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Preparation and applications of perfluorinated ion doped polyaniline based solid-phase microextraction fiber

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ABSTRACT

A perfluorooctanesulfonic acid-doped polyaniline (PFOS-doped PANI) directly electrodeposited onto stainless steel was employed as a solid-phase microextraction (SPME) fiber. Commercial SPME fibers were chosen to compare with the PFOS-doped PANI through extraction of phenols and polybrominated diphenyl ethers (PBDEs). Excellent extraction efficiency of this fiber was demonstrated, indicating its good affinity for both non-/less polar and polar compounds. To achieve maximum response, influential parameters affecting the extraction efficiency were optimized by full-factorial experimental designs. Under the optimized conditions, the analytical features for PBDEs were estimated. The calibration curve was linear approximately 3 orders of magnitude for the target analytes, with linear correlation coefficients greater than 0.99. Detection limits in the range of 0.1–0.2 ng/L were obtained. Repeatability ($n = 5$) was in the range of 4.5–8.3%. The results suggest that the proposed fiber can be applied for the determination of trace PBDEs in environmental water and expected to be extended to other analytes and matrices.

1. Introduction

Solid-phase microextraction (SPME), introduced by Arthur and Pawliszyn in 1990 [1], has been widely applied in many areas. For SPME approach, the crucial part lies in the extraction phase coatings. There are several commercial polymeric coatings available aiming at different analytes. However, some of their limitations have been pointed out in many literatures [2–4] Thus, fabrication of new material for fibers was one of the most important research hotspots during SPME development. For determination of environmental samples, it is very important to obtain high sensitivity. Generally, a thick film is necessary to obtain high extraction ability and consequent high sensitivity. However, the thicker coatings slow down the mass transfer during extraction and desorption procedure, which means longer extraction time and possible carryover effect. In addition, it is difficult to prepare thick and stable coatings. Up to now, the polymer coatings on silica fibers are less than 100 μm (i.e. 100 μm PDMS), which is the most popular fiber in application to environmental matrix. Thus, stable substrates coated with thin coatings with high extraction efficiency are desired.

Among the home made fibers, conductive polymer attracts much attention because of the following inherent properties: (1) using metal wires as substrates which have good mechanical strength, (2) electrochemical deposition applied to synthesize the conductive polymer is easily controllable and reproducible, (3) the coatings with diverse characteristics can be achieved by incorporation of functional counter ions, utilization of derivate monomers, etc. The popular conductive polymers used as SPME candidates include polyaniline, polypyrrole, polythiophene and their derivates. However, there are also some problems to restrict their developments. Scarce reports [5] were available about polythiophene based SPME fiber, which might be due to its poor extraction ability [6]. Polypyrrole and polyaniline were limited by their low thermal stability, i.e. 200 °C for polypyrrole [7] and 220 °C for common PANI [8]. In addition, their extraction efficiency for non-/less polar compounds is relatively low [9,10]. Thus, several methods were proposed to enhance their performance, such as introducing functional group [11,12], mixing with multiwalled carbon nanotubes [13] and nano-structured PANI [14].

In order to improve the application of conductive polymer as the SPME fibers, our group introduced a tri fluoroacetic acid-doped PANI fiber for solid-phase microextraction [6]. The extraction capacity of this coating was much greater than commonly used polyaniline (sulfuric acid-doped PANI) and polythiophene based SPME fibers, and comparable to commercial 30 μm PDMS fiber but with thinner stationary and enhanced thermal stability. Fluorine element in this fiber was thought to play an important role in the explanation of its good performance. In our following studies [15], we found that increasing the thickness of the coatings could improve the extraction efficiency to some extent, but there was no

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obvious improvement. To further increase the extraction efficiency and testify the role of fluorine element, according to recent reports [16], a perfluorinated acid will be introduced to the PANI backbone and applied as the SPME fiber in this study. It is reported that the perfluorooctanesulfonic acid-doped PANI (PFOS-doped PANI) shows superhydrophobic characteristic [16], with a water contact angle of 153°, which makes it might be an ideal candidate as SPME stationary to determine organic compounds in combination with gas chromatography (GC).

Herein, PFOS-doped PANI was pioneered application as SPME coatings. Its performance was evaluated by extraction of non-/less polar and polar compounds, i.e. polybrominated diphenyl ethers (PBDEs) and phenols. The extraction performance was also compared to corresponding commercial SPME fibers. The influential extraction parameters of PFOS-doped PANI including extraction mode, extraction temperature, salt content and pH were optimized by full factor design to obtain the highest extraction efficiency for PBDEs and phenols. Then, the method was applied to determine the real samples.

2. Experimental methods

2.1. Reagents and materials

The reagents used for the PFOS-doped PANI synthesis were: aniline (≥99.8%) was purchased from Acros (New Jersey, America), tetraethylammonium perfluorooctanesulfonate (TEAPFOS, Aldrich, America) and perfluorooctanesulfonic acid (PFOS, TCI, Japan) were used as received. Acetone and acetonitrile of HPLC grade were obtained from Merk (Darmstadt, Germany). Sodium chloride and sulfuric acid (analytical grade), used for the modification of the ionic strength and pH of samples, were of analytical grade and obtained from Shanghai Chemical Company (Shanghai, China). Distilled water was produced by use of a Milli-Q nanopure water system (Milli-Q system, Millipore, Beldford, MA).

Phenol standards (2000 μg/mL for each compound) in dichloromethane, including 4-chloro-3-methylphenol, 2,4-dichlorophenol, 2-nitrophenol, pentachlorophenol and 2,4,6-trichlorophenol were obtained from AccuStandard, Inc. (NewHaven, CT, USA). PBDEs, 50 mg/L for each analytes in isooctane: toluene (v:v = 8:2), containing BDE-28, BDE-47, BDE-100, BDE-99, BDE-154 and BDE-153 was also obtained from AccuStandard, Inc. (NewHaven, CT, USA).

2.2. Apparatus

A CHI 650A Electrochemical Workstation from CH Instrument (TX, USA) was employed for preparation of SPME fibers. A 6890N gas chromatography equipped with split/splitless inlet and μECD/FID (Agilent Technologies, USA) was used in the experiments. A DB-5 capillary column (30 m × 0.32 mm i.d., 0.25 μm film thickness) was used for separation. Commercial SPME fiber holder for manual use and fiber assembly for manual sampling were obtained from Supelco (Bellefonte, PA, USA). 100 μm polydimethylsiloxane (PDMS), 65 μm PDMS/DVB and 85 μm polyacrylate (PA) fibers were chosen for comparison. All fibers were conditioned according to the instructions provided by the manufacturer. A heating magnetic stirrer (Jingfeng Instrument Co. Ltd., Shanghai, China) was used to heat and stir the samples during SPME procedure. Spinbar (10 mm × 3 mm) was purchased from Sigma–Aldrich (St. Louis, MO, USA).

2.3. Chromatographic conditions

For PBDEs, μECD was employed and the carrier gas was helium with a flow rate of 1.5 mL/min. The detector temperature was set at 300 °C with N_2 as make-up gas at the flow rate of 60 mL/min. Chromatographic separation was accomplished with a DB-XLB column (15 m × 0.25 mm × 0.25 μm). Oven temperature program for PBDEs: started at 140 °C, held for 2 min, then up to 200 °C at 20 °C/min, to 260 °C at 6 °C/min and finally to 300 °C at 12 °C/min and held for 5 min.

For phenols, FID was employed and the carrier gas was N_2 with a flow rate of 1.8 mL/min. The detector was maintained at 300 °C with 25 mL/min for N_2 (make-up gas), 400 mL/min for air and 30 mL/min for H_2. A DB-5 capillary column (30 m × 0.32 mm × 0.25 μm) was used for separation. The oven temperature was as following: 40 °C held for 3 min, then up to 140 °C at 8 °C/min and finally to 280 °C at 15 °C/min. The injectors were maintained between 250 °C and 310 °C, depending on the desorption temperature used. The fiber desorption was maintained at injector in splitless mode for 5 min.

2.4. Preparation and characterization of PFOS-doped PANI based SPME coating

The electrochemical polymerization of PFOS-doped and de-doped PFOS PANI was derived from previous report [16] with some modifications. In detail, synthesis was conducted in an electrolytic cell consisting of a saturated calomel reference electrode (SCE), a platinum foil counter electrode and a tip 10 mm segment of the stainless fiber (75 mm length and 350 μm diameter) as working electrode. All the electrodes were polished with alumina slurry and then sonicated in a doubly distilled water bath for 10 min before use. All potentials were referred to a SCE. Chronoamperometry was carried out on a CHI 650A Electrochemical Workstation. The electrolytic solution consisted of 0.1 M aniline, 0.12 M PFOS in acetonitrile–H_2O (v:v = 95:5). Preliminary tests showed that the optimal potential was 1.2 V for polymerization of PFOS-doped PANI. The film thickness used for this experiment was controlled by the charge consumed in the electrolysis, which was 0.5 C in this case. To prepare the de-doped PFOS PANI film, anion-laden film (i.e. PFOS-doped PANI) was subsequently dipped into a solution containing 0.1 M TEAPFOS in acetonitrile under a constant potential of −0.1 V for 10 min. After deposition, the PFOS-doped PANI and de-doped PANI films were washed with methanol and double distilled water several times to remove unwanted compounds and left dry in the air. Then, it was aged in a GC inlet under a gentle stream of N_2. The inlet temperature was initiated at 125 °C for 1 h, then held at 200 °C for 1 h, and finally held at 320 °C for 5 h until clean background was obtained for GC analysis.

Morphology of the PFOS-doped and de-doped PANI films were observed by using a Hitachi S-3400N II scanning electron microscopy (SEM). To study the chemical state of atoms on the polymer surface, EX-250 energy dispersive spectrometer (EDS) (HORIBA, Japan) was employed to semi-quantitative microanalysis of composition of the prepared fibers.

2.5. Solid-phase microextraction procedure

The performance of the PFOS-doped SPME fiber was evaluated through extraction of PBDEs and phenols from aqueous samples. 10 mL water sample was placed into a 15 mL brown glass vial with PTFE-coated septa from Supelco (Bellefonte, PA, USA). 10 μL of 50 μg/L phenols and 50 ng/L PBDEs were spiked respectively to different aqueous solutions to optimize correspondent SPME parameters. The influential parameters to be optimized were extraction mode, extraction temperature and salt content. And the pH was adjusted for phenol but that not for PBDEs because of their absence of protonated forms.

For preliminary comparison of extraction efficiency, the extraction conditions were chosen attending to the properties of the compounds, previous literatures and the experience with this tech-