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Magnetic metal-organic nanotubes: An adsorbent for magnetic solid-phase extraction of polychlorinated biphenyls from environmental and biological samples

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ABSTRACT

A new type of three-dimensional, echinus-like magnetic Fe_3O_4 @ cobalt(II)-based metal-organic nanotube (Fe_3O_4 @ Co-MONT) yolk-shell microspheres, have been designed and synthesized for the first time. Fe_3O_4 @ Co-MONTs yolk-shell microspheres were characterized by scanning electron micrographs, transmission electron microscopy, Fourier transform infrared spectra, X-ray diffraction, and vibrating sample magnetometry. The feasibility of the new material for use as an absorbent was investigated for magnetic solid phase-extraction (MSPE) of polychlorinated biphenyls (PCBs) from environmental water samples and biological samples. The Plackett-Burman design and Box-Behnken design were used to determine and optimize the extraction parameters influencing the extraction efficiency through response surface methodology. Under the optimized conditions, the developed method showed good linearity within the range of 5–1000 ng L^{-1}, low limits of detection (0.31–0.49 ng L^{-1}), and good reproducibility (RSD < 10%). The proposed method was successfully applied for the analysis of PCBs in real environmental water samples. These results demonstrated that Fe_3O_4 @ Co-MONTs is a promising adsorbent material for the MSPE of PCBs at trace levels from environmental water samples and biological samples.
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1. Introduction

Solid-phase extraction (SPE) is a popular sample pretreatment technique for the separation and enrichment of the target compounds from sample solutions. In SPE, the separation occurs based on the analyte partition coefficient between the mobile phase and the solid sorbent [1]. However, typical SPE methods suffer from limited rates of diffusion and mass transfer [2]. Magnetic solid-phase extraction (MSPE) is a relatively new SPE mode where magnetic nanoparticles (MNPs) are added as sorbents to the sample solution in the extraction process. Following the adsorption of the analytes, the adsorbent can be rapidly separated from the sample solution by the application of an external magnetic field. The target compounds are then eluted from the magnetic adsorbent with a small volume of an appropriate organic solvent [3,4]. Unlike the conventional SPE, MSPE can avoid the high back pressure and clogging of the sorbent during the loading that gives rise to an unstable loading flow rate that affects the extraction efficiency [5]. More importantly, MNPs can be modified with special functionalities, increasing their versatility and thus improving the selectivity of the extraction procedures [6]. Various functional materials, such as octadecyl-functionalized monodispersed magnetic ferrite microspheres [7], zeolitic imida zolate framework-8 (ZIF-8) [8], Cd(II)-ion imprinted magnetic mesoporous silica material [9], Fe_3O_4 @ SiO_2 @ UiO-66 microspheres [10], Fe_3O_4 @ metal-organic framework (Fe_3O_4 @ MOF) [11] and Fe_3O_4@3-(Trimethoxysilyl)propyl methacrylate@ ionic liquid nanoparticles [12], have been successfully applied in the MSPE of various pollutants from environmental and food samples.

Metal-organic nanotubes (MONTs) are a novel class of hybrid materials that combines organic ligands and metal ions or metal-containing clusters [13] and which have attracted intense interest from chemists and material scientists. MONTs have been applied for catalytic reduction, ion exchange, gas adsorption and separa-

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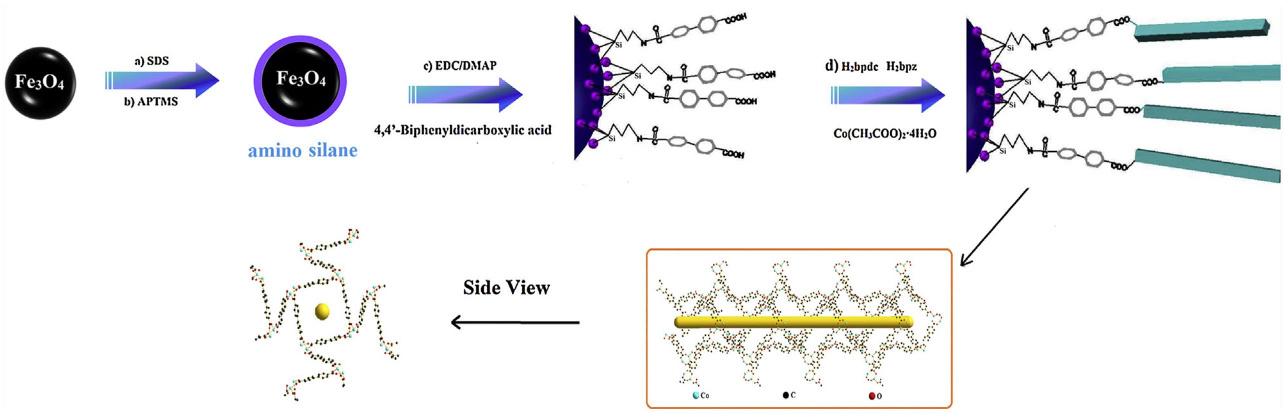

Fig. 1. Synthesis of the Fe_3O_4 @ Co-MONTs magnetic microspheres.

tion, and molecular sensing and recognition [14–16]. As a bridge between the inorganic and organic nanotubes, MONTs possess the advantages of carbon nanotubes (CNTs) and metal-organic frameworks (MOFs), such as an open nanoporous structure, large specific surface area, and exceptional thermal and chemical stability [17,18]. These diverse properties make MONTs promising as adsorbent candidates. However, to the best of our knowledge, there have been no reports on the design, synthesis and application of magnetic metal organic nanotubes for MSPE.

Polychlorinated biphenyls (PCBs) are a class of industrial chemicals in which 1–10 chlorine atoms are attached to a biphenyl molecule [19]. Because of their bioaccumulative, toxic and persistent properties, PCBs were placed on the list of persistent organic pollutants by the Stockholm Convention [20,21]. PCBs had been widely used as industrial oil additives and coolants as well as in some consumer products [22]. They were found to be highly toxic to humans through the food chain accumulation and were shown to be mutagenic by interrupting the action of the hormones in the body [23,24]. Although PCBs manufacturing has been banned by the United States Congress in the late of 1970s, humans and animals are still exposed to these chemicals because of their long-range transport and high stability [25]. Therefore, monitoring of PCBs' content in the environment is important. However, the conventional liquid–liquid extraction (LLE) [26] and solid phase extraction [27] often needs large amount of toxic solvent and time-consuming procedures. Fortunately, various new sample pretreatment techniques, such as solid-phase microextraction (SPME) [13], liquid phase microextraction (LPME) [28] and magnetic solid phase extraction (MSPE) [11,29] have been developed for the extraction of PCBs from environmental and biological samples. These techniques have obvious advantages such as rapidity, high enrichment factor, simplicity of operation, and low cost [11,13,28,29].

Our previous work used Fe_3O_4@MOF core–shell magnetic microspheres for MSPE of PCBs from environmental water samples [11], however, the lack of a strong force between Fe_3O_4 and MOF makes the MOF material prone to being lost during extraction and desorption steps [11]. Generally, chemical bonding can endow the adsorption material with enhanced stability. In addition, analytical area of the paper only includes environmental samples [11]. In order to solve these problems, in this study, a new adsorbent, chemical bonding magnetic Fe_3O_4 @ Cobalt(II)-based metal-organic nanotubes (Fe_3O_4 @ Co-MONTs) yolk-shell microsphere, was designed and prepared for the first time. The novel material was then investigated and used as an adsorbent in the MSPE of PCBs from water and biological samples. Box-Behnken design (BBD) was used to optimize experimental conditions through response surface methodology (RSM). Finally, the proposed method was used to analyze PCBs in real environmental and biological samples.

2. Materials and methods

2.1. Chemicals and reagents

All of the reagents were of analytical grade. Iron(III) chloride hexahydrate (99%), ethanol, sodium dodecyl sulfate (SDS), acetonitrile, N.*N*-dimethylformamide, sodium chloride, dichloromethane, methanol, *n*-hexane, acetone, sodium hydroxide, hydrochloric were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Ethylene glycol, sodium aceticum were obtained from Kermel Chemical Reagent Co. Ltd. (Tianjin, China), (3-aminopropyl)trimethoxysilane (APTMS), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC), 4-dimethylaminopyridine (DMAP), Cobalt(II) acetate tetrahydrate, 4,4′-biphenyldicarboxylic acid (H_2bpdc), 3,3′,5,5′-tetramethyl-4,4′-bipyrazole (H_2bpz) were purchased from Aladdin Reagent Co. Ltd. (Shanghai, China). Seven standards of PCB homologs (Congener Nos.: 28, 52, 101, 118, 138, 153, 180) (1.00 mg L^{-1}) were obtained from Accu Standard (Connecticut, USA). The magnetic separator was bought from the local market and collected with the help of an Nd–Fe–B magnet (350 MT).

2.2. Instrumentation

A Bruker gas chromatography system (436 GC, Bruker, USA) coupled with a triple quadrupole mass spectrometer (SCION TQ, Bruker, USA) was used during the experiment in multiple reaction monitoring (MRM) mode. The inlet was operated in splitless mode. A DB-35 MS fused silica capillary column (30 m × 0.25 mm × 0.25 μm) (Agilent Technologies, USA) was used for GC separation. The oven temperature was programmed as follows: initially held at 150 °C for 1 min and then raised to 290 °C for 4 min at 10 °C min^{-1}. The total analysis time was 19 min. Helium (99.999%) was used as the carrier gas, and the flow rate was set as 1.0 mL min^{-1}. High-purity nitrogen was used as a collision gas (1.5 mL min^{-1}). The mass spectrometer was operated in the electron impact mode (EI) at 70 eV. The temperatures of the injector, interface and ion source were 280, 280 and 250 °C, respectively. Parameters such as the MRM transition (major parent ion → daughter ion) and collision energy are present in Table S1.

Scanning electron microscopy (SEM) images were recorded using on a SUPPA^{TM} 55 (Zeiss, Germany). X-ray diffraction (XRD) were performed with a D/max-r8 diffractometer (Rigaku, Japan) using Cu Kα radiation (λ = 1.5418 Å) over the angular range from 5° to 40°. The morphology of the material was observed by transmis-

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