



Preparation and evaluation of molecularly imprinted ionic liquids polymer as sorbent for on-line solid-phase extraction of chlorsulfuron in environmental water samples

Lu Guo, Qiliang Deng, Guozhen Fang, Wei Gao, Wang Shuo*

Key Laboratory of Food Nutrition and Safety, Ministry of Education of China, Tianjin Key Laboratory of Food Nutrition and Safety, Tianjin University of Science and Technology, Tianjin 300457, China

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ABSTRACT

In this report, vinylimidazolium ionic liquid as a functional monomer for preparation of chlorsulfuron (CS) imprinted polymers were first studied. The imprinted materials showed high selectivity for CS, and fast kinetics so that adsorption equilibrium was achieved within 5 min. These materials have been further employed to detect trace CS from water samples by online preconcentration coupled with HPLC. The sorbent offered good linearity ($0.005\text{--}30\ \mu\text{g L}^{-1}$, $r^2 > 0.99$) for on-line solid-phase extraction of trace chlorsulfuron. Under the optimal experimental conditions, the recovery for chlorsulfuron was in the range of 81.0–110.1% for the water samples, with RSDs ranging from 1.2 to 7.6%.

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1. Introduction

Molecularly imprinted polymers (MIPs) are tailor-made artificial synthetic materials with selective molecular recognition abilities, provided by the copolymerization of functional and cross-linker monomers in the presence of a template (guest) molecule [1]. Owing to the cavities with exposed functional groups specific for the target analyte, MIPs have become increasingly attractive in many fields of chemistry and biology. For example, they were used as an affinity material for sensors [2], binding assays [3], antibody mimics [4] and adsorbents for solid phase extraction [5]. Up till now, most were synthesized using methacrylate acid (MAA) or 2-(dimethylamino) ethyl methacrylate (DAMA) as functional monomer, and nonpolar or aprotic solvent as porogen, in which polar interactions such as hydrogen bonds and electrostatic interaction were responsible for imprinting effect. Thus, it is difficult to apply these MIPs directly to aqueous samples, for water molecules interfere with the interaction of the template and monomers. To overcome this problem, developing MIPs dependent on strong electrostatic interaction could be a promising alternative direction [6,7].

Ionic liquids (ILs) are molten salts containing relatively large asymmetric organic cations and inorganic or organic anions [8] with melting points at or below room temperature ($\sim 25^\circ\text{C}$) [9]. Owing to their non-volatility, non-flammability, high ion density and high ionic conductivity, ILs are now recognized as attractive materials in several research fields. Besides the characteristics aforementioned, it is convenient to change the physical and chemical properties of ILs by varying the nature of cations and anions. Over the last few years, ILs have been widely investigated as reaction solvents [10], separation–extraction solvents [9], and electrolyte materials [11]. In addition, as a result of their strong ionic hydrogen bonding interaction with dissolved molecules, ILs have also been employed to dissolve and stabilize protein [12]. Recently, ILs have been used as polymeric materials for solid-phase microextraction [13], organic surface modifier of polymers [14] or porogens to prepare MIPs [15–18]. To the best of our knowledge, the use of ionic liquids as the unique functional monomer for the synthesis of selective MIPs has not been reported previously.

In this work, chlorsulfuron (CS, 1-(2-chlorophenylsulfonyl)-3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)), one of sulfonylurea herbicides, was chosen as template molecule. It was difficult to detect chlorsulfuron directly by high performance liquid chromatography (HPLC) or gas chromatography (GC) [19] because of its much lower application ranges (between 10 and 100 g of active ingredient per hectare) [20]. A novel imprinted material was fabricated by the copolymerization of vinylimidazolium ionic liquid

* Corresponding author. Tel.: +86 22 6060 1456; fax: +86 22 6060 1332.
E-mail address: S.Wang@tust.edu.cn (S. Wang).

monomer and ethylene glycol dimethylacrylate (EGDMA) cross linker in the existence of CS.

2. Experimental

2.1. Materials

Thifensulfuron methyl (TFSM, 97.6%), 1-vinylimidazole ($\geq 99\%$), and CS (99%) were obtained from Sigma–Aldrich (Steinheim, Germany) and used as received. EDMA (98%) was also purchased from Sigma–Aldrich and distilled under vacuum to remove the polymerization inhibitor. Bensulfuron methyl (BSM, 98%) and pyrazosulfuron (PS, 99%) were obtained from Dr. Ehrenstorfer (Augsburg, Germany). DAMA (99%) was purchased from Tokyo Chemical Industry Corporation (Tokyo, Japan). MAA (99%) and 2,2-azobisisobutyronitrile (AIBN, 99%) were obtained from Tianjin Chemical Reagent Factory (Tianjin, China) and purified before use. All other chemicals/solvents were obtained as either Analar or HPLC reagent-grade materials from normal commercial sources. Ultrapure water (18 M Ω cm, Millipore Corporation, USA) was used for the preparation of all aqueous solutions.

A preconcentration column (1.0 cm \times 8.0 mm i.d.) packed with 40.0 mg MIPs was used for the on-line solid phase extraction (SPE) preconcentration of CS in water samples.

A stock solution of each analyte was initially prepared at 1.0 mg mL $^{-1}$ by dissolving 10.0 mg of individual standard in 10.0 mL of methanol and stored at -18°C in the dark. Working standard solutions were obtained by diluting the individual stock solutions with methanol to desired concentration just before use. The standard mixtures at different concentration levels were prepared by diluting standard solutions of the analytes with methanol. The best composition of the mobile phase for the separation of CS was 37% acetonitrile–methanol 8:2 (v/v) and 63% aqueous solution acidified to pH 3.0 [19].

2.2. Methods

FT-IR spectra (4000–400 cm $^{-1}$) in KBr were recorded using a Vector 22 spectrometer (Bruker, brukeroptics.equips.cn). SEM images were recorded by SS-550 (Shimadzu, Japan). Adsorption/desorption analyses were carried out using a nitrogen surface area analyzer (TriStar 3000, Micromeritics, USA). All separations were performed on a Shimadzu HPLC system (Shimadzu, Japan) equipped with a Shimadzu SPD-20AVP ultraviolet detector and a Hypersil-ODS column (4.6 mm \times 250.0 mm, Thermo) at a mobile flow rate of 1.0 mL min $^{-1}$ under gradient elution conditions at 35 $^\circ\text{C}$ of column temperature. The Class-*vp* software was used to acquire and process spectral and chromatographic data. The ultraviolet detector was operated at 220 nm. A Model FIA-3100 flow injection system (Vital Instruments, Beijing, China) was used for on-line SPE preconcentration. Tygon pump tubes were used for delivering the sample solution. Small-bore (0.5 mm i.d.) PTFE tubes were adapted for all connections, which were kept at the shortest possible length to minimize the dead volume.

2.3. Synthesis of 1-vinyl-3-butylimidazolium chloride (ViBulm $^+\text{Cl}^-$) ionic liquid

1-Vinyl-3-butylimidazolium chloride was synthesized according to the protocol reported by Marcilla et al. [21]. Under vigorous stirring, 1-chlorobutane (37.0 g, 0.4 mol) was added dropwise to 1-vinylimidazole (20.0 g, 0.2 mol) in a flask. The mixture was refluxed at 70 $^\circ\text{C}$ for 50 h. The viscous liquid was allowed to cool to room temperature, and washed several times with ethyl acetate. After being filtered and dried in a vacuum oven until constant weight,

1-vinyl-3-butylimidazolium chloride ionic liquid was obtained as a white solid.

2.4. Preparation of molecularly imprinted ionic liquid polymer

A typical preparation of the MIP was carried out as follows: CS (537.0 mg, 1.5 mmol) and vinylimidazolium ionic liquid (679.5 mg, 3.6 mmol) were dissolved in a mixed solvent of 2.5 mL N,N-dimethylformamide and 4.0 mL toluene and 1.0 mL methanol in a flask. Crosslinker EDMA (1.5 mL, 8.0 mmol) and initiator AIBN (20.0 mg) were then added to the above solution. The solution was degassed ultrasonically and purged with nitrogen for 10.0 min. The flask was sealed under nitrogen and the mixture was heated at 60 $^\circ\text{C}$ for 24 h. The resultant polymer was crushed, ground, and sieved through the stainless steel sieves of 100 meshes. The polymer particles were extracted with a solution composed of 10% acetic acid and 90% methanol using a Soxhlet extraction device for 24 h, and then dried in a vacuum at 60 $^\circ\text{C}$ for 10 h. As a blank, non-imprinted polymer (NIP) was simultaneously prepared and treated in an identical method, in the absence of any template molecule.

2.5. Capacity study on the adsorption of CS

20.0 mg of MIPs or NIPs were mixed with 10.0 mL of CS–methanol solution or CS–water solution in different concentrations (10.0–160.0 mg L $^{-1}$) and shaken for 24 h to measure the static adsorption capacities of the polymer, respectively. The mixture was then separated centrifugally (5000 rpm) for 10 min. The unbound CS in the supernatant was measured by HPLC. The adsorption capacity (Q) was calculated according to the following formula (1):

$$Q = (C_i - C_f) \times \frac{V}{W} \quad (1)$$

Here C_i , C_f were the initial and final concentration of the analytes in the solution, respectively, V and W were the volume of solution and the mass of polymer, respectively.

2.6. Kinetic study on the adsorption of CS

A 20.0 mg amount of sorbents was added to 10.0 mL of 20.0 mg L $^{-1}$ CS–methanol solution. The mixture was mechanically shaken for set times at room temperature and then separated centrifugally (5000 rpm) for 10 min. The unbound CS in the supernatant was measured by HPLC.

2.7. Competitive adsorption analysis

To validate the selectivity of MIPs, BSM, CME, PS and TFMS (see Fig. 1) were chosen as the competitors of CS in competitive recognition studies. The imprinted ionic liquid polymer (20.0 mg) was added to a flask containing 10.0 mL of 100.0 mg L $^{-1}$ BSM, CME, PS, TFMS and CS–methanol mixed solution, shaken at room temperature for 12 h and separated centrifugally. HPLC was used to measure the concentration of the five analytes in the supernatant solution.

2.8. Procedures for on-line SPE–HPLC determination of CS

A stainless steel cartridge (1.5 cm \times 4.0 mm i.d.) packed with 40.0 mg of MIPs was prepared to evaluate the applicability of imprinted ionic liquid polymer sorbent for on-line SPE–HPLC determination of trace CS in water samples. The process of the on-line SPE preconcentration coupled to HPLC for determination of CS was as follows: first, the sample solution was introduced onto the SPE microcolumn at a flow rate of 1.0 mL min $^{-1}$ while the HPLC injector

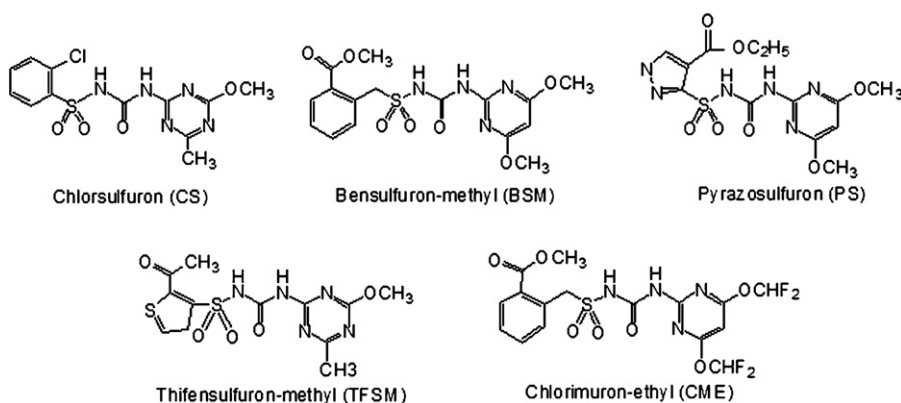


Fig. 1. Template molecule (CS) and its structural analogues.

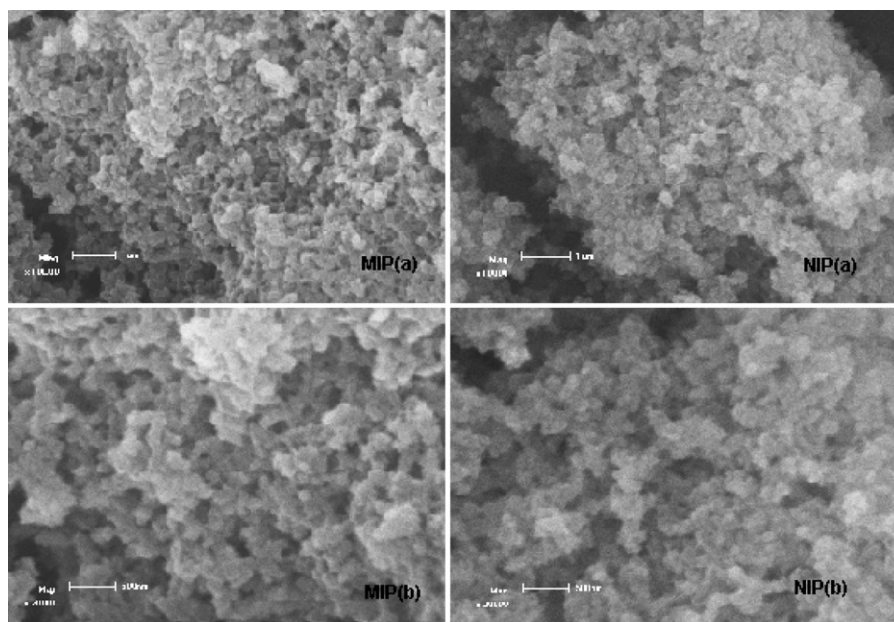


Fig. 2. Scanning electron micrographs of MIP and NIP. Magnification: (a) 10,000 \times ; (b) 20,000 \times .

valve was kept in the load position. This resulted in the CS being preconcentrated by the imprinted material-packed microcolumn, and the unwanted water was sent to the waste. Second, the analytes adsorbed on the microcolumn were eluted in the back-flush mode by the HPLC mobile phase at a flow rate of 1.0 mL min⁻¹ into the chromatographic separation column for 2 min by switching the HPLC valve from “load” to “inject”. Third, the HPLC injector valve was turned to the load position for the next sample preconcentration cycle while the analytes were separated in the separation column to improve sample throughput. Areas of peak at 220 nm were calculated and used for data evaluation.

2.9. Preparation of water samples

Environmental water samples were chosen to evaluate the developed on-line SPE-HPLC method. The reservoir water was collected from suburbs of MiLuo city (surface water 1) and YueYang county (surface water 3) in China. Pond water was taken from Tianjin University of Science and Technology (surface water 2). 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 microfiber filters (0.22 μ m) and adjusted to

pH 4.5 with phosphoric acid to ensure efficient extraction of the analytes.

3. Results and discussion

3.1. Characterization of the synthesized MIP and NIP

3.1.1. Morphological structure

The morphological structures of the MIP and NIP were detected by SEM. From Fig. 2, we could observe that the morphology of the particles obtained by crushing and grinding was irregular. With 10K magnification, the surface of the NIP formed as irregular particles seemed to be compact and less-porous, however, the MIP had many relatively small through pores in comparison with that of NIP synthesized without the addition of CS. In addition, the 20K magnification picture showed that MIP possessed a loose and porous structure.

3.1.2. BET analysis

Fig. 3 shows the nitrogen adsorption/desorption profiles of both the imprinted and the nonimprinted materials. The specific surface area, pore volume and pore size with MIP were 135.7 m² g⁻¹, 0.33 cm³ g⁻¹, 9.7 nm, respectively, which were smaller than those

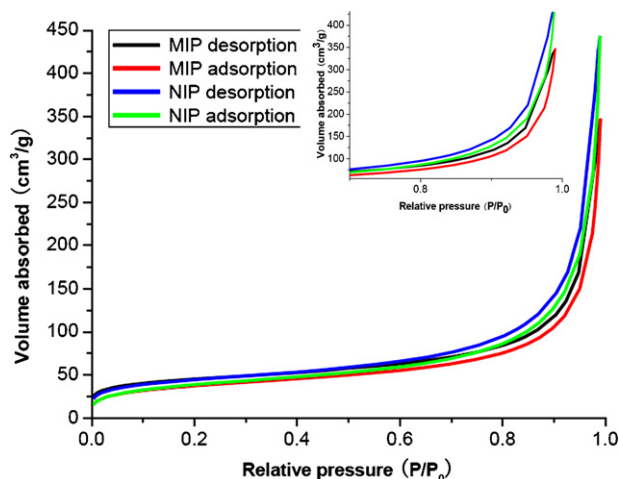


Fig. 3. Nitrogen adsorption/desorption profiles of the imprinted and nonimprinted polymers.

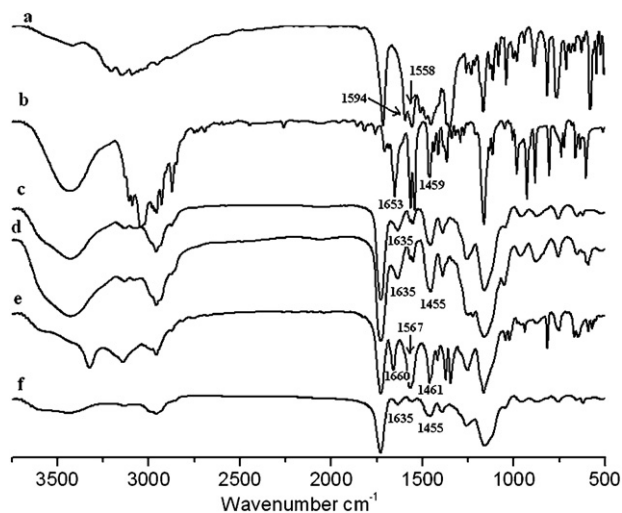


Fig. 4. FT-IR spectra of the (a) CS, (b) vinylimidazolium ionic liquid, (c) non-imprinted polymer before extraction, (d) non-imprinted polymer after extraction, (e) imprinted polymer before extraction, and (f) imprinted polymer after extraction.

with NIP ($142.2 \text{ m}^2 \text{ g}^{-1}$, $0.43 \text{ cm}^3 \text{ g}^{-1}$, 12.3 nm). It might seem confusing that the imprinted materials had many imprinted cavities, and should have larger surface area and pore volume. Nevertheless, it could be realized the functional monomers were distributed orderly at the surface of pores in the imprinted polymer via the imprinting process, and they were distributed disorderly within the nonimprinted polymer. As a result, the imprinted material could absorb much more water molecules than the nonimprinted material, and had less surface area, pore size and pore volume. In addition, template molecules might also affect the polymerization process.

3.1.3. FT-IR analysis

To further determine the characteristics of the MIP, FT-IR (FTIR) spectra of CS imprinted ionic liquid and non-imprinted ionic liquid polymers (before and after extraction of the template) were compared with the spectra of CS and ViBulm⁺Cl⁻ (see Fig. 4). A strong peak was observed near 1653 cm^{-1} due to conjugation of C=C and C=N and overlap of both stretching vibrations (Fig. 4b). The peak shifted to 1635 cm^{-1} for NIP (before and after extraction of the template) resulted from C=C, which attended the polymerization (Fig. 4c and d). For unwashed imprinted polymer, the peak

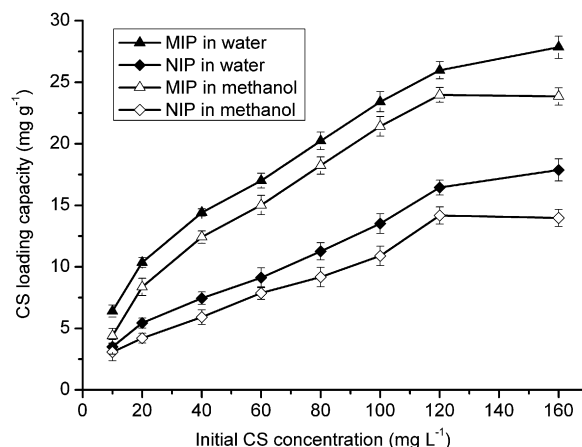


Fig. 5. Loading isotherm of CS onto the imprinted and nonimprinted sorbents. The error bars indicate standard deviations of the results of at least three measurements.

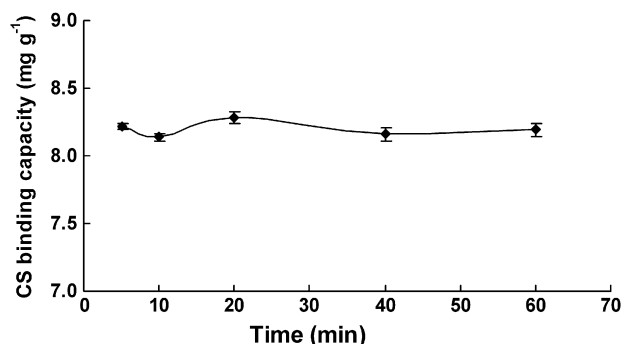


Fig. 6. Kinetic uptake plot of the imprinted polymer. The error bars indicate standard deviations of the results of at least three measurements.

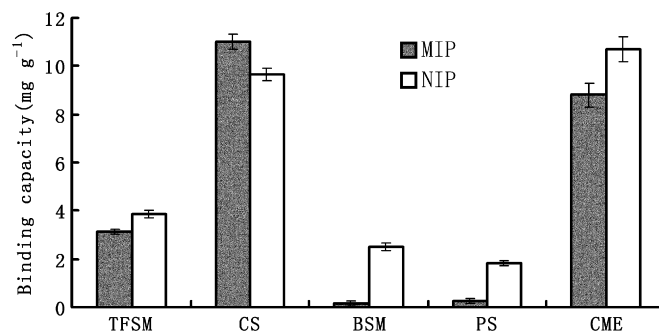


Fig. 7. Selectivity of the imprinted polymer towards the template molecule and its analogues. The error bars indicate standard deviations of the results of at least three measurements.

was observed at 1660 cm^{-1} due to the interaction between the template and imidazole ring, which was further verified by a shift of the peak to 1635 cm^{-1} after washing the template out of the polymer (Fig. 4e and f). Besides these results, there was a peak at 1459 cm^{-1} corresponding to vibration of imidazole ring (Fig. 4b), which was at 1455 cm^{-1} for NIP (before and after extraction of the template) and MIPs (after extraction of the template), and at 1461 cm^{-1} for MIP (before extraction of the template). In addition, peaks at 158 and 1594 cm^{-1} corresponded to NH-CO-NH vibration (Fig. 4a), which were only observed at 1567 cm^{-1} in Fig. 4e as overlapped with the peaks of 1542 and 1565 cm^{-1} corresponding to C-H vibration of imidazole ring (Fig. 4b). For other polymers (Fig. 4c–e), the peaks corresponding to C-H vibration of imidazole ring appeared at 1550 and 1567 cm^{-1} . These results indicated that the vinylimidazolium

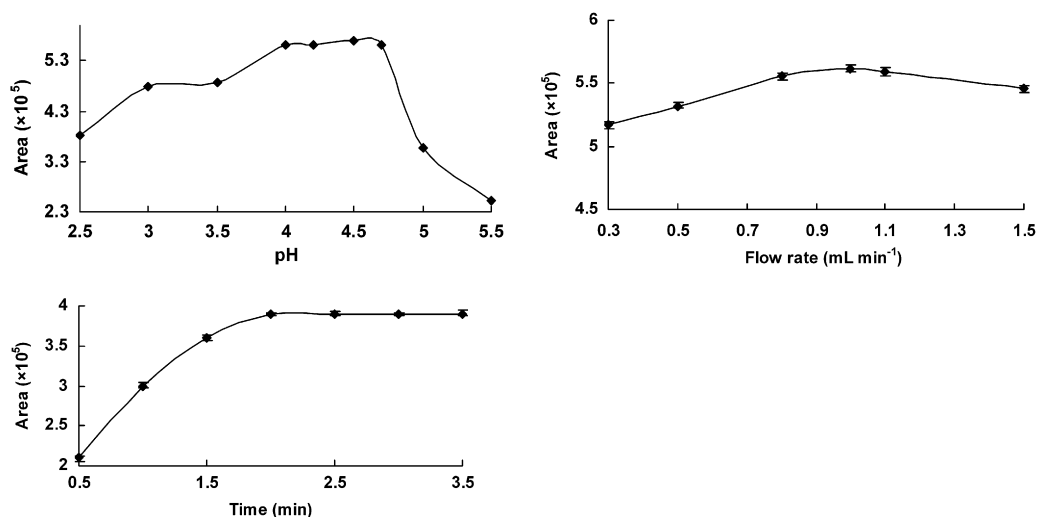


Fig. 8. (a) Effects of pH on peak area of CS, (b) flow rate of loading sample solution on peak area of CS, (c) time of eluting sample solution on peak area of CS. Tests were carried out with $0.5 \mu\text{g L}^{-1}$ CS aqueous solution. The error bars indicate standard deviations of the results of at least three measurements. The standard deviations are smaller than the symbols themselves for those without an error bar.

ionic liquid had been incorporated into polymers, and the hydrogen and/or ionic static interaction between ionic liquid functional monomers and template had formed during the imprinting process.

3.2. Characterization of the molecular recognition

3.2.1. Evaluation of static adsorption

For successful imprinted materials, the specific cavities that complement the size, shape and functionality of the template molecule, should have been formed. Thus, the capability of special adsorption for template molecule is a vital property to evaluate the imprinted materials. The ability of MIP binding CS at each concentration, ranging from 10.0 to 160.0 mg L^{-1} was compared with NIP (Fig. 5). It was found that the binding capacities of MIP and NIP increased with increase of CS initial concentration, however, the MIP showed a higher binding capacity than that of NIP. The results indicated that the MIP had a specific binding capacity for the template molecule. In addition, MIP and NIP show higher adsorption capacity in water than in methanol, this may be attribute to hydrophobic interaction between CS and materials. However, it is worth to note that the imprinting effect has no significant change. Besides the synthesized ionic liquid functional monomer, MAA and DAMA, which both had been widely employed to prepare imprinted materials, were also used here to synthesize imprinted materials under the same condition. The adsorption capacities of MIP and NIP using MAA as functional monomer were 0.67 mg g^{-1} and 0.57 mg g^{-1} , respectively, while using DAMA as functional monomer, they were 3.88 mg g^{-1} and 2.96 mg g^{-1} , respectively.

3.2.2. Kinetics to take up target species

Fig. 6 shows the time dependent evaluation of the CS amount bound by MIP. To our surprise, the adsorption equilibrium was achieved within a short shaking period of 5 min. It was worthy to note that the present MIP was synthesized by bulk molecular imprinting technique, while other MIPs usually showed an unfavorable binding kinetics. Besides, the present ionic liquid polymer even showed a faster binding kinetics than that of surface imprinting polymers [22,23].

3.2.3. Competitive adsorption of MIP for CS in mixture solution

From the previous data, the imprinted materials prepared already had proven imprinting effect as well as binding capacity for CS. The binding selectivity of these materials was further evaluated

Table 1
Selectivity of CS-imprinted ionic liquid polymer in mixture solution toward CS.

	Materials	Imprinted	Non-imprinted
Selectivity	TFSM	13.3	13.6
	CS	47.2	33.8
	BSM	0.6	8.8
	PS	1.1	6.3
	CME	37.8	37.5

by competitive adsorption using the mixture solution composed of CS, TFSM, BSM, PS and CME at 100.0 mg L^{-1} methanol solution. The common fragment in these five molecules is the sulfonylurea moiety. As shown in Fig. 7, the imprinted materials could discriminate CS from its analogues in the solution mixture. The amounts of structural analogues bound by the imprinted materials were much less than that of CS. The imprinted materials also showed a higher capacity for CS than that of nonimprinted one, but negative results were obtained for PS, BSM, and CME. TFSM, which differs from CS only in the 2-chloride phenyl group substituted by thiophene derivative, was equally low absorbed by the imprinted and non-imprinted materials. For CME, although no imprinting effect was observed, the amounts of the compound absorbed by imprinted and nonimprinted materials were both larger than that of BSM. As the difference of the two molecular structures was that CME was fluoric methoxyl pyrimidine ring while BSM was methoxyl groups pyrimidine ring. Thus, the binding of materials to CME could be attributed to nonspecific interaction between cation imidazole ring and fluoric methoxyl group of in pyrimidine. All results indicated that besides the shape of the template, 2-chloride phenyl group played an important role in the imprinting process. Selectivity of each analyte for imprinted materials was listed in Table 1. The selectivity of each analyte was defined as the bound amount of each analogue divided by the total bound amount of all the compounds. As shown in Table 1, the imprinted materials exhibited excellent binding selectivity of 47.2% for the template, which was higher than that for the others. The binding results and the selectivity data confirmed that the selectivity of the imprinted material for CS was significantly superior to that of the nonimprinted one.

3.3. Optimization of on-line SPE-HPLC procedure

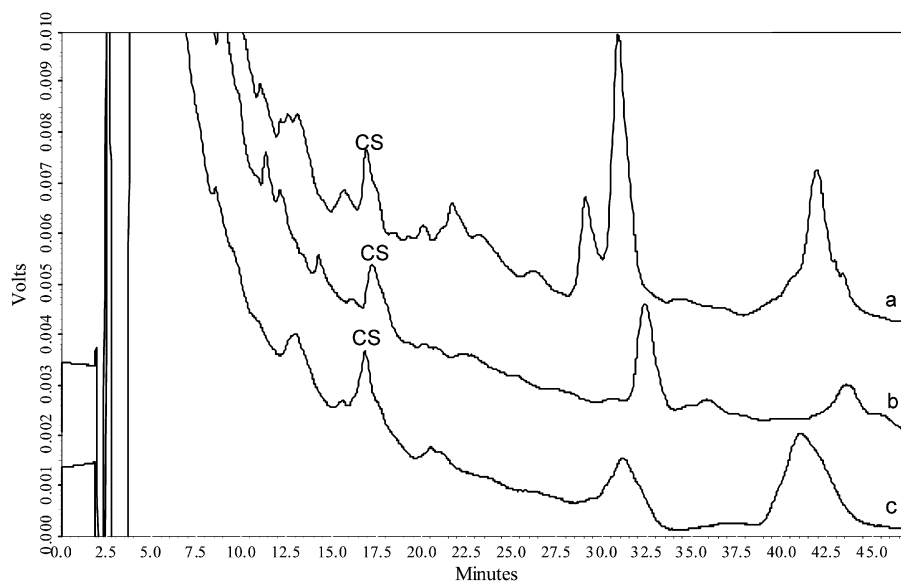
In combination with a C_{18} -SPE column, the applicability of the imprinted ionic liquid polymer sorbent for on-line SPE-HPLC

Table 2
Comparison of the two sorbents for merits of on-line solid-phase extraction coupled with HPLC for determination of trace CS.

Sorbents	MIP	C ₁₈
Enrichment factors ^a	102	90
Detection limit ($\mu\text{g L}^{-1}$)	0.001	0.035
Peak area precision ^b ($n=9$) (RSD, %)	2.2	1.2
Linear equation ^c	$Y=(71554 \pm 301)x+(1745 \pm 57)$ ($n=3$) ($r^2=0.9974$)	$Y=(63046 \pm 335)x+(1986 \pm 61)$ ($n=3$) ($r^2=0.9972$)
Linear range of the calibration graph ($\mu\text{g L}^{-1}$)	0.005–30	0.35–10
Sample consumption (mL)	50	50

^a Compared with direct injection of 20 μL sample solution.^b For 0.5 $\mu\text{g L}^{-1}$ CS standard solution.^c Y: peak areas (μVs); x: concentrations of CS ($\mu\text{g L}^{-1}$).**Table 3**
Comparison of the ionic liquid-functionalized MIP sorbent with the commercial C₁₈ sorbent for the recoveries obtained with the water samples.

Samples	Sorbents	Spiked levels					
		1.0 $\mu\text{g L}^{-1}$		3.0 $\mu\text{g L}^{-1}$		5.0 $\mu\text{g L}^{-1}$	
		Recovery (% , $n=3$)	RSD (% , $n=3$)	Recovery (% , $n=3$)	RSD (% , $n=3$)	Recovery (% , $n=3$)	RSD (% , $n=3$)
Surface water 1	MIP	96.4	2.8	88.6	5.3	103.3	4.5
	C ₁₈	12.0	9.8	38.3	4.7	59.5	0.7
Surface water 2	MIP	100.1	7.6	110.1	5.8	94.2	4.3
	C ₁₈	57.5	5.9	69.6	7.7	60.1	4.5
Surface water 3	MIP	91.3	4.1	81.0	1.2	102.5	6.8
	C ₁₈	45.3	5.8	82.5	4.6	80.6	6.2

**Fig. 9.** Chromatograms of on-line preconcentration coupled with HPLC using imprinted sorbent for 50 mL of surface water 1 (a), surface water 2 (b) and surface water 3 (c) samples spiked with 1.0 $\mu\text{g L}^{-1}$ of CS at the upload rate of 1.0 mL min^{-1} .

determination of trace CS was evaluated (Fig. 8). The general factors, including sample acidity, sample loading flow rate, loading and eluting time were optimized to achieve good sensitivity and precision for the extraction and elution of CS.

3.3.1. Sample pH

The influence of sample acidity on the on-line extraction of 0.5 $\mu\text{g L}^{-1}$ CS was tested at a sample flow rate of 1.0 mL min^{-1} for 50 min (Fig. 8a). The result showed that the maximum chromatographic peak area of CS was achieved in the pH range of 4.2–4.6. Out of the optimum pH range, the chromatographic peak area of CS decreased. These results showed that CS could be effectively adsorbed by the imprinted MIP-SPE column in the pH range of 4.2–4.6.

3.3.2. Flow rate of loading sample

The flow rate of loading sample was optimized by keeping the total sample solution volume constant. With the constant sample loading volume (50.0 mL), the flow rate ranged from 0.25 to 1.5 mL min^{-1} . The adsorption capacity of CS reduced when flow rate exceeded 1.0 mL min^{-1} , which meant that higher speed (>1.0 mL min^{-1}) was not conducive to CS being fully adsorbed onto the MIP-SPE column (Fig. 8b). In order to maximize the efficiency of assay, the flow rate of loading sample was chosen as 1.0 mL min^{-1} .

3.3.3. Time of loading sample

The effect of sample loading time on the on-line solid-phase extraction of 0.5 $\mu\text{g L}^{-1}$ CS was tested at a sample loading flow rate of 1.0 mL min^{-1} . Within 50 min, the chromatographic peak area increased almost linearly as sample loading time increased up.

3.3.4. Time of eluting sample

The time for on-line desorption of analytes was optimized by using the mobile phase for different times, showing that 2 min was sufficient time to desorb all extracted analytes (Fig. 8c).

In this work, sample pH, loading flow rate and the eluting time of MIP materials were established at 4.5, 1.0 mL min⁻¹, 2.0 min, respectively. And for C₁₈-SPE column, the optimum experimental conditions were 4.5 (sample pH), 1.0 mL min⁻¹ (loading flow rate) and 1.5 min (eluting time), correspondingly (Table 2).

3.4. Application of the present on-line SPE-HPLC

The analytical figures of merit for the present on-line SPE using the imprinted ionic liquid polymer sorbent coupled with HPLC for the determination of trace CS were evaluated under optimal experimental conditions. The commercially available C₁₈-SPE column was also used for comparison with the MIP sorbents. The linear ranges of CS were 0.005–30 µg L⁻¹ for MIP packed column and 0.35–10 µg L⁻¹ for C₁₈-SPE. The detection limit of CS was 0.001 µg L⁻¹ for MIP packed column, and increased to 0.035 µg L⁻¹ for C₁₈-SPE. The enrichment factor of MIP was higher than that C₁₈-SPE, and was 102 for MIP and 90 for C₁₈-SPE. In order to investigate recovery, the samples of water determined to be free of CS, were spiked with three levels of CS (1.0 µg L⁻¹, 3.0 µg L⁻¹ and 5.0 µg L⁻¹) and analyzed. At each concentration, three measurements were performed and recoveries of CS had ranged from 81.0% to 110.1% for MIP packed column. Compared with MIP packed column, recoveries of C₁₈-SPE had only ranged from 12.0 to 82.5 (Table 3). The results indicated that MIP was superior to C₁₈-SPE in extraction CS from complicated samples. Typical chromatograms with the level of 1.0 µg L⁻¹ CS are shown in Fig. 9.

4. Conclusion

In this paper, an imprinted vinylimidazolium ionic liquid polymer sorbent was synthesized by bulk polymerization technique. Compared with MIP for chlorsulfuron prepared before [24], the novel material showed high affinity, selectivity, and fast kinetics for the adsorption/desorption for CS and was suitable as sorbent for on-line SPE. The method could successfully detect CS at low concentration levels in water samples with good recoveries. It was

a promising method using the material for selective adsorption and determination of trace CS by on-line SPE-HPLC.

Acknowledgements

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