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Solvent (ionic liquid) impregnated resin-based extraction coupled with dynamic ultrasonic desorption for separation and concentration of four herbicides in environmental water

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ABSTRACT

A new method was developed for the determination of monolinuron, propazine, linuron, and prebane in environmental water samples. The solvent (ionic liquid) impregnated resin (IL-SIR)-based extraction coupled with dynamic ultrasonic desorption (DUSD) was applied to the separation and concentration of the analytes. The high performance liquid chromatography (HPLC) was applied to the determination of the analytes. The ionic liquid [C_6MIM][PF_6] was immobilized on Diaion HP20 resin by immersing the resin in ethanol solution containing [C_6MIM][PF_6]. The effect of extraction parameters, including pH value of sample solution, salt concentration in sample and extraction time, and elution conditions, including the concentration of ethanol in elution solvent, the flow rate of elution solvent and the ultrasonic power, were examined and optimized. The limits of detection and quantification for the analytes were in the range of 0.15–0.29 $\mu g\,L^{-1}$ and 0.51–0.98 $\mu g\,L^{-1}$, respectively. Some environmental water samples were analyzed and the analytical results were satisfactory.

1. Introduction

The herbicides have been widely applied in agriculture for crop protection during the past few decades [1]. However, the herbicides are also chemical pollutants and have the significant impact on the environment and human health. These compounds can be found in water, soil and crop [2–4]. The herbicides are moderately soluble in water and have relatively low soil-sorption coefficients. Because of these properties, the herbicides can contaminate the environment through agricultural run-off and leaching. Therefore, the reliable method to determine the pesticides in environmental water samples should be developed.

Many methods for determining herbicides from water samples have been reported. Most applications are based on chromatographic methods, such as gas chromatography (GC) [3], high-performance liquid chromatography (HPLC) [5], gas chromatography–mass spectrometry (GC–MS) [6], liquid chromatography–mass spectrometry (LC–MS) [7] and micellar electrokinetic chromatography (MEKC) [4]. Because of the relatively low concentrations of herbicides in environmental samples, the extraction step usually becomes necessary for the reliable determination of these compounds. Liquid–liquid extraction (LLE) [8] and solid phase extraction (SPE) [9,10] have been widely applied for the analysis of water samples, but these methods suffer from the disadvantages of being time-consuming, using large amounts of toxic organic solvent, and being relatively expensive. Although solid phase microextraction (SPME) [5,11] is replacing traditional methods, such as LLE, it also has some drawbacks, such as high cost, sample carry-over, and a decline in performance with time. Liquid-phase microextraction (LPME) [12–14] has shown to be an attractive alternative for sample preparation. Ionic liquids (ILs) can be used as extraction solvents in LPME.

ILs are ionic media resulting from the combination of inorganic anions and organic cations (usually heterocycles containing nitrogen, e.g. imidazolium, pyridinium) that are liquids at room temperature [15–17]. The advantages of ILs, such as negligible vapour pressure, large operating range of temperature, high ionic conductivity and ability to solvate compounds of varying polarity, have made them a replacement to organic solvents in extraction processes [15–18]. Although ILs have some advantages, they have some drawbacks, such as high viscosity, low rate of mass transfer and entraining loss of ionic liquid to aqueous phase [19].

Thus, solvent (ionic liquid) impregnated resin (IL-SIR)-based extraction offers a highly attractive strategy to circumvent the drawbacks associated with ILs. The macroporous resins have high surface area and good mechanical stability. When the macroporous resins contain an extractant within their lattice, the macroporous

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resins have higher capacity and more chelating sites available [20,21]. Because IL-SIRs have many pores or cavities filled with ILs, the IL-SIR-based extraction offers a number of important benefits, such as reducing the amount of ILs, retaining properties of ILs, improving mass transfer rate, achieving high recoveries and recovering the adsorbent easily.

Recently, IL-SIR has been used for extraction of rare earth elements and noble metal ions [22,23]. Chen et al. [24] separated Y(III) from rare earths by IL-SIR and indicated that IL-SIR contributed to ameliorating mass transfer efficiency, i.e. shortening equilibrium time from 40 min to 20 min, increasing extraction efficiency from 29% to 80%. However, there is no report of the application of IL-SIR for the extraction of organic compounds. Dai et al. [25] recently reported that the mechanism of adsorbing naphthalene in aqueous phase with IL-SIR, offers an attractive theoretical basis for this study.

Ultrasonic waves promote desorption of adsorbed species from the adsorbent and intensify the mass transfer process, which made the use of ultrasonics for desorption increasing popular [26,27].

In the paper, the IL-SIR was used as adsorbent. The IL-SIR-based extraction coupled with dynamic ultrasonic desorption (DUSD) was applied to the separation and concentration of monolinuron, propazine, linuron and prebane in water samples. The proposed method could be applied to the separation and concentration of other analytes in environmental water samples by changing some experimental conditions.

2. Experimental

2.1. Standards and chemicals

Monolinuron, propazine, linuron, and prebane standards were obtained from National Institute for the Control of Pharmaceutical and Biological Products (Beijing, China). Stock standard solutions of these analytes (100 $\mu g\,mL^{-1}$) were prepared separately by dissolving the proper amount of each analyte in chromatographic grade acetonitrile (ACN) and stored at 4 °C. The mixed stock standard solution containing each analyte at a concentration of 10 $\mu g\,mL^{-1}$ was prepared by diluting the stock standard solutions with acetonitrile. Working standard solutions were freshly prepared by diluting the mixed standard solution with pure water.

Chromatographic grade acetonitrile was purchased from Fisher (Pittsburgh, PA, USA). Analytical grade hydrochloric acid, sodium hydroxide, sodium chloride and ethanol were purchased from Beijing Chemical Co. (Beijing, China). Pure water was obtained from a Milli-Q water system (Millipore, Billerica, MA, USA). 1-Hexyl-3-methylimidazolium hexafluorophosphate ($[C_6MIM][PF_6]$) was purchased from Shanghai Chengjie Chemical Co. (Shanghai, China). The macroporous resins AB-8 and D4020 were purchased from Chemical Plant of Nankai University (Tianjin, China). The Diaion HP20 macroporous resin was purchased from Mitsubishi Chemical Company (Tokyo, Japan). The 860021 macroporous resin was purchased from Shandong Lukang Record Pharmaceutical Group Co., Ltd. (Shandong, China). The D101 macroporous resin was obtained from Haiguang Chemical Co., Ltd. (Tianjin, China). All the resins were pretreated with ethanol, 5% HCl and 5% NaOH sequentially to remove impurities.

2.2. Instruments

The KQ-100DE ultrasonic cleaner was purchased from Kunshan Ultrasonic Instrument Co., Ltd. (Kunshan, China). The frequency and output power of the ultrasonic cleaner are 40 kHz and 40–100 W, respectively. Absorption spectra were recorded with an Australian GBC Cintra 10e UV–vis spectrometer within the wavelength range from 190 to 300 nm. The WZ-50 micro-infusion pump was obtained from Zhejiang Medical Instrument Co., Ltd. (Hangzhou, China). The column (30 mm long, I.D. 4.0 mm) was made of polytetrafluoroethylene.

The 1100 series liquid chromatograph (Agilent Technologies Inc., USA) equipped with UV detection and quaternary gradient pump was used. Eclipse XDB-C18 column (3.5 μm, 4.6 mm × 150 mm, Agilent, USA) was used.

2.3. Preparation of the IL-SIR

The IL used in this study was 1-hexyl-3-methylimidazolium hexafluorophosphate ($[C_6MIM][PF_6]$) [15,18,29]. The IL was immobilized on the surface of macroporous resin by direct impregnation method [22–25]. Before use, the resin was washed with ethanol three times to remove impurities and dried at 50 °C to remove excess ethanol. To immobilize the $[C_6MIM][PF_6]$ on the surface of the macroporous resin, the resin was immersed into ethanol solution containing $[C_6MIM][PF_6]$ at room temperature for 24 h. Then, the volatile components of the mixture were evaporated at 60 °C until the IL-SIR was dried to constant weight.

2.4. Samples

In this work, six samples, including tap water (sample 1), well water (sample 2), snow water (sample 3), river water (sample 4), lake water (sample 5) and waste water (sample 6) were collected from Changchun, China for validating the proposed method. Except for the experiment results mentioned in Sections 3.3.5, 3.4 and 3.5, which were obtained with real sample, other results of the experiments were obtained with pure water. The spiked samples containing the analytes at the concentration levels of 5, 10 and 50 $\mu g\,L^{-1}$ were prepared by spiking the working standard solutions into the samples. Then the water samples were filtered through 0.45 μm filter and stored at 4 °C until analysis.

2.5. IL-SIR-based extraction

100 mg of IL-SIR was accurately weighed and added into 50 mL of water sample. NaCl was added in the water sample and its concentration was 10%. Then, the mixture was stirred for 60 min. Thereafter, the IL-SIR was isolated from the solution by filtering with filter paper (11 cm in diameter). The obtained IL-SIR was placed between two small plugs of glass fiber in the elution column. The elution column was put in ultrasonic bath, which was cooled by flowing water (Fig. 1). The ultrasonic power was 80 W. Meantime, the micro-infusion pump was activated and the eluant (ethanol) was passed through the elution column at the flow rate of 0.1 $mL\,min^{-1}$. The target analytes and $[C_6MIM][PF_6]$ were eluted with 1.0 mL eluant. The eluate was filtered through a 0.45 μm filter, and 20 μL of the eluate was injected into the HPLC system for analysis.

2.6. HPLC conditions

The solvents A and B were water and acetonitrile, respectively. The mobile phase consists of solvents A and B. The isocratic elution was used from 0 to 2 min and mobile phase was 85% solvent A:15% solvent B. The gradient elution was used from 2 to 30 min: from 85% solvent A:15% solvent B to 55% solvent A:45% solvent B from 2 to 10 min; from 55% solvent A:45% solvent B to 45% solvent A:55% solvent B from 10 to 18 min; from 45% solvent A:55% solvent B to 35% solvent A:65% solvent B from 18 to 30 min. The flow rate of the mobile phase was 0.5 $mL\,min^{-1}$. The chromatographic separation was performed at 30 °C [30]. Sample injection volume was 20 μL. The monitoring wavelength was 246 nm for monolinuron, linuron

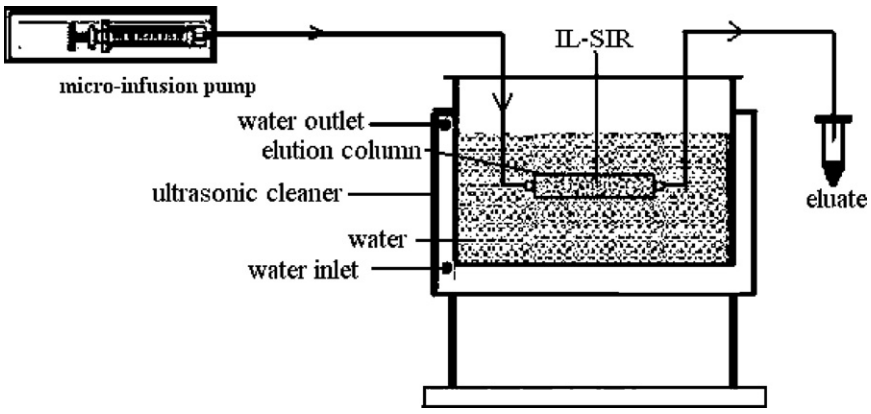

Fig. 1. Dynamic ultrasonic desorption system.

[28,29] and 228 nm for propazine and prebane [29]. The reference wavelength and bandwidth were 360 and 4 nm, respectively. The mobile phase was passed through a 0.45 μm filter and degassed ultrasonically prior to use.

2.7. Liquid–liquid extraction (LLE)

100 mL of water sample was extracted three times with 20, 10 and 10 mL of methylene dichloride, evaporated to dryness and then the residue was dissolved in 1 mL of acetonitrile. The resulting solution was filtered through a 0.45 μm filter membrane and 10 μL of the solution was injected into the HPLC system for analysis [31].

2.8. Ionic liquid dispersive liquid–liquid microextraction (IL-DLLME)

5.0 mL of water sample was placed in a 10-mL conical flask. A mixture of 50 μL [C_6MIM][PF_6] (extraction solvent) and 0.50 mL methanol (disperser solvent) was quickly injected into the sample solution with a 1 mL syringe (Shanghai, China). Cloudy solution was quickly formed. 5 min later, the resulting solution was centrifuged at 4000 rpm for 10.0 min. The IL phase was deposited in the bottom of conical flask. The upper aqueous phase was removed with a syringe, and the IL phase was dissolved in 50 μL of methanol. The resulting solution was filtered through a 0.45 μm filter, and 10 μL of the solution was injected into the HPLC system for analysis [32].

2.9. Method validation

2.9.1. Linearity

Calibration curves were constructed using the standard solutions of analytes in the concentration range of 1.00–100 μg L^{-1}. The each signal on calibration curve represents mean of three measurements. The calibration curves were constructed by plotting the peak areas versus the concentrations of analytes. The calibration curves were also evaluated by using correlation coefficient and *F*-test [33].

2.9.2. Precision and recovery

The intra-day and inter-day precisions were obtained by analyzing spiked water samples at three different concentration levels (5.00, 10.0 and 50.0 μg L^{-1}). The intra-day precision was obtained by analyzing a sample six times in one day. The inter-day precision was obtained by analyzing a sample once a day over six consecutive days. The intra-day and inter-day precisions were expressed as the relative standard deviations (RSDs). Subsequently, the extraction mean recoveries were obtained [33].

2.9.3. Limit of detection (LOD) and limit of quantification (LOQ)

The limit of detection (LOD) was calculated from the calibration curve based on the IUPAC definition [34] and was the analyte concentration giving a signal equal blank signal plus three standard deviations of the blank signal.

The limit of quantitation (LOQ) is defined as the lowest concentration of analyte that can be determined with an acceptable level of uncertainty. Various conventions have been applied to estimating the LOQ. Perhaps the most common recommendation is to quote the LOQ as 3 times the LOD. In this work, the LOQ was defined as the analyte concentration giving a signal equal blank signal plus 10 times the size of the standard deviations of the blank signal [33].

2.9.4. Selectivity and stability

Selectivity was evaluated by examining chromatograms of six kinds of water samples. In addition, the interference of other herbicides was examined by adding 100 μg L^{-1} of monuron, simazine, chlortoluron, isoproturon, atrozine, prometryn, trietazine into spiked water samples, in which the spiked concentration of the analytes was 5 μg L^{-1} [33].

The spiked samples 3 and 5 were used to examine long term stability. A sample was divided into four parts, stored at 4 °C and analyzed after 1, 2, 3 and 4 weeks, respectively. The concentrations of the analytes in the spiked sample were 5 and 50 μg L^{-1}. Each sample was analyzed in triplicate [33].

3. Results and discussion

3.1. Optimization of extraction conditions

3.1.1. Resin evaluation

Five commercial macroporous resins, including D4020, Diaion HP20, AB-8, 860021 and D101, were selected for preliminary investigation. Fig. 2 shows the effect of the types of macroporous resins on the recoveries of target analytes. D4020 and Diaion HP20 can provide the higher recoveries for all the four analytes, compared with AB-8, 860021 and D101 resins. Since the D4020 resin showed a tendency to be pulverized under the ultrasonic action at 100 W. Thus, the Diaion HP20 resin was selected to prepare IL-SIR for further investigation.

3.1.2. Mass ratio between Diaion HP20 resin and [C_6MIM][PF_6]

In this experiment, we also investigate the influence of mass ratio between Diaion HP20 resin and [C_6MIM][PF_6] in IL-SIR prepa-

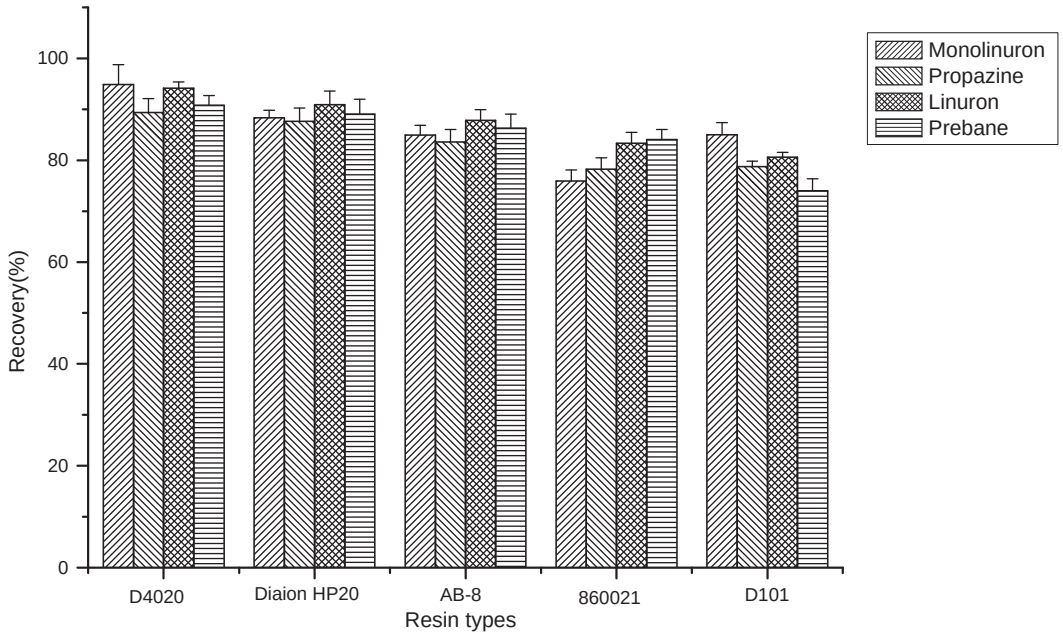

Fig. 2. Effect of resin type. Amount of resin, 100 mg; sample volume, 50 mL; spiked concentration, 10 μg L^{-1}; extraction time, 60 min; eluant volume, 1 mL.

ration on extraction efficiency. The amount of IL, which was immobilized on the macroporous resins, is limited mainly by van der Waals force. As can be seen from Fig. 3 the recoveries decrease with the increase of the amount of $[C_6MIM][PF_6]$. Fig. 3 also shows that the recoveries obtained with IL-SIR are higher than those obtained with Diaion HP20 resin under the same conditions. When the amount of IL used for the preparation of IL-SIR was too large, the amount of IL immobilized on the resin surface was too large and when the IL-SIR was put in samples, a small quantity of $[C_6MIM][PF_6]$ on the resin surface will gradually dissolve in the samples, and part of analytes can transfer into the IL in the samples [35]. The mass ratio 20:1 was selected in the following studies.

3.1.3. The amount of IL-SIR

The effect of amount of IL-SIR on the recoveries of the analytes was investigated. 20 mg, 50 mg, 100 mg and 200 mg of IL-SIR were used, respectively. The recoveries are shown in Fig. 4. The recoveries of analytes increase rapidly with the increase of the amount of IL-SIR from 20 to 100 mg and slightly change from 100 to 200 mg. Therefore, 100 mg of IL-SIR was used in the following experiments.

3.1.4. pH value

The pH value of the sample solution is a crucial factor in the extraction of organic compounds. In this work, the pH value was adjusted to a range of 2–10 by adding 0.1 mol L^{-1} NaOH or 0.1 mol L^{-1} HCl. As can be seen from Fig. 5, an increase of the recoveries is observed when the pH value increases from 2 to 4 and the recoveries remain constant or slightly change in the pH range of 4–10. Considering the environmental water samples are generally neutral, the samples may be directly analyzed without adjusting the pH values except for the special water samples, which are acidic or very alkaline.

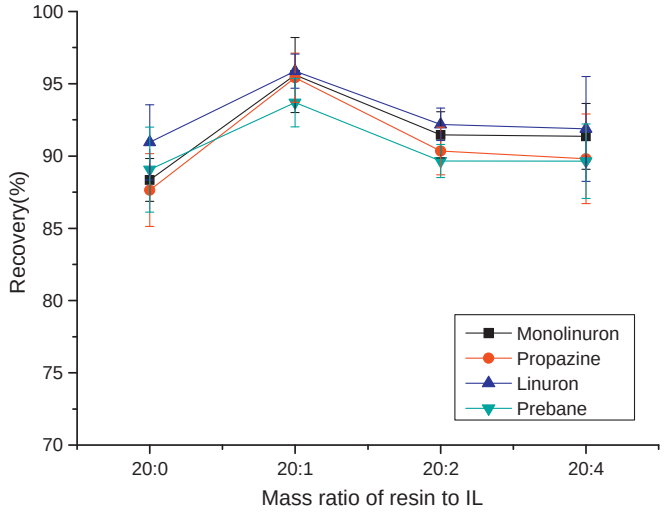

Fig. 3. Effect of mass ratio of resin to IL. Amount of IL-SIR, 100 mg; sample volume, 50 mL; spiked concentration, 10 μg L^{-1}; extraction time, 60 min; eluant volume, 1 mL.

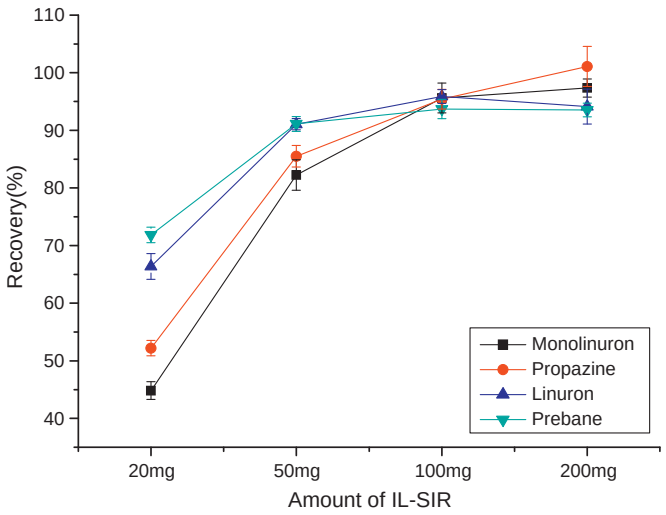

Fig. 4. Effect of amount of IL-SIR. Sample volume, 50 mL; spiked concentration, 10 μg L^{-1}; extraction time, 60 min; eluant volume, 1 mL.

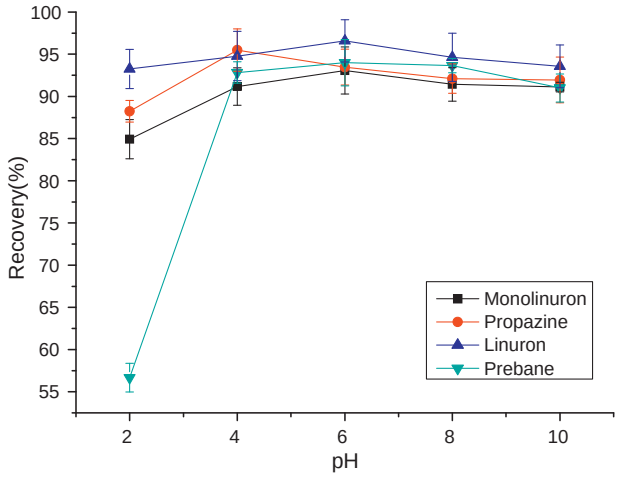

Fig. 5. Effect of pH value of sample solution. Amount of IL-SIR, 100 mg; sample volume, 50 mL; spiked concentration, 10 μg L^{-1}; extraction time, 60 min; eluant volume, 1 mL.

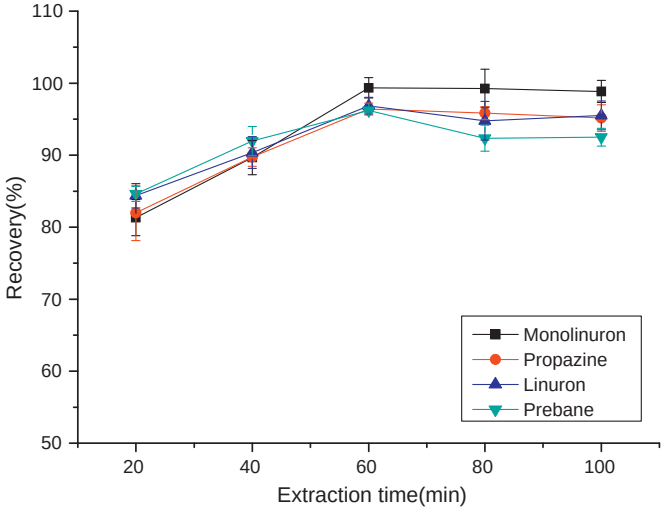

Fig. 7. Effect of extraction time. Amount of IL-SIR, 100 mg; sample volume, 50 mL; spiked concentration, 10 μg L^{-1}; pH value, 6; content of NaCl, 10%; eluant volume, 1 mL.

3.1.5. Ionic strength

In order to survey the influence of ionic strength on the recovery performance, a series of experiments were performed by increasing NaCl concentration in the range of 0–35% (w/v) at an interval of 5% in sample solution. Fig. 6 shows the effect of ionic strength on the recoveries of analytes. The addition of salt to the sample solution can decrease the solubility of the analytes and therefore enhance extraction yields because of the salting-out effect [13]. The recoveries of analytes increase with increasing ionic strength, with a maximum (>95%) being reached at 10% NaCl, followed by a decrease in recoveries with further increase in salt concentration. The crystal of salt ions occupied the superficial area of the IL-SIR at the high salt concentration, which diminishes the IL-SIR available to interact with the analyte and plays a very negative role decreasing the recovery [36]. On the other hand, when the amount of NaCl increased, ion exchange between $[C_6MIM][PF_6]$ and Cl^- occurred, which made $[C_6MIM]Cl$ soluble in water [15]. The concentration of NaCl in water sample was selected as 10%.

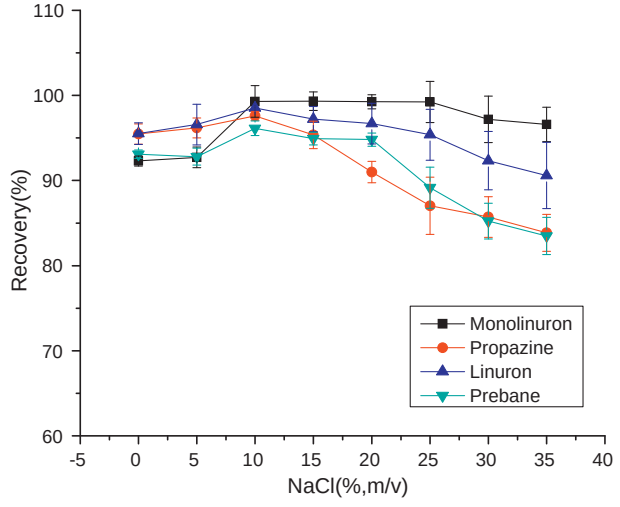

Fig. 6. Effect of ionic strength. Amount of IL-SIR, 100 mg; sample volume, 50 mL; spiked concentration, 10 μg L^{-1}; extraction time, 60 min; pH value, 6; eluant volume, 1 mL.

3.1.6. Effect of extraction time

The effect of extraction time was examined by varying the extraction time from 20 min to 100 min at an interval of 20 min. The recoveries of analytes are shown in Fig. 7. The recoveries of analytes increase rapidly with the increase of the extraction time from 20 to 60 min and arrived to the maximum at 60 min. No obvious recovery change except for linuron and prebane in the extraction time range of 60–100 min was observed. Consequently, 60 min was adopted in the following experiments.

3.2. Optimization of elution conditions

When ethanol was used as elution solvent, the effect of the volume of elution solvent was examined. The results showed that 0.8 mL of ethanol can elute all analytes on IL-SIR and the recoveries were higher than 95%. So 1.0 mL of elution volume was chosen.

In order to reduce the number of the experiments and obtain the desired experimental results, orthogonal design could be very efficient to quickly generate useful information on key variables [37]. In this work, the influential factors in elution step, including (A) concentration of ethanol in elution solvent (A_1, 100%; A_2, 90%; A_3, 80%), (B) flow rate of elution solvent (B_1, 0.1 mL min^{-1}; B_2, 0.5 mL min^{-1}; B_3, 1.0 mL min^{-1}) and (C) ultrasonic power (C_1, 80 W; C_2, 60 W; C_3, 40 W) were investigated and optimized by an orthogonal design L_9 (3^3). The recoveries for the analytes were considered as the experimental response. The factors and the corresponding levels are shown in Table 1. Nine experimental trials were carried out according to the orthogonal design and the results are also shown in Table 1. The K and R values are calculated and listed in Table 2. In the table, K_n is the mean effect of each factor at the different levels and R is the range. The R values are shown in Table 2 indicate that the influences of the factors on the mean recoveries are also not identical, and the influence of ultrasonic power is less significant compared with that of the other factors. According to the largest donating rule, the largest value of K under every level of a variable is the optimized value. Based the results of orthogonal experiment, the optimal conditions to obtain the highest recovery are selected. The concentration of ethanol in elution solvent, the flow rate of elution solvent and ultrasonic power were selected as 100%, 0.1 mL min^{-1} and 80 W, respectively. Under the

Table 1
Experimental results of the orthogonal test ($n = 3$).

Design ID number	Factor			Monolinuron	Propazine	Linuron	Prebane
	(*A*) Concentration of ethanol in elution solvent (%)	(*B*) The flow rate of elution solvent ($mL\,min^{-1}$)	(*C*) Ultrasonic power (W)	Recovery (%)	Recovery (%)	Recovery (%)	Recovery (%)
1	$A_1(100)$	$B_1(0.1)$	$C_1(80)$	99.7	99.4	99.8	103.3
2	A_1	$B_2(0.5)$	$C_2(60)$	96.7	95.5	95.4	96.3
3	A_1	$B_3(1)$	$C_3(40)$	95.0	93.6	92.8	93.8
4	$A_2(90)$	B_1	C_2	98.0	97.2	92.9	93.4
5	A_2	B_2	C_3	92.4	91.0	88.4	88.1
6	A_2	B_3	C_1	91.4	88.1	88.7	88.3
7	$A_3(80)$	B_1	C_3	96.6	92.8	88.3	86.7
8	A_3	B_2	C_1	96.0	91.2	90.2	87.6
9	A_3	B_3	C_2	89.7	85.9	84.5	84.6

Table 2
Analysis of orthogonal test results.

Analyte	Factor	K_1[a]	K_2	K_3	R[b]	Optimal level
Monolinuron	*A*	97.1	93.9	94.1	3.2	A_1
	B	98.1	95.0	92.0	6.1	B_1
	C	95.7	94.8	94.7	1.0	C_1
Propazine	*A*	96.1	92.1	90.0	6.1	A_1
	B	96.5	92.6	89.2	7.3	B_1
	C	92.9	92.9	92.5	0.4	C_1
Linuron	*A*	96.0	90.0	87.6	8.4	A_1
	B	93.7	91.3	88.7	5.0	B_1
	C	92.9	90.9	89.9	3.0	C_1
Prebane	*A*	97.8	89.9	86.3	11.5	A_1
	B	94.5	90.6	88.9	5.6	B_1
	C	93.1	91.4	89.5	3.6	C_1

[a] $K_i^F = (1/3)\Sigma$ the recoveries of target analytes at F_i.
[b] $R_i^F = \max\{K_i^F\} - \min\{K_i^F\}$, here *F* and *i* mean elution factor and setting level, respectively.

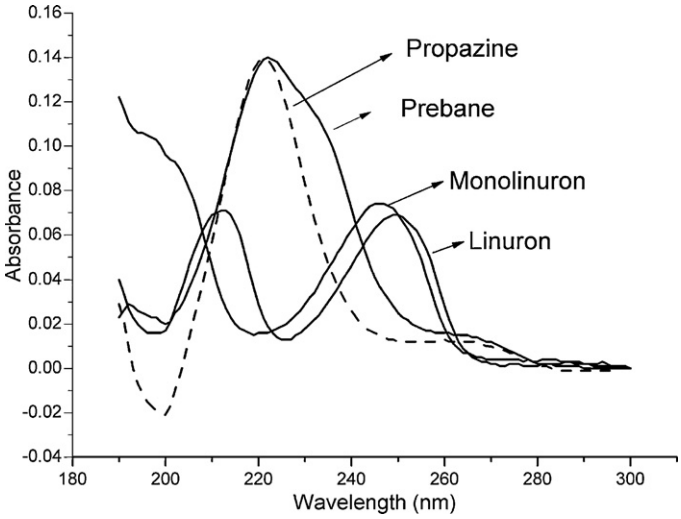

Fig. 8. The absorption spectra of monolinuron, linuron, propazine and prebane.

selected conditions, the recoveries of monolinuron, propazine, linuron and prebane were $100.9 \pm 1.0\%$, $97.3 \pm 0.7\%$, $100.3 \pm 2.0\%$ and $100.9 \pm 1.8\%$ ($n = 3$), respectively.

3.3. Method evaluation

3.3.1. HPLC performances

Fig. 8 shows the absorption spectra of monolinuron, linuron, propazine and prebane. The detection was carried out at 246 nm for monolinuron, linuron and 228 nm for propazine and prebane. The mobile phase consisted of water and organic solvent. A good separation of analytes was achieved when acetonitrile was used as organic phase. The solvent containing acetonitrile and water was used as the mobile phase. The chromatogram of standard solution containing monolinuron, propazine, linuron, and prebane is shown in Fig. 9(a). The baseline separation of all the analytes was achieved. HPLC performance parameters, including retention time (RT), peak symmetry, resolution, selectivity and theoretical plate number are summarized in Table 3.

3.3.2. Linearity

The calibration curves were constructed by plotting the peak areas versus the concentrations of analytes. The corresponding linear regression equations, correlation coefficients and *F* statistics for four analytes are shown in Table 4. Correlation coefficient and *F*-test statistics were obtained with the OriginPro 7.5 software packages (Origin Lab Corporation, Northampton, USA). Correlations were considered statistically significant at $p < 0.005$. The correlation coefficients are between 0.9991 and 0.9999. To judge the correlation *F*-test was applied and the *F* statistics obtained also are listed in Table 4. It is seen from Table 4 that the peak areas should be concentration-dependent because all the *F* values are higher than $F_{0.005\,(1.7)}$ value (16.24).

Table 3
HPLC performances.

Analyte	RT (min)	Resolution	Selectivity	Plate number	Symmetry factor	RT repeatability (RSD %), $n = 5$	Area repeatability (RSD %), $n = 5$
Monolinuron	18.559			59491	1.24	0.06	1.74
		10.11	1.17				
Propazine	21.625			77345	1.04	0.04	1.36
		4.96	1.07				
Linuron	23.268			77723	1.04	0.07	2.04
		9.09	1.14				
Prebane	26.359			88001	0.92	0.06	1.63

Table 4
Analytical performances.

Analyte	Linear range ($\mu g\,L^{-1}$)	Regression equation	Correlation coefficient	*F* statistics	LOD ($\mu g\,L^{-1}$)	LOQ ($\mu g\,L^{-1}$)	RSD[a] (%)
Monolinuron	1.08–108	$A = 0.39294 + 11.47758C$	0.9999	26,332.95	0.15	0.51	4.73
Propazine	1.15–115	$A = 3.32389 + 14.46025C$	0.9991	3814.95	0.29	0.98	7.85
Linuron	0.94–94	$A = -0.54631 + 10.01382C$	0.9998	17,447.99	0.15	0.51	5.47
Prebane	1.20–120	$A = -1.55626 + 17.73924C$	0.9997	11,450.09	0.20	0.67	5.71

[a] RSD values are obtained based on 13 determinations of each analyte at spiked level of 1.00 $\mu g\,L^{-1}$.

Table 5
The intra-day and inter-day precision of the method and recovery of analytes.

Analyte	Added ($\mu g\,L^{-1}$)	Intra-day		Inter-day	
		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Monolinuron	5.00	103.3	2.96	102.9	3.36
	10.0	102.9	1.23	103.5	3.87
	50.0	103.0	1.94	103.8	2.66
Propazine	5.00	98.5	1.60	98.1	3.01
	10.0	98.0	1.76	99.3	4.12
	50.0	102.3	1.65	103.1	2.10
Linuron	5.00	102.4	2.26	102.1	3.89
	10.0	100.4	1.40	102.4	4.30
	50.0	102.6	2.25	101.1	2.46
Prebane	5.00	100.0	3.07	102.4	4.68
	10.0	98.0	1.25	102.4	4.22
	50.0	102.2	1.33	100.7	3.81

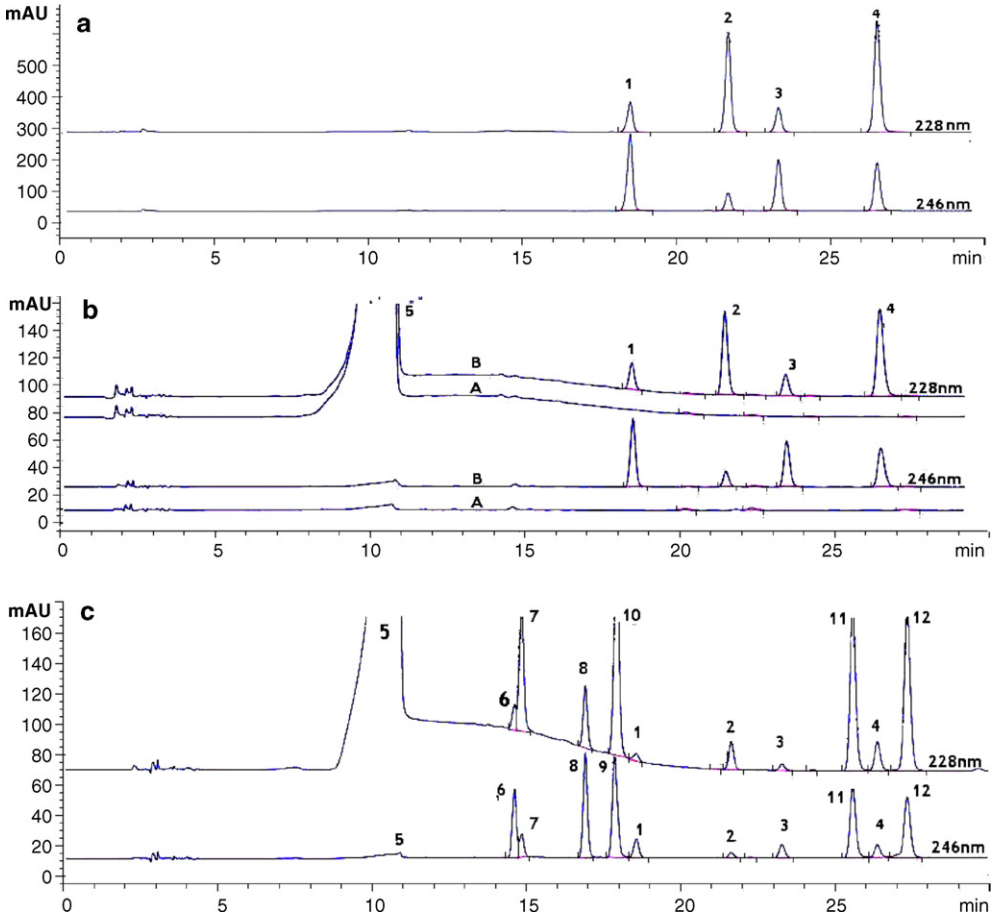

Fig. 9. The chromatograms of (a) the standard solution, (b) the extract of sample 6 (A) and spiked sample 6 (B) and (c) the standard solution in the presence of other herbicides. 1, monolinuron; 2, propazine; 3, linuron; 4, prebane; 5, ionic liquid; 6, monuron; 7, simazine; 8, chlortoluron; 9, isoproturon; 10, atrazine; 11, prometryn; 12, trietazine.

Table 6
Stability of analytes.

Sample	Stored Time (week)	Added ($\mu g\,L^{-1}$)	Monolinuron		Propazine		Linuron		Prebane	
			Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Sample 3	1	5.00	102.4	2.11	98.2	1.41	103.9	2.87	99.4	1.06
		50.0	102.8	1.02	101.4	1.55	104.1	1.63	102.8	1.14
	2	5.00	103.4	4.78	98.7	2.06	100.3	4.55	100.5	4.62
		50.0	103.1	2.87	103.2	1.51	101.2	2.01	101.6	1.45
	3	5.00	101.8	2.52	97.3	3.25	102.2	2.70	105.3	1.93
		50.0	104.3	2.31	103.2	2.21	101.7	1.98	102.6	1.17
	4	5.00	104.8	3.02	99.0	3.15	102.7	2.30	99.4	5.26
		50.0	103.2	3.42	103.0	2.46	100.5	3.20	98.7	4.96
Sample 5	1	5.00	105.2	2.25	99.7	1.08	106.6	4.89	102.0	1.06
		50.0	100.7	1.21	98.6	1.70	101.6	0.82	101.9	1.40
	2	5.00	100.3	1.69	95.5	3.31	99.5	3.02	97.8	3.66
		50.0	106.5	0.54	106.1	1.01	104.8	1.49	105.8	2.54
	3	5.00	101.3	2.63	97.1	3.81	98.1	2.93	98.9	2.56
		50.0	103.4	1.38	103.0	0.93	101.3	0.89	99.7	1.40
	4	5.00	104.5	4.01	99.0	2.39	100.3	5.19	101.8	2.37
		50.0	104.8	0.84	104.3	0.19	101.0	1.90	101.2	1.69

3.3.3. Limit of detection and limit of quantification

LODs and LOQs are considered as the lowest concentrations of analytes that can be confidently identified and quantified by the proposed method, respectively. The LODs of analytes are in the range of 0.15–0.29 $\mu g\,L^{-1}$. The LOQs of analytes are in the range of 0.51–0.98 $\mu g\,L^{-1}$. The results are listed in Table 4.

3.3.4. Precision and recovery

The intra-day and inter-day precision and recovery were evaluated using spiked samples at three concentration levels (5.00, 10.0 and 50.0 $\mu g\,L^{-1}$). The intra-day and inter-day RSDs for all analytes are lower than 5.00% and the recoveries range from 98.0% to 103.8% (Table 5). The precision and accuracy for the proposed method should be satisfactory.

3.3.5. Selectivity and stability

The method shows a good selectivity which is demonstrated in Fig. 9. Six kinds of water samples were analyzed and no interference peak was observed at the retention times of monolinuron, propazine, linuron and prebane. A representative chromatogram of the water sample is shown in Fig. 9(b). The interference of other herbicides was tested. It is seen from Fig. 9(c) that other similar herbicides, including monuron, simazine, chlortoluron, isoproturon, atrozine, prometryn, trietazine, do not interfere with the determination of monolinuron, propazine, linuron and prebane.

The stability of monolinuron, propazine, linuron and prebane during the sample storage and treatment under conditions described above were evaluated. The experimental results shown in Table 6 indicate the stability of the analytes is satisfactory.

3.4. Comparison of IL-SIR-based extraction, LLE and IL-DLLME

The spiked sample 5 was analyzed to compare the IL-SIR-based extraction, LLE and IL-DLLME. The results are shown in Table 7. From these data, it can be seen that there are no significant differences in the results at low concentration levels obtained by three methods. However, the results obtained by the IL-SIR-based extraction are better than those obtained by LLE and IL-DLLME at high concentration level. When LLE was applied, much more samples were consumed compared with IL-SIR-based extraction and IL-DLLME. Considering the accuracy and consumption of sample, the IL-SIR-based extraction should be interesting.

3.5. Analysis of environmental water samples

The practical performance of the present method was validated with six real water samples. No herbicide residues at detectable level were found in these samples. The spiked samples at analyte concentration levels of 5.00 and 50.0 $\mu g\,L^{-1}$ were analyzed. As can be seen from Table 8, the recoveries of the four analytes are

Table 7
Comparison of IL-SIR-based extraction, LLE and IL-DLLME.

Analyte	Added ($\mu g\,L^{-1}$)	IL-SIR-based extraction		LLE		IL-DLLME	
		Found ($\mu g\,L^{-1}$)	RSD (%)	Found ($\mu g\,L^{-1}$)	RSD (%)	Found ($\mu g\,L^{-1}$)	RSD (%)
Monolinuron	5.00	5.41	0.26	4.91	4.85	4.76	3.21
	50.0	50.3	1.45	45.4	3.46	39.7	4.44
Propazine	5.00	5.06	0.49	4.86	1.34	4.49	2.35
	50.0	49.3	1.96	47.2	4.35	40.8	2.80
Linuron	5.00	5.31	1.22	5.04	3.22	5.28	2.71
	50.0	50.8	1.40	48.7	2.42	39.4	5.00
Prebane	5.00	5.19	2.02	4.97	2.06	5.14	1.14
	50.0	50.4	2.76	48.0	3.37	39.3	2.53

Table 8
Analytical results of environmental water samples ($n = 3$).

Sample	Added ($\mu g\,L^{-1}$)	Monolinuron			Propazine			Linuron			Prebane		
		Found ($\mu g\,L^{-1}$)	Recovery (%)	RSD (%)	Found ($\mu g\,L^{-1}$)	Recovery (%)	RSD (%)	Found ($\mu g\,L^{-1}$)	Recovery (%)	RSD (%)	Found ($\mu g\,L^{-1}$)	Recovery (%)	RSD (%)
Sample 1	5.00	5.19	103.8	2.48	4.84	96.9	1.53	5.05	101.1	2.99	5.06	101.1	1.20
	50.0	49.6	99.1	1.82	48.6	97.3	1.16	49.7	99.5	2.40	49.1	98.1	0.93
Sample 2	5.00	5.49	109.9	1.55	4.76	95.3	0.51	5.22	104.5	0.85	4.98	99.6	1.62
	50.0	51.3	102.5	1.77	50.3	100.6	1.69	51.7	103.3	1.47	50.4	100.7	2.06
Sample 3	5.00	5.06	101.1	2.91	4.68	93.5	1.36	5.03	100.7	1.92	4.91	98.2	1.66
	50.0	51.3	102.6	1.11	50.3	100.5	1.69	52.0	103.9	1.01	51.3	102.6	2.20
Sample 4	5.00	5.16	103.2	1.21	4.78	95.5	1.34	5.09	101.8	1.28	4.98	99.6	2.60
	50.0	49.4	98.9	1.70	49.1	98.2	2.47	50.1	100.3	1.61	50.1	100.2	2.28
Sample 5	5.00	5.41	108.1	0.26	5.06	101.3	0.49	5.31	106.2	1.22	5.19	103.9	2.02
	50.0	50.3	100.6	1.45	49.3	98.5	1.96	50.8	101.7	1.40	50.4	100.7	2.76
Sample 6	5.00	5.15	103.0	1.22	4.79	95.9	1.81	5.11	102.2	2.10	4.95	99.1	1.61
	50.0	48.9	97.8	2.04	48.2	96.5	2.42	49.5	99.1	2.48	48.9	97.7	3.10

between 93.5% and 109.9% and the RSDs of the four compounds are between 0.26% and 3.10%. These results showed that the proposed method can be applied to the determination of herbicide residues in environmental water samples.

4. Conclusions

In this work, IL-SIR was used as adsorbent to extract herbicides from environmental water samples and DUSD was applied to the desorption of herbicides from the IL-SIR. The proposed method has some advantages, such as increase of contact area between IL and water, reduction of amount of IL and little loss of IL in the water samples. This method provides satisfactory selectivity for the determination of herbicides in environmental water samples and would be applied for the determination of other pesticides in water samples.

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