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Mixed functional monomers-based monolithic adsorbent for the effective extraction of sulfonylurea herbicides in water and soil samples



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ABSTRACT

Effective extraction is a key step in the determination of sulfonylurea herbicides (SUHs) in complicated samples. According to the chemical properties of SUHs, a new monolithic adsorbent utilizing acrylamidophenylboronic acid and vinylimidazole as mixed functional monomers was synthesized. The new adsorbent was employed as the extraction phase of multiple monolithic fiber solid-phase microextraction (MMF-SPME) of SUHs, and the extracted SUHs were determined by high-performance liquid chromatography with diode array detection (HPLC-DAD). Results well evidence that the prepared adsorbent could extract SUHs in environmental waters and soil effectively through multiply interactions such as boronate affinity, dipole-dipole and π - π interactions. Under the optimized extraction conditions, the limits of detection for target SUHs in environmental water and soil samples were 0.018–0.17 $\mu\text{g/L}$ and 0.14–1.23 $\mu\text{g/kg}$, respectively. At the same time, the developed method also displayed some analytical merits including wide linear dynamic ranges, good method reproducibility, satisfactory sensitivity and low consume of organic solvent. Finally, the developed were successfully applied to monitor trace SUHs in environmental water and soil samples. The recoveries at three fortified concentrations were in the range of 70.6–119% with RSD below 11% in all cases. The obtained results well demonstrate the excellent practical applicability of the developed MMF-SPME-HPLC-DAD method for the monitoring of SUHs in water and soil samples.

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1. Introduction

Sulfonylurea herbicides (SUHs) are a class compounds which composed of a sulfonyl structure linked to a urea group. Since the introduction by Dupont Corporation in 1982, SUHs have been widely applied to control the road leaf weeds and some grasses in agriculture [1,2]. However, the SUHs may be released into environmental waters and field soils during the application procedure. Residual SUHs have been found in environmental waters and soils [3,4]. Studies have verified that residual SUHs have phytotoxicity towards sensitive crops [5] and potential impact on aquatic ecosystems [6,7]. Therefore, there is an urgent need to develop sensitive

and reliable analytical method for the monitoring of SUHs residues in environmental waters and soils.

Because of the simplicity and high performance in qualitative and quantitative, high-performance liquid chromatography with diode array detection (HPLC-DAD) or mass spectrometry (HPLC-MS) has become the popular technology to separate and detect SUHs. However, the concentrations of SUHs existed in waters and soils are usually at trace level. To enrich the analytes and reduce the interferences of sample matrices, appropriate sample pretreatment should be performed before chromatographic separation and detection. So far, adsorbent-based extraction (ABE) and solvent-based extraction (SBE) methods have been developed to analyze SUHs in various samples [8,9]. Compared to SBE, ABE is more attractive because less organic solvent is demanded. Some ABE methods such as solid phase extraction (SPE) [10,11], dispersive solid-phase extraction (DSPE) [12] and magnetic solid-phase extraction (MSPE) [13,14] have been utilized to extract SUHs from all kinds of complicated samples. However, these methods still suffer from some disadvantages such as laborious extraction and

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cleanup steps, consume of substantial organic solvent, low extraction capacity and unsatisfactory reproducibility. Hereby, efforts still should be paid to develop sample preparation method with simple operation, high extraction performance and environmental friendliness for the monitoring of SUHs.

Recently, a new extraction format, namely, multiple monolithic fiber solid-phase microextraction (MMF-SPME) was developed in our group [15,16]. MMF-SPME shares the extraction principle of conventional solid-phase microextraction (SPME). However, MMF-SPME utilizes four thin monolithic fibers as extraction phase (adsorbent). Thus, the MMF-SPME possesses higher extraction capacity than SPME. In addition, MMF-SPME employs porous monoliths as extraction media. There are many attractive features for monolithic materials, including simplicity of preparation, fast mass-transfer, low cost and abundant raw materials. It is noteworthy that the monolith-based adsorbents can be designed and fabricated according to the properties of target analytes. In our previous works, a series of monolith-based adsorbents were designed and synthesized according to the characteristics of target analytes such as fluoroquinolones [17], fluorobenzenes [18] and nitrophenols [19]. Although some monolith-based adsorbents have been synthesized, the extraction performance of these adsorbents for SUHs is not as good as expected. Hereby, to extract SUHs effectively, new extraction media should be designed and synthesized. In the present work, six SUHs including triflurosulfuron-methyl (TRM), thifensulfuron-methyl (THM), metsulfuron methyl (MEM), chlor-sulfuron (CHS), prosulfuron (PRS) and halosulfuron methyl (HAM) were selected as target analytes. It can be clearly seen from their molecular structures that there are ample urea, sulfonyl and phenyl groups (Supplementary material, Table S1). To extract these compounds effectively, there should be multi-interactions between the adsorbent and analytes. For this purpose, acrylamidophenylboronic acid (ABA) and vinylimidazole (VI) were used as mixed functional monomers to in-situ co-polymerize with divinylbenzene (DB)/ethylenedimethacrylate (ED) to fabricate the monolithic adsorbent. In the prepared adsorbent, the boronic acid, imidazole and phenyl groups can produce B-N coordination, dipole-dipole and π - π interactions with target SUHs, respectively. Therefore, it is reasonable to believe that the proposed MMF-SPME can enrich SUHs effectively. To the best of our knowledge, this is the first time to utilize MMF-SPME to extract SUHs. After optimizing the extraction factors, MMF-SPME was combined with HPLC-DAD to direct monitor trace SUHs in environmental water and soil samples

2. Experimental

2.1. Chemicals and materials

ABA (98%) was purchased from SuKaiLu Chemical Co. LTD (Suzhou, China). VI (99%), DB (80%) and ED (98%) were supplied by Alfa Aesar Ltd. (Tianjin, China). Initiator azobisisobutyronitrile (AIBN) (97%), dimethyl sulfoxide (DMSO) (98%) were purchased from Shanghai Chemical Co. (China). Acetonitrile (ACN) and methanol were HPLC-grade and they were purchased from Tedia Company (Fairfield, USA). Ultrapure water (18.2 M Ω cm) was obtained using a Milli-Q Reference water-purification system (Merck Millipore, Germany). The purity of reference standards of TRM, THM, MEM, CHS, PRS and HAM is above 99% and they were bought from Testing Center of the Shanghai Pesticide Research Institute (China). The molecular structures and chemical properties of these SUHs are listed in Table S1. The stock solution of each analyte was prepared at 100.0 mg/L in methanol and stored at 4 °C in dark. Working standard solutions were prepared by appropriate dilution of stock solutions with methanol. The other reagents used in this work are analytical reagent.

Environmental water samples including river, lake and well waters were collected from Jiulong river in Zhangzhou city, Xiang'an campus of Xaimen University and Xiang'an district of Xiamen city, respectively. Two soil samples were obtained by quincunx sampling from farmland and a grove in Xiang'an district of Xiamen city and Xiang'an campus of Xaimen University, respectively.

2.2. Apparatus and analytical conditions

Chromatographic analysis of SUHs was performed on a HPLC system (Shimadzu, Japan) consisting of a binary pump (LC-20AB) and a DAD (SPD-M20A). Sample injection was carried out using an auto sample injector (SIL-20A). Chromatographic separations were performed on a Kromasil C18 column (250 mm \times 4.6 mm i.d., 5.0 μ m) which was purchased from FLM Scientific Instrument Co. Ltd (Guangzhou, China). A binary mobile phase composed of phosphoric acid aqueous (0.4% v/v) (solvent A) and ACN (solvent B) was used as optimal mobile phase to separate target SUHs. The gradient elution program was as follows: 0.0–5.0 min = 30% B, 5.0–10.0 min = 30% B–55% B, 10.0–13.0 min = 55% B–60% B and kept to 15.0 min, 15.0–18.0 min = 60% B–90% B, 18.0–23.0 min = 90% B–30%B and kept to 28.0 min. The detector wavelength, flow rate and injection volume were 230 nm, 1.0 mL/min and was 20 μ L, respectively. Under above-mentioned conditions, all target SUHs were well resolved from each other.

Characterizations of prepared adsorbent were conducted on elemental analysis (EA, PerkinElmer-Model PE 2400, Shelton, CT, USA), Fourier transform infrared spectrum (FT-IR, Avatar-360, Thermo Nicolet, Madison, WI, USA). Model XL30 scanning electron microscopy (SEM, Philips, Eindhoven, The Netherlands) was employed to investigate the morphology. The pore size distribution (PSD) of the adsorbent was checked on a mercury intrusion porosimeter (MIP) Model PoreMaster-60 (Quantachrome Instruments, Florida, USA).

2.3. Synthesis of MMF-SPME

To obtain the MMF-SPME, single thin poly (ABA/VI-co-DB/ED) monolithic fibers were synthesized in the first step. In present study, in-situ polymerization technique of monolith was utilized to prepare the monolithic fibers. ABA and VI were used as mixed functional monomers, and the mixture of DB and ED (w/w = 1/2), DMSO and AIBN (1% (w/w) of the total amount) were used as cross-linker, porogenic solvent and initiator, respectively. To obtain the expected extraction performance and life-span, different concentration of monomer, cross-linker and porogenic solvent in polymerization solution were used to prepare the monolithic fibers (Table 1). ABA/VI, DB/ED, DMSO and AIBN were weighed accurately and mixed ultrasonically into a homogenous solution, and then high purity nitrogen was used to remove the air in the polymerization solution for 5 min. After that, the solution was infused into a glass capillary (0.5 mm in diameter and 10.0 cm in length) with a syringe. After the infusion, using silicon rubbers to seal the both ends of capillary, and the filled glass capillary was placed in an oven for polymerization at 70 °C for 12 h. When the polymerization reaction was finished, using a cutter of capillary to remove 2.0 cm length of glass capillary carefully, and white, elastic and thin monolithic fiber (0.5 mm in diameter) could be obtained. In the following step, parafilm was utilized to tie up four thin monolithic fibers at the glass part of fibers to form the MMF-SPME. The residual monomers, porogenic solvent and uncross-linked compounds in the monolith were removed by dipping the MMF-SPME in methanol or ACN for 24 h. After that, the monolithic fibers were dried in air for 0.5 h to obtain the final MMF-SPME. The polymerization sketch of poly (ABA/VI-co-DB/ED) monolith is showed in Fig. 1. It can be seen from the above description that the preparation of MMF-SPME is quite con-

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