



# Magnetic solid-phase extraction using nanoporous three dimensional graphene hybrid materials for high-capacity enrichment and simultaneous detection of nine bisphenol analogs from water sample



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## ARTICLE INFO

### Article history:

Received 19 May 2016

Received in revised form 31 July 2016

Accepted 2 August 2016

Available online 3 August 2016

### Keywords:

Three dimensional graphene/ZnFe<sub>2</sub>O<sub>4</sub>

Magnetic solid-phase extraction

Bisphenol analogs

Water sample

## ABSTRACT

The synthesis of a magnetic nanoporous three dimensional graphene (3DG)/ZnFe<sub>2</sub>O<sub>4</sub> composite has been achieved. Through formation of graphene hydrogel, ZnFe<sub>2</sub>O<sub>4</sub> magnetic particles was successfully introduced into the nanoporous 3DG, resulting in a magnetic porous carbon material. The morphology, structure, and magnetic behavior of the as-prepared 3DG/ZnFe<sub>2</sub>O<sub>4</sub> were characterized by using the techniques of SEM, XRD, BET, VSM, FTIR, Raman and TGA. The 3DG/ZnFe<sub>2</sub>O<sub>4</sub> has a high specific surface area and super paramagnetism. Its performance was evaluated by the magnetic solid-phase extraction of nine bisphenol analogs (BPs) from water samples followed by HPLC analysis, and showed excellent adsorption capability for the nine target compounds. Under optimized condition, the lower method detection limits (0.05–0.18 ng mL<sup>-1</sup>), the higher enrichment factors (800 fold) and good recoveries (95.1–103.8%) with relative standard deviation (RSD) values less than 6.2% were achieved. The results indicated that the developed method based on the use of 3DG/ZnFe<sub>2</sub>O<sub>4</sub> as the magnetic adsorbent has the advantages of convenience and high efficiency, and can be successfully applied to detect the nine BPs in real water samples.

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## 1. Introduction

In an overall analytical process, miniaturization has become an important issue in the development of sample preparation techniques, since it has a multifarious role related to the extraction, preconcentration, and cleanup of the analytes from the coexisting species in the sample. Furthermore, miniaturization is greatly beneficial not only to the environment but also to the economy.

Recently, a variety of the sorbent-based extraction methods, including solid phase extraction (SPE) [1], solid phase microextraction (SPME) [2], molecularly imprinted solid-phase extraction (MISPE) [3], magnetic solid-phase extraction (MSPE) [4,5], stir bar sorptive extraction (SBSE) [6], dispersive micro-solid-phase extraction (D- $\mu$ -SPE) [7], have been developed for sample preparation. In these techniques, porous carbon materials as adsorbent have received great interest from researchers. Since their unique physical and chemical properties, such as high surface area, large pore volume, tunable pore sizes, interconnected frameworks and mechanical stability [8], porous carbon materials could interact with target molecules and ions not only at their surface. Porous carbon materials have been explored as the efficient adsorbents

for the separation of organic dyes [9], tetracycline [10], aniline [11], bisphenol A [12], pesticides [13], bromide ions [14] and chromium [15] from aqueous solutions. The results indicated that porous carbon materials were the most efficient and promising adsorbents with rapid rate of adsorption and high binding capacities. However, porous carbon materials were difficult to be separated and recovered from the solution because of their small sizes, which could hinder their reusability. The incorporation of magnetic components into porous carbon materials could be an effective approach to address the above problem [16]. Recently, a series of magnetic porous carbon materials have been successfully used as the adsorbent for isolation and enrichment of dye [17], phenolic derivatives [18] and chromium [19], etc. So far, porous silica [11,13], calcium acetate [20], magnesium oxide [21], zeolites [18,22], nickel foam [23] and metal-organic frameworks (MOFs) [24,25] have been used as the templates for the fabrication of porous carbon materials. However, these methods are also somewhat time-consuming and costly since it involved complicated multistep synthetic processes.

More recently, porous 3DG quickly drew extensive research interest [26,27]. This graphene-based monolith could be synthesized by hydrothermal process without any templates [26,28]. More importantly, compared to graphene, 3DG can effectively avoid layer-layer aggregation and retain the large specific surface. 3DG usually has a low-density porous structure which allows diffusion of molecules and ions throughout [29,30]. Increasing studies

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have shown the good adsorption capability of 3DG for pollutants such as oil [31], heavy metal ions [32], organic solvents [33], dyes and aromatic pollutants [34]. Hao et al. used 3DG-Fe<sub>3</sub>O<sub>4</sub> as the adsorbent for the extraction of four phthalate esters from fruit juice [35]. Liu et al. used 3DG-Fe<sub>3</sub>O<sub>4</sub> as the adsorbents for the preconcentration of three endocrine disrupting phenols from honey peach juice samples [36]. Up to date, the applications of magnetic 3DG powder for the enrichment and determination of trace pollutants from real samples has remained still rarely touched [37].

Hence, in this paper, a novel magnetic nanoporous 3DG hybrid material was synthesized. This hybrid material not only possesses high specific surface area but also has sufficient magnetism due to the incorporate of magnetic ZnFe<sub>2</sub>O<sub>4</sub> nanoparticles into nanoporous 3DG. 3DG/ZnFe<sub>2</sub>O<sub>4</sub> as the adsorbent was evaluated for the extraction of nine bisphenol analogs (BPs) including bisphenol S (BPS), bisphenol F (BPF), 4,4'-Thiodiphenol (TDP), bisphenol A (BPA), bisphenol AF (BPAF), bisphenol AP (BPAP), bisphenol C (BPC), tetrachlorobisphenol A (TCBPA), tetrabromobisphenol A (TBBPA). Studies have shown that BPs can affect endocrine systems due to BPs's toxicities (e.g., genotoxicity, immunotoxicity and neurotoxicity) [38,39], and cause adverse effects such as endocrine dyscrasia, precocity and even cancer [40,41]. Very recently, it has been reported that BPs had been found at concentrations ranging from ng mL<sup>-1</sup> to ng L<sup>-1</sup> in different environmental matrices [42–46] (mainly in water and sediment) and foodstuffs [47]. This may pose a potential hazard to both human health and ecosystem. Thus, a rapid, simple, effective and sensitive method that MSPE followed by HPLC, is proposed to detect nine BPs in environmental water samples. Various factors affecting preconcentration of the analytes were discussed in details. The developed method was successful applied to the simultaneous determination of trace levels of nine BPs in large-volume real water samples.

## 2. Materials and methods

### 2.1. Chemicals and reagents

Graphite powder (natural flake graphite, 325 mesh) was purchased from Alfa Aesar. BPS, BPF, TDP, BPA, BPAF, BPAP, BPC, TCBPA and TBBPA (the structural formula of nine BPs was shown in Fig. 1) standards was purchased from Aladdin Chemistry Co. Ltd. (Shanghai, China). All other chemicals were of analytical reagent grade and produced by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

The stock standard solutions (1.0 mg mL<sup>-1</sup>) were individually prepared by dissolving corresponding standard compound in methanol and stored at 4 °C under dark conditions. The working standard solutions were obtained daily by appropriately diluting the stock solution with ultrapure water. Analytical grade sodium chloride were purchased from Beijing Chemical Co. (Beijing, China). Ultrapure water used throughout experiments was purified using a Sartorius Arium 611 system (Sartorius, Göttingen, Germany). Chromatographic grade methanol was purchased from Fisher Corporation (Pittsburgh, PA, USA). HPLC grade ultrapure water (18.2 MΩ cm<sup>-1</sup> resistivity) was obtained from a MilliQ water purification system (MilliQ Water; Molsheim, France).

### 2.2. Preparation of 3DG/ZnFe<sub>2</sub>O<sub>4</sub> composites

#### 2.2.1. Synthesis of magnetic ZnFe<sub>2</sub>O<sub>4</sub> nanoparticles

Briefly, 0.8925 g of Zn(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O, 2.424 g of Fe(NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O and 0.20 g urea were added to 60 mL of absolute ethanol with stirring for 30 min at room temperature and then transferred to a teflon-lined stainless-steel autoclave (100 mL capacity). The autoclave was heated to and maintained at 180 °C for 12 h and then naturally cooled to room temperature. Finally, the obtained

ZnFe<sub>2</sub>O<sub>4</sub> precipitate was thoroughly rinsed with ultrapure water for several times, and dried in vacuum at 60 °C for 24 h.

#### 2.2.2. Synthesis of 3DG/ZnFe<sub>2</sub>O<sub>4</sub> composite

Graphene oxide (GO) was synthesized from graphite powder using a modified Hummers method [48]. The 3DG/ZnFe<sub>2</sub>O<sub>4</sub> composite was fabricated by a facile one-step hydrothermal method. Firstly, 120 mg of GO was dispersed into 60 mL of ultrapure water with sonication for 1 h. Secondly, 60 mg of ZnFe<sub>2</sub>O<sub>4</sub> were added to the above solution and vigorously stirred for 10 min to obtain a homogeneous suspension. The suspension was then poured into a 100 mL teflon-lined autoclave and heated to 180 °C for 12 h. Finally, the 3DG/ZnFe<sub>2</sub>O<sub>4</sub> composite are obtained by freezing dry. The pure 3DG were synthesized through the same method without adding ZnFe<sub>2</sub>O<sub>4</sub>.

### 2.3. Characterization of 3DG/ZnFe<sub>2</sub>O<sub>4</sub>

The morphologies and microstructures of the 3DG/ZnFe<sub>2</sub>O<sub>4</sub> were observed by scanning electron microscopy (HITACHI SU8000). The BET surface area and pore distribution were analyzed using N<sub>2</sub> adsorption/desorption isotherms on a Tristar 3020 volumetric adsorption analyzers manufactured by Micromeritics (Norcross, GA). The structure of the 3DG/ZnFe<sub>2</sub>O<sub>4</sub> was identified by the Powder X-ray diffraction (XRD) using Cu Kα radiation (Diffractometer D8, Bruker AXS, Germany). Raman spectra were measured using Laser Confocal Micro-Raman Spectroscopy (LabRAM XploRA, HORIBA JOBIN YVON S.A.S, France). FTIR spectra of the 3DG/ZnFe<sub>2</sub>O<sub>4</sub> was recorded by AVATAR 330 Fourier transform infrared spectroscopy (FTIR) (NICOLET Co., USA). Thermogravimetric analysis (TGA) was carried out using a SDT Q 600 thermoanalyzer at a ramping of 10 °C min<sup>-1</sup> with a nitrogen or air flow rate of 100 mL min<sup>-1</sup>. The magnetic property was characterized by vibrating sample magnetometry (VSM, Lakeshore-7407) at room temperature.

### 2.4. Chromatographic system and conditions

Chromatographic analyses were carried out on Agilent 1100 HPLC system (Palo Alto, CA, USA) equipped with an automatic sampler and diode array detector (DAD). The Agilent ZORBAX SB-C18 HPLC column (150 mm × 4.6 mm, 5 μm) was used to separate analytes for the whole experiment. The mobile phase was methanol (A) and water (B) at a flow rate of 1.0 mL min<sup>-1</sup> in gradient. Gradient elution was performed as follows: 0–10.0 min, 40.0–80.0% (A); 10–15 min, 80.0% (A); 15–20 min, 80.0%–100.0% (A); 20–25 min, 100.0–40.0% (A); and 25–30 min, 40.0% (A). The column temperature was 30 °C and the detection wavelength was set at 275 nm, and the injection volume was 20 μL.

### 2.5. MSPE procedure

The MSPE procedure was carried out as follows: 3DG/ZnFe<sub>2</sub>O<sub>4</sub> powder (60.0 mg) were added into 25 mL of the working standard solution (or 400 mL of the spiked water samples), and the extraction was performed at a stirring rate of 1000 rpm for 15 min. After extraction, the 3DG/ZnFe<sub>2</sub>O<sub>4</sub> were isolated rapidly from the solution by an external magnet, and the supernatant was decanted away. The target compounds were ultrasonically eluted from the 3DG/ZnFe<sub>2</sub>O<sub>4</sub> with 2.0 mL of MeOH-2.0% NaOH (0.1 mol mL<sup>-1</sup>) for 2 min. The eluent was separated from the 3DG/ZnFe<sub>2</sub>O<sub>4</sub> by a magnet. Then the eluent was evaporated to dryness under a mild nitrogen stream at room temperature. Finally, the residue was redissolved with 500 μL MeOH and filtered through a 0.45 mm PTFE filter membrane for HPLC analysis (as shown in Fig. 2).

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