.5	349.9	162.5	148.2	3.3	hard
6	45	55	30	70	234.6	391.1	367.9	172.0	161.1	2.7	hard
7	45	55	35	65	207.8	355.7	350.4	165.5	143.4	3.3	hard
8	45	55	45	55	201.1	341.0	354.6	185.8	162.1	4.6	very hard
9	45	55	50	50	200.9	346.6	335.0	180.2	168.2	5.4	very hard

[a] Ultrapure water was used as sample matrices, and the spiked concentration was 100 μg/L for each targeted analytes.
[b] Methanol passed through the MCC/MNPs with 0.10 mL/min flow rate.

Fig. 2. Magnetization curves at 300 K (red line) and 5 K (blue line) (a) and magnetization curves at 300 K (dots-line, black, the blue line shows the sharp linear increase in the region of approximately 0–70 Oe) (b) of VIED/MCMC.

the optimal synthesized parameters, preparation repeatability was investigated. Results indicated that the relative standard deviations (RSDs) of column-to-column repeatability for studied analytes were in the range of 6.0–8.6% ($n = 4$). The satisfying preparation repeatability is in favor of the popularization of the introduced MB-MR/IT-SPME.

3.2. Characterization of VIED/MCMC

The C, N and H contents of VIED/MCMC synthesized in the optimized conditions were inspected by EA, and the results indicated that the corresponding contents were 56.1%, 4.8% and 8.6% (w/w), respectively. FT-IR was employed to confirm the main functional groups in the adsorbent. As shown in Fig. S1, the adsorption bands around 2981 cm^{-1} and 2914 cm^{-1} can be ascribed to the vibrations of CH$_3$ and CH$_2$ groups. The strong band located at 1732 cm^{-1} and the weak bands appeared at 1463 cm^{-1} reveal the existence of carbonyl and imidazole groups, respectively. The vibrations of Fe–O–Fe can be demonstrated by the bands around 667 cm^{-1} and 466 cm^{-1}. The EA and FT-IR results indicate the successful polymerization of VI and ED.

In the present study, SEM and TEM were employed to inspect the morphologies of VIED/MCMC. As shown in the SEM at 3000× magnification (Fig. S2a), uniform globular and porous structure of monolith can be found obviously. At the same time, the monolith is closely bonded to the inner wall of capillary, and there is no obvious cleft between monolith and the wall. The above-mentioned features guarantee the good permeability and stability of the microextraction column. The existence of magnetic nanoparticles was evidenced by TEM (Fig. S2b) and EDS. It can found from TEM that the Fe$_3$O$_4$ nanoparticles disperse in the monolith but there is a little accumulation of nanoparticles in part of monolith. The reason might be that the Fe$_3$O$_4$ nanoparticles deposited partly during polymerization. The EDS results reveal the Fe content in the monolith is 3.75% (w/w). Fig. S3 shows the pore size distribution of the VIED/MCMC inspected with MIP. Result clearly evidences that most of the pore sizes are around at 300 nm, which ensuring the high permeability of the microextraction column.

In MB-MR/IT-SPME, the magnetization properties of the monolith embedded Fe$_3$O$_4$ nanoparticles play an important role in the extraction performance. Fig. 2a displays the magnetization curves of the prepared VIED/MCMC at room temperature (300 K) and low temperature (5 K). As shown, the both magnetization versus field curve display s-shaped curves, which indicating there is no obvious hysteresis and remanence. When the applied magnetic field intensity increases to 10,000 Gs, the magnetization of adsorbent tends to be saturated. It can be seen from Fig. 2b that the magnetization of VIED/MCMC shows a linear trend in the range of 0–70 Gs, and the magnetic susceptibility of VIED/MCMC has reached 16.6% of the saturation value at this field. The magnetization curves evidence that prepared adsorbent possesses superparamagnetism and can be rapidly magnetized in a low external magnetic field. At the same time, it can be easily demagnetized when the magnetic field is disappeared.
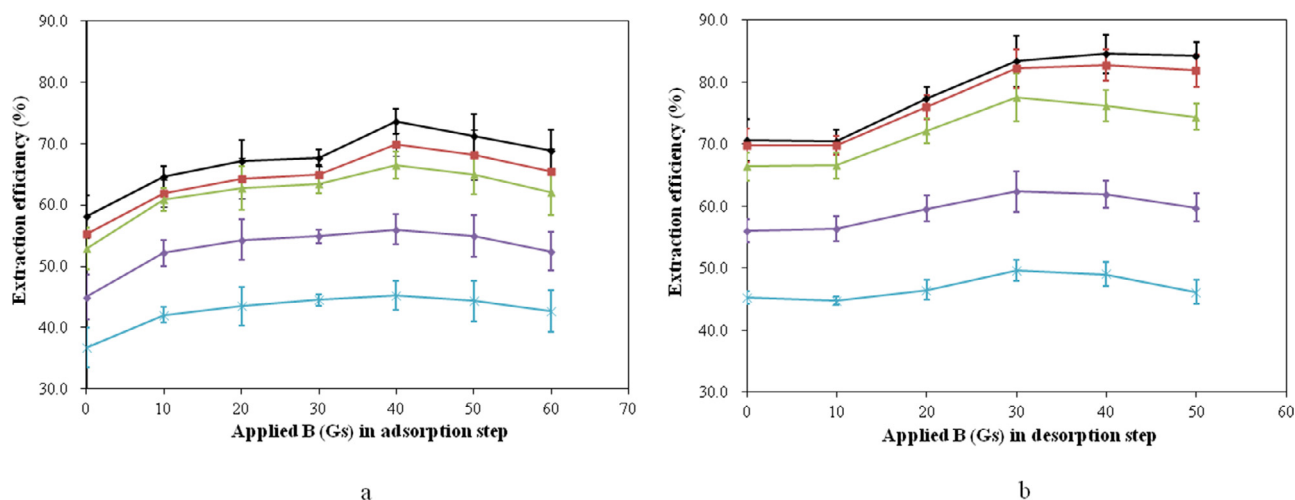
Fig. 3. The influences of the intensity of magnetic field in adsorption (a) and desorption (b) steps on extraction efficiency. Experimental parameters: (a) the intensity of magnetic field in desorption step was 0.0 Gs; the sample volume and eluent were 3.0 mL and 0.10 mL ACN/FA (95/5.0, v/v), respectively; the adsorption and desorption flow rates were 0.08 mL/min and 0.10 mL/min, respectively; the pH value and ionic strength did not be adjusted. The spiking concentration for each compound was 100.0 μg/L; (b) the intensity of magnetic field in desorption step was 40 Gs; the other conditions were the same as in Fig. 3a.
Symbols: ◆ THM; ■ MEM; ▲ CHS; ◆ PRS; ✳ TRM.

3.3. Selection of MB-MR/IT-SPME conditions

To obtain satisfying extraction performance for studied SUHs, various experimental variables including the intensity of magnetic field, sample volume, adsorption flow rate, eluent, eluent volume, desorption flow rate, sample pH value and ionic strength were inspected in detail.

3.3.1. The intensity of magnetic field

According to the characteristic results shown in 3.2 part, the synthesized VIED/MCMC doped with Fe_3O_4 nanoparticles is super paramagnetic. As a result, different magnetic field gradients can be engendered in the VIED/MCMC when magnetic field is exerted. Based on the magnetic microfluidic principles [27], the diamagnetic SUHs molecules will tend to locate at the adsorbent where the magnetic field is minimal, resulting in the enhancement of extraction performance. In the present study, different intensity of magnetic field ranging from 0 to 60 Gs was applied in absorption procedure. As shown in Fig. 3a, the extraction efficiencies for the target SUHs enhance with the increase of magnetic field from 0 to 40 Gs, and then declining gradually from 40 to 60 Gs. Accordingly, 40 Gs was selected as the optimum intensity of magnetic field in adsorption procedure. The influence of the intensity of magnetic field in desorption step was inspected by changing the intensity from 0 to 50 Gs with an interval of 10 Gs. The results shown in Fig. 3b well evidence that the exertion of magnetic field favors the elution of the retained SUHs from the adsorbent, and the best extraction efficiencies are achieved at 30 Gs.

3.3.2. Sample volume and flow rate of sample loading

Sample volume is an important parameter that should be taken into consideration in the MB-MR/IT-SPME. In this work, different volumes (2.0–7.0 mL) of the SUHs aqueous solutions containing each SUH at 100 μg/L were loaded on VIED/MCMC. As shown in Fig. S4, when the sample volume is increased from 2.0 mL to 5.0 mL, the extraction recoveries for all of the studied analytes almost keep constant, and then decreasing when the sample volume enhances from 5.0 mL to 7.0 mL. Hence, 5.0 mL sample solution was selected for the following experiments. In IT-SPME, the flow rate of sample loading can influence the extraction performance and whole analytical time. Low flow rate favors the extraction procedure, but longer extraction time should be spent. Contrarily, high

flow rate can shorten the extraction time, however, the extraction efficiency will be reduced due to there is no enough time for analytes to interact with adsorbent. At the same time, high flow rate will cause high column pressure. The changed profiles shown in Fig. S5 clearly indicate that there is no obvious decrease in extraction efficiency when the adsorption flow rate enhances from 60 μL/min to 160 μL/min, which means that the VIED/MCMC possesses high permeability. Comprehensively balancing the sensitivity, extraction time and pressure drop, 140 μL/min was adopted as the favorable flow rate of sample loading.

3.3.3. Sample pH value and salinity

Sample pH value will affect influence the existing forms of adsorbent and target SUHs due to there are abundant polar groups in both of them, and thus, influencing the extraction performance. As indicated in Fig. S6, the extraction efficiency of MB-MR/IT-SPME for studied SUHs strongly relies on the sample pH value. At low pH values, the nitrogen atoms in SUHs and adsorbent were all protonated, resulting in the decrease of hydrophobic interaction. At this stage, only π-π interaction was involved in the enrichment. Therefore, low extraction efficiencies were obtained at low sample pH values. However, when the sample pH value increased to 5.0, deprotonation procedure occurred on the nitrogen atoms in VIED/MCMC and analytes, as a result, increasing the hydrophobic interaction. Simultaneously, hydrogen-bonding and dipole-dipole interactions also contributed to the capture of SUHs. And thus, the extraction efficiencies enhanced with the increase of sample pH value. When the pH value was enhanced continuously, the favorable hydrogen-bonding and dipole-dipole interactions were weakened by the superfluous hydroxide in solution, resulting in the decline of extraction efficiencies. According to the results, sample pH was adjusted to 5.0 in the subsequent experiments.

When salinity in sample matrix is changed, the extraction performance will be influenced obviously due to the existence of two opposite effects, salting-out and salting-in effects [28]. In the present study, different amount of NaCl was added to adjust the salinity in sample solution. As shown in Fig. S7, the extraction efficiencies for all analytes declined dramatically when the salinity increased from 0.0% to 8.0% (w/v). The reason might be that SUHs molecules participated in electrostatic interaction with the salt ions when NaCl was added, thus, reducing its ability to move into the adsorbent and resulting in the decrease of extraction
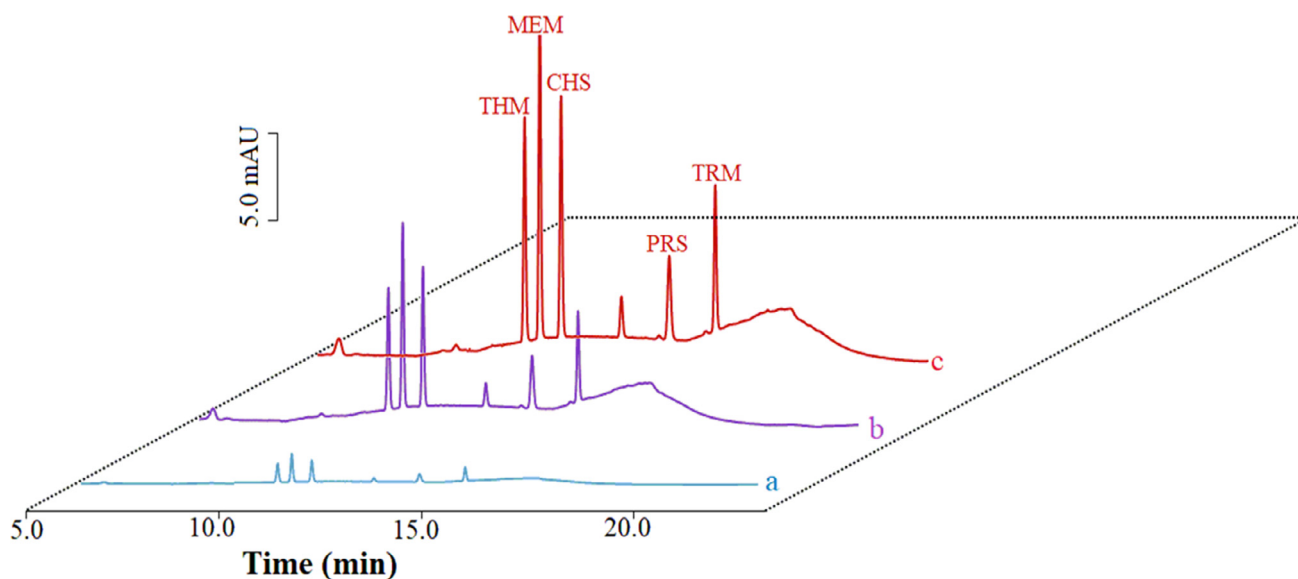
Fig. 4. Chromatograms of studied SUHs direct injection without enrichment (a), after treatment with IT-SPME (b) and treatment with MB-MR/IT-SPME (c). Experimental parameters: the intensity of magnetic field in adsorption and desorption steps were 40 Gs and 30 Gs, respectively; the sample volume and adsorption flow rate were 5.0 mL and 140 μL/min, respectively; the desorption flow rate was 20 μL/min and 80 μL ACN/FA (98/2.0, v/v) was used as desorption solvent; the sample pH value was 5.0 and the ionic strength did not be adjusted. The spiked concentration for each studied analyte was 100.0 μg/L.

performance. Therefore, salinity in sample matrix did not be changed when using MB-MR/IT-SPME to extract SUHs.

3.3.4. Desorption conditions

To release the retained SUHs from adsorbent and avoid the carry-over effect, selection of desorption conditions including eluent, eluent volume and desorption flow rate is very important. In our preliminary study, the adsorptive SUHs could not be desorbed from the VIED/MCMC completely when pure ACN was employed as eluent. Considering that dipole-dipole and hydrogen-bond interactions were involved in the extraction, addition of acid in eluent might favor the release of analytes. The results shown in Fig. S8 indicate that the best extraction efficiencies can be achieved when the eluent contains 2.0% (v/v) FA. Hence, the mixture of ACN/FA (98/2.0, v/v) was selected as the optimal eluent. The influence of eluent volume (from 70 μL to 110 μL with an interval of 10 μL) on extraction efficiency was investigated and the results were shown in Fig. S9. The results evidence that the extraction efficiencies increase with the enhancement of eluent volume from 70 μL to 80 μL, and then declines when more eluent is used.

Desorption flow rate plays an important role in extraction performance and desorption time. As shown in Fig. S10, the extraction efficiencies almost keep constant when the flow rate increases from 10 μL/min to 20 μL/min. However, the extraction efficiencies for all studied SUHs decrease obviously when the desorption flow rate increases continuously. Based on the above-mentioned results, 80 μL the mixture of ACN/FA (98/2.0, v/v) was used as eluent and the flow rate was controlled at 20 μL/min in the subsequent experiments.

According to experimental results and above-mentioned discussions, the most favorable conditions of MB-MR/IT-SPME for SUHs were tabulated in Table S2. Fig. 4 displays the typically chromatograms of studied SUHs before and after extraction under the optimal conditions. As shown, the peaks of analytes were very small when fortified sample was analyzed without enrichment (Fig. 4a). The analytes could be extracted by IT-SPME without the exertion of magnetic field during extraction procedure (Fig. 4b). However, the extraction efficiencies were unsatisfactory (36.8–58.1%). It also could be seen from the Fig. 4c that the peak heights of targeted SUHs were further enhanced when using the

MB-MR/IT-SPME to treat the sample. The extraction efficiencies in this case were increased to 82.6–94.5%. The comparison results well evidence that the introduced MB-MR/IT-SPME can enrich the studied SUHs effectively. At the same time, the MB-MR/IT-SPME possesses good stability. It can be reused to extract studied SUHs more than 50 times including real samples, and there is no obvious decline in extraction performance during continuous application.

3.4. Validation of the current approach

To validate the introduced online MB-MR/IT-SPME-HPLC/DAD approach, various parameters including linearity, limits of detection (LODs), limits of quantification (LOQs) and precision were inspected under the optimized working conditions. For avoiding the effect of sample matrices, matrix-matched calibration curves for water and soil were constructed. The related listed in Table 2 indicate that in water sample, the linear ranges are 0.1–200 μg/L for THM, MEM and CHS, and 0.5–200 μg/L for PRS and TRM. In soil sample, the linear ranges are 1.0–300 μg/kg for THM and CHS, 2.0–300 μg/kg for PRS and TRM, 5.0–300 μg/kg for MEM. Good linearity was obtained for all analytes in water and soil samples, with the correlation coefficients ranging from 0.9900 to 0.9992. The method LOD and LOQ values defined as the concentration of analyte giving a signal equivalent to the blank signal plus three times (LOD) or ten times (LOQ) its standard deviation, were calculated for each individual SUHs. As shown in Table 2, the LOD and LOQ values for water sample are in the ranges of 0.030–0.15 μg/L and 0.10–0.50 μg/L, respectively. For soil sample, the corresponding values are 0.30–1.5 μg/kg and 1.0–5.0 μg/kg, respectively. The LODs can be further decreased if more sensitive detector such as mass spectrometry (MS) is employed. At the same time, the approach precision was inspected in term of intra-day and inter-day assay variability with low and high fortified concentrations. It can be found that the RSDs are all below 10% for all analytes in water and soil samples. The validation results well demonstrate that the current online approach possesses wide linear ranges, satisfying sensitivity and good precision. And thus, it can be applied to analyze trace levels of SUHs in water and soil samples.

Table 2
The analytical parameters of current method for studied SUHs.

Samples	Compounds	Linear range[a] (μg/L or μg/kg)	R^2	LOD[b] (μg/L or μg/kg)	LOQ[c] (μg/L or μg/kg)	Intra-day assay Variability (RSD, %, $n=4$) Spiked(μg/L or μg/kg) Low[d]	High[e]	Inter-day assay Variability (RSD, %, $n=4$) Low[d]	High[e]
Water	THM	0.1–200	0.9995	0.031	0.10	6.2	3.5	6.1	1.2
	MEM	0.1–200	0.9992	0.031	0.10	4.2	4.0	6.7	1.4
	CHS	0.1–200	0.9900	0.030	0.10	8.0	4.1	6.7	4.2
	PRS	0.5–200	0.9974	0.15	0.50	3.9	2.6	8.3	4.3
	TRM	0.5–200	0.9973	0.15	0.50	3.9	4.1	6.2	1.5
Soil	THM	1.0–300	0.9994	0.30	1.0	4.9	5.8	8.5	8.1
	MEM	5.0–300	0.9991	1.5	5.0	6.0	2.3	7.6	5.9
	CHS	1.0–300	0.9966	0.30	1.0	6.8	4.4	5.9	9.7
	PRS	5.0–300	0.9993	1.5	5.0	9.8	7.2	8.3	8.0
	TRM	5.0–300	0.9990	1.5	5.0	6.2	8.2	8.4	8.6

[a] Water sample spiked level included 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, 10, 50, 100, 200 μg/L for each targeted analytes; soil samples spiked level included 1.0, 2.0, 5.0, 10, 20, 50, 100, 200, 300 μg/kg for each targeted analytes;.
[b] $S/N=3$.
[c] $S/N=10$.
[d] Low spiked level at 1.0 μg/L for water samples and 5.0 μg/kg for soil samples.
[e] High spiked level at 100 μg/L for water samples and 200 μg/kg for soil samples.

Table 3
Results of determination and recoveries of real water and soil samples spiked with studied SUHs.

Samples	Spiked (μg/L or μg/kg)	Detected (μg/L or μg/kg) / recovery (% RSD, $n=3$) THM		MEM		CHS		PRS		TRM	
Farmland water	0.0	ND		ND		ND		0.79		ND	
	1.0	1.17	117 (2.4)	0.98	98.0 (5.1)	1.10	110 (4.7)	1.88	110 (7.9)	0.82	82.5 (8.7)
	10.0	8.10	81.0 (7.6)	11.5	115 (6.5)	8.28	82.8 (7.8)	9.58	87.9 (9.4)	11.4	114 (3.5)
	50.0	54.6	109 (0.9)	55.1	110 (1.6)	50.1	100 (1.0)	41.9	82.2 (3.8)	47.5	95.0 (8.8)
Lake water	0.0	ND		0.11		ND		ND		0.96	
	1.0	1.07	107 (4.8)	1.01	90.4 (9.0)	1.12	112 (4.2)	0.88	88.1 (9.4)	1.92	96.6 (8.2)
	10.0	8.11	81.1 (2.0)	10.7	106 (7.4)	9.65	96.5 (3.9)	8.45	84.5 (2.7)	8.97	80.1 (2.5)
	50.0	49.1	98.2 (7.3)	51.2	104 (7.5)	44.3	88.5 (8.8)	45.7	91.5 (5.7)	41.9	83.9 (3.5)
Tap water	0.0	ND		ND		ND		ND		ND	
	1.0	1.02	99.1 (5.5)	0.98	98.0 (5.2)	1.14	114 (7.0)	0.86	85.7 (8.3)	1.03	103 (10)
	10.0	9.22	91.9 (8.8)	9.68	96.8 (8.2)	8.99	89.9 (4.3)	9.43	94.3 (7.8)	100	100 (1.5)
	50.0	45.2	90.3 (5.4)	44.8	89.6 (4.9)	46.2	92.4 (4.0)	41.4	82.8 (1.2)	41.5	82.9 (3.2)
Soil 1	0.0	14.7		18.5		ND		20.7		30.8	
	5.0	20.1	107 (6.4)	23.5	101 (5.9)	5.56	111 (6.1)	25.5	97.0 (5.1)	35.1	86.1 (4.9)
	50.0	55.0	80.6 (3.2)	73.5	110 (2.9)	45.3	90.6 (8.7)	68.9	96.4 (6.4)	74.4	87.1 (6.8)
	200	177	81.0 (2.6)	217	99.4 (7.0)	220	110 (1.3)	202	90.4 (2.5)	234	102 (1.5)
Soil 2	0.0	ND		8.00		ND		14.8		20.4	
	5.0	4.30	86.0 (4.6)	12.8	95.1 (3.8)	5.90	118 (6.2)	19.3	90.9 (3.5)	25.8	108 (4.8)
	50.0	49.2	98.4 (2.3)	55.7	95.4 (7.5)	47.0	94.0 (6.2)	67.9	106 (1.6)	66.6	92.4 (6.8)
	200	234	117 (6.3)	241	116 (4.9)	184	92.2 (6.9)	181	83.2 (8.6)	181	80.4 (5.3)
Soil 3	0.0	ND		16.2		ND		5.00		34.2	
	5.0	5.70	114 (5.8)	21.1	98.6 (4.7)	5.60	112 (3.1)	10.0	100 (4.5)	38.5	86.1 (3.3)
	50.0	41.3	82.6 (3.5)	63.3	94.2 (5.4)	55.1	110 (3.2)	57.1	104 (0.7)	83.1	97.8 (5.2)
	200	167	83.3 (2.6)	201	92.5 (7.3)	175	87.3 (1.3)	194	94.6 (4.4)	257	111 (5.2)

3.5. Assay of real samples

To evaluate the applicability and reliability of the introduced online MB-MR/IT-SPME-HPLC/DAD method, it was used to analyze the concentrations of the dissolved SUHs in farmland water, lake water, tap water and three farmland soils. The related results are listed in Table 3. It can be seen that several target SUHs are found in farmland and lake waters, but the concentrations are very low. For tap water, no analytes is detected. For soil samples, the detected concentrations are higher than that found in water samples. The contents are in the range of several to dozens μg/kg. For evaluation of the accuracy, fortified recovery with low, medium and high spiked concentrations were investigated. As listed in Table 3, the spiked recoveries range from 79.5% to 114% for water samples, and 80.6% to 117% for soil samples. At the same time, the RSDs for precision are 0.9–10% and 0.7–8.7% for water and soil samples, respectively. Fig. 5 displays the typical chromatograms of non-fortified (Fig. 5a) and fortified samples (Fig. 5b) treated with the developed MB-MR/IT-SPME. It can be seen that after the treatment of the current technology, there is no interfering substance that affecting the detection of studied analytes. These results well demonstrate the good feasibility of current approach in the analysis of low levels of SUHs in water and soil samples.

3.6. Comparison with reported approaches

To further exhibit the merits of the introduced method in the analysis of SUHs, key analytical factors including the consumptions of sample and organic solvent, LODs and recoveries obtained in the current study and previously reported adsorbent-based approaches with ultraviolet (UV) or DAD detection are compared. The comparative results are summarized in Table 4. As displayed, the consumption of organic solvent in the present method is lower than that used in reported approaches [11,18,19,29–38]. In addition, most of the existing studies need more sample than that used in the current study [18,19,29–38]. It also can be seen from the
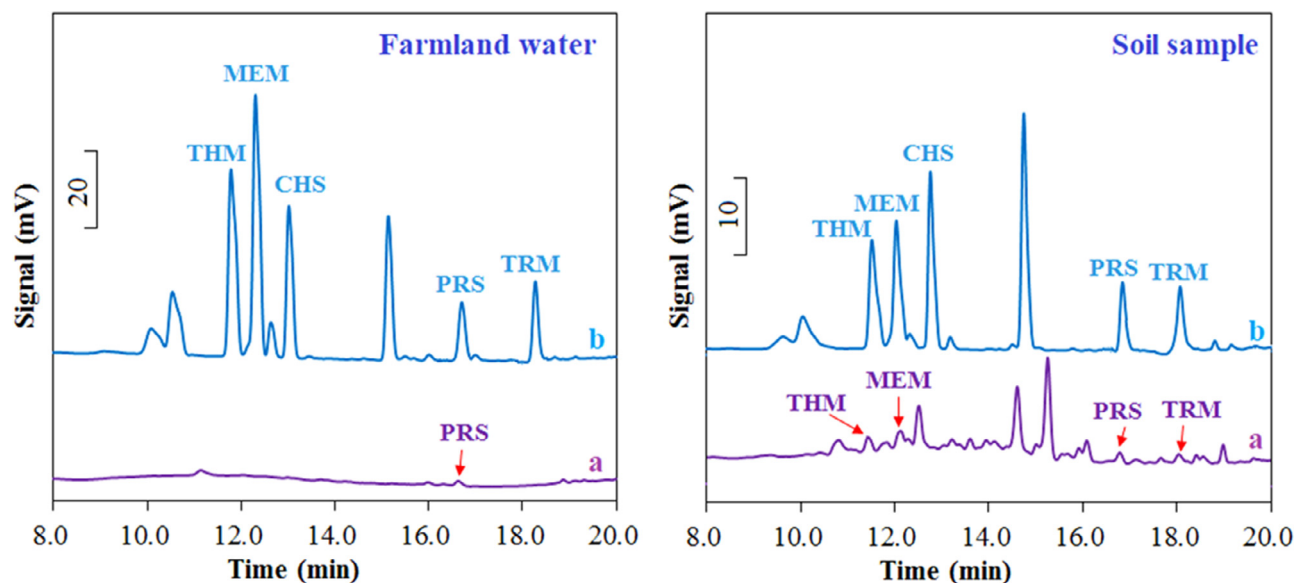
Fig. 5. Typical HPLC chromatograms of studied SUHs in water and soil samples (a) real samples treated with MB-MR/IT-SPME; (b) spiking samples (each analyte at 10.0 μg/L for water sample and 50.0 μg/kg for soil sample) treated with MB-MR/IT-SPME. The experimental parameters were the same as in Fig. 4.

Table 4
Comparison of current method with reported approaches for the determination of SUHs in water and soil samples.

Samples	Methods	Sorbents	Usage of sample	Consumption of solvent (mL)	LODs (μg/L or μg/kg)	Recoveries (%)	Ref.
Water	SPE-HPLC/DAD	Single walled carbon nanotubes	1000 mL	10 (MeOH)+1 (ACN)	1.1~7.2	79~102	29
	SPE-HPLC/UV	MIP	250 mL	12.65 (ACN)	0.1~2.0	90.2~92.7	30
	SPE-HPLC/UV	IL-functionalized silica	250 mL	23.8 (DCM[c])+1.7 (MeOH)	0.012~0.14	53.8~118	31
	MSPE-HPLC/UV	IL-functionalized magnetic particles	300 mL	0.3 (MeOH) +1.5 (acetone)	0.053~0.091	77.8~104	32
	MSPE-HPLC/DAD	Fe$_3$O$_4$@DODMAC@silica particles	300 mL	0.3 (MeOH) +1.5 (acetone)	0.078~0.10	82.9~106	18
	MSPE-HPLC/DAD	Magnetic MWCNTs[a]	100 mL	5 (MeOH) +5 (acetone) +0.08 (ACN)	0.01~0.03	69.5~115	19
	MSPE-HPLC/DAD	IL-functionalized Fe$_3$O$_4$	50 mL	6.5 (ACN)	1.1~2.9	90.4~98.7	33
	SBSE-HPLC/UV	MIP	100 mL	13 (ACN)	0.31~4.92	81.3~93.4	34
	SPME-HPLC/UV	UIO-66(Zr)-NH$_2$[b]	20 mL	0.18 (MeOH)	0.19~1.45	82.2~95.3	35
	MMF/SPME-HPLC/DAD	Porous monolith	20 mL	0.4 (ACN) +0.1 (MeOH)	0.018~0.17	70.6~119	11
	MB-ME/IT-SPME-HPLC/DAD	Poly (VI-ED) monolith	5 mL	0.08 (ACN)	0.030~0.15	79.5~114	This work
Soil	SPE-HPLC/MS-MS	Graphene	0.5 g	10.1 (ACN)	0.08~0.26	84.2~109	36
	SPE-HPLC/UV	MIP	5 g	12.6 (ACN) +35 (MeOH)	0.1~2.0	90.2~92.7	30
	SPE-HPLC/UV	IL-functionalized silica	50 g	23.8 (DCM[c]) +1.7 (MeOH)	0.08~1.00	60.9~121	31
	SPE-HPLC/UV	MIP	10 g	0.2 (ACN)	4.1~4.8	81.9~99.1	37
	SPE-HPLC/UV	MIP	10 g	3.2 (MeOH) +0.14 (ACN) +3.66 (DCM[c])	5~12	71~139	38
	SBSE-HPLC/UV	MIP	10 g	13 (ACN)	0.31~4.92	81.3~93.4	34
	SPME-HPLC/UV	UIO-66(Zr)-NH$_2$[c]	10 g	0.18 (MeOH)+15 (acetone)	0.19~1.45	75.7~94.2	35
	MMF/SPME-HPLC/DAD	Porous monolith	0.5 g	2.4 (ACN)+0.1 (MeOH)	0.018~0.17	72.1~119	11
	MB-ME/IT-SPME-HPLC/DAD	Poly (VI-ED) monolith	0.5 g	0.08 (ACN)	0.30~1.5	80.6~117	This work

[a] Multiwalled carbon nanotubes.
[b] Metal-organic frameworks.
[c] Dichloromethane.

comparison that the developed method displays better sensitivity than part of previous methods [29, 30, 33-35, 37, 38], and at the same level as some of reported studies [11,18,31,32,36]. Furthermore, the spiked recoveries got in the introduced method and previous studies are at the same level [11,18,19,29–38]. Most of important is that the extraction and HPLC analytical procedures in reported approaches are offline. However, the introduced MB-MR/IT-SPME procedure is online combined with HPLC/DAD. It can be concluded from the comparison that the proposed online MB-

MR/IT-SPME -HPLC/DAD approach displays some features such as convenience, environmental friendliness and good sensitivity in the quantification of SUHs.

4. Conclusions

In summary, a novel analytical approach for the determination of SUHs in water and soil samples was developed by the MB-MR/IT-SPME online combined with HPLC/DAD. According to the

chemical properties of SUHs and magnetic microfluidic principles, a porous monolith-based microextraction column doped with magnetic particles was prepared and used as the extraction phase of magnetism-reinforced IT-SPME. Results well demonstrated that application of magnetic field during adsorption and desorption steps afforded satisfying extraction efficiencies (82.6–94.5%), which were obviously higher than that achieved in traditional IT-SPME format (36.8–58.1%). Under the most favorable conditions, the introduced approach was successfully used to quantify trace levels of studied SUHs in environmental water and soil samples. Comparing with existing approaches, the current method exhibits some merits such as convenient operation, high sensitivity, low consumptions of sample and organic solvent. Therefore, the developed method can be used to regularly monitor low contents of SUHs in water, soil and other complex samples. Although the current displays some attractive features, the extraction capacity of the MCMC can be further improved. In our future study, new MCMC with high extraction capacity will be designed and prepared, and combining with magnetism-reinforced IT-SPME to develop online couplable sample preparation technology for the monitoring of ultra-trace pollutants.

Author contribution statement

The authors' individual contributions are as follows:

Dr. Jinling Pang: Optimizing the extraction parameters, assaying real samples, and writing the manuscript.

Xiaochong Song: Preparation and characterization of VIED/MCMC.

Dr. Xiaojia Huang: Conceptualization of MB-MR/IT-SPME and data analysis.

Dr. Dongxing Yuan: Refining the manuscript.

Declaration of interest statement

The work described in this manuscript titled "Porous monolith-based magnetism-reinforced in-tube solid phase microextraction of sulfonylurea herbicides in water and soil samples" has not been published previously and is not under consideration for publication elsewhere. The submitting is approved by all authors and our responsible authorities. All authors agreed with the order of authorship.

CRediT authorship contribution statement

Jinling Pang: Data curation, Investigation, Writing - original draft. **Xiaochong Song:** Methodology, Validation. **Xiaojia Huang:** Conceptualization, Supervision, Project administration, Writing - review & editing. **Dongxing Yuan:** Writing - review & editing.

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Supplementary materials

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