



A water resistant solid-phase microextraction fiber with high selectivity prepared by a metal organic framework with perfluorinated pores



Jiajia Niu^a, Zhongyue Li^{b,*}, Huijuan Yang^b, Changwen Ye^a, Chen Chen^a, Dong Li^a, Jun Xu^b, Li Fan^{a,*}

^a Zhengzhou Tobacco Research Institute of China National Tobacco Corporation, Zhengzhou, Henan 450001, China

^b Department of Physics–Chemistry, Henan Polytechnic University, Jiaozuo, Henan 454000, China

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ABSTRACT

A novel solid-phase microextraction (SPME) fiber was fabricated by the construction of fluorinated metal organic frameworks (FMOF) and a polyimide (PI) composite strategy. As an auxiliary material, PI was expected to help FMOF particles form well-knit film on the surface of stainless steel wire and reinforce the coating, and FMOF was expected to afford a special structure to absorb, extract and enrich. Furthermore, it was explored for the headspace SPME (HS-SPME) of six volatile aromatic compounds (VACs) from water samples followed by gas chromatographic (GC) separation with flame ionization detection. Under the optimized conditions, the fiber afforded wide linear ranges (1–1000 $\mu\text{g L}^{-1}$), low detection limits (0.15–0.9 $\mu\text{g L}^{-1}$) and acceptable repeatability (<4.6%) and reproducibility (<7.3%). The FMOF@PI coated fiber not only offered large enhancement factors for benzene (1227) but also exhibited high extraction selectivity for benzene to other benzene homologues, hydrocarbons and phenols; for example, the extraction ratio of benzene to toluene, *n*-hexane and phenol could be as high as 10.2, 64.1 and 32.3, respectively. Moreover, the FMOF@PI-coated fiber afforded good thermal, water and organic solvent stabilities, and a long lifetime (over 200 times). The developed method was successfully applied to the determination of VACs in wastewater samples.

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1. Introduction

Solid-phase microextraction (SPME) is a highly effective solvent-free sample pretreatment and enrichment method [1] and has been widely used in environmental engineering, biology, clinical medicine, the food industry, etc. [2,3]. The sorbent coatings of SPME fibers are the key to effective extraction, so exploring novel SPME coatings is of great significance and interest. A number of custom-made fiber coating materials have been reported, such as organic polymer [4,5], ion liquid [6,7], carbon nanomaterials [8,9], molecular imprinted polymers [10,11] and mesoporous materials [12], but highly sensitive, selective and stable fiber coating is still scanty.

Metal organic frameworks (MOFs) have been considered to be appropriate candidates materials for SPME fiber coatings because of their special properties such as large surface area, good thermal

stability and uniform structure [13]. Owing to their programmable pore structures and pore size, MOFs especially have great potential for preferential adsorption and selective extraction on the basis of the molecular sieve effect [14]. It is very important for SPME technology to selectively extract target analytes in complex real samples. Several SPME fibers with MOF coatings have been developed since MOF-199 film was applied in the SPME field for the first time in 2009 [15–21]. Unfortunately, bad tolerance for ambient moisture has been recognized as a barrier to their practical applications [15,22]. To enhance the moisture resistant MOFs, additional water repellent processing increased the difficulty of preparation [23,24]. Fluorinated metal organic frameworks (FMOFs) are a class of special MOFs whose pore surfaces are fluorine-lined and hydrogen-free that possess a highly hydrophobic character [25]. The perfluorinated inner surface of FMOFs offers not only water or moisture stability but also potential property for enhancing adsorption of hydrophobic volatile organic compounds in the presence of water or moist air [25]. Another technical problem for applying MOFs as SPME fiber coatings is that MOF particles are easy to fall off as a result of inadequate link strength between the coatings

* Corresponding authors.

E-mail addresses: lizhongyue@hpu.edu.cn (Z. Li), fanl@ztri.com.cn (L. Fan).

and the substrate. Recently, Yu and Yan improved the link strength between MOF coating and silica fiber by a chemical-bonded strategy [26]. However, this method could be applicable only to silica fiber whose lifetime must be improved. In contrast, the stainless steel wire substrate has obvious advantages owing to its high strength and toughness. At present, the main preparation methods of MOF coatings on stainless steel wire are as follows: (1) in situ growth and layer by layer deposition method [15,27–29], but weak forces between the MOF coating and stainless steel wire causes that MOF coating to easily fall off; (2) physical adhesion between MOFs and the surface of stainless steel wire by commercial adhesive such as epoxy resin and silicone [30–32], but the components of commercial adhesive are complex and its thermal stability is poor, and interferent could also be released during the SPME process leading affected test results; (3) sol–gel method [33,34], but cumbersome modifications to MOFs are needed to help MOFs participate in the sol–gel reaction authentically. Therefore, the development of novel stable MOF coating preparation methods based on stainless steel wire substrate is still a challenge of great significance.

As a developing research area, MOF composites can overcome the drawbacks, such as low mechanical stability and fine powder of MOFs and offer improved properties. Polyimide (PI) is a polymer of imide monomers that is prepared by condensation reaction of a dianhydride and a diamine [35]. PI is an ideal choice to prepare MOFs@polymer composite owing to its high thermal stability, strong link strength with stainless steel and good film-forming property on the surface of stainless steel wire. However, the relevant research has not been reported.

In this paper, a new composite material that formed rapidly by a combination of Zn-FMOF and PI under high temperature conditions was initially explored as the SPME fiber coating. Zn-FMOF [$\text{Zn}(\text{C}_{17}\text{H}_8\text{F}_6\text{O}_4)$] is the FMOF used here and is constructed by zinc(II) and 4,4'-(hexafluoroisopropylidene) bis(benzoic acid). The large surface area, high hydrophobicity, fluorine-lined channels (6.5 Å), good thermal characteristics, and solvent stability make Zn-FMOF a potential novel sorbent for the SPME of VACs in water [36]. With regard to Zn-FMOF@PI composite, PI was expected to help FMOF particles form well-knit film owing to its good film-formation, and Zn-FMOF was expected to afford a special structure to absorb, enrich and detect VACs. Parameters affecting extraction efficiency, including extraction temperature, extraction time, salt concentration, desorption conditions and agitation speed were optimized for the Zn-FMOF@PI coated fiber. Finally, the developed method was successfully applied to the determination of VACs in wastewater samples.

2. Experimental

2.1. Reagents and materials

Analytical grade zinc nitrate hexahydrate and sodium acetate trihydrate were bought from Aladdin Chemistry Co., Ltd. Analytical grade *N,N'*-dimethylformamide, isopropanol and hydrofluoric acid were bought from Tianjin Weichen Chemical Reagent Technology and Trade Co., Ltd. (Tianjin, China). 4,4'-(hexafluoroisopropylidene) bis(benzoic acid) was bought from Sigma–Aldrich Co., Ltd. 4,4'-Diaminodiphenyl ether (98%) and pyromellitic dianhydride (99.5%) were bought from Beijing J&K Technology Co., Ltd. Benzene (99.5%), *o*-xylene (96%), *m*-xylene(99%) and *p*-xylene (99%) were bought from Alfa Aesar. Toluene (99.8%) was bought from Tianjin Kemiou Chemical Reagent Co., Ltd. (Tianjin, China). Mesitylene (98%), fluorobenzene (99%), chlorobenzene (99%), bromobenzene (99%), iodobenzene (99%), *n*-hexane (99.5%), cyclohexane (99.8%) were bought from Beijing J&K Technology Co., Ltd. Phenol and cresols (99.5%) were bought from Dr. Ehrenstorfer GmbH. Stainless steel

wire (diameter of 0.1 mm) was bought from Shenzhen Kang Hong Metal Products Co., Ltd. (Shenzhen, China). 5 μL microliter syringes were bought from Shanghai Gaoge Industrial and Trading Co., Ltd. (Shanghai, China). The commercially available fibers for comparison including polydimethylsiloxane (PDMS, 100 μm), polyacrylate (PA, 85 μm) and carbowax/polyethylene glycol CW/PEG (60 μm) were purchased from Supelco.

2.2. Instrumentation

Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 Advance X-ray (Cu-K α radiation) diffractometer. The voltage and current were set to be 40 kV and 40 mA, respectively. The measuring 2θ range was from 4° to 40°. The scan speed is 6° min^{-1} . N_2 adsorption and desorption were performed on Quantachrome Autosorb-1C at 77 K. The scanning electron microscope (SEM) images were obtained on a JSM-6010LA (JEOL, Japan). Thermogravimetric analyses (TGA) were performed under N_2 with a heating rate of 5 °C min^{-1} using a TA (USA) DISCOVERY TGA.

All analyses were carried out with gas chromatography (GC) on an Agilent 6890 N system (USA) equipped with a flame ionization detector (FID). An HP-INNOWAX capillary column (30 m \times 0.25 mm i.d. \times 0.25 μm) (Agilent) was used to separate the target analytes. The injector temperature and detector temperature were set as 230 and 250 °C, respectively. The injection was conducted in the splitless mode. Highly pure helium was used as carrier gas at a flow rate of 1.0 mL min^{-1} , and nitrogen was used as a makeup gas at a rate of 25 mL min^{-1} . Hydrogen and air were maintained at flow rates of 40 mL min^{-1} and 400 mL min^{-1} , respectively. The GC–FID column-temperature program was as follows: the initial temperature of 40 °C (held for 3 min) was ramped to 130 °C at a rate of 10 °C min^{-1} (held for 3 min) and then ramped to 200 °C at 20 °C min^{-1} and maintained at this temperature for 3 min (15 min for phenols test).

2.3. Preparation

2.3.1. Synthesis of Zn-FMOF

A mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 4,4'-(hexafluoroisopropylidene) bis(benzoic acid) and CH_3COONa at a stoichiometric ratios of 1:1:1 was added into 60 mL of water/isopropanol (v/v, 9:1) solution and then stirred until well distributed at room temperature. The mixture was transferred into a stainless reaction kettle with Teflon lining and placed at 180 °C for 1 day. Colorless needlelike crystals were obtained. The product was filtered and washed by water, dried at 80 °C, and milled sufficiently.

2.3.2. Synthesis of polyamide acid (PAA) prepolymer solution

2.5 mmol of 4,4'-diaminodiphenyl ether was completely dissolved into 10 mL of anhydrous *N,N'*-dimethylformamide. Equimolar of pyromellitic dianhydride was added into the aforementioned solution slowly under an ice water bath condition while stirring. When the reaction was finished, the product appeared as a yellow viscous solution.

2.3.3. Preparation of the SPME fiber

2.3.3.1. Pretreatment of stainless steel wire. The stainless steel wire was washed in turns by acetone, ethanol and deionized water under a supersonic wave and dried at room temperature. One end (approximately 3 cm in length) of the clean stainless steel wire was treated in hydrofluoric acid for 5 min to generate a rough surface, washed with deionized water and dried in air.

2.3.3.2. Zn-FMOF-coated SPME fiber. Zn-FMOF coating was prepared via a hydrothermal growth method. The preformed Zn-FMOF particles were put into an agate mortar and milled with a pestle, and then 0.2 g of well-milled powers was put to the mixture of

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