Trace Bensulfuron-Methyl Analysis in Tap Water, Soil, and Soybean Samples by a Combination of Molecularly Imprinted Stir Bar Sorption Extraction and HPLC-UV

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ABSTRACT: A molecularly imprinted stir bar was prepared using bensulfuron-methyl as the template molecule and methacrylic acid as the functional monomer. The imprinted and nonimprinted stir bars were characterized by scanning electron microscopy, nitrogen sorption porosimetry, thermogravimetric analysis, and differential scanning calorimetry. Extraction time, desorption time and pH value affecting extraction efficiency of the stir bar have been evaluated to achieve the selectively direct preconcentration of the template from aqueous samples. Competitive sorption experiments demonstrated that the imprinted stir bar gave high selectivity and imprinted effect on the template bensulfuron-methyl compared to the nonimprinted stir bar. Based on S/N of 3, LOD was 0.83 n*M*. The method showed good recoveries and precision, 92.4% (RSD 1.5%, $n = 3$) for tap water spiked with 126 ng (100 mL sample), 84.6% (RSD 2.2%, $n = 3$) for soil spiked with 210 ng (100 g sample) and 73.7% (RSD 2.1%, $n = 3$) for soybean spiked with 250 ng (5 g sample), suggesting that the imprinted stir bar sorption extraction can be successfully applied to the preconcentration of bensulfuron-methyl in real samples. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 1198–1205, 2011

Key words: bensulfuron-methyl; *in situ* polymerization; molecularly imprinted polymers; stir bar sorption extraction

INTRODUCTION

Sulfonylureas are a class of herbicides that can function by inhibiting the action of acetolactate synthase, which is a key enzyme in the biosynthesis of amino acids in plants. As herbicides used for crops protection, sulfonylureas have been widely used for weed control in cereals such as wheat, rice, corn, and other crops such as potatoes, sugar beet, and turnip.[1] Although they are applied at rates that are typically much lower than those used for triazine herbicides most commonly used in agriculture, the sulfonylurea herbicide residues are highly phytotoxic to some plants at only 1% or even less of originally applied amount.[2]

Many methods such as supercritical fluid chromatography, GC, HPLC have been proposed for sulfonylurea analysis.[3–5] HPLC is the most commonly used one because of the polarity and thermal instability of sulfonylureas. But pretreatments of the methods are tedious and time-consuming, and require large amounts of organic solvents. Therefore, the development of more efficient and robust pretreatment methods to meet the need for detecting sulfonylureas is very necessary.

Molecular imprinting is a well established approach to develop artificial recognition systems capable of mimicing features of the corresponding biological systems. This imprinting is a relatively inexpensive procedure for preparation of the synthetic receptors with appreciable affinity, selectivity, and toughness. The advantages have led to various applications of molecularly imprinted polymers (MIPs), including catalysis, SPE, chemical sensors.[6–8] Although some disadvantages are the site heterogeneity and a slow mass transfer, MIPs have been applied to the extraction of pollutants in the environmental area, such as rivers and soils.[9,10]

Stir bar sorption extraction (SBSE) introduced by Sandra's group[11] is a very elegant enrichment technique for complicated samples. The SBSE has been widely used for enrichment and trace determination of contaminants such as pesticides, volatile phenols, and fungicide in food or environmental samples.[12–14] To date, poly(dimethylsiloxane) and sol-gels are mainly coating materials.[15,16] However, they have some disadvantages, such as shortage of specific

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recognition on target molecules because they can adsorb some concomitant substances in samples.

Recently, Wu et al. and Yang et al. have reported the preparation of nylon-6-based monocrotophos or L-glutamine-imprinted polymer coatings for a stir bar and the application of stir bars coated with nicosulfuron imprinted polymer.[17,18] The preliminary investigations extend application of molecular imprinting techniques, and it is necessary to develop other imprinted coating materials. In the study, a new stir bar coated with bensulfuron-methyl imprinted polymer monolith (IPSB) was prepared using the functional monomer methacrylic acid and the crosslinking monomer ethylene glycol dimethacrylate commonly used in molecular imprinting. The IPSB combined the flexibility and simplicity of SBSE with the high selectivity and good permeability of MIPs. The advantages of the stir bar sorption extraction approach are higher selectivity, flexibility, and simplicity for extraction of target analytes compared to the more common SPE one. The procedures were successfully applied to selective preconcentration of the target analyte bensulfuron-methyl in top water, soil, and soybean.

EXPERIMENTAL

Materials and instruments

Materials

Methacrylic acid (MAA) and ethylene glycol dimethacrylate (EDMA) were purchased from Sigma-Aldrich and distilled before use. Azodiisobutyronitrile (AIBN) was also obtained from Sigma-Aldrich and recrystallized from methanol. Nicosulfuron (99.7%, NS), metsulfuron-methyl (99.5%, MSM), bensulfuron-methyl (99.5%, BSM), thifensulfuron-methyl (99.4%, TFM) were generously provided by College of Plant Protection Science, Shandong Agricultural University (Taian, China). All other chemicals were of analytical grade, and solvents were of HPLC-grade. All the solvents were passed through a 0.45 μm cellulose filter from Feiluo men Chemical Co. Ltd. prior to use. Analyzed samples (standards and recovered herbicides) were dissolved in acetonitrile. An iron bar (20 mm ×1.0 mm o.d.) was placed in the glass tube (1.1 mm i.d.), and then two ends of the tube were sealed with an alcohol blast burner.

Instruments

The morphology, specific surface areas, and thermal properties of the prepared stir bars were characterized with scanning electron microscopy (SEM; Hitachi, *S*-570, Japan), a multipoint Brunauer-Emmett-Teller (BET) apparatus (HuiHaiHong, 3H-2000III, China), thermogravimetric analysis (TGA; Shimadzu, DTG-60A/60AH, Japan), and differential scanning calorimetry (DSC; TA, Q10). All chromatographic evaluations were performed isocratically using a Waters HPLC system (a pump, Model 600; a manual injector, Model Rheodyne 7725i; CAPCELL PAK C_{18} column, 250 mm ×4.6 mm i.d., 5μm particle size; Model 2487 UV absorbance detector). The mobile phase consisted of acetonitrile/water/trifluoroacetic acid (50/50/0.1, v/v/v). The mobile phase flow-rate through the column was 1.0 mL/min. UV detection wavelength was set at 254 nm. The injection volume was 20 μL.

Pretreatment of the stir bar

The bare glass bar was sequentially cleaned with redistilled water (1 h) and methylene dichloride (1 h), and then treated with 1.0*M* NaOH for 8 h, redistilled water for 1 h, 0.10*M* HCl for 8 h, washed with redistilled water for 1 h and acetone for 30 min. After that, the bar was dried with a stream of nitrogen. Double bonds were connected on the outer surface of the glass bar by the procedure for creating double bonds on the inner surface of a capillary using γ-methacryloxypropyltrimethoxysilane (γ-MAPS) as a coupler.[15] Pyridine (0.3% of volume of γ-MAPS) was added into the reactant as a catalyst to favor the reaction of γ-MAPS with silanol.[16]

Preparation of IPSB

The molecularly imprinted monolithic coating was prepared by an *in situ* polymerization. BSM (198 mg, 0.5 mmol), MAA (258 mg, 3 mmol), EDMA (2379 mg, 12 mmol), and AIBN (57 mg, 2% w/w total monomers) were added to 15 mL of acetonitrile in a 25-mL flask. The solution was then purged with nitrogen for 15 min. Subsequently, the reactant mixture was injected into a polytetrafluoroethylene tube with 4.0 mm inner diameter, in which a pretreated stir bar was vertically fixed in the center of the tube bottom by aid of the fixed base. The solution was ultrasonicated for 10 min and sealed, then kept at 60°C for 24 h. After the polymerization, the stir bar was taken out and washed with acetonitrle-acetic acid (95 : 5, v/v), acetonitrile and doubly distilled water until the template BSM could not be detected with UV. The blank stir bar coated nonimprinted polymer (NIPSB) was prepared with the same polymerization conditions in the absence of the template.

Preparation of aqueous standards

10.0 μ*M* individual stock solutions of NS, MSM, BSM, TFM, were prepared by dissolving certain amount of each sulfonylurea in acetonitrile. 10.0*M* stock mixed solution of the four sulfonylurea was

also prepared by dissolving 1.00 mol of each sulfonylurea with acetonitrile in a 100-mL volumetric flask. The stock solutions were stored at 4°C. Aqueous standards at various concentrations were daily prepared by diluting each stock solution with doubly distilled water and adjusting to pH 4.0 with 3*M* HCl.

Water sample preparation

Drinking water sample was collected from the tap in our laboratory and spiked with BSM to the final concentration 1.185 μg/L, then adjusted to pH 4.0 with 3*M* HCl.

Soil sample preparation and extraction

The soil (water content 2.36%) used was collected from dry flower bed of Shandong agricultural university (China). The sample was ground to 100–200 mesh. The soil sample was prepared by adding 0.50 mL of standard aqueous solution (1.0 μ*M* of BSM) to 100.0 g subsamples of sieved soil, and the sample was thoroughly mixed and stood for 1 h. Three replicates were prepared. Then, soil extraction was based on the method reported previously.[19] The sample was extracted with aqueous sodium hydrogen carbonate solution (0.1*M*, pH 8.2, 200 mL). The suspension was stirred and ultrasonicated for 5 min. Following centrifugation (20 min, 4800 rpm), the aqueous solution was decanted and the extraction procedure was repeated twice. The combined extracts were concentrated to 100 mL under reduced pressure, and then adjusted to pH 4.0 with 3*M* HCl.

Soybean sample preparation and extraction

The soybean used was bought from a local farm produce market and was ground to 100–200 mesh. The soybean sample was prepared by adding 1.20 mL of standard solution (0.5 μ*M* of BSM) to 5.0 g subsamples of sieved soybean. The sample was extracted with aqueous sodium hydrogen carbonate solution (0.1*M*).[17] To the ground soybean, 40 mL of aqueous sodium hydrogen carbonate solution (0.1*M*, pH 8.2) were added and oscillated in a constant temperature bath oscillator for 10 min at 25°C. The mixture samples were then centrifuged at 6000 rpm for 15 min. The supernatant was transferred to a 500-mL separatory funnel. The extraction procedure was repeated twice. The combined supernatant was washed with *n*-hexane (20 mL ×3). Following centrifugation (15 min, 6000 rpm) to prevent emulsification, the sample solution was diluted to 100 mL with doubly distilled water, and then adjusted to pH 4.0 with 3*M* HCl.

Stirring extraction and desorption modes

The stir bar was used to extract the sulfonylurea herbicides from 100 mL aqueous standards or water samples at room temperature, using a stirring speed of 600 rpm. After reaching adsorption equilibrium, the stir bar was removed and immersed in 10 mL of acetonitrile-trifluoroacetic acid (99.5/0.5, V/V), stirred for a certain time to release the adsorbed analytes until the chromatographic peak areas of the sulfonylureas in 10 mL of acetonitrile-trifluoroacetic acid reached a maximum. After desorption process was completed, the stir bar was removed with a clean magnetic rod, and the solvent was evaporated to dryness under reduced pressure. The dry residues were redissolved in 1.00 mL acetonitrile, and analyzed with HPLC-UV. The bound amounts of analytes were calculated by subtracting the free concentration from the initial analyte concentration.

RESULTS AND DISCUSSION

Preparation of IPSB and NIPSB coatings

Successful MIPs coating on the glass surface of a stir bar was prepared using the reported preparation methodology.[15] In this study, BSM was used as the template, the functional monomer MAA, the crosslinking monomer EDMA, and the porogen acetonitrile were used. The MIP coating was covalently attached to the stir bar surface via the double bonds linked to the stir bar surface using γ-MAPS as a coupler prior to MIP synthesis. Upon radical formation, initiated thermally, the polymerization reaction was carried out (Fig. 1). The thickness of the MIP coating depended on the difference between the inner diameter of the used polytetrafluoroethylene tube and the outer diameter of the stir bar. To compare with IPSB, NIPSB was prepared with the same procedure in the absence of BSM.

Morphology characterization and physical property of IPSB and NIPSB

After removal of the template, the imprinted polymeric material attached to the pretreated stir bar was white and smooth by macroscopic observation. There was no difference between IPSB and NIPSB in visual topography at the macroscopic level. The SEM images of IPSB and NIPSB were shown in Figure 2. Compared with NIPSB, IPSB had obvious differences in morphology, such as irregular and bigger pores in nanometer level. This test verify that the template BSM play an important role in the preparation of IPSB, which exerts a decisive impact on IPSB selectivity.

To confirm the conclusion, nitrogen sorption measurement on IPSB and NIPSB was performed

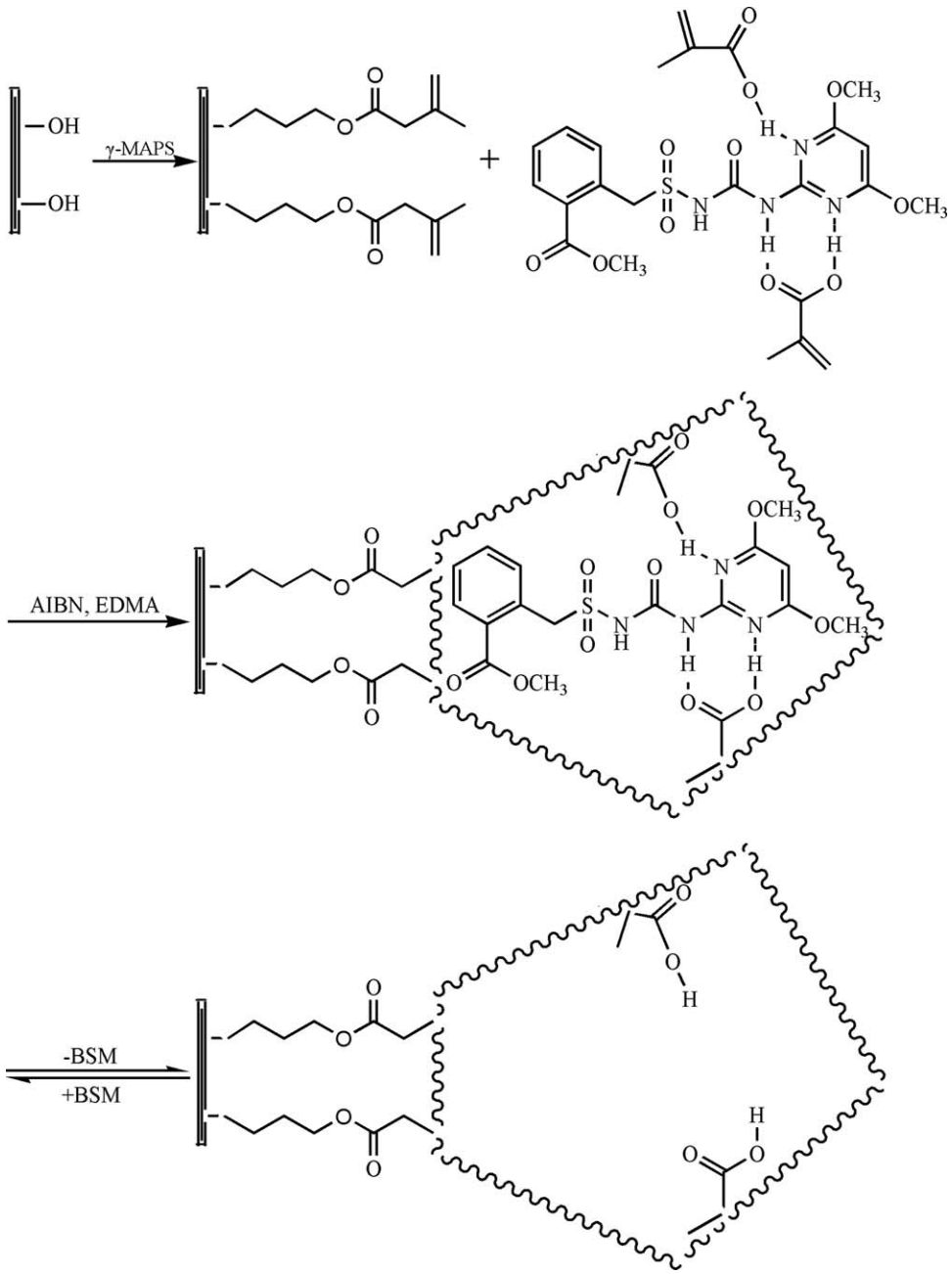

Figure 1 Schematic representation of preparation procedures of MIPs monolithic coating on the surface of a stir bar.

and the specific surface areas were found to be 291.75 m^2/g and 193.64 m^2/g, respectively. This demonstrated that IPSB and NIPSB had obvious differences in specific surface areas

Thermal analysis of IPSB and NIPSB

The thermal properties of the stir bar coatings were studied with TGA and DSC. The TGA curves of IPSB and NIPSB were given in Figure 3(A). When the temperature was less than 250°C, both IPSB and NIPSB had good thermal stability. Linear decreases in weight appeared from ~ 250°C to ~ 450°C because of thermal decomposition of the polymers. However, the weight loss of IPSB was slower than that of NIPSB due to the presence of imprinting cavities. The DSC thermograms of IPSB and NIPSB shown in Figure 3(B) showed that the glass-transition temperature (T_g) was 64.30°C and 73.77°C, respectively. The T_g of IPSB shifted to a lower temperature by about 9°C than that of NIPSB. These observations indicated that the polymeric chain movement of IPSB became easier and the T_g was decreased.

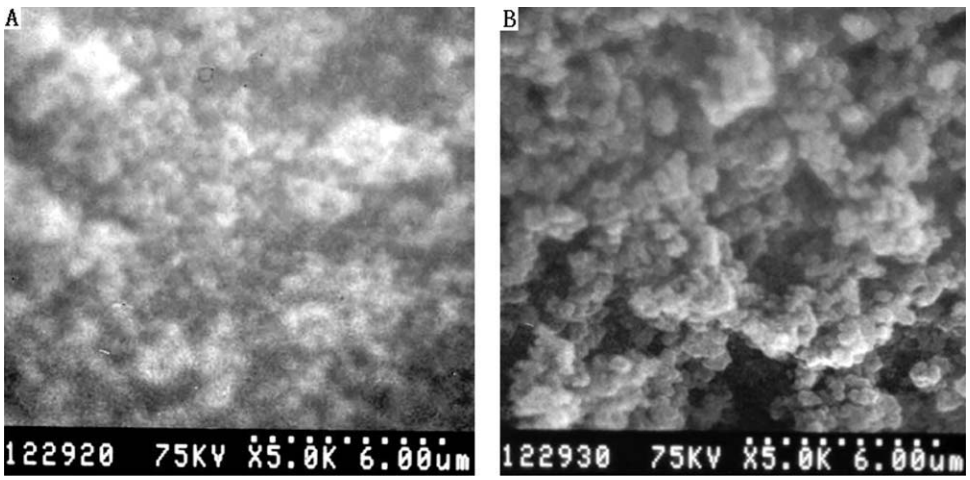

Figure 2 Scanning electron micrographs of NIPSB (A) and IPSB (B).

Optimization of IPSB stirring extraction operating conditions

To optimize the IPSB stirring extraction operating conditions for BSM analysis, several parameters that could influence the IPSB extraction were studied in standard aqueous samples spiked at 0.50 μ*M* levels. According to the literature,[19] the stirring speed may have a significant effect on the SBSE stirring extraction efficiency. But the tests performed at 600, 750, and 1000 rpm demonstrated that the differences of extraction efficiency observed were negligible. The difference maybe was the fact that the imprinting process created more expedite channels, through which analyte molecules could desorbed more easily. Therefore, a 600 rpm stirring speed was used in our research.

To estimate the adsorption equilibrium time, the sorption experiments were performed for the BSM aqueous solution (0.5 μ*M*) at room temperature. The extraction efficiency increased rapidly with adsorption time and reached a maximum at 2 h, then leveled off as shown in Figure 4(A). To compare with the adsorption speed of conventional imprinted polymers for the template molecules, the imprinted polymer coating was peeled off from the glass stir bar, then ground, and sieved. The fraction of particles having an average size ranging from 25 to 75 μm was collected. The batch experiments for the obtained particles were carried out. The experimental results indicated that the particulate imprinted polymer took 3.5 h to reach the equilibrium for BSM by shaking adsorption [Fig. 4(A) curve 2]. This demonstrated that the equilibrium for IPSB stirring adsorption was fast in that the template molecules were incorporated into the polymer matrix in solution by the stirring process. Accordingly, the reintroduction equilibrium was attained rapidly (~ 2 h). We also studied the effect of liquid desorption time in 10 mL of acetonitrle-trifluoroacetic acid (99.5/0.5, V/V). It was found that the desorption efficiency reached a maximum after 2 h of desorption as

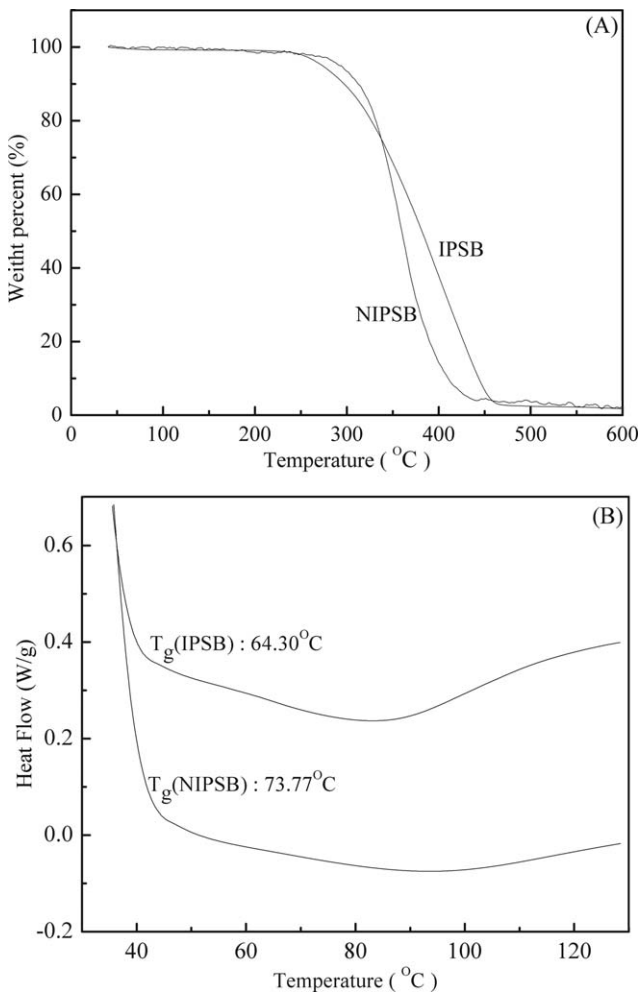

Figure 3 The TGA curves (A) and DSC heating thermograms (B) of IPSB and NIPSB.

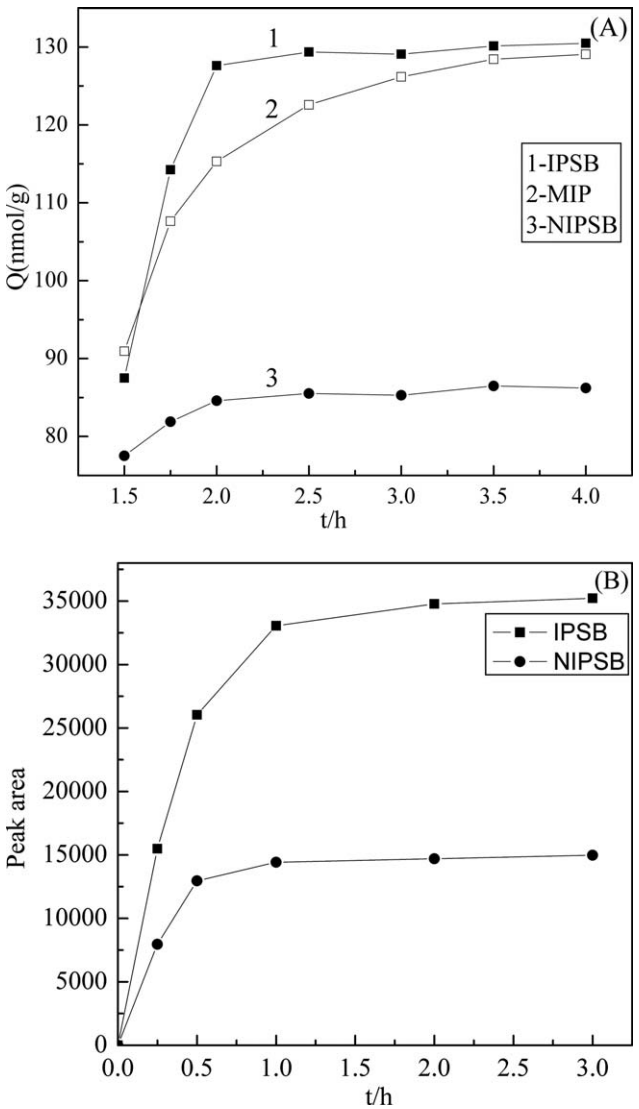

Figure 4 Time sorption (A) curves of the IPSB, MIP, and NIPSB and Time desorption (B) curves of the IPSB and NIPSB obtained at BSM concentration of 0.50 μ*M* and pH 4.0.

shown in Figure 4(B). Thus 2 h were used for the adsorption and desorption time in the following research.

The effect of sample pH on the extraction efficiency was investigated in the pH range from 2.0 to 8.0 in the BSM aqueous sample spiked at 0.50 μ*M* level (Fig. 5). Figure 5 showed that the extraction efficiency increased slowly from pH 2.0 to 4.0, a little decreased from pH 4.0 to 5.0, and decreased drastically from pH 5.0 to 8.0. The changes can be explained that BSM binds to the imprinted sites of the IPSB by hydrogen bonds. Most of the carboxyl groups on the imprinted sites exist in the free acidic form in the pH range 4–5, and there are stronger hydrogen-binding interaction between BSM and the MIPs coating. BSM in the aqueous solution is protonated when the pH is less than 4.0, and the carboxyl group on the imprinted sites is ionized when pH is more than 4.0. Both cases can weaken the hydrogen-binding interaction between BSM and the MIPs coating. This results in less extraction efficiency of the IPSB. So setting the pH value of aqueous matrix at 4.0 was recommended for adsorption of BSM with the IPSB.

Selectivity of IPSB

To evaluate the high selectivity and imprinted effect of the IPSB for the template and its structural analogues, four different sulfonylurea herbicides (NS, MSM, BSM, and TFM) were selected to test the extraction characteristic of the IPSB under the optimized conditions. A total of 100 mL of an aqueous mixture of 0.3 μ*M* of each sulfonylurea tested was applied to a competitive stirring adsorption and desorption experiment using the IPSB or NIPSB. After adsorption, desorption, and evaporation under vacuum, the residue was redissolved in 1 mL of acetonitrile and analyzed by HPLC-UV. The chromatograms obtained were shown in Figure 6. We define that the selective factor is the ratio of amount of the template BSM adsorbed to that of BSM analogues adsorbed for the IPSB, and the imprinted factor the ratio of amount adsorbed by IPSB to that adsorbed by NIPSB for the same sulfonylurea. The selective and imprinted factors obtained for the tested sulfonylureas were given in Table I. These imprinted factors indicate that the BSM-imprinted stir bar (IPSB) exhibits high affinity for the investigated sulfonylurea herbicides than the NIPSB, moreover, has the highest affinity for the template BSM. These selective factors show that the IPSB have higher selectivity for the template BSM than its structural analogues. This

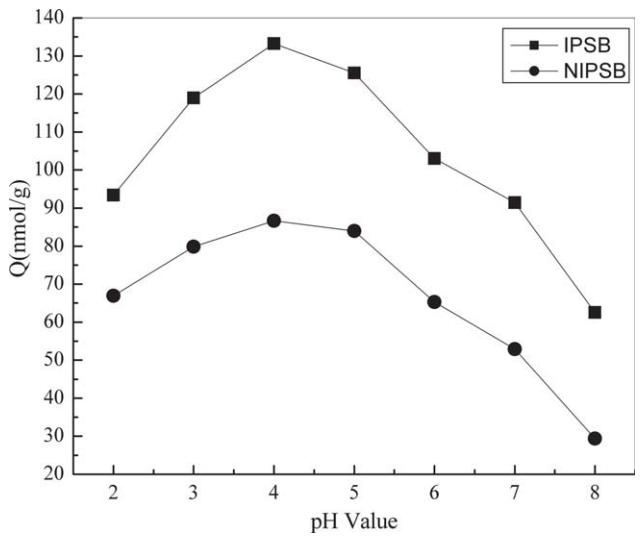

Figure 5 Effects of pH in the sample matrix on the IPSB and NIPSB extraction efficiencies at BSM concentration of 0.50 μ*M*.

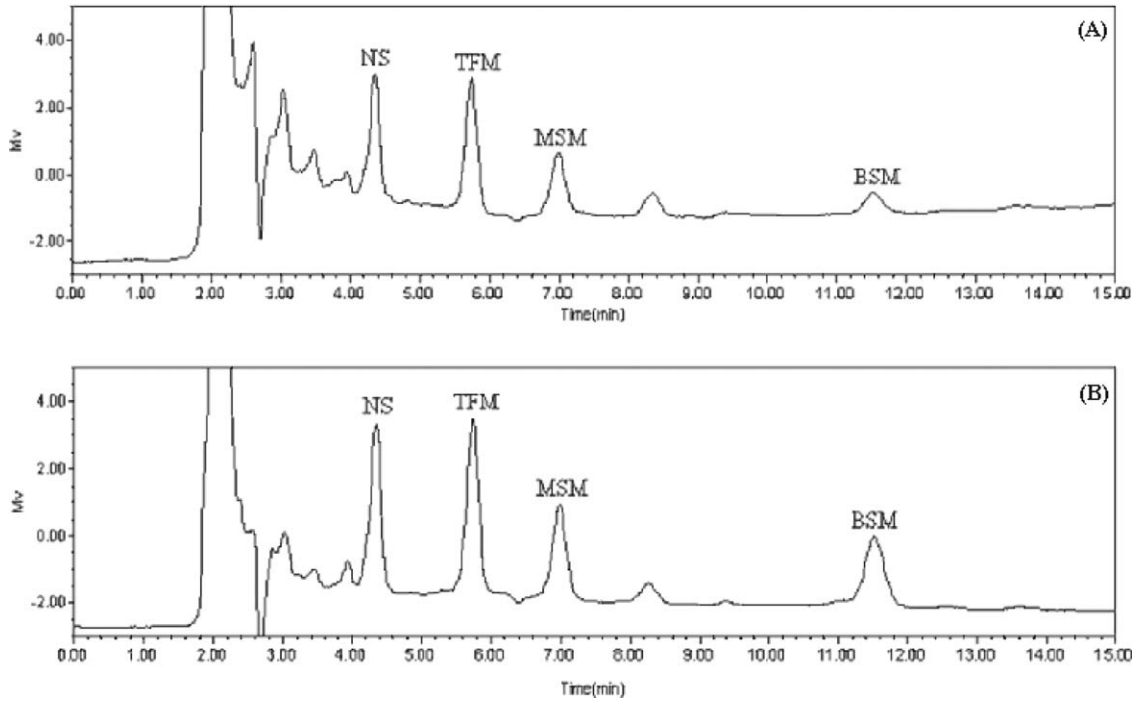

Figure 6 HPLC-UV chromatograms of four sulfonylurea herbicides in standard aqueous sample with 0.3 μ*M* of each sulfonylurea after (A) NIPSB extraction and (B) IPSB extraction.

difference between IPSB and NIPSB is due to the imprinted binding sites created in the imprinting process and does not result from nonspecific sorption.

Calibration and sensitivity

In real samples, the quantity of sulfonylurea herbicides is usually very low. To develop a highly sensitive method for the determination of BSM by coupling IPSB stirring extraction and HPLC-UV, 13 BSM standard aqueous samples with the tested sulfonylurea herbicides were prepared, which consisted of 1.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 12.0, 14.0, 16.0, 18.0 n*M* of BSM, respectively. To generate the calibration, the peak area obtained from the extracted BSM was plotted against the concentrations of the initial samples (Fig. 7). In Figure 7, we found that the calibration graph for BSM was linear in the concentration range from 5.0 to 10.0 n*M*, in which the linear regression equation was: $y = 1692.1x - 402.2$ with a correlation coefficient of 0.9935 (y, peak area; x, initial BSM concentration with the unit of n*M*). Based on an S/N of 3, the LOD was 0.83 n*M*.

TABLE I
Selective Factors and Imprinted Factors of the IPSB in an Aqueous Mixture of 0.3 μ*M* of Each Sulfonylurea Tested

Substrates	Selective factors		Imprinted factors
	IPSB	NIPSB	
BSM	1.00	1.00	2.60
TFM	1.33	0.68	1.33
MSM	1.43	0.72	1.29
NS	1.85	0.89	1.25

Selectivity factor: amount of BSM extracted/amount of BSM analogues extracted for the IPSB. Imprinted factor: peak area of the chromatogram measured after stirring extraction by the IPSB/peak area of the chromatogram measured after stirring extraction by the NIPSB for the same substrate.

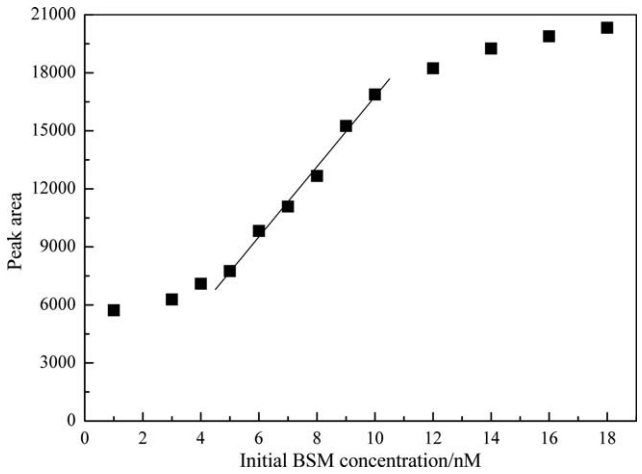

Figure 7 Plot of chromatographic areas obtained from the extracted BSM against initial BSM concentration.

TABLE II
Average Recoveries (%) and RSD (%) Obtained After Stirring Extraction by the IPSB for 100 mL Tap Water, 100 g Soil, and 5 g Soybean Samples Spiked at 126 ng, 210 g, and 250 ng of BSM, respectively, (n = 3)

		IPSB-HPLC-UV	
Sample	Spiked level (ng)	Found level, ng, (RSD %)	Recoveries (%)
Tap water	126	114.7 (1.5)	92.4
Soil	210	177.7 (2.2)	84.6
Soybean	250	184.2 (2.1)	73.7

Trace analysis of BSM in tap water, soil, and soybean samples

The presence of matrix components in real samples may significantly decrease the stirring extraction efficiency of BSM on the IPSB.[20] To evaluate the applicability of the optimized IPSB stirring extraction procedure to the analysis of trace BSM in real samples, the tap water (100 mL), soil (100 g), and soybean samples (5 g) were spiked with 126 ng, 21 ng, and 250 ng BSM and analyzed by the optimized methodology. According to the above regression equation, the recovery data for BSM spiked into the tap water, soil, and soybean were presented in Table II. The recoveries were 92.4% for tap water, 84.6% for soil, and 73.7% for soybean with good reproducibility. For being a UV-based method, the results demonstrate the broad applicability of the IPSB for extraction of BSM in real samples, and this method has highly sensitive and selective for the determination of BSM compared to other methods.[5,21,22]

Finally, it is important to stress that the same IPSB can be reused without losing its extraction ability. The IPSB was used for 150 times for extraction of 0.50 μM BSM in an aqueous sample and the recovery of the average of all 150 measurements and precision of the first result obtained are 91.6% and 2.1%, respectively.

CONCLUSIONS

In this study, a molecularly imprinted stir bar for selective trace-enrichment of BSM was prepared. The imprinted stir bar not only exhibited high affinity for the template molecule BSM in aqueous samples, but also had the flexibility and simplicity of stir bar sorption extraction. The highly sensitive detection method developed by coupling to HPLC-UV was successfully applied to the analysis of BSM in tap water, soil, and soybean samples and provided good recoveries and reproducibility. The molecularly imprinted stir bar could be reused more than 150 times for extraction of BSM in aqueous samples without losing its extraction efficiency. The optimized methodology is promising for the determination of BSM in other samples.

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