Journal of Chromatography A, 1388 (2015) 9–16

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Polydopamine-based immobilization of zeolitic imidazolate framework-8 for in-tube solid-phase microextraction

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ARTICLE INFO

Article history:
Received 15 January 2015
Accepted 3 February 2015
Available online 11 February 2015

Keywords:
Zeolitic imidazolate framework-8
Polydopamine
Polycyclic aromatic hydrocarbons
Solid-phase microextraction
HPLC

ABSTRACT

Zeolitic imidazolate frameworks (ZIFs), a subfamily of metal-organic frameworks (MOFs), have received considerable attention as a novel porous material for sample preparation due to their fascinating structures and unique properties. Here, we developed a novel bio-inspired polydopamine (PDA) method to immobilize ZIFs inside the chemical resistance poly(ether ether ketone) (PEEK) tube for online solid-phase microextraction (SPME). Firstly, PDA layer was assembled inside the PEEK tube. Secondly, attributing to its noncovalent adsorption and covalent reaction ability, PDA could attract and anchor ZIF-8 nutrients onto the inner surface of PEEK tube to promote the nucleation and growth of ZIF-8. The morphology and surface properties of the prepared ZIF-8-PDA-PEEK tube were characterized by scanning electron microscopy and energy dispersive X-ray spectrometry. The ZIF-8-PDA-PEEK tube exhibits excellent extraction efficiency toward six polycyclic aromatic hydrocarbons (PAHs), with enrichment factor from 550 to 734. The developed online SPME–HPLC method shows good linearity (10–5000 pg/mL) and low detection limits (0.5–5 pg/mL) for six PAHs. It also has been used to determine PAHs in environmental samples, with recoveries in the range of 82.5–98.6%.

1. Introduction

Metal-organic frameworks (MOFs) are a new class of hybrid crystalline porous materials that consist of inorganic sub-units and multidirectional organic linker by strong noncovalent or dative bonds [1–4]. These high ordered porous materials possess extended periodic one-dimensional, two-dimensional, and three-dimensional hybrid networks. Due to their fascinating structures and unique properties, MOFs have received remarkable attention. MOFs are considered as one of the most promising materials for catalysis [5], gas storage and adsorption [6], sensor technology [7], imaging and drug delivery [8]. Their unusual properties such as large surface area, good thermal and mechanical stability, uniform nanoscale porosity, tunable cavities, adsorption affinities and multiple interactions have made MOFs as potential candidates for highly efficient separation materials and sorbents [9–13]. Zeolitic imidazolate frameworks (ZIFs), a commonly used subfamily of MOFs, combining highly desirable properties of both zeolites and MOFs, are regarded as novel coating materials have been used in sample preparation [14–17].

Solid-phase microextraction (SPME) is a novel and simple sample pretreatment technique [18,19]. SPME which integrates sampling, extraction, concentration and sample introduction into a single step, was first introduced by Arthur and Pawliszyn [20]. Thereafter, various SPME based on coated fibers, vessels, stirrers and membranes are booming [21,22]. In comparison with traditional solid-phase extraction (SPE) and liquid-liquid extraction, it has the merits of rapidity, simplicity of operation, and low sample and solvent consumption. For coupling of SPME with HPLC, fiber-based SPME has the shortcomings of swelling in solvent, coating stripping, and low capacities in early time which limit its application [23]. To address these problems, in-tube SPME, a novel microextraction technique with the extraction medium in micro-tube was introduced. Fused-silica capillaries have been widely used for in-tube SPME because of their abundant active silanol groups which can be further modified to form coating material [24,25]. However, the silica capillaries are fragile and easily broken down. The ends of the capillary are also easily crushed when connected to the HPLC system. Poly(ether ether ketone) (PEEK) tube with high-pressure resistance, good flexibility, especially commonly used as HPLC pipelines, is a good alternative for in-tube SPME material.

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http://dx.doi.org/10.1016/j.chroma.2015.02.010
0021-9673/

They are convenient to couple with HPLC because of the ready-made interfaces and connectors. However, due to its high chemical resistance, it is difficult to immobilize sorbents such as ZIFs on the inner-wall of PEEK tubes. To our knowledge, no work has been reported for immobilization of ZIFs onto chemically resistant microtubes for online SPME.

Inspired from the highly bio-adhesive ability of mussel, a polydopamine (PDA)-based surface modification method has been developed by Messersmith's group [26,27]. Polydopamine and its derivatives, which can be modified on the surface of various substrates, including inorganic or organic materials, have wide applications in sensor [28], biomedical science [29], water treatment [30] and separation [31]. In our previous works, we have explored the PDA modification method inside the plastic microtubes [23,32] and fused-silica capillaries [33,34], and successfully realized the mobilization of graphene and monolith for microextraction and hydroxyapatite and graphene for separation by capillary electrochromatography. Recently, highly permselective ZIFs molecular sieve membranes were prepared for gas separation by using PDA as a molecular linker to promote the nucleation and crystal growth of the ZIFs membrane layer [35]. Inspired by this ZIFs synthesis route, along with our successful attempts of PDA modification inside microtubes in our previous works, it is also promising to fabricate ZIFs inside PEEK microtubes for microextraction.

In this work, we describe a novel method to prepare ZIFs in chemically resistant plastic microtubes for SPME. Firstly, a PDA layer formed on the inner surface of PEEK microtubes by spontaneous oxidative polymerization of dopamine; then, ZIFs can be grown on the PDA modified PEEK microtubes attributing to noncovalent adsorption and covalent reaction ability between PDA and ZIFs. The merit of this synthesis method is that special linkage groups were not required on the ZIFs to react with the supports. Therefore, various ZIFs can be grown on the PDA modified PEEK microtubes conveniently and can be further used for online SPME. The general morphology and surface properties of the PEEK tube were characterized by scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDS). Extraction efficiency of ZIFs modified microtube was systematically investigated and more than 500-fold enrichment was obtained for polycyclic aromatic hydrocarbons (PAHs). To the best of our knowledge, this is the first time that ZIFs is fabricated on chemically resistant microtubes for sample preparation.

2. Experimental

2.1. Chemicals and instruments

Six polycyclic aromatic hydrocarbons (PAHs) standards including fluoranthene (FLU), pyrene (PYR), benz[a]anthracene (B[a]AN), benzo[a]fluorathene (B[a]FL), benzo[a]pyrene (B[a]PY), and dibenz[a,h]anthracene (D[a,h]AN) and dopamine hydrochloride were purchased from Sigma–Aldrich (MO, USA). Zinc chloride, sodium formate were obtained from Shenshi Chemical Reagent and Instrumental Company (Wuhan, China). 2-Methylimidazole was purchased from Aladdin (Shanghai, China). All above chemicals were of analytical grade. Acetonitrile and methanol were HPLC grade and purchased from Tedia (OH, USA). Deionized water used was purified by a Milli-Q system (MA, USA). Poly(ether ether ketone) (PEEK) tubes (1/16 in. o.d., 250 μm i.d.) were obtained from Haohai Chemical (Wuhan, China).

All the experiments were carried out on a Shimadzu 20 A HPLC system (Tokyo, Japan), equipped with two Shimadzu 20 A pumps, a Shimadzu six-port valve, a house-made modified PTFE tube for SPME, a temperature controlled column compartment, a 10 A fluorescent detector and a syringe pump for sampling (KDs, MA, USA). A C18 column (250 mm × 4.6 mm i.d.) with 5 μm particle size from GL Science (Tokyo, Japan) was used for chromatographic separation. Data collection was performed on Shimadzu LC Solution software. The detection wavelength was set at 300 nm for exiting wavelength and 440 nm for emission wavelength. The temperature of SPME and HPLC separation was set at 30 °C. Surface characteristics and element analysis of the ZIF-8 modified PEEK microtubes were obtained on scanning electron microscope (SEM) and energy dispersive X-ray spectrometry (EDS) (FEI quanta 200, Netherlands), respectively.

2.2. Sample preparation

Six PAHs standards including FLU (3.0 mg), PYR (3.0 mg), B[a]AN (3.0 mg), B[a]FL (3.0 mg), B[a]PY (3.0 mg) and D[a,h]AN (3.0 mg) were weighed accurately, and dissolved with acetonitrile (5 mL), respectively, to obtain six PAHs standard solution with both concentration of 600 μg/mL. PAHs mixed stock solutions (100 μg/mL) were prepared by mixing equal amount of above solution and were stored at 4 °C in a refrigerator. PAHs stock solutions were diluted to certain concentrations with acetonitrile step-by-step to obtain standard solutions for further use. Sampling solutions for condition optimization of SPME were prepared by 20 μL of PAHs standard solution diluted into 20 mL water containing 400 μL acetonitrile.

Water and soil samples were used to prove the feasibility of this method in real environmental samples. Tap water from our lab including 2% acetonitrile was directly loaded onto the ZIF-8-PDA-PEEK tubes after filtering with 0.22 μm membrane filter. Soil samples were obtained from the side of the road. Then, it was dried at 60 °C in an oven overnight and grounded into small particles. After that, the soil (5.0 g) were weighed accurately and mixed with 30 mL acetonitrile for extraction [23,36,37]. The above solution was sonicated for 3 h and the supernatant was collected after centrifugation (10,000 rpm, 10 min). At last, the supernatant was concentrated by rotary evaporation and redissolved with 1 mL acetonitrile to obtain soil sample solution. 100 μL soil sample solution and 300 μL acetonitrile were diluted into 20 mL with water and loaded for SPME–HPLC.

For recovery test, 20 mL water was spiked 20 μL of 20 μg/mL PAHs standard solution (20 pg six PAHs respectively per mL of water) and 5 g soil sample was spiked 10 μL of 20 μg/mL PAHs standard solution (40 pg six PAHs respectively per gram of soil). The two real samples were preconditioned as above procedures.

2.3. Preparation of ZIF-8-PDA-PEEK tube

The preparation procedure of ZIF-8-PDA-PEEK tube is schematically shown in Fig. 1. Briefly, PEEK tube was washed by methanol, deionized water for several hours and dried by nitrogen stream. Then, 2 mg/mL dopamine hydrochloride solution in 10 mM Tris–HCl buffer was continually injected into the PEEK tube with a syringe pump for 24 h at room temperature, leading to PDA layer being deposited on the inner-wall of PEEK tube. The formation mechanism of PDA was based on oxidation of catechol under alkaline condition and further oxidized and polymerized to form highly cross-linked homopolymer [26,38]. Zinc chloride (0.0538 g), 2-methylimidazole (0.0648 g) and sodium formate (0.0268 g) were weighed accurately and dissolved in 5 mL methanol by ultrasonication to obtain a transparent solution. After that, the PEEK tube was filled with the solution and both ends were sealed; it was then put into the water bath to react for 24 h at 85 °C. Finally, it was taken out of the water bath and washed with methanol to obtain ZIF-8-PDA-PEEK tube.