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# Core–shell indium (III) sulfide@metal-organic framework nanocomposite as an adsorbent for the dispersive solid-phase extraction of nitro-polycyclic aromatic hydrocarbons

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ABSTRACT

A core–shell discoid shaped indium (III) sulfide@metal-organic framework (MIL-125(Ti)) nanocomposite was synthesized by a solvothermal method and explored as an adsorbent material for dispersive solid-phase extraction (*d*-SPE). The as-synthesized sorbent was characterized by scanning electron microscopy, energy-dispersive spectroscopy, transmission electron microscopy, powder X-ray diffraction, $N_2$ adsorption–desorption analysis, and Fourier transform infrared spectroscopy. The extraction performance was evaluated by the *d*-SPE of 16 nitro-polycyclic aromatic hydrocarbons (NPAHs) from water samples. The analysis was carried out by gas chromatography (GC) coupled with triple quadruple mass spectrometer in negative chemical ionization (NCI) mode. The selected ion monitoring (SIM) was used in the quantification of the target NPAHs. Extraction factors affecting the *d*-SPE, including the ionic strength, extraction temperature, and extraction time were optimized by the response surface methodology. The developed *d*-SPE method showed good linear correlations from 10 to 1000 ng $L^{-1}$ ($r > 0.99$), low detection limits (2.9–83.0 ng $L^{-1}$), satisfactory repeatability (relative standard deviation of <10%, $n = 6$), and acceptable recoveries (71.3%–112.2%) for water samples. The developed method was used for the food and environmental sample analysis. The results demonstrated that the method could be used for sample preparation of trace NPAHs in real samples.

## 1. Introduction

Persistent organic pollutants (POPs) can accumulate and move through the food chain, and they have long lifetimes. These compounds are known for their high toxicity, carcinogenicity, durability, and bioaccumulation. They have been considered to be a major concern for human health and ecological safety [1,2]. Nitro-polycyclic aromatic hydrocarbons (NPAHs) are a class of derivatives of PAHs, which have one or more nitro groups connected to the benzene ring of PAHs as a substituent [3]. NPAHs mainly come from the incomplete combustion of fossil fuels and biomass pyrolysis [4]. They are commonly found in the atmosphere, water, soil, and food [5–13]. It has been reported that the direct mutagenicity and potential carcinogenicity of NPAHs are higher than those of their related parent PAHs [14].

Metal–organic frameworks (MOFs) have been extensively studied in analytical chemistry in recent years. The unique structural and chemical properties of MOFs meet the demands for various analytical sciences. For instance, they have been explored as the stationary phase of a column for isomer separation in high-performance liquid chromatography (HPLC) [15,16], the coating of capillaries for high-resolution gas chromatography (GC) [17,18], and the porous stationary phase for thin-layer chromatography (TLC) plates [19]. MOFs have also been used as adsorbent materials for the effective extraction of analytes at trace levels from various matrices [20–35]. Typical MOFs, such as MIL-101 [20–22], MIL-53 [23], ZIF-8 [24,25], PCN-222 [26], and UiO-66 [27,28] have been used as sorbents for micro-solid-phase extraction ($\mu$-SPE) [20,25], solid-phase extraction (SPE) [24], solid-phase microextraction (SPME) [23,26], and stir bar sorptive extraction (SBSE) [21].

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The interactions between pristine MOFs and aromatic pollutants are usually weak and physical in nature. Researchers have tried to combine metal/metal oxide nanoparticles with MOFs to improve the adsorption performance of MOFs [36–39]. In the current study, a core–shell discoid shape $In_2S_3$@MIL-125(Ti) nanocomposite was prepared by a solvothermal method and was used as an adsorbent material for dispersive solid-phase extraction (*d*-SPE). Sixteen NPAHs were used as probe analytes to access the extraction behavior and performance. The structures of the selected NPAHs are shown in Table S1. The target analytes in the samples were quantified through gas chromatography coupled with negative chemical ionization mass spectrometry (GC-NCI-MS). The extraction conditions affecting the extraction performance were studied by using a response surface methodology (RSM). Finally, the proposed method was successfully applied to the analysis of NPAHs in food and environmental samples.

## 2. Experimental

### 2.1. Reagents and materials

All reagents used were of analytical grade. 2-Aminoterephthalic acid (99%) ($NH_2$-BDC) was purchased from the Sigma-Aldrich Co., Ltd. N,N-dimethyl formamide (99%) (DMF), thioacetamide (99%) ($CH_3CSNH_2$) and ethanol (99.7%) were obtained from the Sinopharm Chemical Reagent Co., Ltd. Titanium(IV) isopropoxide (99.9%) (TPOP) and indium nitrate hydrate (99.9%) ($In(NO_3)_3{\cdot}xH_2O$) were obtained from the Aladdin Reagent Co., Ltd. Carbon disulfide (99%) ($CS_2$) was obtained from the Tianjin Kermel Chemical Reagent Company, China. Deionized water ($18.2\ M\Omega\ cm^{-1}$) obtained from a Millipore Milli-Q system (Millipore, Bedford, MA, USA) was used to prepare aqueous solutions. Acetonitrile (ACN), methanol, acetone, tetrahydrofuran (THF), *n*-hexane, and dichloromethane (DCM) were purchased from the Tedia Company Inc., USA. 16 NPAHs including Nitronaphthalene (1N-NAP), 2-Nitronaphthalene (2N-NAP), 2-Nitrobiphenyl (2N-BiPh), 3-Nitrobiphenyl (3N-BiPh), 5-Nitroacenaphthene (5N-ACE), 2-Nitrofluorene (2N-FLO), 9-Nitroanthracene (9N-ANT), 9-Nitrophenanthrene (9N-PHE), 3-Nitrophenanthrene (3N-PHE), 2-Nitroanthracene (2N-ACE), 2-Nitrofluoranthene (2N-FLA), 3-Nitrofluoranthene (3N-FLA), 1-Nitropyrene (1N-PYR), 7-Nitrobenz[a]anthracene (7N-BaA), 6-Nitrochrysene (6N-CHR), 6-Nitrobenzo[a]pyrene (6N-BaP), were used as target analytes. The standard mixtures of the selected NPAHs ($10\ \mu g\ mL^{-1}$) in (1:1, v/v) were purchased from AccuStandard (New Haven, CT, USA, www.accustandard.com) and stored in a dark room at 4 °C. A working standard solution ($1.0\ \mu g\ mL^{-1}$ in methanol) was prepared weekly.

### 2.2. Instrumentation

Morphology of the as-obtained materials was characterized using scanning electron microscopy (SEM) (SWPRA$^{TM}$55, Carl Zeiss Micro Imaging Co., Ltd., Germany) and transmission electron microscopy (TEM) (JEM-2010, JEOL Ltd.). Powder X-ray diffraction (PXRD) patterns were acquired at room temperature (298 K) on a Bruker SMART APEX CCD-based diffractometer. The specific surface areas (Brunauer–Emmett–Teller), pore size, and their distributions in materials were measured with an ASAP 2020 porosimeter (Micromeritics, USA). Fourier transform infrared (FTIR) spectra were obtained on a Nicolet Magna 750 FTIR spectrometer. All the experiments were performed by using an Agilent GC system (7890A, Palo Alto, USA) and a triple quadruple (QqQ) mass spectrometer (7001B, Agilent, USA).

### 2.3. Preparation of nanocomposite

#### 2.3.1. Synthesis of MIL-125(Ti)

The MIL-125(Ti) was synthesized through a solvothermal method [40]. Typically, $NH_2$-BDC (0.56 g, 3.1 mmol) was dissolved in a solvent mixture of DMF and methanol (40 mL, $V_{DMF}/V_{methanol} = 9:1$). Then, TPOT (0.6 mL, 2.0 mmol) was directly added into the solution and mixed under ultrasonic conditions for 5 min. Afterwards, the mixture was carefully transferred into a Teflon-lined steel autoclave (100 mL) and heated at 150 °C for 24 h in an oven. The yellow solid products were collected by centrifugation after cooling to room temperature. It was washed several times with DMF and methanol. Finally, the products were dried at 60 °C for several hours.

#### 2.3.2. Synthesis of $In_2S_3$@MIL-125(Ti)

The solid powder MIL-125(Ti) (50 mg) was well-dispersed in ethanol under ultrasonication. Then, $In(NO_3)_3{\cdot}xH_2O$ (0.3 g, 1.0 mmol) and $CS_2$ (2.0 mL) were added to the solution with ultrasonication for 30 min to form a homogeneous mixture of solutions. Subsequently, $CH_3CSNH_2$ (0.075 g, 1.0 mmol) was added. After dissolving completely, the mixture was transferred into a 100 mL Teflon-lined steel autoclave and heated at 150 °C for 12 h in an oven. The solid yellow products were collected by centrifugation and washed with ethanol. The products were dried at 60 °C for several hours. The scheme of the material synthesis is shown in Fig. 1.

### 2.4. Extraction procedure

All extraction experiments were carried out in 50 mL plastic tubes. To conduct extraction, 10 mL of the aqueous sample solution was firstly added into the tube. 1.0 mg of sorbent was subsequently added into the solution. Then, the mixture was ultrasonicated for 10 min to 60 min. After adsorption, the sorbents were collected by centrifugation. After removing the solution, 2 mL of elution solvent was added into the tube for desorption under ultrasonic conditions for a certain time, and the residue was collected after centrifugation. The eluent was collected and dried by using stream of nitrogen at room temperature. The obtained residue was re-dissolved to 100 μL, from which 1.0 μL was used for instrumental analysis.

### 2.5. Real sample preparation

Water samples: Drinking water samples were taken from barreled purified water for daily drinking. Snow water samples were collected from water melted from snow during the winter of January 2017. The water sample was firstly filtered through a 0.45 μm membrane filter and then stored in brown glass bottles at 4 °C. Food samples: The grilled pork and smoked sausages were purchased from a local market and barbecued in a restaurant in Jinan. The meat samples were minced and homogenized, and 2 g samples were accurately weighed and then added to a 50-mL plastic centrifuge tube. The sample was extracted by sonication for 1 h with 10 mL of DCM in an ultrasonic bath. After centrifugation, the supernatant was collected and cleaned by a LC-alumina-NSPE column. The eluent was evaporated to almost dryness and finally dissolved to 10 mL with deionized water to form the homogeneous solution for *d*-SPE use.

### 2.6. GC-NCI-MS analysis

The GC was equipped with a HP-5MS column (5% phenyl-95% methyl-polysiloxane, 30 m long × 0.25 mm diameter × 0.25 μm film thickness). The MS was equipped with a chemical ionization

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