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Graphene reinforced multiple monolithic fiber solid-phase microextraction of phenoxyacetic acid herbicides in complex samples

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ABSTRACT

To increase the specific surface area (SSA) of monolith-based adsorbent for the extraction of phenoxyacetic acid herbicides (PAAs) in complex samples, graphene was embedded in an adsorbent based on poly (4-vinylpyridine-*co*-ethylene glycol dimethacrylate) monolith (GEM). The new adsorbent was employed as extraction phase of multiple monolithic fiber solid-phase microextraction (MMF-SPME). The influences of preparation conditions and extraction parameters on the enrichment performance of GEM/MMF-SPME for PAAs were investigated in detail. Results well indicated that the embedded graphene could obviously enhance the SSA of the adsorbent and introduce π-π electrostatic stacking groups. The prepared GEM/MMF-SPME could extract PAAs effectively by means of π-π electrostatic stacking, hydrophobic, ion-exchange and hydrogen bonding interactions. Under the most favorable conditions, a convenient, sensitive, cost-effective and environmentally friendly method for the determination of trace PAAs in water and rice samples was developed by the combination of GEM/MMF-SPME and high performance liquid chromatography-diode array detection (HPLC-DAD). Results showed that for water sample, the limits of detection (LOD, S/N = 3) and limit of quantification (LOQ, S/N = 10) values were in the range of 0.093–0.12 μg/L and 0.31–0.41 μg/L, respectively. The corresponding values in rice sample were 0.36–0.66 μg/kg and 1.18–2.27 μg/kg, respectively. The proposed method was successfully applied to quantify trace PAAs in water and rice samples. Recoveries achieved for water and rice samples at different spiked concentrations were in the ranges of 70.0–118% and 70.0–117%, respectively. The RSDs varied from 0.3% to 10% for all analytes. The results well revealed the potential application of GEM/MMF-SPME as an effective sample preparation processes for the monitoring of PAAs in water, rice and other complex samples.

1. Introduction

Phenoxyacetic acid herbicides (PAAs) are widely applied to control the growth of broad-leaf weeds in corn, tobacco and other crops [1,2]. However, due to their strong polarity, nature persistence and high water solubility, PAAs are present in various environmental waters such as river, lake and wastewaters [3–5]. Furthermore, the PAAs may be absorbed by the leaves and roots during application, and then concentrated in the meristematic regions. Finally, the PAAs will remain in the fruits such as rice and soybean [6,7]. Studies have evidenced that residual PAAs can cause uncontrolled growth of meristematae and restrain both DNA and protein synthesis [8,9]. To protect human's safety, the maximum residue levels (MRLs) of PAAs in water and grain have been regulated in several organizations and countries [10,11]. For example, the Chinese Ministry of Health has regulated that the MRL for 2,4-dichlorophenoxyacetic acid (DCPA) in drinking water was 30 μg/L [10]. The 0.1 mg/kg MRL for DCPA in rice was set by the European Commission [11]. Herein, developing sensitive and robust method for the monitoring of trace-level PAAs in water and rice is highly desired.

So far, chromatographic methods including high performance liquid chromatography (HPLC) [12,13] and gas chromatography (GC) [14,15] have become the preferred methods to analyze PAAs. For GC, additional inconvenient derivatization step of PAAs should be carried out, while the related step is unnecessary in HPLC. Considering the complexity of sample matrices and the low concentrations of PAAs in real samples, appropriate sample preparation is necessary before chromatographic analysis. The most frequent technologies used for the sample preparation of PAAs in complex samples are liquid-liquid extraction (LLE) [16], solid-phase extraction (SPE) [17,18], solid phase microextraction (SPME) [19] and quick, easy, cheap, effective, rugged and

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safe method (QuEChERS) [7,20]. However, the LLE requires a large amount of sample and organic solvent. For SPE and QuEChERS, several procedures are involved in the whole operation process. Low extraction capacity and high cost of extraction fibers limit the wide application of SPME. Therefore, there is an urgent need to develop new sample pretreatment with convenient operation, satisfactory extraction capacity, cost-effectiveness and eco-friendliness, for the monitoring of trace PAAs.

Multiply monolithic fiber solid-phase microextraction (MMF-SPME) is a new extraction format which was developed in our group [21,22]. MMF-SPME shares the same extraction principle as the conventional SPME, but MMF-SPME possesses higher extraction capacity because more adsorbents can be utilized. Furthermore, MMF-SPME utilizes porous monolith as extraction phase, as a result, it displays some advantages such as easy synthesis, various chemical properties, fast mass-transfer and environmental friendliness. Based on these advantages, MMF-SPME is an ideal sample preparation method for the analysis of PAAs. In our previous studies, several MMF-SPMEs based on different kinds of monoliths have been prepared [21–24]. However, when these MMF-SPMEs were applied to extract PAAs, the extraction performance was not as high as expected. The reason may be that the functional groups in these monoliths can't produce suitable interactions with PAAs. At the same time, the typical specific surface areas (SSA) of monoliths-based adsorbents are only dozens of m^2/g, resulting in insufficient sorptive sites to extract PAAs. Hereby, to utilize MMF-SPME to extract PAAs effectively, new monolithic fibers with abundant functional groups and large SSA should be prepared.

In this work, five PAAs including phenoxyacetic acid (POA), 4-chloro-2-methylphenoxyacetic acid (CMPA), DCPA, 2-nitrophenoxyacetic acid (NPA) and 4-chlorophenoxyacetic acid (CPA) were selected as target analytes. Based on the principle of "like dissolves like", 4-vinylpyridine (VP) was used as functional monomer to copolymerize with ethylene glycol dimethacrylate (ED) to prepare the monolithic fiber. Furthermore, to increase the SSA of monolith and introduce π groups, graphene which contains extra high SSA and π-π electrostatic stacking properties was embedded in the monolith by addition of suitable amount of graphene in the polymerization solution. The prepared graphene embedded monolith (GEM) was used as the extraction phase of MMF-SPME. Because there are large SSA and abundant active groups in the GEM/MMF-SPME, therefore, the proposed GEM/MMF-SPME can enrich target PAAs effectively. Under the optimized conditions, the GEM/MMF-SPME was combined with HPLC with diode array detection (DAD) for the sensitive and robust monitoring of PAAs in rice and environmental water samples.

2. Experimental

2.1. Chemical reagents

VP (95%), ED (98%) and graphene were obtained from Aladdin Chemical Co. (Shanghai, China), Alfa Aesar Ltd. (Tianjin, China) and TCI Shanghai Co. (China), respectively. Azobisisobutyronitrile (AIBN, 97%), 1-propanol (97%), 1,4-butanediol (98%) and trifluoroacetic acid (98%, TFA) were supplied by Shanghai Chemical Co. (China). Chromatographic grade acetonitrile (ACN) and methanol were purchased from Tedia Company (Fairfield, USA). Milli-Q water-purification system (Millipore, USA) was utilized to purify water used throughout the study. Five target PAAs including POA (98%), DCPA (97%), CMPA (98%), NPA (98%) and CPA (99%) were bought from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Table S1 shows the related chemical properties of the target PAAs. Stock standards solutions of each PAA were prepared in methanol at a concentration of 100.0 mg/L and stored at 4 °C. Ultra-pure water was used to dilute the stocks to the required working solutions of PAAs.

Environmental water samples including river, lake and wastewaters were collected from Jiulong river in Zhangzhou city, Furong lake in Simin campus of Xiamen University and influent of sewage treatment plant in Xiang'an campus of Xiamen University, respectively. Three rice samples were obtained from a local market.

2.2. Instruments and analytical conditions

The HPLC analyses of target PAAs were carried out on a LC chromatographic system (Shimadzu, Japan) equipped with a binary pump (LC-20AB) and a diode array detector (SPD-M20A). Sample injection was conducted with a RE3725i automatic sample injector coupled with a 20 μL loop (Rheodyne, Cotati, CA, USA). The chromatographic separation of PAAs was achieved on a reversed phase Hypersil C18 column (250 mm × 4.6 mm i.d., 5 μm particle size). The mobile phase consisted of 0.1% (v/v) phosphoric acid aqueous (solvent A) and ACN/methanol (2/3, v/v) (solvent B). Isocratic elution mode was utilized to achieve the separation of PAAs. The ratio of solvent A to solvent B was kept at 55/45 (v/v), the flow rate and detection wavelength were 1.0 mL/min and 200 nm, respectively.

The prepared GEM was characterized by Fourier transform infrared spectroscopy (FT-IR) (Avatar-360, Thermo Nicolet, Madison, WI, USA); scanning electron microscopy (SEM) (Philips, Eindhoven, the Netherlands) and transmission electron microscopy (TEM) (JEOL 2011 microscope, Japan).

2.3. Preparation of GEM/MMF-SPME

Two simple steps are involved in the preparation of GEM/MMF-SPME. In the first step, thin monolithic fibers were synthesized according to the *in-situ* polymerization of porous monolith. In this study, VP, ED, the mixture of 1-propanol/1,4-butanediol (2/3, v/v) and AIBN were used as functional monomer, cross-linker, porogenic solvent and initiator, respectively. For the increase of the SSA of the monolith, graphene was added in the polymerization solution to synthesize the GEM. The effect of the additional amount of graphene on the extraction performance was investigated in detailed (Table 1). Typically, 4.0 mg AIBN, 47.5 mg VP, 47.5 mg ED, 40 mg 1-propanol, 60 mg 1,4-butanediol and 5.0 mg graphene were weighed accurately and put into a beaker. Under the ultrasonication for 10 min, the mixture became a

Table 1
The extraction performance of different GEM/MMF-SPME for PCAs.

GEMs	Monomer mixture			Polymerization mixture		Peak area				
	VP (%, w/w)	ED (%, w/w)	Graphene (%, w/w)	Monomer mixture (%, w/w)	Porogenic solvent (%, w/w)	NPA	POA	CPA	DCPA	CMPA
1	50	50	0	50	50	199,336	200,962	299,471	549,179	567,620
2	47.5	47.5	5	50	50	256,755	272,255	414,263	714,633	764,739
3	45	45	10	50	50	243,209	224,916	339,088	605,159	637,939
4	42.5	42.5	15	50	50	251,307	168,623	246,862	434,732	462,721
5	40	40	20	50	50	220,910	181,277	240,108	411,187	447,174
6	37.5	37.5	25	50	50	162,515	118,999	159,378	316,200	316,694