



Determination of six sulfonylurea herbicides in environmental water samples by magnetic solid-phase extraction using multi-walled carbon nanotubes as adsorbents coupled with high-performance liquid chromatography



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ABSTRACT

Magnetic solid-phase extraction (MSPE) using magnetic multi-walled carbon nanotubes (mag-MWCNTs) as adsorbents, coupled with high-performance liquid chromatography–diode-array detector (HPLC–DAD), was developed for the simultaneous separation and determination of six types of sulfonylurea herbicides (SUs) in environmental water samples. Several variables affecting MSPE efficiency were systematically investigated, including the type and volume of desorption solvent, sample solution pH, salt concentration, amount of mag-MWCNTs, and extraction and desorption time. Response surface was employed to assist in the MSPE optimization. Under optimized conditions, excellent linearity was achieved in the range of 0.05–5.0 µg/L for all six SUs, with coefficients of correlation $r > 0.9994$, and preconcentration factors ranging from 178 to 210. Limits of detection and quantification were 0.01–0.04 µg/L and 0.03–0.13 µg/L, respectively. The intra-day and inter-day precision (relative standard deviations, $n = 6$, %) at three spiked levels were 2.0–11.0% and 2.1–12.9% in terms of peak area, respectively. The method recoveries at three fortified concentrations were obtained within 76.7–106.9% for reservoir water samples and 78.2–105.4% for tap water samples. The developed MSPE–HPLC method demonstrated high sensitivity, repeatability, simplicity, rapidity, and excellent practical applicability.

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1. Introduction

Sulfonylurea herbicides (SUs) are one class of widely used herbicides with high efficiency and low toxicity. These herbicides provide efficient, broad-spectrum control of broad-leaved weeds and some grasses. To date the class has expanded to include over 30 commercial herbicides. These compounds generally have low mammalian toxicity, but plants demonstrate a wide range of sensitivities to SUs. Some have demonstrated residual phytotoxicity, including rotation crops such as corn, sunflowers, sugar beets and dry beans [1]. SUs can be released into environmental water and endanger human health. Hence, the presence and levels of SUs in environmental water must be monitored and detected.

Determination of trace SUs is very challenging. The most common analytical methods for SUs are high-performance liquid chromatography coupled with an ultraviolet or diode-array detector (HPLC–UV/DAD) [2–6] and mass spectrometry (HPLC–MS) [7,8]. However, for low concentration of SUs in water, UV detectors cannot provide high sensitivity without enrichment prior to analysis. HPLC–MS instrumentation is expensive and not available in every laboratory. Therefore, pretreatment techniques are imperative for the enrichment and cleanup of SUs in environmental samples in order to achieve the ideal sensitivity and effectively eliminate contaminants from complex matrices. Currently reported pretreatment techniques for SUs in environmental water samples mainly include solid-phase extraction (SPE) [2,5,7,8], dispersive liquid–liquid microextraction [4], stir-bar sorptive extraction [9], and salting-out assisted liquid–liquid extraction [10]. SPE, due to its high recovery, short extraction time, high enrichment factor, low consumption of organic solvents, and ease of automation and

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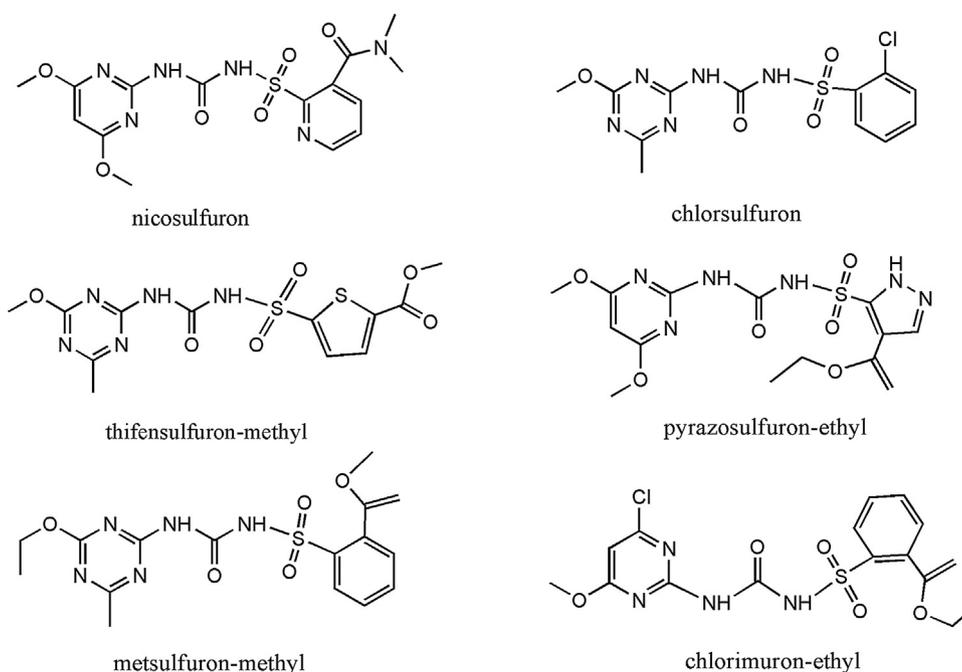


Fig. 1. Chemical structures of six analyzed SUs.

operation, has been widely used to concentrate organic compounds in water samples. In SPE, the choice of adsorbents is very important for obtaining high-enrichment efficiency.

Magnetic SPE (MSPE) has received increasing attention as a relatively new mode of SPE based on the adsorption and release of target analytes by a small amount of magnetic nanoparticles (e.g., Fe₃O₄ nanoparticles) dispersed in solution. The Fe₃O₄ nanoparticle-adsorbed target compounds can be easily collected by an external magnetic field without additional centrifugation or filtration of samples [11,12]. For example, He et al. [13] have used Fe₃O₄@dioctadecyl dimethyl ammonium chloride@silica magnetic particles as MSPE adsorbents for enrichment of SUs in environmental water samples.

Carbon nanotubes (CNTs) have also attracted much interest owing to their unique thermal, mechanical, electronic and chemical properties [14]. Multi-walled CNTs (MWCNTs) composed of several layers of rolled graphite sheets display large specific surface areas and have high adsorption capacities, making them especially useful [15]. As SPE adsorbents, MWCNTs have shown very strong adsorption of phthalate esters [16], chlorophenols [17], 4-*tert*-octylphenol [18], etc. We have used MWCNTs as SPE adsorbents for the successful enrichment of polycyclic aromatic hydrocarbons [19], pyrazole and pyrrole pesticides [20] in environmental water samples.

Inspired by these studies, we used magnetic MWCNTs (mag-MWCNTs) as MSPE adsorbents to enrich six SUs in environmental water samples, followed by HPLC-DAD determination. Several methods have previously been developed using mag-MWCNTs as the adsorbent for analysis of estrogens [21], nerve agents [22], aconitines [23] and so on. However, to the best of our knowledge, no methods based on mag-MWCNTs have been established for determination of SUs. In this work, mag-MWCNTs were prepared and characterized using scanning electron microscope (SEM) and X-ray diffraction (XRD). Several key factors influencing MSPE efficiency were investigated in detail, including the type and volume of desorption solvent, sample solution pH, salt concentration, amount of mag-MWCNTs, and extraction and desorption time. Response surface methodology was employed for multi-variable optimization.

The MSPE-HPLC method was validated and applied to the simultaneous separation and determination of six SUs in reservoir and tap water samples.

2. Experimental

2.1. Chemical reagents and materials

Carboxylic MWCNTs (>50 nm I.D., 10–20 μm length) were obtained from Chengdu Organic Chemistry Co., Ltd, Chinese Academy of Sciences (Chengdu, China). Ferric chloride hexahydrate (FeCl₃·6H₂O) was purchased from Sinopharm Chemical Reagent Co. Ltd. (China). Ethylene glycol was supplied by Fuyu Fine Chemical Co., Ltd. (Tianjin, China). Sodium acetate, sodium hydroxide and absolute ethyl alcohol were purchased from Aibi Chemical Reagent Limited Company (Shanghai, China). Anhydrous sodium chloride was purchased from Jiangsu Powerful Function Chemical Co., Ltd. Phosphoric acid was purchased from Kaixin Chemical Industry Co., Ltd (Tianjin, China). Chemicals were of at least analytical grade. Solvents including methanol, acetonitrile and acetone were of HPLC grade and supplied by TEDIA (USA). Ultrapure water (18.2 MΩ cm) was obtained from a model Synergy 185 ultra-pure water system (Millipore, USA).

Analytical standards of the six SUs (>99% purity), namely, nicosulfuron, thifensulfuron methyl, metsulfuron methyl, chlorsulfuron, pyrazosulfuron-ethyl, and chlorimuron-ethyl (Fig. 1), were purchased from the Testing Center of the Shanghai Pesticide Research Institute (China). A stock solution of each analyte was prepared at 1000 mg/L in acetonitrile, and stored at –18 °C in the dark. Working standard solutions were prepared by appropriate dilution of stock solutions into an acetonitrile-water solution (20:80, v:v).

Surface water samples were collected from the Qingdao Jihongtan Reservoir, and tap water samples were collected from our laboratory. All water samples were filtered through 0.45-μm membranes (Tianjin Jinteng Experiment Equipment Ltd, Co., Tianjin, China) and stored in brown glass bottles at 4 °C prior to analysis.

2.2. Apparatus and software

Experiments were performed on an Agilent 1100 liquid chromatographic system consisting of a quaternary delivery pump, an auto-sampler, a thermostatic column compartment and a DAD detector. A personal computer equipped with Agilent ChemStation for HPLC was used to process the chromatographic data. An analytical Agela Venusil ASB C₁₈ (250 × 4.6 mm, 5 μm) was used to analyze the SUs at 30 °C. The sample injection volume was 20 μL. Absorbance was monitored at 230 nm. The mobile phase was a gradient prepared from acetonitrile (solvent A) and water (solvent B), the pH of which was adjusted to 3.0 with phosphoric acid. Gradient elution conditions were as follows: 20% A (0 min), 40% A (8 min, hold 9 min), 45% A (18 min, hold 12 min). The flow rate was 1 mL/min. Under these optimum conditions, all studied SUs were well resolved from each other.

Characterization of mag-MWCNTs were conducted on a Tescan XM 5136 scanning electron microscope (SEM, Tescan, Czech Republic) and an X-ray diffractometer (XRD) (Bruker D8 Advance). Matlab 7.5.0.342 (Mathworks Corporation, USA) was employed for study of the response surface.

2.3. Preparation of mag-MWCNTs

Mag-MWCNTs were synthesized using a published solvothermal method [24] with slight modification, as schematically shown in Fig. S1. Briefly, 0.5 g of carboxylic MWCNTs was suspended in 50 mL of ethylene glycol containing 3 g of FeCl₃·6H₂O in a 100-mL beaker. After 3.5 g of sodium acetate was added, the mixture was stirred for 30 min. The resulting solution was allowed to stand at room temperature for 30 min and the obtained mixture was transferred to a Teflon-lined stainless steel autoclave (100 mL) and heated to 200 °C for 16 h. After cooling to room temperature, the synthetic product was sequentially washed with 50 mL of absolute ethyl alcohol and then three times with 50 mL of ultra-pure water. The purified mag-MWCNTs were dried under vacuum.

2.4. MSPE procedure

Before extraction, 40 mg of mag-MWCNTs were added to a 250-mL beaker and conditioned with 5.0 mL of methanol and 10.0 mL of ultra-pure water by stirring for 1 min. The mag-MWCNTs were forced to settle by placing a strong magnet near the bottle, and the water was decanted. Then, 100 mL of a spiked water sample (pH adjusted to 3.0 with phosphoric acid) was added and dispersed with stirring for 8 min. Mag-MWCNTs were again forced to settle to the bottom and the supernatant water was decanted and discarded. Wet mag-MWCNTs were then washed twice with 5 mL of acetone. All acetone extracts were combined and transferred into an autosampler vial. The collected eluate was concentrated with a gentle stream of nitrogen at room temperature, diluted to 0.4 mL with an acetonitrile-water solution (20:80, v:v), and filtered through a 0.45-μm nylon membrane for HPLC analysis. The MSPE procedure is shown schematically in Fig. S1.

3. Results and discussion

3.1. Characterization of the mag-MWCNTs

The micro-morphologies of the mag-MWCNTs were observed by SEM. As shown in Fig. 2, the spherical Fe₃O₄ nanoparticles were well wrapped by the MWCNT bundles to give magnetic-responsive MWCNTs, which could be separated from the matrix solution using an external magnet. Accordingly, Fig. S2 shows observations before and after the MSPE procedure. As shown, the SU solution became black and turbid when mag-MWCNTs were dispersed (Fig. S2A),

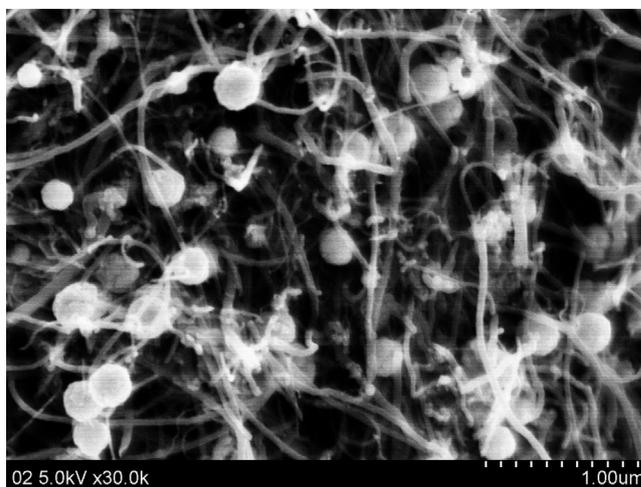


Fig. 2. SEM image of mag-MWCNTs.

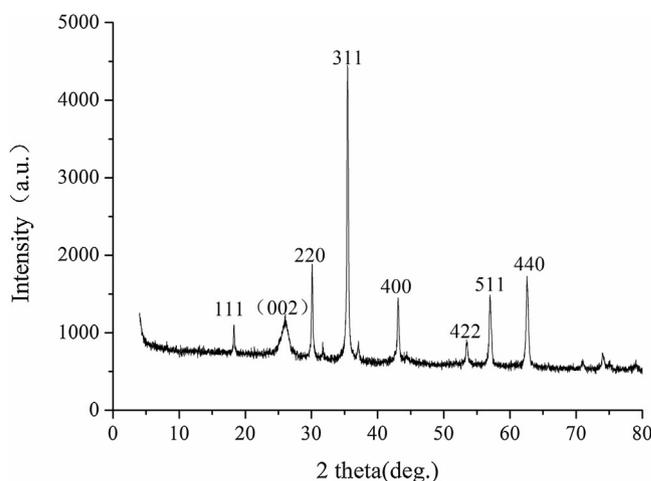


Fig. 3. XRD pattern of mag-MWCNTs.

but the mag-MWCNTs with adsorbed SUs adhered to the inner side wall of the vial when the external magnetic field was applied. As a result, the turbid solution again became clear and transparent, as shown in Fig. S2B. Thus a fast simple magnetic separation was attained.

The mag-MWCNTs were also characterized by XRD. As shown in Fig. 3, peaks at 2θ values of 30.02° (220), 35.06° (311), 43.32° (400), 53.05° (422), 57.08° (511), and 62.92° (440) can be attributed to the inverse spinel crystalline structure of Fe₃O₄, consistent with previous reports [25]. The diffraction peak at 2θ of 26.04° is the typical Bragg peak of pristine MWCNTs and can be indexed to the (002) reflection of graphite [26]. Therefore, the mag-MWCNTs were successfully prepared.

3.2. Optimization of MSPE procedure

MSPE efficiency is mainly subject to the following major factors: amount of mag-MWCNTs, sample solution pH, extraction and desorption time, amount of salt added, and type and volume of desorption solvent. In this study, these were investigated using a spiked ultrapure water sample (0.5 μg/L). First, the type and volume of desorption solvent, sample solution pH, and the amount of salt added were investigated individually. The other three factors

(amount of mag-MWCNTs, extraction time and desorption time) were evaluated using response surface experiments.

3.2.1. Effect of type of desorption solvent

Desorption solvent is known to be an important factor that can significantly affect MSPE efficiency. Three solvents—methanol, acetonitrile and acetone—were studied as desorption solvents to examine their effect on extraction efficiency. Fig. 4A shows that acetonitrile and acetone provided better results than methanol. The best extraction efficiency was obtained by using acetone, which can disrupt interactions between mag-MWCNTs and SUs, and elute SUs effectively. Therefore, acetone was adopted as the desorption solvent for the remainder of this study.

3.2.2. Effect of volume of desorption solvent

The volume of desorption solvent is thought to have a marked effect on the desorption efficiency of MSPE and thereby the analytical sensitivity of the proposed method. To investigate the effect of volume of desorption solvent, 5, 10 and 15 mL of acetone were used. The results shown in Fig. 4B reveal that 10 mL of acetone is sufficient for quantitative desorption. This volume is low while still offering quantitative and reproducible elution. In further experiments, 10 mL of acetone was selected for desorption.

3.2.3. Effect of sample pH

It is well known that the analyte species in solution usually depends on solution pH, as does analyte stability. The pH of the sample solution plays an important role in the adsorption of SUs by affecting both the form of the SUs and the surface binding sites of the mag-MWCNTs. The effect of solution pH (ranging from 2 to 7) on SU extraction was investigated. As shown in Fig. 4C, at low pH (pH = 2.0), the recoveries of all SUs were low. This was probably due to partial decomposition of the SUs in acidic condition. The extraction efficiencies for the six SUs increased at pH 2–3. The highest signals were obtained when the samples were prepared at pH 3; signals again decreased when pH > 3. There was no marked difference between pH 4.0 and 7.0. It is very likely that the six SUs are weakly acidic herbicides whose pKa values lie between 3.3 and 4.6, and they are extracted through both electrostatic interaction and π - π stacking. The carboxyl groups on carboxylic MWCNTs surfaces enhance electrostatic interactions and may serve as chelation sites for the formation of hydrogen bonds that increase extraction efficiency. At pH 5–7, most SUs are negatively charged, the carboxylic MWCNTs are ionized and negative, and SUs can no longer interact with MWCNTs through electrostatic interactions. At pH 3.0, SUs are neutral and have high affinity for the adsorbent through hydrogen bonds and π - π interactions. Therefore, sample solutions at pH 3 were used in further experiments.

3.2.4. Effect of salt

Salt content in water samples can disrupt the solvation cage of water-soluble analytes or alter the diffusion rate of analytes from aqueous to solid phases. To investigate the effect of salt on the extraction of SUs, various amounts of NaCl (0, 0.5, 1, 5 and 10%, w/v) were added into solution to adjust salinity. As shown in Fig. 4D, recovery of SUs decreased when the concentration of NaCl varied from 0 to 0.5%, but remained nearly constant for pyrazosulfuron-ethyl and chlorimuron-ethyl, while increasing for other SUs as the NaCl concentration increased from 0.5 to 10%. Notably, the highest recoveries were obtained when no NaCl was added. Possible explanations are as follows. NaCl may reduce mass transfer by increasing the thickness of the Nernst diffusion layer [27], since in sample solutions at pH 3, the carboxyl groups on mag-MWCNTs surfaces were charged and showed partial electrostatic interactions with NaCl. Accordingly, the diffusion rate of SUs to the surface of the MWCNTs

decreased, resulting in longer adsorption times to reach equilibrium and decreased extraction efficiency when NaCl increased from 0 to 0.5%. Alternatively, the addition of salt could decrease SU solubility in aqueous samples and thus benefit the extraction [27], leading to increased efficiency as the NaCl content increased from 0.5 to 10%. On the basis of these results, considering the slight difference in extraction efficiency between 0 and 10% NaCl (Fig. 4D), and for the sake of simplicity and economy, NaCl was not added in subsequent experiments.

3.2.5. Response surface for optimization of other conditions of MSPE

The remaining three parameters (amount of mag-MWCNTs, extraction time and desorption time) were optimized by response surface experimental design. These response surfaces were obtained for two experimental factors while the third was held constant at its optimum level. The amount of mag-MWCNTs can directly affect extraction efficiency for SUs. Insufficient mag-MWCNTs might cause breakthrough of SUs, whereas excessive mag-MWCNTs will increase the cost and time of analysis. Fig. 5 shows a three-dimensional representation of the response surfaces (in recovery) for metsulfuron methyl, as an example. As shown in the figure, high extraction recovery was achieved when 40 mg of mag-MWCNTs were added with an extraction time of 8 min and desorption time of 2 min. The highest extraction recoveries were not achieved for nicosulfuron and chlorimuron-ethyl (data not shown) when 40 mg mag-MWCNTs were added. Nevertheless, when considering the overall high extraction recoveries for all six SUs, the three optimal parameters were established: mag-MWCNTs, 40 mg; extraction time, 8 min; desorption time, 2 min.

3.3. Analytical performance of the mag-MWCNTs-MSPE-HPLC method

Under the above-optimized MSPE conditions, the six SUs were separated well by HPLC and the analytical performance of the mag-MWCNTs-based MSPE method was assessed. Six SU standard solutions with different concentrations (0.05, 0.1, 0.4, 1.0, 2.0, and 5.0 $\mu\text{g/L}$ for individual SU) were obtained by serial dilution with pure water from a stock solution. Calibration curves were obtained using a least-squares linear regression analysis of peak area versus SU concentration. The method gives excellent linearity in the range of 0.05–5.0 $\mu\text{g/L}$ for six SUs, with coefficients of correlation (r) ranging from 0.9994 to 0.9998, as listed in Table 1.

The preconcentration factors for all six SUs, which were obtained by comparing the slopes of the calibration curves before and after the MSPE procedure, ranged from 178 to 210, as shown in Table S1. This suggested that MSPE has high enrichment ability. The limits of detection (LODs) for the method, calculated according to peak height by analyzing the spiked water sample after pretreatment using a signal-to-noise ratio of 3, ranged from 0.01 to 0.04 $\mu\text{g/L}$ (Table 1). With a target of peak height that is 10-fold higher background noise ($S/N = 10$), the limits of quantification (LOQs) were obtained from 0.03 to 0.13 $\mu\text{g/L}$ (Table 1). The LODs for all six SUs are much lower than both the maximum residue level (MRL) of 0.1 $\mu\text{g/L}$ for a single pesticide in drinking water (98/83/EC by the European legislation) [28] and the MRL of 1 $\mu\text{g/L}$ in European Union surface water intended for use in drinking water regulations (75/440/EEC) [29]. Thus, this method meets the requirements of MRL detection for these six SUs in drinking water and surface water samples. The intra-day and inter-day precision in terms of peak area, based on six consecutive injections, are shown in Table 2. As shown, the relative standard deviations (RSDs) of peak area, obtained from a working solution containing each of six herbicides at three spiked concentrations (0.1, 2 and 4 $\mu\text{g/L}$) based on intra-day precisions, were 2.0–11.0%, while the RSDs based on inter-day

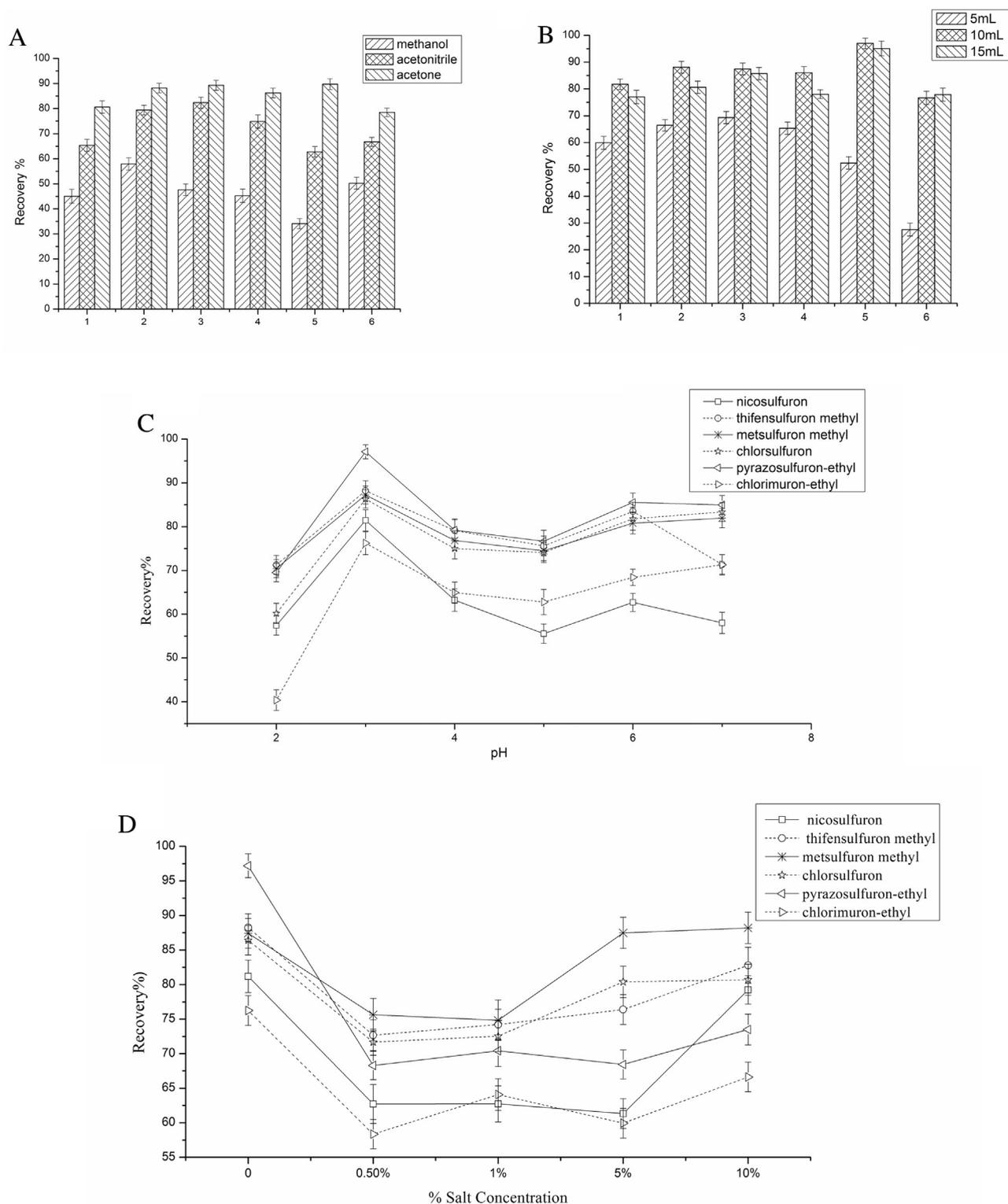


Fig. 4. Effect of (A) type of desorption solvent, (B) volume of desorption solvent, (C) pH of sample solution and (D) amount of salt added on the extraction efficiency of mag-MWCNTs MSPE for six SUs. Peak identification: (1) nicosulfuron, (2) thifensulfuron methyl, (3) metsulfuron methyl, (4) chlorsulfuron, (5) pyrazosulfuron-ethyl, and (6) chlorimuron-ethyl. Extraction conditions: sample volume, 100 mL; concentration of pesticide, 0.5 $\mu\text{g/L}$. (A) Mass of mag-MWCNTs, 40 mg; extraction time, 8 min; sample pH, 3.0; volume of desorption solvent, 5 mL; desorption time, 2 min. (B) Mass of mag-MWCNTs, 40 mg; extraction time, 8 min; sample pH, 3.0; desorption solvent, acetone; desorption time, 2 min. (C) Mass of mag-MWCNTs, 40 mg; extraction time, 8 min; desorption solvent, 2 \times 5 mL of acetone; desorption time, 2 min. (D) Mass of mag-MWCNTs, 40 mg; extraction time, 8 min; sample pH, 3.0; desorption solvent, 2 \times 5 mL acetone; desorption time, 2 min.

precision ranged from 2.1–12.9%. Thus, mag-MWCNTs are ideal candidate adsorbents for MSPE, and the MSPE-HPLC method is proven highly sensitive and accurate for simultaneous enrichment and determination of six SUs at trace levels.

3.4. Method performance comparison

Analytical performance of the developed MSPE-HPLC-DAD method for the detection of SUs was compared with reported

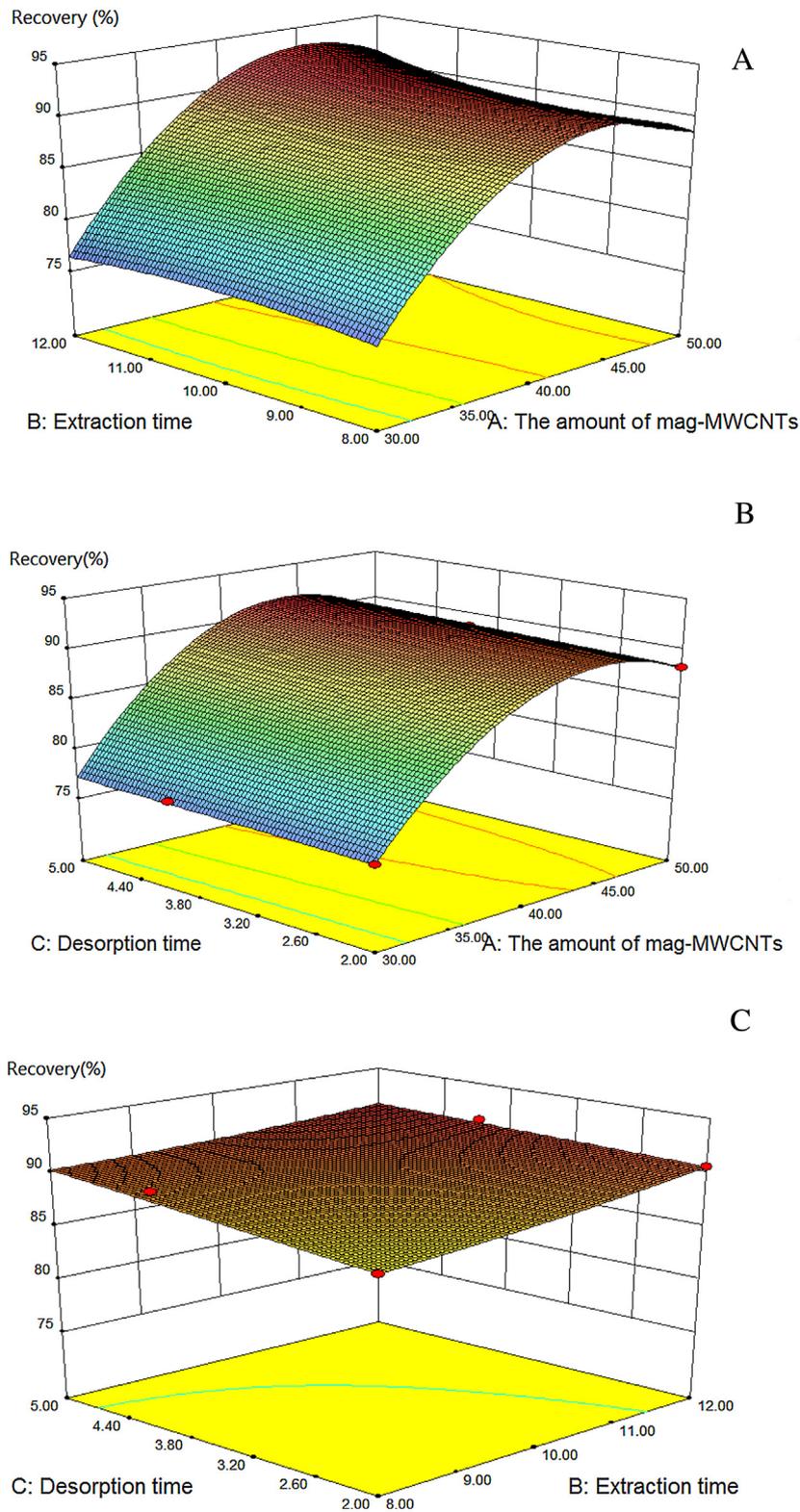


Fig. 5. Three-dimensional representation of response surfaces (in recovery) of metsulfuron methyl. (A) Adsorbent amount vs. extraction time; desorption time, 2 min. (B) Adsorbent amount vs. desorption time; extraction time, 8 min. (C) Desorption time vs. extraction time; adsorbent mass, 40 mg.

HPLC methods. As shown in Table S2, a pretreatment time of less than 15 min is significantly shorter than conventional SPE (2–7 h) [2,5,8]. In comparison with reported MSPE-based methods [13,30], our method presents lower LODs for more SUs. Furthermore, considering economic costs, MWCNTs and iron salt precursors are

commercially available and relatively inexpensive. Mag-MWCNTs can be reused for at least six adsorption–desorption cycles, as nearly constant recovery values are obtained with relative error less than 3%. Thus, the method presented here has advantages of high sen-

Table 1
Related analytical parameters of the mag-MWCNT-MSPE-HPLC method for determination of six SUs.

| SUs | Regression equation ^a | Coefficient of correlation (r) | Linear range (μg/L) | LOD (μg/L) | LOQ (μg/L) |
|-----------------------|----------------------------------|--------------------------------|---------------------|------------|------------|
| Nicosulfuron | $y = 9.473x + 0.258$ | 0.9997 | 0.05–5.0 | 0.04 | 0.13 |
| Thifensulfuron methyl | $y = 15.70x + 0.467$ | 0.9997 | 0.05–5.0 | 0.03 | 0.10 |
| Metsulfuron methyl | $y = 17.39x + 0.432$ | 0.9997 | 0.05–5.0 | 0.01 | 0.03 |
| Chlorsulfuron | $y = 17.89x + 0.328$ | 0.9998 | 0.05–5.0 | 0.01 | 0.03 |
| Pyrazosulfuron-ethyl | $y = 11.94x + 0.457$ | 0.9994 | 0.05–5.0 | 0.02 | 0.07 |
| Chlorimuron-ethyl | $y = 11.88x + 0.444$ | 0.9996 | 0.05–5.0 | 0.02 | 0.07 |

^a x means concentration of SUs (μg/L), y means peak area.

Table 2
Intra-day and inter-day precisions (RSD, %) for MSPE-HPLC determination of the six SUs.

| SUs | Spiked (μg/L) | Intra-day (n=6) | Inter-day (n=6) |
|-----------------------|---------------|-----------------|-----------------|
| Nicosulfuron | 0.1 | 8.1 | 12.9 |
| | 2 | 6.0 | 5.9 |
| | 4 | 3.9 | 7.3 |
| Thifensulfuron methyl | 0.1 | 9.3 | 11.0 |
| | 2 | 5.6 | 5.7 |
| | 4 | 2.0 | 4.1 |
| Metsulfuron methyl | 0.1 | 8.0 | 8.2 |
| | 2 | 4.4 | 2.2 |
| | 4 | 5.1 | 4.4 |
| Chlorsulfuron | 0.1 | 7.6 | 8.8 |
| | 2 | 4.7 | 3.4 |
| | 4 | 2.4 | 4.5 |
| Pyrazosulfuron-ethyl | 0.1 | 11.0 | 10.5 |
| | 2 | 3.3 | 5.6 |
| | 4 | 4.4 | 7.8 |
| Chlorimuron-ethyl | 0.1 | 8.6 | 11.1 |
| | 2 | 3.7 | 2.1 |
| | 4 | 6.7 | 8.2 |

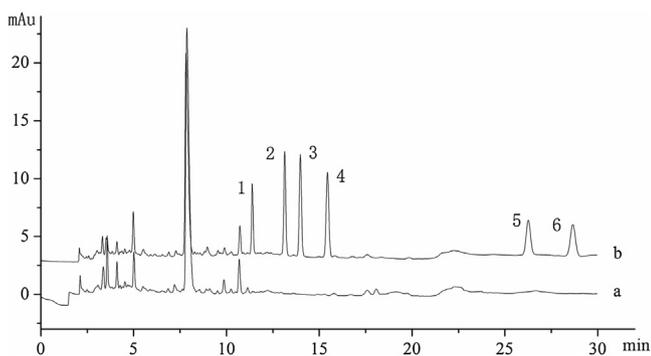


Fig. 6. HPLC chromatograms of six SUs in real-life water samples after MSPE without spiking (a) and with spiking (b). Spiked concentration of SU standard was 4.0 μg/L. MSPE conditions: sample volume, 100 mL; amount of mag-MWCNTs, 40 mg; extraction time, 8 min; desorption solvent, 10 mL acetone; desorption time, 2 min; sample pH, 3. Peak identification as described in Fig. 4.

sitivity, cost-effectiveness, excellent reusability and rapid, simple magnetic separation.

3.5. Application of the MSPE-HPLC to real environmental water samples

To further evaluate the practical applicability of the MSPE-HPLC method, two water samples from reservoir water and tap water were analyzed. The MSPE elution solutions were analyzed by HPLC and the results are shown in Fig. 6. No endogenous SUs were detected in the real water samples (Fig. 6a), and significant peaks appeared after spiking (Fig. 6b). The recoveries were obtained with spiked real water samples with 0.1, 2.0 and 4.0 μg/L individual herbicides, which were averaged from three replicates. As listed

in Table 3, the recovery of six SUs ranged from 76.7–106.9% with RSDs of 0.7–9.8% for reservoir water samples, and ranged from 78.2–105.4% with RSDs of 1.6–11.3% for tap water samples. The results indicate that the MSPE-HPLC method is practically feasible for highly efficient separation, extraction and determination of trace SUs in complex water samples.

4. Conclusions

In conclusion, a simple, sensitive, and robust mag-MWCNTs-based MSPE method was successfully developed for the simultaneous determination of six SUs in environmental water samples followed by HPLC-DAD. High extraction efficiency and low LODs/LOQs were obtained. The assay requires no complex devices, as the mag-MWCNTs are separated quickly from solutions by an external magnet. The processes of enrichment, separation, and desorption for six SUs are convenient, rapid, cost/labor-effective and eco-friendly. The developed MSPE-HPLC-DAD method provides great potential for analyzing SUs in real water samples.

Conflict of interest

The authors declare no conflict of interest.

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Table 3
Determination of six SUs and method recoveries in real water samples.

| SUs | Spiked (µg/L) | Reservoir water | | Tap water | |
|-----------------------|---------------|-----------------|--------------------------|--------------|----------------------|
| | | Found (µg/L) | Recovery (% , n = 3) | Found (µg/L) | Recovery (% , n = 3) |
| Nicosulfuron | 0 | ND ^a | | ND | |
| | 0.10 | 0.107 | 106.9 ± 9.8 ^b | 0.097 | 96.8 ± 8.0 |
| | 2.00 | 1.75 | 87.3 ± 8.0 | 1.67 | 83.3 ± 8.0 |
| | 4.00 | 3.67 | 91.8 ± 3.7 | 3.98 | 99.5 ± 6.7 |
| Thifensulfuron methyl | 0 | ND | | ND | |
| | 0.10 | 0.085 | 84.9 ± 7.5 | 0.069 | 99.3 ± 2.0 |
| | 2.00 | 1.99 | 99.7 ± 3.4 | 1.73 | 86.3 ± 7.9 |
| | 4.00 | 4.06 | 101.5 ± 4.9 | 3.89 | 97.2 ± 2.7 |
| Metsulfuron methyl | 0 | ND | | ND | |
| | 0.10 | 0.090 | 90.2 ± 6.3 | 0.090 | 90.0 ± 5.4 |
| | 2.00 | 1.95 | 97.7 ± 4.8 | 1.66 | 83.2 ± 10.3 |
| | 4.00 | 3.95 | 98.7 ± 8.2 | 3.71 | 92.8 ± 3.7 |
| Chlorsulfuron | 0 | ND | | ND | |
| | 0.10 | 0.077 | 76.7 ± 7.2 | 0.105 | 105.4 ± 9.3 |
| | 2.00 | 1.95 | 97.4 ± 4.9 | 1.75 | 87.3 ± 11.3 |
| | 4.00 | 4.06 | 101.4 ± 2.7 | 4.04 | 101.1 ± 3.3 |
| Pyrazosulfuron-ethyl | 0 | ND | | ND | |
| | 0.10 | 0.087 | 87.3 ± 9.5 | 0.081 | 81.5 ± 4.2 |
| | 2.00 | 1.85 | 92.6 ± 0.7 | 1.74 | 86.8 ± 5.0 |
| | 4.00 | 4.01 | 100.4 ± 3.0 | 3.97 | 99.3 ± 7.5 |
| Chlorimuron-ethyl | 0 | ND | | ND | |
| | 0.10 | 0.106 | 105.7 ± 7.9 | 0.078 | 78.2 ± 1.6 |
| | 2.00 | 1.92 | 96.0 ± 5.5 | 1.86 | 93.0 ± 4.3 |
| | 4.00 | 4.07 | 101.7 ± 7.9 | 4.12 | 103.1 ± 3.2 |

^a Not detected.^b RSD.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chroma.2016.08.065>.

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