



N-Methylimidazolium ionic liquid-functionalized silica as a sorbent for selective solid-phase extraction of 12 sulfonylurea herbicides in environmental water and soil samples

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ABSTRACT

A novel material for solid-phase extraction (SPE) was synthesized by chemical immobilization of a functionalized N-methylimidazolium ionic liquid on silica gel. Cartridges packed with the synthetic material were successfully applied to the pre-concentration of trace-level thifensulfuron-methyl, metsulfuron-methyl, chlorsulfuron, sulfometuron-methyl, rimsulfuron, ethametsulfuron, tribenuron-methyl, bensulfuron-methyl, prosulfuron, pyrazosulfuron, chlorimuron-ethyl and primisulfuron from environmental water and soil samples. The 12 sulfonylurea herbicides (SUs) obtained a good resolution in less than 50 min using HPLC with a UV detector. The recovery studies using the ionic liquid-functionalized silica as a sorbent were performed by three consecutive extractions of water and soil samples at two spiked levels. The average recovery for each analyte was in the range of 53.8–118.2% for the water samples and 60.9–121.3% for the soil sample, with RSDs lower than 11.3% in all cases. The ionic liquid-functionalized silica cartridges showed higher selectivity for the SUs than commercially available C₁₈ cartridges did.

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1. Introduction

Sulfonylurea compounds, which are composed of a sulfonyl structure linked to a urea group, represent one of the largest classes of herbicides. The first commercialized sulfonylurea herbicide, sulfometuron-methyl, was registered by DuPont Agricultural Products in 1982. To date, this class has expanded to include over 31 commercial herbicides. As a family, sulfonylurea herbicides are noted for their high specific activity in controlling a wide range of annual and perennial grasses and broadleaf weeds at very low application levels. Compared with other herbicides, the SUs are characterized by their low mammalian toxicity and their degradation to innocuous compounds after application [1,2]. However, the SUs have now been found in natural waters since they are increasingly being used for weed control in cereals and other crops. As reported by Perreau et al. [3], more than half the rivers in the mid-western United States have been found to contain nicosulfuron and chlorimuron-ethyl at quantifiable levels. Recently, there has been ever-increasing concern about the adverse impact of the SUs on soils and their subsequent contamination of natural or irrigating water sources. Simultaneous monitoring of sulfonylurea herbicides

in complex environmental samples is very challenging due to their active physical–chemical properties.

Analytical methods related to series of these herbicides generally include a combination of SPE and highly sensitive instruments to detect trace-level residues in water and soil samples. Because of their low volatility and thermal instability [4], the SUs cannot be directly detected by gas chromatography (GC) without time-consuming derivatization procedures. In this respect, the analytical mode of SPE coupled with HPLC or HPLC–MS has great potential to provide both high sensitivity and high selectivity for trace analysis of multiresidue SUs. A rapid and economical SPE technique is particularly used for clean-up and concentration of aqueous and soil samples. Octadecyl-bonded silica [3,5–10], polystyrene divinylbenzene polymeric phase [3,7,9], a co-polymer of polydivinylbenzene-co-N-vinyl pyrrolidone [8,9], polystyrene polymer [10], magnesium silicate [11] and graphitized carbon black [12] have been reported as nonspecific materials in the SPE procedure for the extraction of SUs from water, soil or plant samples.

Room temperature ionic liquids (RTILs) containing relatively large asymmetric organic cations and inorganic or organic anions have recently been used as “green solvents” to replace traditional organic solvents for chemical reactions. Due to their low volatility, high stability and good solubility for organics and inorganics, ILs have been successfully applied in the field of analytical chemistry [13,14] such as in liquid–liquid extraction [15],

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liquid-phase microextraction [16–18], solid-phase microextraction [19,20], mobile phase additives in HPLC [21,22], electrolyte additives in CE [23] and stationary phases in GC [24–29] and CE [30]. The application of immobilized ionic liquids in separation and clean-up procedures has recently aroused much interest. The ionic liquids bond on silica as an HPLC stationary phase have been reported to separate mixtures of inorganic anions, organic anions and some organic compounds [31,32], ephedrine [33] and aromatic carboxylic acids [34]. Li et al. [35], Myasoedova et al. [36] and Li et al. [37] have reported the use of immobilized ILs prepared by physically adhering ionic liquids to different support materials to extract α -tocopherol, trace elements (Pt and Pu) and five phthalates. To our knowledge, the use of the synthesized *N*-methylimidazolium ionic liquid-functionalized silica as an adsorbent for the selective extraction of multiresidue SUs has not been reported previously.

In this work, a novel ionic liquid-functionalized silica was prepared by chemically bonding the functionalized *N*-methylimidazolium ionic liquid on the silica surface. A convenient and sensitive method for trace analysis of 12 SUs using the synthesized ionic liquid-functionalized silica coupled with HPLC is proposed. The factors impacting the HPLC separation and SPE procedure are discussed in detail. The extraction character of the ionic liquid-functionalized silica is compared with that of a commercial C_{18} sorbent. The developed method was successfully applied to the simultaneous detection of 12 SUs in water and soil samples.

2. Experimental

2.1. Materials and reagents

Silica gel (80–100 mesh) used as the support material was obtained from Qing Dao Ocean Chemical Co., China. The solvents for preparing the ionic liquid-functionalized silica were at least of analytical grade. *N*-Methylimidazole and potassium hexafluorophosphate (KPF_6) were obtained from Sinopharm Chemical Reagent Beijing Co., Ltd., and Beijing Sanshengtengda Technology Co., Ltd., respectively. The silylant agent 3-chloropropyltrimethoxysilane was obtained from JingZhou JiangHan Fine Chemical Co., Ltd. Acetonitrile, methanol and dichloromethane (HPLC grade) were purchased from Tianjin Concord Technological Corporation. Trifluoroacetic acid (TFA), used to regulate the pH of the mobile phase, was purchased from Tianjin KLES Industry of Fine Chemicals Co., Ltd. The mobile phase was filtered through a 0.22 μ m nylon membrane and degassed ultrasonically prior to use. Sodium hydrogen phosphate and sodium dihydrogen phosphate (Tianjin Chemical Factory) were also used to prepare the soil-extraction solution. Doubly deionized water (DDW; 18 $M\Omega\text{ cm}^{-1}$) prepared by a Milli-Q water purification system (Labconco Corporation, Kansas City, MO, USA) was used throughout the experiment.

The analytical grade standards of metsulfuron-methyl, sulfometuron-methyl, bensulfuron-methyl, chlorimuron-ethyl, tribenuron-methyl, pyrazosulfuron, ethametsulfuron and prosulfuron were purchased from Dr. Ehrenstorfer (Augsburg, Germany). The other 4 SUs, thifensulfuron-methyl, chlorsulfuron, rimsulfuron

and primisulfuron, were from Sigma–Aldrich Chemie (Madrid, Spain). A stock solution of each analyte was initially prepared at 1000 mg L^{-1} by dissolving 10 mg of individual standard in 10 mL of acetonitrile and stored at -18°C in the dark. Working standard solutions were obtained by diluting the individual stock solutions with acetonitrile to desired concentrations just before use. The standard mixtures at different concentration levels were prepared by diluting standard solutions of the analytes with DDW.

200 mg of ionic liquid-functionalized silica packed into an empty polypropylene cartridge (200 mg/3 mL, United Chemical Technologies, Inc., USA) was used to pre-concentrate the 12 SUs in solution. The commercially available C_{18} cartridges (200 mg/3 mL, United Chemical Technologies, Inc., USA) were also used for comparison with the ionic liquid-functionalized silica sorbent.

2.2. Apparatus

Analysis was performed using a Shimadzu high-performance liquid chromatographic instrument equipped with an SPD-10Avp ultraviolet detector. Chromatographic data were collected and processed by a chromatographic software Class VP 5.0 package. Optimal separation of the 12 SUs was achieved on an analytical reversed-phase column (Alltima- C_{18} , 5 μ m, 4.6 mm \times 250 mm, Alltech, USA) at a mobile flow rate of 1.0 mL min^{-1} under gradient elution conditions. During the analytical process, the UV detection was set at a wavelength of 230 nm and the column temperature was held constant at 30 $^\circ\text{C}$. The SPE procedure using a Visiprep-DL SPE vacuum from SUPELCO (Bellefonte, PA, USA) was applied to the sample pre-concentration. The ionic liquid synthesized in this study, *N*-methylimidazolium hexafluorophosphate silane, was confirmed on an ion trap mass spectrometer (LCQ; Thermo Finnigan, Advantage MAX, USA) equipped with an electrospray ion source. A Vector 22 spectrometer (Bruker, Germany) was employed for FT-IR spectra recording.

2.3. Preparation of ionic liquid-functionalized silica sorbent

Silica gel used as the support material was activated in order to enhance the content of silanol groups on the silica surface. 8 g of silica gel was mixed with 60 mL of 33% methanesulfonic acid and refluxed with stirring for 8 h. The solid product was recovered by filtration, washed with DDW to a neutral pH, and dried under vacuum at 70 $^\circ\text{C}$ for 8 h [38].

The synthesis process was carried out in the presence of acetonitrile with three steps (see Fig. 1). 15 mM of *N*-methylimidazole (1.2 mL) was mixed with 16.5 mM of 3-chloropropyltriethoxysilane (silane-coupling agent, 4.0 mL) in a 500 mL round bottomed flask, and the mixture was refluxed with stirring for 48 h. After the reaction had cooled to room temperature, 2.8 g of KPF_6 dissolved in 50 mL acetonitrile was slowly added and the anion-exchange reaction was allowed to take place over the next 26 h. 0.25 g of activated silica was mixed with silane-coupling agent attached with *N*-methylimidazolium ionic liquid and the mixture was refluxed with stirring for 24 h, after which the product was recovered by filtration

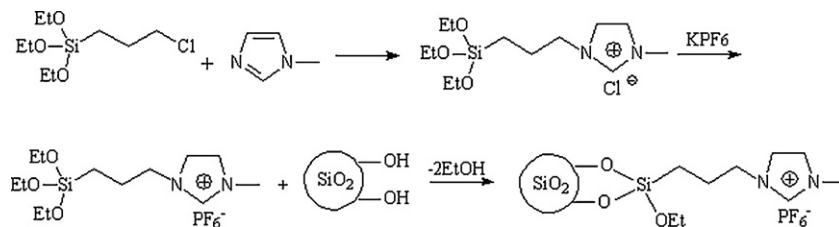


Fig. 1. Synthetic scheme for *N*-methylimidazolium ionic liquid-functionalized silica.

and consecutively rinsed with ether (100 mL), acetonitrile (100 mL) and DDW (100 mL). The obtained ionic liquid-functionalized silica was dried under vacuum at 80 °C for 8 h.

2.4. Conditions for the HPLC analysis

In order to obtain optimal separation of the 12 SUs, analysis was carried out under a linear gradient program. The initial composition of the mobile phase was 37% acetonitrile–methanol 8:2 (v/v) and 63% aqueous solution acidified to pH 3.0. After 25 min, the concentration of organic phase was linearly increased to 59% over 16 min and then maintained at this level for 9 min. Within 50 min, all the analytes were fully separated with sharp and symmetrical peaks. Other conditions for HPLC analysis were described in Section 2.2.

2.5. Pretreatment of samples

Environmental water and soil samples were chosen to evaluate the developed SPE–HPLC method. Mineral water was taken from JiXian in Tianjin. The reservoir waters were collected from a suburb of GuangZhou city (surface water 1) and the downtown area of HeYuan city (surface water 2) in China. Water samples were stored in precleaned polypropylene bottles (thoroughly washed with detergent, tap water and DDW and finally dried before use), and kept at 4 °C in the dark. All samples were filtered through glass microfibre filters (0.45 μm) and adjusted to pH 4.8 (or pH 4.5 for C₁₈ sorbents) with phosphoric acid or ammonium acetate to ensure efficient extraction of the analytes.

The soil sample was randomly sampled from a playground located in the Tianjin University of Science and Technology in China. The soil taken from 20 cm below the surface was collected in a black plastic bag and dried overnight at room temperature. The sample was sieved through a 40 mesh screen to remove stones and achieve uniform soil particle sizes. 50 g of soil sample was weighed into a 250 mL conical flask and extracted by 100 mL of 0.1 M, pH 6.8 phosphate buffer solution (PBS). After sonication for 20 min, the mixture was separated by centrifugation at 5000 rpm for 15 min. The supernatant acidified to pH 4.8 (or pH 4.5 for C₁₈ cartridges) was adjusted to a quantity of 60 mL before uploading the cartridge.

2.6. Pre-concentration procedure for SPE cartridges

Cartridges packed with 200 mg of the ionic liquid-functionalized silica were equilibrated with 10 mL of dichloromethane–methanol 95:5 (v/v) and DDW. The aqueous sample (250 mL of water sample or 60 mL of soil-extraction solution) acidified to pH 4.8 was uploaded onto a cartridge at a flow rate of 1.5 mL min⁻¹ during the whole SPE procedure. After washing with 5 mL of DDW, the cartridge was dried under vacuum for about 30 min. The analytes retained on the cartridge were eluted with 15 mL of dichloromethane–methanol 95:5 (v/v), and the extract was evaporated to dryness under a stream of dry nitrogen. The residues were redissolved in 0.5 mL of methanol and filtered through a PTFE filter (0.22 μm) before analysis by HPLC.

The C₁₈ cartridge was preconditioned with 5 mL of methanol followed by 5 mL of DDW. After the pH 4.5 aqueous samples had passed through the sorbents, 5 mL of methanol–DDW (2:8, v/v) was used to remove interferences. The 12 adsorbed SUs were quantitatively eluted from the C₁₈ sorbent with 10 mL of acetonitrile after drying the cartridge. The eluate was evaporated to dryness and the residues were redissolved using 0.5 mL methanol. The obtained SUs methanol solution was filtered through a 0.22-μm PTFE filter before analysis by HPLC.

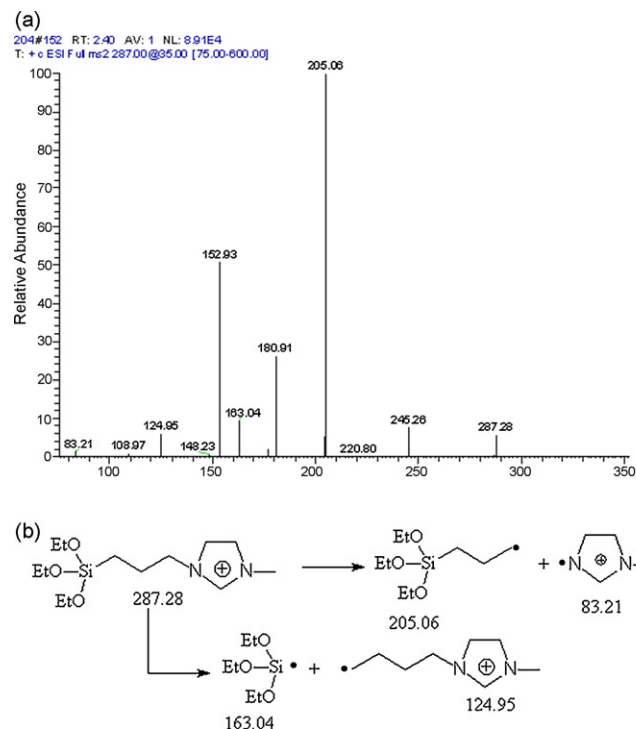


Fig. 2. (a) Mass spectrum of the functionalized *N*-methylimidazolium ionic liquids acquired with a collision energy of 35% in positive ion mode and (b) structures and masses of product ions obtained from the functionalized *N*-methylimidazolium cations.

3. Results and discussion

3.1. Characterization of the synthesized ionic liquid and ionic liquid-functionalized silica

3.1.1. Mass spectral analysis

The functionalized ionic liquids have been synthesized in this paper. In contrast to the process reported by Tian et al. [39], the water-insoluble anion [PF₆] was added to exchange with the water-soluble anion [Cl] in order to increase the hydrophobic property of the synthesized ionic liquids in our synthesis process. The synthesized ionic liquids were analyzed by electrospray ionization mass spectroscopy (ESI–MS) and precursor ion peaks at *m/z* 287.28 and *m/z* 145.52 in positive and negative ion modes were obtained, respectively. In order to further identify the structure of the compound, the peak at *m/z* 287.28 was fragmented as shown in Fig. 2a. At least four target product ions were obtained to confirm the structure of the functionalized ionic liquids synthesized (seen in Fig. 2b).

3.1.2. FT-IR analysis

In order to confirm the immobilization reaction, FT-IR spectra of activated silica and ionic liquid-functionalized silica were compared between 4000 and 400 cm⁻¹. As shown in Fig. 3, no significant differences were observed between the spectra with respect to the wave numbers of major bands for the activated silica and the ionic liquid-functionalized silica. The bond at 3435 cm⁻¹ was mainly assigned to stretching vibrations of the O–H bonds of silanol groups. The difference on the intensity of the OH vibration indicated that the free silanols were engaged in the silylation process as suggested by the decrease of the isolated silanol band in the functionalized silica spectrum. In the spectrum of ionic liquid-functionalized silica, a characteristic frequency at 2960 cm⁻¹ was attributed to the C–H stretching of the tetrahedral carbon, which confirmed the anchoring of the organic molecule onto the silica surface [31].

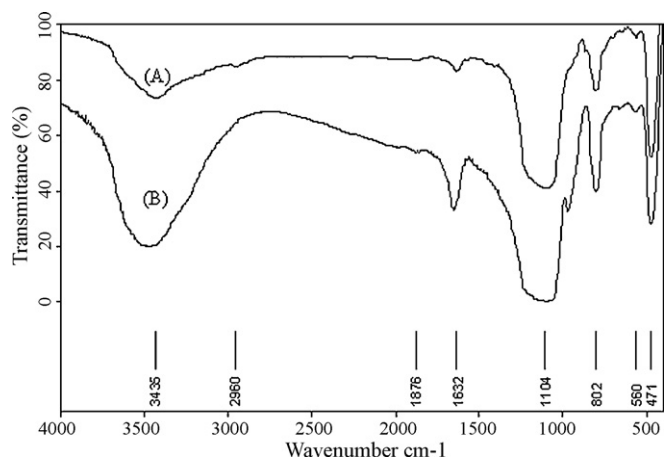


Fig. 3. FT-IR spectra of (A) *N*-methylimidazolium ionic liquid-functionalized silica and (B) activated silica.

3.2. Optimization of SPE procedure

To achieve accurate and sensitive chromatographic quantification of trace SUs in complex samples, the optimum conditions for SPE using ionic liquid-functionalized silica sorbents were investigated by comparison with those for the commercial C_{18} sorbents. SPE parameters including the sample pH, the type and the amount of eluent were optimized following a factor by factor technique. The experiments were performed in duplicate under the following conditions: 250 mL of $3.0 \mu\text{g L}^{-1}$ SUs standard aqueous solution at a flow rate of 1.5 mL min^{-1} , without any washing step.

3.2.1. Effect of sample pH on the absorption efficiencies of the two sorbents

The pH value of the sample solution plays an important role in the extraction of the selected SUs because it not only determines the state of the analytes in solution as ionic or neutral molecules, but also influences the stability of the SUs. The SUs with pK_a values ranging from 3.3 to 5.2 were evaluated to be more extractable at a rather acidic pH but not below 3 [11], since a pH below 3 could accelerate their hydrolysis, particularly for tribenuron-methyl. However, a strong alkaline environment could lead to

breakage of the sulfonylurea bridge structure. Preliminary experiments were carried out using 15 mL of dichloromethane–methanol 95:5 (v/v) as the initial eluent. As Fig. 4(a and b) shows, the influence of sample pH was estimated in the pH range of 3.0–6.5. The results illustrated that the sample pH greatly affected the absorption efficiencies of all the analytes in the pH range examined. The peak areas of the target compounds tended to increase as the pH value increased from 3.0 to 4.5. Typically, the maximum chromatographic peak area of each analyte was achieved in the pH range of 4.5–5.0. The SUs were not effectively absorbed on the ionic liquid-functionalized silica at pH values higher than 5.0. This result could not be explained in accordance with the main strong anion-exchange mechanism of the phase based on *N*-methylimidazolium chloride immobilized on silica [31]. In this work, the water-insoluble anion $[\text{PF}_6]$ was exchanged with the water-soluble anion $[\text{Cl}]$ to produce the *N*-methylimidazolium ionic liquid with a higher hydrophobic property. It may be concluded that the hydrophobic interaction became predominant as the 12 SUs were absorbed by the ionic liquid-functionalized silica sorbent. Thus, a sample pH of 4.8 was applied to subsequent studies.

On the C_{18} cartridge, the influence of sample pH on the adsorption efficiency was studied over a pH range of 3.0–6.5 using 15 mL of acetonitrile as the initial eluent. As can be seen in Fig. 4(c and d), remarkable changes in the adsorption efficiencies of the 12 SUs were observed in this pH range. The maximum chromatographic peak area for each analyte was basically obtained in the pH range of 4.2–4.8. Therefore, pH 4.5 was chosen to simultaneously quantify the 12 SUs. In addition, the loading pH 4.8 of the ionic liquid-functionalized silica sorbent was very close to the optimized pH 4.5 of the C_{18} sorbent. This could further demonstrate that the absorption of the 12 SUs on the ionic liquid-functionalized silica sorbents is mainly attributable to hydrophobic interactions, as for the SUs on the C_{18} sorbents.

3.2.2. Optimization of elution conditions for the two sorbents

Elution solvent and elution volume are essential parameters to be investigated in SPE procedures. The tests were carried out with the pH 4.8 and 4.5 standard solutions for the ionic liquid-functionalized silica and C_{18} sorbents, respectively. Acetonitrile, a satisfactory eluent, has been reported to elute SUs absorbed on C_{18} sorbents [7–10]. In this work, however, acetonitrile can dissolve the functionalized ILs (*N*-methylimidazolium

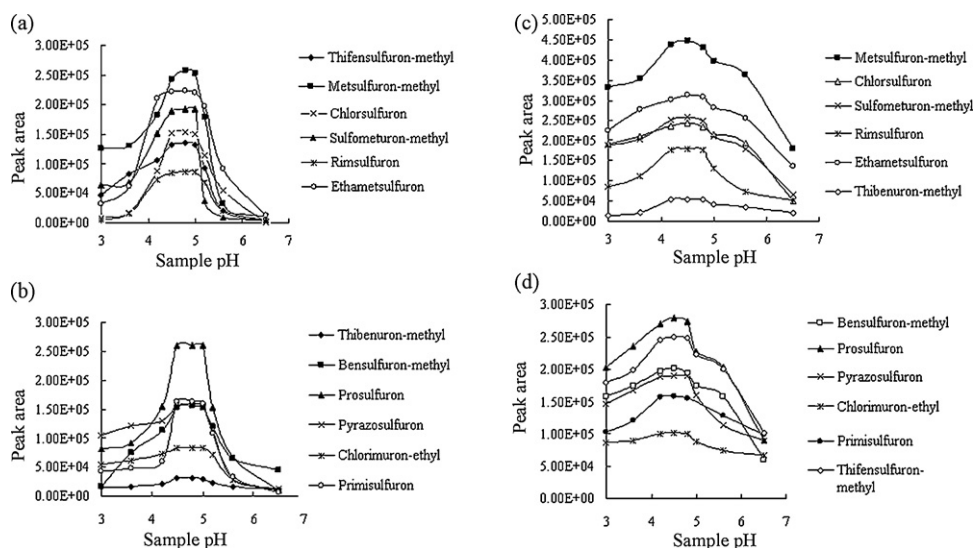


Fig. 4. Effect of sample loading pH on the peak areas of the 12 SUs (a and b) using the ionic liquid-functionalized silica sorbent and 15 mL of dichloromethane–methanol 95:5 (v/v) as the eluent; (c and d) using the C_{18} sorbent and 15 mL of acetonitrile as the eluent. Experimental conditions for both sorbents: 250 mL of $3.0 \mu\text{g L}^{-1}$ SUs working solution at a flow rate of 1.5 mL min^{-1} .

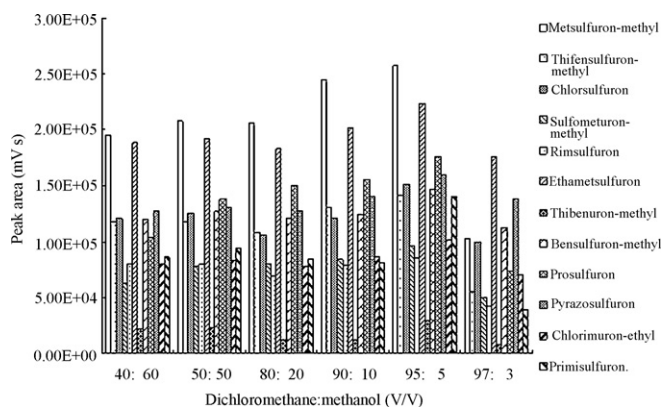


Fig. 5. Effect of different elution solvents on the peak areas of the 12 SUs using the ionic liquid-functionalized silica sorbent for 250 mL of $3.0 \mu\text{g L}^{-1}$ SUs working solution (acidified to pH 4.8) at a 1.5 mL min^{-1} flow rate and 15 mL elution volume.

hexafluorophosphate silane) immobilized on the silica. In order to allow the ionic liquid-functionalized silica sorbent to be reused effectively, methanol and dichloromethane were chosen to elute the 12 adsorbed SUs. Elution solvents with different polarities consisted of dichloromethane–methanol 50:50, 60:40, 80:20, 90:10, 95:5 and 97:3 (v/v) mixtures. As Fig. 5 illustrates, dichloromethane–methanol 95:5 (v/v) provided the strongest chromatographic signals for all the analytes. The peak areas of the target compounds tended to rise with a reduction in the percentage of methanol; however, the peak areas of the 12 SUs decreased dramatically over the optimal volume ratio. Therefore, dichloromethane–methanol 95:5 (v/v) was selected as the final eluting agent in the following experiments. For the C_{18} sorbent, acetonitrile was used to elute the SUs absorbed, in accordance with the previously published literature [7–10], without further optimization.

Elution volume is also a significant factor that needs to be considered. It must be sufficient to elute all the analytes from the sorbent. Different elution volumes of 5, 8, 10, 15 and 18 mL were investigated after passing $3.0 \mu\text{g L}^{-1}$ standard solutions through the ionic liquid-functionalized silica sorbent. The results demonstrated that an elution volume of 15 mL was enough to achieve satisfactory extraction yields, since an additional 3 mL still provided similar extraction yields. Hence, 15 mL of dichloromethane–methanol 95:5 (v/v) was selected to accomplish the quantitative elution of the adsorbed SUs. The extraction yields of the SUs absorbed by C_{18} cartridges were determined by using acetonitrile as the eluant with volumes of 5, 8, 10 and 15 mL. No significant differences were noted between the extraction yields of the analytes when $3.0 \mu\text{g L}^{-1}$ standard solutions were eluted with 10 and 15 mL of acetonitrile, respectively. As a result, 10 mL of acetonitrile was adopted as the optimal elution volume.

3.3. Evaluation of adsorption capacity of the two sorbents

The adsorption capacity of a sorbent is an important parameter in assessing its ability to retain selected analytes. The kinetic adsorption curves for both sorbents were identified by successively loading 1 mL of 10 mg L^{-1} standard solution through the 200 mg sorbent under the following conditions: a loading flow rate of 1.5 mL min^{-1} , a loading sample pH of 4.8 for the ionic liquid-functionalized silica sorbent and a pH of 4.5 for the C_{18} sorbent. The column effluents were collected in tubes and the 12 SUs were detected by HPLC. The curves present the peak areas of target compounds in the effluents versus the loading amounts of each analyte. In terms of the amounts of SUs retained per mass of the sorbent, chlorsulfuron and ethamet-

sulfuron gave the lowest adsorption capacity at $1950 \mu\text{g g}^{-1}$. The curves of thifensulfuron-methyl, metsulfuron-methyl and bensulfuron-methyl became almost smooth when the total loading amount was over $1020 \mu\text{g}$. Accordingly, the adsorption capacities of these 3 SUs were $5100 \mu\text{g g}^{-1}$. With an increase of loading analytes, sulfometuron-methyl reached its adsorption capacity at $6350 \mu\text{g g}^{-1}$. Rimsulfuron, tribenuron-methyl, chlormuron-ethyl and primisulfuron achieved adsorption capacities of $7600 \mu\text{g g}^{-1}$ when the gross loading amount was up to $1520 \mu\text{g}$. The highest adsorption capacities were obtained by prosulfuron and pyrazosulfuron with $8850 \mu\text{g g}^{-1}$. The above results demonstrated that the ionic liquid-functionalized silica sorbent possessed a high relative adsorption capacity for the target compounds, which could be sufficient to analyze samples for the presence of these SUs.

Typically, the adsorption capacity acquired with the C_{18} sorbent was higher than $6000 \mu\text{g g}^{-1}$ for all SUs tested except for thifensulfuron-methyl, which displayed the lowest adsorption capacity, between 4300 and $5500 \mu\text{g g}^{-1}$. With an increased loading of the analytes, tribenuron-methyl, chlorsulfuron, sulfometuron-methyl, metsulfuron-methyl and rimsulfuron obtained adsorption capacities in the range of 6500 – $7500 \mu\text{g g}^{-1}$. The capacities of the C_{18} sorbent to retain ethametsulfuron, bensulfuron-methyl, prosulfuron, pyrazosulfuron and chlormuron-ethyl ranged from 16,250 to $18,750 \mu\text{g g}^{-1}$. The best performance was obtained by primisulfuron with an adsorption capacity of $18,750 \mu\text{g g}^{-1}$.

3.4. Optimization of extraction conditions for real samples

3.4.1. Extraction of water samples

250 mL of the water samples (non-spiked and spiked with 12 SUs) acidified to pH 4.8 and 4.5 were passed through the two respective sorbents. 5 mL of DDW was sufficient to wash the interferences co-absorbed with the 12 SUs on the ionic liquid-functionalized silica sorbent, and 15 mL of dichloromethane–methanol 95:5 (v/v) could accomplish quantitative elution of the adsorbed SUs. In the process of the C_{18} SPE, 10 mL of acetonitrile could quantitatively elute the 12 SUs. However, matrix components absorbed on the sorbent could be co-eluted with target compounds and present chromatographic peaks very close to those of the analytes. Therefore, washing solvents for the elimination of interferences were investigated, including 5 mL of DDW and methanol–DDW 1:9, 2:8 and 3:7 (v/v). Basically, an increase in the percentage of methanol enhanced the washing strength of the mixture. On the other hand, 5 mL of methanol–DDW 3:7 (v/v) significantly decreased the extraction yields of most analytes. As a compromise, 5 mL of methanol–DDW 2:8 (v/v) was selected to wash the interferences co-absorbed with the 12 SUs on the C_{18} sorbent, since the extraction yields were in the range of 50–120%.

3.4.2. Extraction of soil sample

The migration of SUs from soil to aqueous solution is mainly dependent on the properties of the soil and the soil-extraction solution. As the SUs are weakly acidic solutes that are stable in solution in the form of anions, the extraction of SUs from the test soil sample is largely influenced by the ionic mobile character of the analytes and the properties of the soil-extraction solution system. Based on previous reports [5,8], we selected 0.1 M PBS as the soil-extraction solution.

To make all the analytes migrate efficiently from the soil matrix to the extraction solution in an anionic form, pH 7.2 PBS was initially chosen [8]. As the SUs can be readily dissolved in organic solvents including methanol and acetonitrile, we studied the impacts of the methanol and acetonitrile contents in the PBS on the extraction efficiency. 50 g of soil samples spiked with each analyte at a

Table 1
Analytical characteristic data for the developed SPE–HPLC method with the ionic liquid–functionalized silica sorbent for the determination of 12 SUs.

Analyte	Linear equation	Correlation coefficient (r^2)	Linear range ^b ($\mu\text{g L}^{-1}$)	RSD ^a ($n=7$) (%)
Thifensulfuron-methyl	$Y=(35,377 \pm 0.08)x + (-4297.3 \pm 0.28)$	0.9997	0.010–5.0	3.7
Metsulfuron-methyl	$Y=(38,504 \pm 0.09)x + (-3822.2 \pm 0.47)$	0.9993	0.020–5.0	2.5
Chlorsulfuron	$Y=(34,153 \pm 0.02)x + (-162.1 \pm 1.41)$	0.9992	0.010–5.0	3.8
Sulfometuron-methyl	$Y=(18,684 \pm 0.01)x + (217.6 \pm 1.41)$	0.9999	0.015–5.0	3.0
Rimsulfuron	$Y=(29,635 \pm 0.01)x + (-3521.3 \pm 0.06)$	0.9999	0.020–5.0	4.4
Ethametsulfuron	$Y=(21,512 \pm 0.01)x + (-836.1 \pm 1.41)$	0.9999	0.060–5.0	6.9
Thibenuron-methyl	$Y=(8522.3 \pm 0.02)x + (-1035.8 \pm 0.05)$	0.9996	0.250–5.0	5.3
Bensulfuron-methyl	$Y=(36,084 \pm 0.10)x + (-6008.7 \pm 0.34)$	0.9998	0.010–5.0	5.3
Prosulfuron	$Y=(32,767 \pm 0.01)x + (416.2 \pm 1.05)$	0.9998	0.010–5.0	3.2
Pyrazosulfuron	$Y=(18,573 \pm 0.01)x + (1728.0 \pm 0.25)$	0.9992	0.060–5.0	2.4
Chlorimuron-ethyl	$Y=(14,350 \pm 0.04)x + (-522.45 \pm 1.41)$	0.9995	0.100–5.0	2.6
Primisulfuron	$Y=(33,115 \pm 0.02)x + (4307.3 \pm 0.11)$	0.9986	0.100–5.0	7.2

Y: peak areas (μVs); x: concentrations of 12 SUs ($\mu\text{g L}^{-1}$).

^a Using a standard mixture of 12 SUs at a $0.5 \mu\text{g L}^{-1}$ level for each analyte.

^b Using standard working solutions at different concentration levels for each analyte.

concentration of 4.0 mg kg^{-1} were extracted with 0.1 M PBS (pH 7.2), PBS–methanol (9:1, v/v), PBS–methanol (8:2, v/v), PBS–acetonitrile (9:1, v/v) and PBS–acetonitrile (8:2, v/v), respectively. The results indicated that analytes extracted by the PBS alone achieved higher relative extraction yields. In addition, the chromatogram for the soil sample extracted by the PBS alone was basically free of matrix interferences. In contrast, interference peaks were present in the regions of the target compounds in the chromatograms for soil samples extracted by PBS–organic solvent systems. This might be due to organic interferences that were co-extracted with the SUs in these solvent systems. In order to minimize the matrix effect, 0.1 M PBS was chosen as the soil-extraction solution for further experiments.

The impact of the pH of the PBS on the extraction efficiency was also evaluated over a pH range of 5.6–8.0. The results showed that below pH 6.4 the chromatographic peak areas of the analytes increased greatly with the buffer pH, whereas over pH 7.2 the chromatographic peak areas for each analyte decreased dramatically as the buffer pH increased. The optimal pH range of PBS for effective extraction of the 12 SUs was found to be in the range of 6.4–7.2, so we selected a pH 6.8 PBS as the final soil-extraction solution.

60 mL of the above soil extract (acidified to pH 4.8 or 4.5) was passed through the two sorbents, respectively. It had been indicated that the SPE conditions used for the water samples, including the washing for the interferences and the elution of the 12 SUs from the two sorbents, could satisfy the soil sample. Hence, the same washing and elution conditions as those used for the water samples were applied to the soil sample.

3.5. Analytical performance characteristics

The external standard method for quantification was used in this analytical process. A calibration plot of the peak area as a function of the concentration of each analyte was used for quantification of the analytes in the water and soil samples and the recovery study. The analytical characteristic data for the ionic liquid–functionalized silica sorbent coupling with HPLC are shown in Table 1. Calibration curves were measured by analyzing five concentrations of standard mixtures, with three replicates at each concentration level. Good linearity for each analyte was obtained in the range of $0.25\text{--}5.0 \mu\text{g L}^{-1}$ with correlation coefficients higher than 0.9986 for all the analytes. The precisions were evaluated by pre-concentrating seven replicate runs of $0.5 \mu\text{g L}^{-1}$ SUs standard solution. The LODs of the 12 SUs in water and soil samples are compared and summarized in Table 2, mainly depending on UV absorbance characteristics of individual analytes and the nature of the samples. The LODs calculated for the water sample using ionic liquid–functionalized silica and C_{18} as sorbents were in the range of $0.012\text{--}0.142$ and $0.011\text{--}0.175 \mu\text{g L}^{-1}$, respectively. The two sorbents had no significant differences in their LODs, except for tribenuron-methyl, bensulfuron-methyl and sulfometuron-methyl. For tribenuron-methyl and bensulfuron-methyl, lower LODs were achieved using the ionic liquid–functionalized silica sorbent, while the LOD of sulfometuron-methyl was lower using the C_{18} sorbent. The LODs of the soil sample varied from 0.080 to $1.000 \mu\text{g kg}^{-1}$ using the ionic liquid–functionalized silica sorbents, whereas the matrix effect of the soil sample made accurate determination of the LODs difficult, especially for thifensulfuron-methyl,

Table 2
Comparison of the LODs of 12 SUs in water and soil samples using the ionic liquid–functionalized silica and the C_{18} as sorbents.

Analyte	LOD ($\mu\text{g L}^{-1}$) ^a	LOD ($\mu\text{g L}^{-1}$) ^b	LOD ($\mu\text{g kg}^{-1}$) ^c	LOD ($\mu\text{g kg}^{-1}$) ^d
Thifensulfuron-methyl	0.019	0.014	0.100	–
Metsulfuron-methyl	0.012	0.013	0.080	0.050
Chlorsulfuron	0.014	0.019	0.100	0.250
Sulfometuron-methyl	0.054	0.016	0.400	0.450
Rimsulfuron	0.015	0.018	0.150	0.350
Ethametsulfuron	0.021	0.019	0.500	1.200
Thibenuron-methyl	0.100	0.122	1.000	1.780
Bensulfuron-methyl	0.076	0.175	0.200	–
Prosulfuron	0.040	0.026	0.150	0.500
Pyrazosulfuron	0.023	0.011	0.200	0.850
Chlorimuron-ethyl	0.142	0.127	0.200	0.800
Primisulfuron	0.016	0.014	0.200	–

(–): The determination of LODs for the analytes was seriously influenced with interference peaks very close to the analytes.

^a LOD, water sample, the ionic liquid–functionalized silica sorbent.

^b LOD, water sample, the C_{18} sorbent.

^c LOD, soil sample, the ionic liquid–functionalized silica sorbent.

^d LOD, soil sample, the C_{18} sorbent.

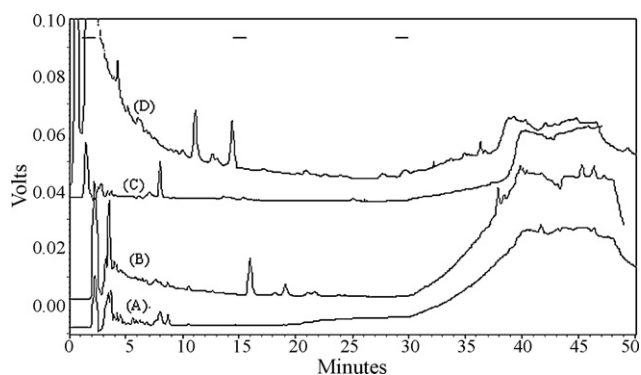


Fig. 6. Chromatograms of (A) SPE of 250 mL of surface water 2 (acidified to pH 4.8) using ionic liquid-functionalized silica sorbent combined with HPLC; (B) SPE of 250 mL of surface water 2 (acidified to pH 4.5) using the C_{18} sorbent coupled to HPLC; (C) SPE of 60 mL of soil extract acidified to pH 4.8 (non-spiked soil sample) using ionic liquid-functionalized silica sorbent combined with HPLC; and (D) SPE of 60 mL of soil extract acidified to pH 4.5 (non-spiked soil sample) using the C_{18} sorbent coupled to HPLC. Chromatographic conditions: solvent A, acetonitrile–methanol (8:2, v/v); solvent B, DDW with the addition of TFA (pH 3.0); gradient elution conditions are shown in Section 2.4. Other conditions for HPLC analysis are displayed in Section 2.2.

bensulfuron-methyl and primisulfuron, with the developed C_{18} SPE–HPLC method. The LODs calculated for the other 9 SUs were basically higher than those obtained with the ionic liquid-functionalized silica sorbents.

To evaluate the usefulness of the developed method, real environmental water and soil samples were analyzed under the optimal conditions. Representative chromatograms of the water and soil samples after pre-concentration by the two sorbents are presented in Fig. 6. The 12 SUs in the samples pre-concentrated by the ionic liquid-functionalized silica were under the limits of detection and the chromatograms were basically free from matrix interferences in the regions of all the analytes (shown in Fig. 6A and C). For comparison, interference peaks very close to the analytes (particularly for thifensulfuron-methyl and bensulfuron-methyl) were observed using conventional C_{18} sorbents for pre-concentration (shown in Fig. 6B and D), which makes accurate quantification of each analyte difficult or impossible.

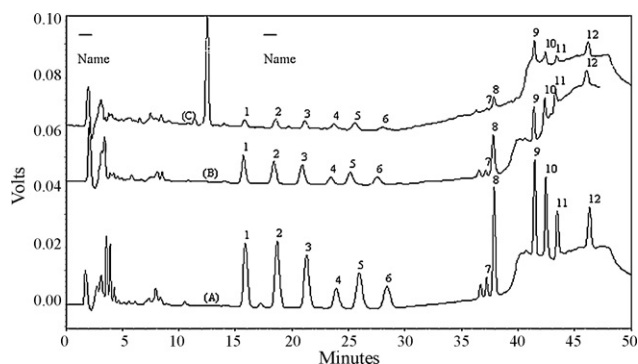


Fig. 7. Chromatograms of (A) SPE of 250 mL of $3.0 \mu\text{g L}^{-1}$ SUs working solution (acidified to pH 4.8) using ionic liquid-functionalized silica sorbent coupled with HPLC; (B) SPE of 250 mL of surface water 2 (acidified to pH 4.8) at a $1 \mu\text{g L}^{-1}$ fortification level for each analyte using ionic liquid-functionalized silica sorbent coupled with HPLC; (C) SPE of 60 mL of soil extract acidified to pH 4.8 (soil sample spiked with $4 \mu\text{g kg}^{-1}$ SUs) using ionic liquid-functionalized silica sorbent combined with HPLC. Chromatographic conditions were described in Fig. 6. Chromatographic peaks: (1) thifensulfuron-methyl; (2) metsulfuron-methyl; (3) chlorsulfuron; (4) sulfometuron-methyl; (5) rimsulfuron; (6) ethametsulfuron; (7) tribenuron-methyl; (8) bensulfuron-methyl; (9) prosulfuron; (10) pyrazosulfuron; (11) chlorimuron-ethyl and (12) primisulfuron.

Table 3

Comparison of the ionic liquid-functionalized silica sorbent with the commercial C_{18} sorbent for the recoveries obtained with the water sample (surface water 2) (mean \pm RSD, %, $n = 3$).

Analyte	Spiked level ($0.5 \mu\text{g L}^{-1}$)		Spiked level ($1.0 \mu\text{g L}^{-1}$)	
	ILs	C_{18}	ILs	C_{18}
Thifensulfuron-methyl	72.2 ± 4.8	175.4 ± 3.0	100.2 ± 6.3	153.6 ± 2.7
Metsulfuron-methyl	61.7 ± 5.2	33.8 ± 5.0	94.4 ± 5.3	44.2 ± 3.7
Chlorsulfuron	100.2 ± 6.0	94.7 ± 1.9	118.2 ± 5.4	97.3 ± 2.9
Sulfometuron-methyl	67.4 ± 5.5	30.5 ± 4.9	75.9 ± 6.7	48.5 ± 5.4
Rimsulfuron	79.2 ± 6.1	76.3 ± 6.7	98.1 ± 4.9	83.1 ± 4.7
Ethametsulfuron	53.8 ± 7.6	60.8 ± 8.3	98.2 ± 4.9	80.3 ± 7.8
Thibenuron-methyl	78.2 ± 11.2	102.4 ± 7.3	69.3 ± 8.6	113.7 ± 6.6
Bensulfuron-methyl	88.2 ± 8.5	39.2 ± 5.5	90.1 ± 5.5	50.3 ± 4.8
Prosulfuron	54.3 ± 3.1	44.9 ± 5.6	80.0 ± 3.7	57.6 ± 3.2
Pyrazosulfuron	67.4 ± 5.4	110.4 ± 3.7	105.0 ± 6.0	117.8 ± 4.2
Chlorimuron-ethyl	85.7 ± 5.6	66.3 ± 2.9	102.1 ± 5.4	70.4 ± 4.0
Primisulfuron	76.1 ± 10.9	147.1 ± 8.4	87.5 ± 4.6	154.7 ± 6.9

The recovery study was conducted by spiking the water and soil samples at 0.5 and $1.0 \mu\text{g L}^{-1}$ levels and at 2.0 and $4.0 \mu\text{g kg}^{-1}$ levels, respectively. Typical chromatograms of spiked samples pre-concentrated by the ionic liquid-functionalized silica sorbents are shown in Fig. 7, and the recovery results are summarized in Tables 3 and 4. Mean recoveries at each spiked level ranged from 53.8 to 118.2% with RSDs of 3.1–11.2% for the water sample (surface water 2), and from 60.9 to 121.3% with RSDs of 3.7–11.3% for the soil sample. The recovery results of the C_{18} sorbents are also summarized in Tables 3 and 4 for a comparison with those of the ionic liquid-functionalized silica sorbents. The average recoveries of thifensulfuron-methyl and primisulfuron in the water and soil samples were far beyond the limit of 120%, while the average recoveries for sulfometuron-methyl in the water sample were reduced to 30.5% and that for chlorimuron-ethyl in the soil sample decreased to 27.4%. According to the contrast experiment, it was indicated that the ionic liquid-functionalized silica sorbent could better simultaneously quantify 12 SUs in complex samples than the C_{18} sorbent do.

Table 4

Comparison of the ionic liquid-functionalized silica cartridge with the commercial C_{18} cartridge for the recoveries obtained with the soil sample (mean \pm RSD, %, $n = 3$).

Analyte	Spiked level ($2.0 \mu\text{g kg}^{-1}$)		Spiked level ($4.0 \mu\text{g kg}^{-1}$)	
	ILs	C_{18}	ILs	C_{18}
Thifensulfuron-methyl	112.5 ± 5.1	142.9 ± 6.4	108.2 ± 4.0	172.7 ± 5.5
Metsulfuron-methyl	73.7 ± 3.8	96.8 ± 3.5	74.6 ± 4.5	89.7 ± 4.9
Chlorsulfuron	82.8 ± 4.5	67.3 ± 4.0	111.6 ± 3.7	129.0 ± 4.6
Sulfometuron-methyl	65.3 ± 6.5	58.8 ± 3.8	65.2 ± 5.4	69.6 ± 5.0
Rimsulfuron	118.7 ± 5.9	57.4 ± 10.4	106.3 ± 4.4	78.7 ± 12.6
Ethametsulfuron	117.9 ± 5.7	56.8 ± 4.7	93.6 ± 4.8	59.6 ± 4.8
Thibenuron-methyl	72.6 ± 10.2	63.1 ± 10.5	76.4 ± 6.8	44.7 ± 10.8
Bensulfuron-methyl	75.5 ± 7.3	116.9 ± 6.6	69.3 ± 9.0	792.2 ± 4.0
Prosulfuron	88.6 ± 4.4	46.7 ± 10.4	88.7 ± 3.8	71.2 ± 7.6
Pyrazosulfuron	60.9 ± 6.0	48.0 ± 12.8	120.1 ± 4.7	31.4 ± 6.3
Chlorimuron-ethyl	118.3 ± 11.3	27.4 ± 7.7	121.3 ± 8.4	76.7 ± 6.7
Primisulfuron	116.2 ± 8.7	145.3 ± 6.7	105.8 ± 6.0	133.6 ± 5.0

4. Conclusion

A simple procedure for the synthesis of *N*-methylimidazolium ionic liquid-functionalized silica sorbent was developed by grafting the functionalized *N*-methylimidazolium ionic liquid on silica. The prepared ionic liquid-functionalized silica sorbent exhibits high selectivity for the 12 SUs, making the sorbent very suitable for SPE of trace SUs, and has been successfully applied to the quantification of 12 SUs in complex water and soil matrices.

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