



Original article

Preconcentration of chlorophenols in water samples using three-dimensional graphene-based magnetic nanocomposite as adsorbent



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ABSTRACT

In this paper, a novel magnetic solid-phase extraction method using three-dimensional graphene-based magnetic nanocomposite as adsorbent for the preconcentration of several chlorophenols from water samples prior to high-performance liquid chromatography analysis was developed. Various experimental parameters were investigated. Under the optimum conditions, the enrichment factors of the method were in the range of 186–312, and the limit of detection ($S/N = 3$) was 0.10 ng/mL. The recoveries of the method were in the range between 85.1% and 101.2%. The developed method has been successfully applied to the determination of chlorophenols in environmental water samples.

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1. Introduction

In recent years, magnetic solid-phase extraction (MSPE) as a relatively new mode of solid-phase extraction (SPE) has received much attention in sample pretreatment [1]. MSPE is based on the use of magnetic or magnetically modified adsorbents [2], which can be readily separated from sample solution using an external magnet [3]. In comparison with the conventional SPE techniques, the MSPE further simplifies the separation process and can avoid the time-consuming column passing operations [4]. In MSPE, the adsorbent material is a key factor because it determines both the selectivity and sensitivity of the method [5]. Therefore, the current research in MSPE is oriented on the development of novel adsorbents with high adsorption capacity and good reusability.

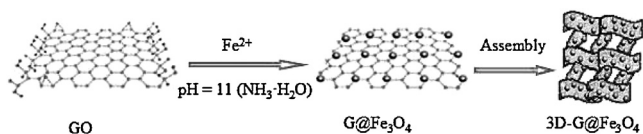
Graphene (G), one-atom-thick two-dimensional (2D) layers of sp^2 -bonded carbon material, has sparked great excitement in scientific and engineering communities since its discovery by Novoselov *et al.* in 2004 [6]. Due to a hexagonal, packed-lattice structure and large delocalized π -electron system, G can form strong hydrophobic and π -stacking interactions with certain organic molecules, which makes G a good adsorbent for some organic compounds [7]. So far, G-based composites have been used as adsorbent in many sample preparation techniques [8,9]. However, two-dimensional G tends to agglomerate or re-stack

into graphite, which may decrease the specific surface area and hinder the effective elution of analytes [10]. To solve the above problems, the synthesis of three-dimensional graphene (3D-G) has attracted much more attention [11]. 3D-G has interconnected network structures and provides high specific surface area, strong mechanical strength, large mesopore volume, and fast mass and electron transport kinetics. Due to its unique property, 3D-G has been widely applied in the fields of energy storage, catalysis, stretchable conductors *etc.* [12]. However, the application of 3D-G as adsorbent for the extraction of environmental pollutants has not been reported yet.

In this article, we prepared a novel 3D-G-based magnetic nanocomposite (3D-G@Fe₃O₄) and applied it as MSPE adsorbent. The introduction of magnetic properties into 3D-G can combine the separation convenience of the magnetic materials and the high adsorption capacity of 3D-G. To the best of our knowledge, this may be the first report that 3D-G@Fe₃O₄ was used as an adsorbent for the enrichment of organic pollutants. To evaluate the performance of the 3D-G@Fe₃O₄, four chlorophenols (CPs) were selected as the model analytes. CPs are important organic compounds with high toxicity and have been widely used in many fields such as pharmaceuticals, preservatives, and pesticides [13]. Due to their widespread use, the CPs could exist in and contaminate our environment [14]. Therefore, there is a need for the development of efficient methods for the determination of CPs in environmental samples. To date, a number of sample preparation techniques have been developed to isolate CPs from different samples, such as solid phase extraction [15], solid-phase microextraction [16], liquid-phase microextraction [17] and

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Scheme 1. Synthesis process of 3D-G@Fe₃O₄.

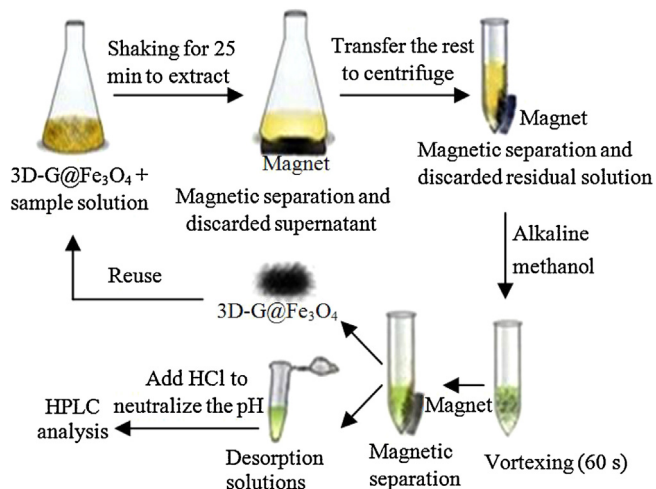
liquid–liquid–liquid microextraction [18]. In this work, a rapid, simple and effective analytical method of 3D-G@Fe₃O₄-MSPE coupling with high performance liquid chromatography (HPLC) was established.

2. Experimental

The HPLC system was LC-20AT (Shimadzu, Japan), which consists of a SPD-20A UV/vis detector and two LC-20AT pumps. Chromatographic separations were performed on a Promosil C18 column (150 mm × 4.6 mm I.D., 5.0 μm) from Bonna-Agela technologies (Tianjin, China). The mobile phase was a mixture of methanol–water (65/35, v/v) at a flow rate of 1.0 mL/min. The UV monitoring wavelength was chosen at 280 nm. A mixture stock solution containing 2-chlorophenol (2-CP), 3-chlorophenol (3-CP), 2,3-dichlorophenol (2,3-DCP) and 3,4-dichlorophenol (3,4-DCP) at 50.0 μg/mL was prepared in methanol. All the standard solutions were stored at 4 °C and protected from light. Tap water was collected from the Key Laboratory of Bioinorganic Chemistry of Agricultural University of Hebei (Baoding, China). River water was collected from Tang River (Baoding, China). Sea water was collected from Rushan (Shandong, China). All the solvents and water samples were passed through a 0.45-μm membrane filter to remove the particulate matters prior to use.

The synthetic process of the 3D-G@Fe₃O₄ is illustrated in Scheme 1. To a 50 mL aqueous suspension of graphene oxide (GO, which was prepared according to the method in our previous work [19]) at the concentrations of 2 mg/mL, was added 0.695 g of FeSO₄·7H₂O under sonication for 5 min. Then, the pH value of the resulting mixture was adjusted to 11 with 25% NH₃·H₂O. The resulting slurry was then heated at 90 °C for 6 h in an oil bath without stirring. The resultant 3D-G@Fe₃O₄ was separated by filtration, washed with water and then freeze-dried under vacuum to remove absorbed water. The size and morphology of the synthesized 3D-G@Fe₃O₄ were determined by transmission electron microscopy (TEM) using a JEOL model JEM-2011(HR) (Tokyo, Japan) at 5 kV and scanning electron microscopy (SEM) using an S-3000N microscope (Hitachi, Japan). The infrared spectra (IR) were obtained by a WQF-510 FT-IR Spectrometer (Ruili, China). The magnetic properties were analyzed using a JDM-13 vibrating sample magnetometer (VSM, Jilin University, Changchun, China) at room temperature.

The MSPE extraction procedures are shown in Scheme 2: 15 mg of 3D-G@Fe₃O₄ was placed in a conical flask containing 100 mL water sample. After the pH value of the mixture was adjusted to 5.0, the mixture was shaken for 25 min. Subsequently, the 3D-G@Fe₃O₄ adsorbent was isolated from the solution by placing a magnet at the bottom of the conical flask. The supernatant was discarded and then the rest was transferred to a 10-mL centrifuge tube. Next, the 3D-G@Fe₃O₄ was aggregated again by the magnet to remove the residual solution using a pipette. Finally, 0.3 mL of alkaline methanol (1% 1 mol/L NaOH) was added to elute the analytes. Then, the desorption solution was transferred to a 1-mL microcentrifuge tube and 3.0 μL of 1 mol/L HCl solution was added to neutralize the solution. Then 20.0 μL of the resultant desorption solution was injected into the HPLC system for analysis.



Scheme 2. The MSPE procedure.

3. Results and discussion

3.1. Characterization of 3D-G@Fe₃O₄

The size and morphology of the synthesized 3D-G@Fe₃O₄ were determined by TEM (Fig. 1a) and SEM (Fig. 1b), respectively. Fig. 1a shows that the Fe₃O₄ nanoparticles were uniformly coated on the surface of the G. The SEM image in Fig. 1b reveals that there was an interconnected 3D porous network structure for the 3D-G@Fe₃O₄ nanoparticles. Fig. 2 shows the FTIR spectra of GO and 3D-G@Fe₃O₄. The observed representative peaks of GO confirm the presence of the oxygen-containing functional moieties in the carbon frameworks. The spectrum of GO illustrates the presence of C–O (1400 cm⁻¹) and C=O (1730 cm⁻¹) in carboxylic acid and carbonyl moieties. However, for the 3D-G@Fe₃O₄ sample, all these absorption peaks related to the oxidized groups vanish in the FTIR spectrum, confirming the reduction of the above-mentioned functional groups. The saturation magnetization intensity of 3D-G@Fe₃O₄ was 62.3 emu/g, which was sufficient for magnetic separation with a conventional magnet.

3.2. Optimization of extraction conditions

To achieve an optimal extraction efficiency, several experimental parameters that could influence the extraction efficiency were investigated and optimized, such as the dosage of 3D-G@Fe₃O₄, extraction time, sample pH value, salinity, and desorption conditions.

In order to choose the optimum amount of the adsorbent (3D-G@Fe₃O₄) for the extraction of the CPs, different dosages of the 3D-G@Fe₃O₄ were investigated in the range from 5 mg to 20 mg. The results shown in Fig. 3a revealed that the peak areas for the analytes increased rapidly when the amount of the 3D-G@Fe₃O₄ was increased from 5 mg to 15 mg and then plateaued. Therefore, 15 mg 3D-G@Fe₃O₄ was used in the following experiments.

Extraction time is an important parameter for the extraction performance of the method. A sufficient extraction time was required to obtain the adsorption equilibrium for the analytes on the adsorbents. In the present work, the extraction time was changed from 10 min to 30 min to investigate its influence on extraction efficiency. Fig. 3b shows that when the extraction time was increased to 25 min, the extraction recovery for all the analytes maximized and then remained almost unchanged. Therefore, an extraction time of 25 min was selected for further experiments.

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