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Phytic acid-stabilized super-amphiphilic Fe_3O_4-graphene oxide for extraction of polycyclic aromatic hydrocarbons from vegetable oils

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ABSTRACT

Phytic acid-stabilized Fe_3O_4-graphene oxide (GOPA@Fe_3O_4) was assembled by microwave-enhanced hydrothermal synthesis and super-amphipathicity was demonstrated by measurement of dynamic oil and water contact angles. GOPA@Fe_3O_4 was used as a sorbent for enrichment of eight polycyclic aromatic hydrocarbons (PAHs) from vegetable oils by magnetic solid-phase extraction (MSPE). The extraction-desorption factors were systematically investigated and, under optimum conditions, the super-amphiphilic sorbent achieved wide linear ranges (0.2–200 ng g^{-1}), satisfactory precision (3.44–6.64% for intra-day and 5.39–8.41% for inter-day) and low limits of detection (LODs, 0.06–0.15 ng g^{-1}) for PAHs. Excellent recoveries (85.6–102.3%) for spiked PAHs were obtained with genuine vegetable oil samples. These results indicate that MSPE using GOPA@Fe_3O_4 as the sorbent, coupled with high performance liquid chromatography (HPLC), is an efficient and simple method for the detection of low concentrations of PAHs in vegetable oils.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous organic chemical contaminants that contain two or more fused aromatic rings (Bansal & Kim, 2015). PAHs normally originate from geochemical processes and incomplete combustion of organic compounds. Because of their carcinogenic and mutagenic properties, PAHs have been characterized as priority pollutants by the International Agency for Research on Cancer (IARC, 2010). European Commission Regulation No. 835/2011 has also established maximum levels for pyrene (PYR) and for the sum of four PAHs used as markers for the presence of PAHs in foodstuffs: PYR, anthracene (ANT), fluoranthene (FLT), and chrysene (CHR) (European Communities, 2011). For fats and oils, the maximum limit is 2.0 ng g^{-1} for PYR and 10.0 ng g^{-1} for the sum of the four PAHs (EFSA, 2008; European Communities, 2011).

PAHs have a very strong affinity for oil matrices because of their high hydrophobicity, which means that detection of low concentrations of PAHs in vegetable oils is difficult. The analysis of PAHs in vegetable oil samples typically requires sample pretreatment steps, such as solid phase extraction (Chung & Lau, 2015; Dost & Ideli, 2012; Wu & Yu, 2012), solid-phase microextraction (Purcaro, Morrison, Moret, Conte, & Marriott, 2007) or ultrasound-assisted emulsification microextraction (Cacho, Campillo, Viñas, & Hernández-Córdoba, 2016), together with gas chromatography (GC) or high-performance liquid chromatography (HPLC). The adsorption-desorption steps used in these methods are, however, time-consuming and laborious. Rapid and efficient procedures for determining low concentrations of PAHs in vegetable oil matrices are thus urgently needed.

Magnetic solid-phase extraction (MSPE), a new SPE method based on the combination of a non-magnetic adsorbent material and an inorganic magnetic material, has recently attracted considerable interest in the field of separation science (Rocío-Bautista et al., 2016; Shi et al., 2016; Yu, Ang, Yang, Zheng, & Zhang, 2017; Zheng et al., 2016). Graphene oxide (GO) has a higher adsorption capacity than other MSPE sorbents that have been evaluated and is particularly suitable for the preparation of magnetic composites (Mehdinia, Khodaee, & Jabbari, 2015; Shi et al., 2015; Sitko, Zawisza, & Malicka, 2013). GO is a nanoscale carbonaceous material, with sp^2-hybridized carbon atoms in a honeycomb pattern, which can make strong π-π stacking interactions with aromatic compounds (Georgakilas et al., 2016). Different types of

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magnetic GO have been developed, including zero-valent iron/iron oxide-oxyhydroxide/graphene (Karamani, Douvalis, & Stalikas, 2013), Fe_3O_4 grafted graphene oxide (Zeng et al., 2013), Fe_3O_4/SiO_2-GO nanocomposite (Yao et al., 2012) and magnetic Fe_3O_4-graphene oxide/polystyrene (Kassaee, Motamedi, & Majdi, 2011). The ability of magnetic GO to strongly absorb PAHs from aqueous samples has been attributed mainly to its good compatibility with aqueous media (Cacho et al., 2016; Mehdinia et al., 2015; Shi et al., 2015). The poor dispersibility of GO in hydrophobic media, however, limits its application for the separation and enrichment of organic molecules from hydrophobic media. To the best of our knowledge, there have been no earlier reports describing the use of magnetic GO as an MSPE sorbent to enrich PAHs from vegetable oils.

Because of these limitations, we have devised a simple strategy for assembling super-amphiphilic GOPA@Fe_3O_4, based on stabilization by phytic acid (PA), using microwave-enhanced hydrothermal synthesis. Fe_3O_4 particles acted as the “core” and GO was chemically modified by PA on the surface of the Fe_3O_4 within 60 s. The resulting product showed super-amphipathicity, which overcame the problem of uneven dispersibility of magnetic GO sorbents in hydrophobic media. The GOPA@Fe_3O_4 obtained using this process was fully characterized and its performance as a sorbent was systematically investigated by analyzing eight PAHs typically found in vegetable oils.

2. Materials and methods

2.1. Compounds

Eight typical PAHs, PYR, ANT, CHR, FLT, benzo[*g,h,i*]pyrene (BghiP), indeno[1,2,3-cd]pyrene (INPY), dibenzo[*i,a,h*]anthracene (DiahA) and benzo(a)pyrene (BaP), were obtained from Alfa Aesar (Shanghai, China). GO, ethylene glycol, NaOAc, and $FeCl_3$ were purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China). Aqueous phytic acid solution (50%, *w*/*w*) was bought from Sigma-Aldrich China Inc. (Shanghai, China). HPLC grade solvents were purchased from Thermo Fisher Scientific (Fair Lawn, NJ, USA). All analytical grade reagents were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

2.2. Synthesis of super-amphiphilic GOPA@Fe_3O_4

The procedure for preparation of GOPA@Fe_3O_4 is shown in Fig. 1. The Fe_3O_4 microspheres were synthesized as previously described (Ji et al., 2016; Xu et al., 2006). Briefly, $FeCl_3$ (2.7 g) and ethylene glycol (200 mL) were stirred for 30 min and NaOAc (7.4 g) was then added to the clear yellow solution. After stirring for 30 min, the mixture was divided into two portions and each portion was heated at 180 °C for 10 h in a hydrothermal synthesis reactor (200 mL capacity). After cooling to 25 °C, the Fe_3O_4 microspheres were collected using a magnet, washed with H_2O and MeOH, and dried under vacuum at 60 °C for 6 h.

The super-amphiphilic GOPA@Fe_3O_4 was synthesized using microwave-enhanced synthesis (Zhang et al., 2011). Typically, a mixture of Fe_3O_4 microspheres (100 mg), GO (50 mg) and PA solution (1.0 mL) was ultrasonicated and then stirred in a 25 mL crucible for 30 min. The sealed crucible was then heated in a microwave oven (Glanz G8023N2L-G1HCB0, Shenzhen, China). The reaction temperatures were determined to be in the range 250–270 °C using an infrared thermometer. After irradiating for 60 s, the reactor was allowed to cool naturally to room temperature. The product was removed and washed three times with 0.1 M HCl and then three times with methanol. During washing, the GOPA@ Fe_3O_4 was carefully collected using a magnet. The GOPA@ Fe_3O_4 was then dried at 60 °C under vacuum for 12 h.

2.3. Instrumentation

A Nicolet 710 Fourier transform infrared (FT-IR) spectrometer (Thermo Scientific, San Jose, USA) was used to confirm the chemical structure of GOPA@Fe_3O_4. Scanning electron microscopy (SEM)

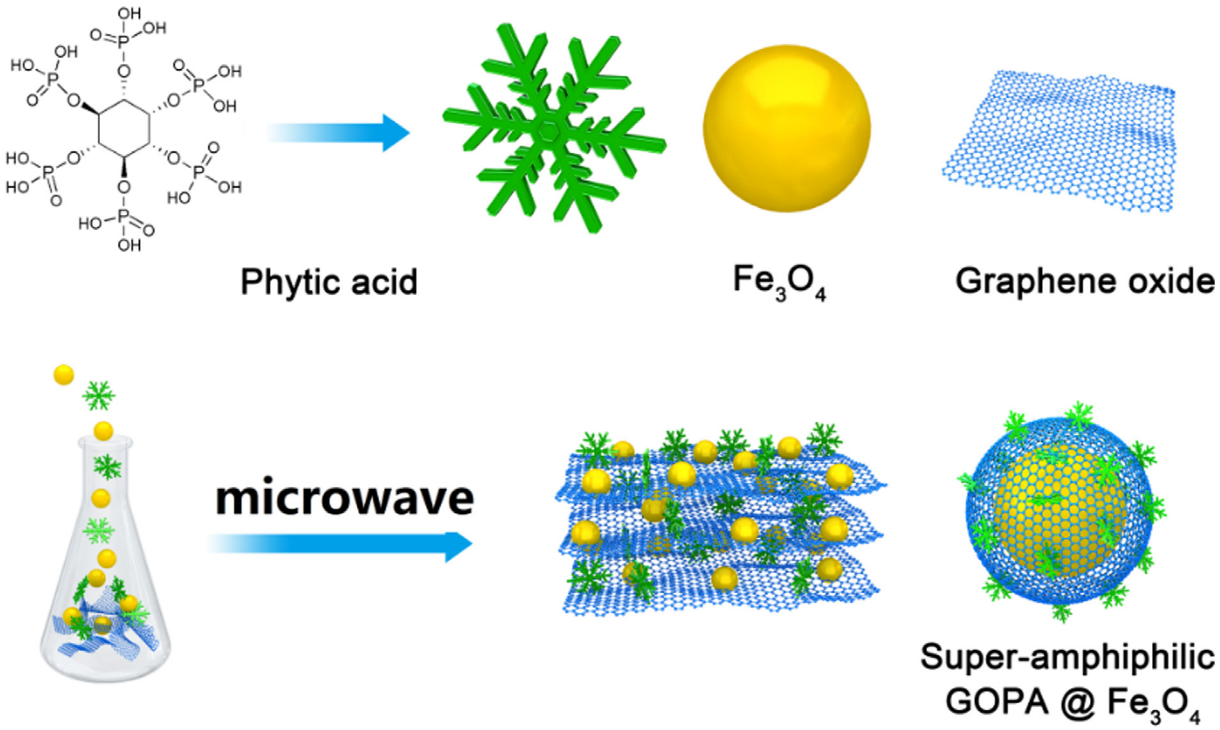

Fig. 1. Fabrication of super-amphiphilic GOPA@ Fe_3O_4.