Original article

Metal-organic framework derived magnetic nanoporous carbon as an adsorbent for the magnetic solid-phase extraction of chlorophenols from mushroom sample

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A B S T R A C T

In this work, a metal-organic framework derived nanoporous carbon (MOF-5-C) was fabricated and modified with Fe_3O_4 magnetic nanoparticles. The resulting magnetic MOF-5-derived porous carbon (Fe_3O_4@MOF-5-C) was then used for the magnetic solid-phase extraction of chlorophenols (CPs) from mushroom samples prior to high performance liquid chromatography–ultraviolet detection. Scanning electron microscopy, transmission electron microscopy, X-ray diffraction, and N_2 adsorption were used to characterize the adsorbent. After experimental optimization, the amount of the adsorbent was chosen as 8.0 mg, extraction time as 10 min, sample volume as 50 mL, desorption solvent as 0.4 mL (0.2 mL × 2) of alkaline methanol, and sample pH as 6. Under the above optimized conditions, good linearity for the analytes was obtained in the range of 0.8–100.0 ng g^{-1} with the correlation coefficients between 0.9923 and 0.9963. The limits of detection ($S/N = 3$) were in the range of 0.25–0.30 ng g^{-1}, and the relative standard deviations were below 6.8%. The result showed that the Fe_3O_4@MOF-5-C has an excellent adsorption capacity for the analytes.

1. Introduction

Metal-organic frameworks (MOFs) are highly ordered crystal-line materials prepared by self-assembly of metal ions with organic linkers to yield low density network structures of diverse topology [1]. MOFs, with their fascinating diverse structures, permanent nanoscale porosity, high surface area and uniform structured cavities [2–4], have become a rapidly developing research area and have attracted much attention in the last few years [5,6]. They have been considered as alternative precursors to construct nanoporous carbons since the use of MOFs as hard templates to synthesize nanoporous carbon materials through high temperature carboni-zation process can offer the resulting nanoporous carbons with ordered micro-, meso-, and macropores depending on the original hard templates. Also, their synthesis process is easy and favorable for large scale production. So far, MOF-5 [7], ZIF-8 [8], ZIF-67 [9], Ni-MOF [10], and Al-MOF [11] have been demonstrated as promising precursors for yielding highly nanoporous carbons. MOFs derived nanoporous carbons (MOF-C) have shown good thermal and chemical stability, highly ordered mesoporous structure and high surface area [12–14]. They have been reported for the use in adsorption [15–17], catalysis [18], and electrochem-ical capacitance [19]. It has been reported that MOF-C materials were promising and efficient adsorbents with fast adsorption rate and high adsorption capacities [15,20]. However, their nanoscale sizes and light weight can make them difficult to separate and recover from sample solution. On the other hand, the incorporation of magnetic property into the MOF-C materials can make the separation easier and convenient by using magnetic solid-phase extraction (MSPE).

MSPE is a mode of solid-phase extraction based on the use of magnetic adsorbents. In MSPE, a magnetic adsorbent is first dispersed in a sample solution. After adsorption for an appropriate time, the powdery magnetic material can be easily separated from the solution by using an external magnet without the need of additional filtration or centrifugation procedures, which makes the separation rapid and effective. When the external magnetic field is removed, the separated powdery magnetic material can be redispersed in a solution, which makes the following washing and desorption operations convenient [21,22]. Since the magnetic adsorbent can be suspended in sample solution, the contact area between the analytes and the adsorbent is large, which is favorable

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for fast mass transfer and rapid reach of extraction equilibrium [23]. For the above reasons, MSPE has been increasingly explored in the field of sample preparation.

The MOF-5 framework is one of the most representative MOFs, in which oxocentered Zn_4 tetrahedra are connected through linear terephthalic acid to give a cubic network structure and a three-dimensional channel system [4]. The terephthalic acid in MOF-5 is rich in carbon and therefore it can serve as both the carbon precursor and as the template for the synthesis of nanoporous carbon materials.

In this work, a MOF-5-derived porous carbon MOF-5-C was synthesized by the direct carbonization of MOF-5 as both the precursor and template. Then, the magnetic MOF-5-derived porous carbon (Fe_3O_4@MOF-5-C) was fabricated by the chemical copre-cipitation method. The prepared Fe_3O_4@MOF-5-C showed a high specific surface area and also strong magnetism due to the presence of iron oxide nanoparticles. Chlorophenols (CPs) are widely used as herbicides, insecticides, wood preservatives and disinfectants [24] and they are also often used in mushroom compost, although they are toxic and carcinogenic for human beings [25]. With the growth of mushrooms, the chlorophenols could remain in them. Considering that the Fe_3O_4@MOF-5-C could have a good adsorption capacity towards the benzene-ring structured compounds such as CPs via van der Waals forces, π–π stacking and hydrophobic interactions, some CPs were selected as the model analytes to evaluate the extraction performance of the Fe_3O_4@MOF-5-C. The relevant experimental parameters were optimized, and as a result, a simple and sensitive analytical method for the determination of CPs in mushrooms by Fe_3O_4@MOF-5-C based MSPE followed by HPLC was established.

2. Experimental

2.1. Reagents and chemicals

HPLC-grade methanol was purchased from Sinopharm Chemi-cal Reagent Co., (Beijing, China). $Zn(NO_3)_2 \cdot 6H_2O$, terephthalic acid (benzene-1,4-dicaboxylic acid), N,N-dimethylformamide (DMF), acetonitrile, acetone, hydrochloric acid, and sodium hydroxide were purchased from Beijing Chemical Reagents Company. The water used throughout the work was double-distilled on an SZ-93 automatic double-distiller (Shanghai Yarong Biochemistry Instru-mental Factory). 2-Chlorophenol (2-CP), 3-chlorophenol (3-CP), 2,3-dichlorophenol (2,3-CP), and 2,4-dichlorophenol (2,4-CP) were purchased from Agricultural Environmental Protection Institution (Tianjin, China). A mixture stock solution containing 2-CP, 3-CP, 2,3-CP, and 2,4-CP each at 40.0 $\mu g\ mL^{-1}$ was prepared in methanol. A series of standard solutions was prepared by mixing an appropriate amount of the stock solution with methanol in a 10 mL volumetric flask. All the standard solutions were stored at 4 °C in the dark.

2.2. Instruments

An Agilent Technologies 1260 Infinity LC/G1314F with 1260 VWD detector was used for all the experiments. A Centurysil C18 column (250 mm × 4.6 mm id, 5.0 μm) from Dalian Johnsson Separation Science Technology Corporation (Dalian, China) was used for separations. The mobile phase was a mixture of methanol–water (60:40 v/v) at a flow rate of 1.0 mL min^{-1}. The UV monitoring wavelength was chosen at 280 nm.

Scanning electron microscopy (SEM) images were observed on an S-4300 SEM instrument (HITACHI, Japan). Transmission electron microscopy (TEM) was conducted on a JEOL model JEM-2011(HR) (Tokyo, Japan). X-ray diffraction (XRD) (Brooker D8 ADVANC, Germany) measurements were made with Cu $K\alpha$

radiation. The Brunauer–Emmett–Teller (BET) surface areas were determined from the N_2 adsorption at 300 K using V-Sorb 2800P (China). The magnetic property was analyzed using an MPMS-XL-7 vibrating sample magnetometer (Quantum Design, USA) at room temperature.

2.3. Preparation of Fe_3O_4@MOF-5-C

MOF-5 was prepared according to the reported method [26]. The carbonization of the MOF-5 nanoparticles was performed at 900 °C for 6 h under Ar flow to get the nanoporous carbon MOF-5-C. For the preparation of the magnetic composite Fe_3O_4@MOF-5-C, 0.2 g MOF-5-C was first suspended in 150 mL water at 50 °C under N_2 atmosphere, and then, 0.46 g (1.724 mmol) $FeCl_2 \cdot 4H_2O$ and 0.24 g (0.86 mmol) $FeCl_3 \cdot 6H_2O$ were added. After the solution was sonicated (200 W, 40 kHz) for 10 min, the pH of the solution was adjusted to 11 with 25% $NH_3 \cdot H_2O$ to precipitate the iron oxides. Then, the reaction was carried out at 50 °C for 1 h under constant mechanical stirring. The resulting powdery magnetic material was separated from the aqueous dispersion by an external magnet. Then, the precipitate was washed with double-distilled water until the pH reached 7. Finally, the Fe_3O_4@MOF-5-C composite was dried under vacuum. The schematic illustration for the synthesis of the Fe_3O_4@MOF-5-C is shown in Fig. 1. The reproducibility of the formation of Fe_3O_4@MOF-5-C from five different batches of Fe_3O_4@MOF-5-C was investigated. The experimental results showed that the adsorption capacity of the adsorbent for the analytes has no obvious changes with a relative standard deviation (RSD) of 6.1% from batch to batch.

2.4. Sample preparation

Fresh mushroom samples were homogenized in a laboratory homogenizer. A 200.0 g portion of the homogenized mushroom sample was accurately weighed, and then placed in four 50 mL screw capped PTFE centrifugal tubes with a conical bottom. The samples were centrifuged at 9000 rpm for 20 min. Then, the sedimented phase in each tube was washed with 25 mL of double-distilled water twice. All the supernatants were combined together in a 500 mL volumetric flask, to which double-distilled water was added to complete the volume. The obtained sample solution was stored at 4 °C for the following MSPE extractions.

2.5. MSPE procedures

For the MSPE, 8.0 mg of Fe_3O_4@MOF-5-C was added to 50 mL sample solution in a conical flask. The mixture was shaken on a slow-moving platform shaker for 10 min. Subsequently, the Fe_3O_4@MOF-5-C was separated from the sample solution by putting an external magnet at the bottom of the conical flask and the resulting supernatant was discarded. Next, the Fe_3O_4@MOF-5-C and the residual solution were all transferred to a 10 mL centrifuge tube. A magnet was put outside of the tube wall to aggregate the Fe_3O_4@MOF-5-C, and the residual supernatant was completely removed by a pipette. Finally, 0.4 mL (0.2 mL × 2) of alkaline methanol (1% 1 mol L^{-1} NaOH) as the desorption solution

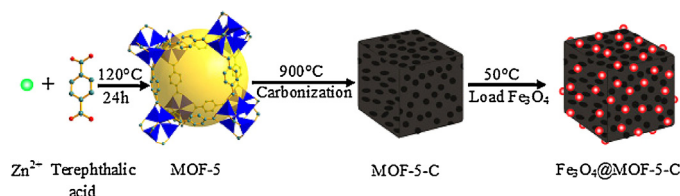**Fig. 1.** Schematic illustration of the synthetic process of Fe_3O_4@MOF-5-C.