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Magnetic porous carbon derived from a bimetallic metal–organic framework for magnetic solid-phase extraction of organochlorine pesticides from drinking and environmental water samples

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ABSTRACT

In this work, magnetic porous carbon material derived from a bimetallic metal–organic framework was explored as an adsorbent for magnetic solid-phase extraction of organochlorine pesticides (OCPs). The synthesized porous carbon possessed a high specific surface area and magnetization saturation. The OCPs in the samples were quantified using gas chromatography coupled with a triple quadrupole mass spectrometer. The experimental parameters, including the desorption solvent and conditions, amount of adsorbent, extraction time, extraction temperature, and ionic strength of the solution, were optimized. Under optimal conditions, the developed method displayed good linearity ($r > 0.99$) within the concentration range of 2–500 ng L^{-1}. Low limits of detection (0.39–0.70 ng L^{-1}, signal-to-noise ratio = 3:1) and limits of quantification (1.45–2.0 ng L^{-1}, signal-to-noise ratio = 10:1) as well as good precision (relative standard deviation < 10%) were also obtained. The developed method was applied in the analysis of OCPs in drinking and environmental water samples.

1. Introduction

Solid-phase sorption-based extraction techniques, including solid-phase extraction (SPE) [1], solid-phase microextraction (SPME) [2], micro-solid-phase extraction [3], magnetic solid-phase extraction (MSPE) [4], and stir-bar sorptive extraction (SBSE) [5], have been extensively used in sample pretreatment. The sorbent material plays a key role in these extraction techniques. The nature of the sorbents determines their affinity to the target compounds, thereby determining the selectivity of the extraction method [6,7]. To improve the extraction capability, many types of nano-materials have been introduced as adsorbents in extraction techniques [8–15].

Porous carbon materials have attracted considerable interest in analytical science because of their distinct chemical properties and extensive applications as adsorbents for various analytes [16]. The porosity and surface compositions of carbon materials are strongly dependent on the fabrication process, and they can be modified according to the requirement. For example, the surface of bamboo charcoal contains various oxygen-functional groups, such as hydroxyl and carboxyl groups; thus, they can be used to absorb analytes with a wide range of polarities [17,18]. Porous carbon materials can also be fabricated from metal–organic frameworks (MOFs) through facile pyrolysis [19,20]. The well-organized skeleton of MOFs can be converted to porous carbon with uniform heteroatom decoration. Notably, the long-range ordering and high porosity of MOFs can also be partially preserved, rendering carbon as an excellent adsorbent with size selectivity. Recently, the potential usage of MOF-derived carbon as an adsorbent for solid-phase sorption-based extraction techniques has been reported. For example, Co-based magnetic nanoporous carbon has been used as a sorbent for the MSPE of neonicotinoid insecticides, trizine herbicides, and chlorophenols from many sample matrices [21,22]. Magnetic carbon derived from a zeolitic imidazolate framework (ZIF)-67 has also been used as a fiber coating for SPME [24]. ZIF-8-derived magnetic carbon has been tested as a sorbent for the *d*SPE of benzoylurea insecticides [23].

The degree of graphitization and the stability of the MOF-derived carbon are considerably important for their practical application. Among the various ZIFs, ZIF-8 and ZIF-67 are character-

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ized by their low cost and easy fabrication. Unlike ZIF-8, ZIF-67 can provide satisfactory graphitized carbon and good stability. However, ZIF-67 does not possess high surface area, porosity, and N content, whereas ZIF-8 does. It has been reported that the carbon derived from ZIF-8 is in an amorphous state [20]. Therefore, the combination of ZIF-8 and ZIF-67 to form bimetallic ZIFs (BMZIFs) could allow an integration of their structural properties, thereby providing a promising template for carbonization.

Although the production of the majority of organochlorine pesticides (OCPs) has been terminated for many years, their adverse and lasting influence on aquatic biota, wildlife, and human health still exists [25,26]. Routine OCPs analysis methods, such as liquid–liquid extraction or SPE, suffer from large volume organic solvent consumption or time costs. In the present work, a BMZIF comprising ZIF-8 and ZIF-67 was synthesized. The BMZIF-derived porous carbon was used as an adsorbent for the MSPE of OCPs. OCPs analysis was performed by combining gas chromatography with triple quadrupole mass spectrometry (GC-QqQ). The parameters affecting extraction performance were optimized in detail. The method was applied in the OCPs analysis of environmental and drinking water samples.

2. Experimental design

2.1. Reagents and materials

All reagents were of analytical grade. 2-Methylimidazole was obtained from Aladdin Reagent Co., Ltd. (China). Zinc nitrate hexahydrate, cobalt chloride hexahydrate, and ethanol were purchased from Tianjin Kermel Chemical Reagent Company (Tianjin, China). De-ionized water (18.2 MΩ cm^{-1}) obtained from a Millipore Milli-Q system (Millipore, Bedford, MA, USA) was used to prepare aqueous solutions for further experiments. A standard mixture of eight OCPs containing α; β; γ; δ-HCH; p,p′-DDE; p,p′-DDD; o,p′-DDT; and p,p′-DDT at a concentration of 50 μg mL^{-1} in *n*-hexane was purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). These standards were stored in the dark at 4 °C and used for the preparation of standard working solutions. A working standard (200 ng mL^{-1} in methanol) was prepared every week. Dichloromethane (DCM) was obtained from Tedia Company, Inc. (USA).

2.2. Instrumentation

The morphology of the as-synthesized crystals was observed using scanning electron microscopy (SEM) (SWPRATM55, Carl Zeiss Micro Imaging Co., Ltd., Germany) and a transmission electron microscope (TEM) (JEM-2100, JEOL, Ltd., Japan). Powder X-ray diffraction (PXRD) patterns were obtained at room temperature (300 K) on a Bruker SMART APEX CCD-based diffractometer. Thermogravimetric analyses (TGA) were performed under flowing nitrogen at a heating rate of 10 °C min^{-1} on a STA449C integration thermal analyzer (NETZSCH, Germany). The Brunauer–Emmett–Teller specific surface areas of typical products were measured using an ASAP 2020 porosimeter (Micromeritics, USA). Magnetization curves were obtained at room temperature on a MPMS-SQUID-VSM (Quantum Design, USA). An Agilent GC system (7890A, Boston, USA)–triple quadrupole mass spectrometer (7001B, Boston, USA) was used for sample quantification. Sorbent collection from the solution was conducted using an external magnet (Shanghai, China). Vortexing was conducted using the VORTEX-5 machine (Haimen, China). Furthermore, X-ray photoelectron spectroscopy (XPS) spectra were obtained using an XPS Thermo Scientific 250Xi (USA). The size distributions of the MOF-derived carbon material were tested using Malvern Zetasizer Nano ZS90 (Malvern, UK). The zeta potentials of the porous carbon in water were measured using Brookhaven Zeta PALS (Brookhaven, USA).

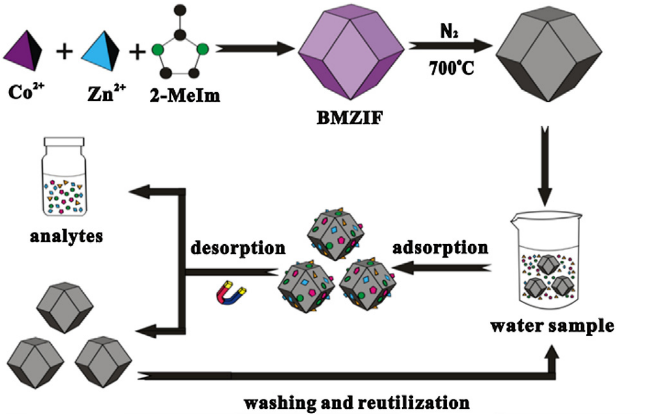

Fig. 1. Schematic diagram for the synthesis of magnetic porous carbon and the magnetic solid-phase extraction procedure.

2.3. Synthesis of porous carbon

The synthesis diagram of porous carbon is shown in Fig. 1. Briefly, zinc nitrate hexahydrate (1.12 g, 3.8 mmol) and cobalt chloride hexahydrate (0.45 g, 1.9 mmol) were dissolved in 80 mL of methanol at room temperature. 2-Methylimidazole (3.70 g, 45.0 mmol) was also dissolved in 80 mL of methanol at room temperature. Subsequently, the two solutions above were mixed together, and approximately 160 mL of bright purple solution was obtained. The solution was stirred for 24 h at room temperature. The product was separated via centrifugation, washed thoroughly for four times with methanol, and dried overnight at 60 °C. The purple powder was carbonized in a tube furnace, which was heated to 700 °C at a heating rate of 4 °C min^{-1} under a N_2 flow (40 mL min^{-1}) atmosphere, and gradually cooled to room temperature. The black powder obtained above was washed thoroughly with ethanol to remove impurities and dried for 3 h at 60 °C. Finally, magnetic porous carbon materials were obtained.

2.4. Procedure of MSPE

All extraction experiments were conducted in 20 mL glass vials. At the beginning of the extraction, 10 mL of samples were added to the vial, and 6.0 mg of porous carbon was added to the aqueous solution. Extraction was conducted on a vortex mixer for 10 min. The adsorbent was collected using an external magnet placed beside the glass vial, and the aqueous solution was removed. The sorbent was then dried under a gentle stream of nitrogen at 40 °C. Approximately 2 mL of DCM was added into the vials as an eluent, and the solution was vortexed for 5 min twice. The magnetic sorbent was collected via magnetic separation, and the collected elute was concentrated by means of a gentle stream of nitrogen at 40 °C. Finally, the obtained extract was diluted with DCM to 100 μL, from which 1 μL was used for the GC–MS/MS analysis.

2.5. GC–MS analysis

GC separation was performed using a fused silica HP-5MS capillary column with a length of 30 m × 0.25 mm and film thickness of 0.25 μm (Agilent Technologies, Inc., USA). The oven temperature was held at 80 °C for 1.0 min and programmed to increase at a rate of 20 °C min^{-1}until 130 °C. Subsequently, the temperature was increased to 250 °C at a rate of 5 °C min^{-1}and finally increased to