Polydimethylsiloxane/metal-organic frameworks coated stir bar sorptive extraction coupled to high performance liquid chromatography-ultraviolet detector for the determination of estrogens in environmental water samples

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ABSTRACT

In this work, three kinds of metal-organic frameworks (MOFs), MOF-5, MOF-199 and IRMOF-3, were introduced in stir bar sorptive extraction (SBSE) and novel polydimethylsiloxane (PDMS)/MOFs (including PDMS/MOF-5, PDMS/MOF-199 and PDMS/IRMOF-3) coated stir bars were prepared by sol–gel technique. These PDMS/MOFs coatings were characterized and critically compared for the extraction of seven target estrogens (17-β-estradiol, dienestrol, diethylstilbestrol, estrone, 4-t-octylphenol, bisphenol-A and 17α-ethynylestradiol) by SBSE, and the results showed that PDMS/IRMOF-3 exhibited highest extraction efficiency. Based on the above facts, a novel method of PDMS/IRMOF-3 coating SBSE-high performance liquid chromatography ultraviolet (HPLC-UV) detection was developed for the determination of seven target estrogens in environmental waters. Several parameters affecting extraction of seven target estrogens by SBSE (PDMS/IRMOF-3) including extraction time, stirring rate, pH, ionic strength, desorption solvent and desorption time were investigated. Under the optimal experimental conditions, the limits of detection (LODs, $S/N = 3$) were found to be in the range of 0.15–0.35 μg/L. The linear range was 2–2500 μg/L for 17α-ethynylestradiol and 1–2500 μg/L for other estrogens. The relative standard deviations (RSDs) were in the range of 3.7–9.9% ($n = 8$, $c = 20\,\mu$g/L) and the enrichment factors were from 30.3 to 55.6-fold (theoretical enrichment factor was 100-fold). The proposed method was successfully applied to the analysis of estrogens in environmental water samples, and quantitative recoveries were obtained for the spiking experiments.

1. Introduction

Estrogens, as a group of endocrine-disrupting chemicals, have attracted a great deal of scientific and public attention due to their presence in environmental waters and their high estrogenic activities. Estrogens could enter human body through food chain, and interfere with the normal functions of the endocrine systems. They would interfere with the mineral-, fat-, sugar- and protein-metabolization in human body [1], even cause tumors such as the breast cancer and prostate cancer [2]. Thus, the development of highly sensitive and selective methodologies for determination of estrogens in environmental waters is of great significance for environment safety supervision.

Conventional methods for the determination of estrogens are based on chromatography techniques, such as gas chromatography (GC), high-performance liquid chromatography (HPLC) and capillary electrophoresis (CE). GC is rapid and sensitive, but it often involves a derivatization step to convert the analytes into more volatile derivatives through silylation or acylation [2]. CE has very high separation efficiency, but it lacks stability and sensitivity during the analysis of real-world samples with complicated matrix [3]. HPLC is the most commonly used technique for analysis of estrogens in different samples because it permits direct analysis of estrogens without derivatization and exhibits good reproducibility of which CE analysis is often lacking. However, it is still difficult to directly use HPLC for determination of these contaminants at a very low concentration level in environmental samples with complex matrix. Therefore, a sample pretreatment step prior to HPLC analysis is usually necessary, such as liquid-liquid extraction (LLE) and solid-phase extraction (SPE). Unfortunately, these conventional

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sample pretreatment methods require a large sample volume, and they are tedious and time-consuming. In recent years, several environmental friendly sample pretreatment techniques have been appeared for the determination of estrogens, including liquid phase microextraction (LPME) [4,5], solid phase microextraction (SPME) [6–8] and stir bar sorptive extraction (SBSE) [9–14]. These techniques minimize the use of organic solvents (green chemistry) and analysis time, and improve the sensitivity of the global analytical method.

SBSE was introduced as a novel sample preparation technique in 1999 by Baltussen et al. [15]. Similar to SPME, SBSE is an equilibrium technique, which possesses many merits such as high sensitivity, good reproducibility, but the coating amount on the stir bar is 50–250 times higher than that on SPME fiber, which results in a significant increase in recovery and extraction capacity [16]. In the last decade, SBSE has been successfully applied to the analysis of various analytes in environmental, food and biological samples. However, a drawback of SBSE is that only polydimethylsiloxane (PDMS), ethylene glycol (EG)-silicone and polyacrylate (PA) are the commercially available coatings for stir bar at present, limiting their extraction efficiency toward polar and less polar compounds. Therefore, the need to develop novel stir bar coating materials with a high affinity toward polar or less polar analytes, thus improving the selectivity and widening the applicability of SBSE, is of interest. So far, several SBSE coatings have been applied in the determination of estrogens, including commercial PDMS [9], PDMS/β-cyclodextrin (PDMS/β-CD) [10], PDMS/β-cyclodextrin/divinylbenzene (PDMS/β-CD/DVB) [14], poly (methacrylic acid stearyl ester-ethylene dimethacrylate) and poly (vinylpyridine-ethylene dimethacrylate) monolithic stir bars [11,13]. However, these coatings also have several drawbacks such as slow extraction kinetics and low extraction efficiency for some estrogens.

In recent years, metal-organic frameworks (MOFs) have received extensive attention due to their fascinating structures and intriguing wide range of applications. MOFs are a new class of exotic topologies and porous solid material, which were self-assembled by metal ions and organic ligands [17]. MOFs have been widely applied in hydrogen storage, gas separation, catalysis, sensors and imaging for their unique structure and properties. The large diversity of structure and pore size, high surface area, good adsorption affinity and selective penetration has made MOFs attractive as sorbents [18]. de Carvalho et al. [19] prepared a 2D networks as a SPE adsorbent for the determination of pesticides in plant. Aquino et al. [20] prepared a coordination polymer as matrix solid phase dispersion sorbent for the analysis of pesticides in medical plants. Cui et al. [21] and Swayze et al. [22] employed MOFs as SPME fiber coating for the determination of gaseous benzene homologue and chemical warfare agent, respectively. Huo et al. [23] and Chen et al. [24] selected MOFs as magnetic solid phase extraction (MSPE) and SPME fiber coatings, respectively, for the determination of polycyclic aromatic hydrocarbons. All these works have demonstrated the potential application of MOFs as the high efficient adsorbent in different extraction techniques. However, to the best our knowledge, the application of MOFs as SBSE coating has not been reported yet.

In this work, three kinds of MOFs (MOF-5, MOF-199 and IRMOF-3) were synthesized at room temperature, and novel PDMS/MOFs coatings were prepared with sol–gel technique for the extraction of seven target estrogens in environmental water samples by SBSE. The extraction efficiency of three laboratory-made PDMS/MOFs (PDMS/MOF-5, PDMS/MOF-199 and PDMS/IRMOF-3) coated stir bars for the extraction of seven target estrogens was compared and PDMS/IRMOF-3 coated stir bar was found to be the most efficient. The operation conditions affecting the extraction of seven estrogens by PDMS/IRMOF-3 coated stir bars

were optimized and the analytical performance of the developed method of SBSE (PDMS/IRMOF-3)-HPLC-UV was evaluated. The developed method was applied to the analysis of seven estrogens in the environmental water samples to demonstrate its applicability.

2. Experimental

2.1. Reagents and standards

Hydroxyl-terminated polydimethylsiloxane (OH-PDMS) was purchased from Sigma–Aldrich (Milwaukee, WI, USA). Methyltrimethoxysilane (MTMS) and poly(methylhydrosiloxane) (PMHS) were purchased from the Chemical Plant of Wuhan University (Wuhan, China). Sodium dihydrogen phosphate (NaH_2PO_4), sodium chloride (NaCl), hydrochloric acid (HCl), sodium hydroxide (NaOH), methanol, ethanol, acetonitrile, trifluoroacetic acid (TFA), dichloromethane (CH_2Cl_2), N, N-dimethylformamide (DMF), zinc acetate dehydrate ($Zn(OAc)_2 \cdot 2H_2O$), copper acetate monohydrate ($Cu(OAc) \cdot H_2O$) and terephthalic acid were purchased from China Medicine (group) Chemical Reagent Corporation (Shanghai, China). 2-Amino terephthalic acid was purchased from Alfa Aesar (Tianjing, China), benzenetricarboxylic acid was purchased from Aladdin (Shanghai, China). All solid reagents and solvents used in this study were of analytical grade. High purity water obtained by a Milli-Q water purification system (18.25 MΩ cm, Millipore, Molsheim, France) was used throughout the whole experiments. Commercial stir bars (Twister™) of 20 mm length coated with a 0.5 mm thickness PDMS were purchased from Gerstel GmbH (Mülheim an der Ruhr, Germany).

17-β-Estradiol (E_2), dienestrol (DES) and diethylstilbestrol (DIS) were purchased from J&K Acros Organics (Dr. Ehrenstorfer GmbH, Germany). Estrone (E_1), 4-t-octylphenol (4-t-OP) and bisphenol-A (BPA) were obtained from Aladdin (Shanghai, China). 17α-Ethynylestradiol (EE) was purchased from Sigma–Aldrich (Saint Louis, USA). The chemical structures, log Ko/w and pK_a values of the target estrogens are shown in Fig. 1. Each standard solution of estrogens was prepared in methanol at a concentration of 1 mg/mL, and a mixed standard solution containing 0.1 mg/mL of each estrogen was also prepared in methanol. All standard stock solutions were stored at 4 °C in the refrigerator.

2.2. Instrumentation

An Agilent 1100 series HPLC system (Agilent Technologies, USA) with a variable wavelength UV detector was used for identification and quantification of estrogens. The separation was performed on a reversed phase C_{18} HPLC column (Merck ODS, 5 mm, 4.6 mm × 250 mm, Germany). The gradient elution was performed with methanol (solvent A), acetonitrile (solvent B) and 10 mmol/L NaH_2PO_4 aqueous solution (pH = 3, solvent C). The gradient program was as follows: 0.00–15.00 min, solvent A/solvent B/solvent C (14/43/43, v/v/v); 15.01–21.00 min, solvent A/solvent B/solvent C (45/43/12, v/v/v). The flow rate, injection volume and UV wavelength were 1 mL/min, 50 μL and 230 nm, respectively.

An X-650 scanning electron microscope (HITACHI, Japan) at an acceleration voltage of 30 kV was used for characterization of the morphology and thickness of PDMS/MOFs coated stir bar. An energy dispersive X-ray analysis (HITACHI, Japan) was used for elemental analysis of MOFs. An X' Pert PRO X-ray diffractometer (PANalytcial, Netherland) was used for characterization of MOFs. A 170SX FT-IR (NICOLET, USA) was used for characterization of the structure of PDMS/MOFs coating.