



Preparation of core-shell structured magnetic covalent organic framework nanocomposites for magnetic solid-phase extraction of bisphenols from human serum sample



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ARTICLE INFO

Keywords:

Magnetic covalent organic frameworks
Magnetic solid-phase extraction
Bisphenols
Human serum
Liquid chromatography-tandem mass spectrometry

ABSTRACT

Core-shell structured magnetic covalent organic framework (Fe₃O₄@COF) nanocomposites were synthesized via a facile approach at room temperature and explored as an adsorbent for magnetic solid-phase extraction (MSPE) of bisphenols (BPs) from human serum sample. The as-prepared Fe₃O₄@COF nanocomposites with core-shell structure possessed high specific surface area (181.36 m²/g), uniform mesoporous size (~ 3.6 nm), high saturation magnetization (42.7 emu/g), and excellent thermal and chemical stability, rendering it as an ideal adsorbent with high adsorption efficiency and size selectivity. The experimental parameters influencing extraction efficiency, including adsorbent dosage, extraction time, pH and ion strength, desorption solvent and time, were investigated in detail. Taking these advantages together, a simple, fast, effective and sensitive method that MPSE followed by HPLC-MS, was proposed to detect five BPs, which exhibited good linearity ($r > 0.9982$) within the concentration ranges of 0.1–50 µg/L. Moreover, the low detection limits (1.0–78.1 ng/L), signal-to-noise ratio ($S/N = 3$), the high enrichment factors (56–95 fold), and good recoveries (93.0–107.8%) with relative standard deviations (RSDs) less than 3.4% for inter-day and 6.9% for intra-day were achieved. The developed method was also successfully applied to the analysis of trace BPs in human serum sample, which demonstrated the most promising potential of the Fe₃O₄@COF nanocomposites as good adsorbent in sample pretreatment.

1. Introduction

Bisphenol A (BPA) is a chemical used primarily to produce polycarbonate plastics and epoxy resins, which are often applied in a wide variety of consumer products [1]. Numerous studies have shown that BPA and its metabolites exhibit estrogenic and endocrine activities [2], which can induce a decrease in daily sperm count and fertility [3], disrupt chromosome alignment [4] and affect sexual maturation or synaptogenesis in human [5]. These potential health risks have attracted considerable attention and strict regulations have been implemented by the EU Commission and the U.S Environmental Protection Agency (US EPA), in which the tolerable daily intake (TDI) are both 0.05 mg BPA/kg body weight/day [6]. Due to these restrictions, a series of structural analogs (also called bisphenols, BPs), such as bisphenol B (BPB), bisphenol F (BPF), bisphenol S (BPS) and bisphenol AF (BPAF) were considered as substitutes for BPA in industrial applications and their structures are shown in Fig. S1 (Supplementary information).

Nevertheless, limited studies have indicated that the aforementioned BPs possess estrogenic activity similar to BPA [7,8], provoking many adverse health effects. Therefore, development of a simple and sensitive method for the quantitative analysis of BPs in biological sample is of great significance to environmental exposure and human health assessments.

Due to the ultralow concentrations of BPs and the complexity of biological samples, pretreatment and enrichment processes are indispensable for their analysis by liquid chromatography-mass spectrometry (HPLC-MS). In the past few years, a variety of solid phase extraction (SPE) including dummy molecularly imprinted mesoporous silica [9], molecularly imprinted polymer microspheres [10] and hollow porous carbon spheres [11] have been successfully used for extraction of BPs. As an important branch of SPE, magnetic solid phase extraction (MSPE) can dramatically simplify the procedure because they can be separated easily by an external magnetic field and has recently attracted much attention as an interesting alternative [12–15].

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Using MSPE, some issues related to sorbent packing, high back pressures, or packed bed clogging can be avoided. At present, a number of magnetic sorbent for MSPE have been developed and applied in the extraction and enrichment of bisphenolic compounds, including magnetic metal-organic frameworks (MOFs) [16], polydopamine-coated magnetic composite nanoparticles [17], magnetic nanoporous three dimensional graphene (3DG/ZnFe₂O₄) [15], magnetic activated carbon [18] and molecularly imprinted magnetic nanoparticles [19]. However, the above functional magnetic sorbents suffer from some drawbacks, such as low selectivity, tedious synthesis procedures or poor structural stability [20].

Covalent organic frameworks (COFs), as a class of novel crystalline porous polymer with well-defined structural regularity, large surface area and tunable pore structure, have attracted increasing attention since the first report in 2005 [21]. Different from MOFs, the fascinating features of COFs like tunable pore size, high chemical stability and outstanding thermal stability, enable their superior potential in a wide variety of applications, such as catalysis [22], sensing [23], optoelectronics device [24] and separation [25–27]. Against such a backdrop, the incorporation of the merits of COFs and magnetic nanoparticles to construct a novel type of nanocomposites with both enhanced functionality and magnetic separability is great of significance. In 2016, Tan et al. [28] first presented a thermodynamic control approach for the preparation of core-shell structured magnetic COFs and then applied them in phototherapy. Li et al. [29] reported a monomer-mediated in situ growth strategy for the controllable synthesis of porous magnetic COFs via solvothermal reaction. The resultant nanocomposites were successfully utilized as an adsorbent for rapid adsorption and removal of chemical pollutants from aqueous solution. However, the above mentioned strategies were both based on solvothermal synthesis, which was rather tedious, labor-intensive and time-consuming. Just recently, an encouraging breakthrough in room-temperature synthesis of core-shell structured magnetic COFs was achieved by our group [30], which have been successfully applied to capture peptides with simultaneous exclusion of proteins from complex biological samples. Nevertheless, the potential advantages of the magnetic COFs and the facile synthetic strategy have not been fully demonstrated. Further development is very necessary to address the advantages and explore new applications of this type of the magnetic COFs.

Herein, we developed a facile approach for rapid room-temperature synthesis of core-shell structured magnetic covalent organic framework (Fe₃O₄@COF) nanocomposites by using the monodisperse Fe₃O₄ nanoparticles as magnetic core and 1,3,5-tris(4-aminophenyl)benzene (TAPB) and terephthalaldehyde (TPA) as two building units in the presence of dimethyl sulfoxide (DMSO). The as-prepared Fe₃O₄@COF nanocomposites were characterized by several techniques, and then their adsorption performance and MSPE abilities for BPs were investigated in detail. In addition, with the new Fe₃O₄@COF nanocomposites as an adsorbent, a Fe₃O₄@COF-based enrichment coupled with HPLC-MS method was developed and successfully applied to the determination of trace BPs in human serum sample.

2. Experimental

2.1. Chemicals and reagents

All the chemical reagents were of analytical grade or better. Ferric chloride hexahydrate (FeCl₃·6H₂O), sodium citrate dehydrate (Na₃Cit·2H₂O), ethylene glycol (EG) and TAPB were purchased by J&K Chemical Ltd (Shanghai, China). TPA, BPA, BPB, BPF, BPS, and BPAF were obtained from Aladdin Chemistry Co. Ltd (Shanghai, China). BPA-d₁₆, obtained from Cambridge Isotope Laboratories Inc. (Andover, MA, USA), served as internal standard for the quantification. Deionized water (18.2 MΩ cm⁻¹) was obtained from a Milli-Q water purification system (Millipore, Milford, USA).

The stock standard solutions of BPs were individually prepared at

the concentration of 1000 µg/mL in methanol, and stored at 4 °C before use. The working standard solutions were obtained daily by appropriately diluting with deionized water. Healthy human serum was kindly donated by Fujian Provincial Official Hospital (Fuzhou, China) and stored at -20 °C prior to use. The frozen serum samples were thawed at room temperature and diluted 50-fold with deionized water before analysis. The study protocol and written informed consent were approved by the Fujian Province Official Hospital Ethics Committee (2014-KFFJJ-PT-2). All serum-related experiments were performed according to the Declaration of Helsinki.

2.2. Apparatus

Scanning electron microscopy (SEM) images were obtained with a FEI Emission Scanning Electron Microscope (SU8020, Hitachi, Japan). Transmission electron microscopy (TEM) images were recorded by a FEI Tecnai G20 (USA). Fourier-transform infrared spectroscopy (FT-IR) was taken on Nicolet 6700 spectrometer (Thermo Fisher, USA). The magnetization curves were calculated by a superconducting quantum interference device magnetometer (SQUID) MPMS XL-7 (Quantum Design, USA). Thermogravimetric analysis (TGA) was performed using a Shimadzu thermogravimetric analyzer (Model DTG-60). The nitrogen adsorption and desorption isotherms were measured by using an ASAP 2020 (Micromeritics, USA). The crystal structure of the Fe₃O₄@COF nanocomposites was determined by X'Pert-Pro MPD (Philips, Holland).

2.3. Preparation of Fe₃O₄@COF nanocomposites

2.3.1. Synthesis of Fe₃O₄ magnetic nanoparticles

Monodisperse Fe₃O₄ magnetic nanoparticles (MNPs) were synthesized according to the previous report with minor modification [31]. Briefly, FeCl₃·6H₂O (6.8 g), Na₃Cit·2H₂O (2.0 g) and sodium acetate (12.0 g) were dissolved in EG (200 mL). The obtained homogeneous yellow solution was transferred to autoclave, and then heated to 200 °C for 12 h. After reaction, the product was collected by magnet and washed with water and ethanol for several times and then dried at 25 °C.

2.3.2. Synthesis of Fe₃O₄@COF nanocomposites

The obtained Fe₃O₄ MNPs were further coated with COF shells through the template-controlled precipitation polymerization of TAPB and TPA. Typically, Fe₃O₄ (0.15 g), TAPB (0.106 g) and TPA (0.06 g) were added into 60 mL DMSO and ultrasonically dispersed for 5 min to form a stable dispersion. Afterwards, 2 mL acetic acid (17.5 M) was slowly added with sonication and the brown precipitates (Fe₃O₄@COF nanocomposites) were formed during this process (~10 min). After incubation for 30 min, the obtained brown precipitates were collected by magnetic separation and washed with anhydrous tetrahydrofuran and methanol for three times. Finally, the resultant Fe₃O₄@COF nanocomposites were dried at 25 °C for further use.

2.4. Procedures of MSPE

All extraction experiments were conducted in 50 mL centrifuge glass tubes. 20 mg of Fe₃O₄@COF nanocomposites was dispersed into 10 mL standard solution or 10 mL of 50-fold diluted human serum sample. The mixture solution was incubated for 10 min by a slow-moving platform shaker at room temperature. Then, the Fe₃O₄@COF nanocomposites were collected by applying a magnet to the outer wall of the vial and the supernatant was discarded. Afterwards, the analytes were desorbed from the Fe₃O₄@COF nanocomposites with 0.5 mL of *i*-propanol under vigorous vortex for 2 min, and the eluate was collected by magnetic separation. Three such replicate elutions were required for quantitative desorption of the analytes from the sorbent. The collected eluate (1.5 mL of *i*-propanol) was dried with a gentle stream of nitrogen at room temperature. Finally, the analytes were redissolved in 0.1 mL of deionized water for HPLC-UV/vis and HPLC-MS analysis.

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