Simultaneous extraction and determination of phthalate esters in aqueous solution by yolk-shell magnetic mesoporous carbon-molecularly imprinted composites based on solid-phase extraction coupled with gas chromatography–mass spectrometry

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A R T I C L E   I N F O

A B S T R A C T

A rapid, sensitive and accurate method for the simultaneous extraction and determination of five types of trace phthalate esters (PAEs) in environmental water and beverage samples using magnetic molecularly imprinted solid-phase extraction (MMIP–SPE) coupled with gas chromatography–mass spectrometry (GC–MS) was developed. A novel type of molecularly imprinted polymers on the surface of yolk-shell magnetic mesoporous carbon (Fe_3O_4@void@C–MIPs) was used as an efficient adsorbent for selective adsorption of phthalate esters based on magnetic solid–phase extraction (MSPE). The real samples were first preconcentrated by Fe_3O_4@void@C–MIPs, subsequently extracted by eluent and finally determined by GC–MS after magnetic separation. Several variables affecting the extraction efficiency of the analytes, including the type and volume of the elution solvent, amount of adsorbent, extraction time, desorption time and pH of the sample solution, were investigated and optimized. Validation experiments indicated that the developed method presented good linearity ($R^2 > 0.9961$), satisfactory precision (RSD < 6.7%), and high recovery (86.1–103.1%). The limits of detection ranged from 1.6 ng/L to 5.2 ng/L and the enrichment factor was in the range of 822–1423. The results indicated that the novel method had the advantages of convenience, good sensitivity, and high efficiency, and it could also be successfully applied to the analysis of PAEs in real samples.

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1. Introduction

Phthalate esters (PAEs), or plasticizers, are widely used as polymer additives to improve flexibility in the manufacture of plastics, medical devices, children's toys and food packaging [1]. However, several studies have shown that the effects of PAEs are similar to those of estrogen, which can cause feminization of male infants and disturbances in the development and maturation of the genitals [2–4]. Laboratory tests on rodents showed that a high exposure to PAEs damages the liver, kidneys, and lungs [5]. Moreover, PAEs can easily leach from plastic packaging to the contents and into the environment [6]. The United States Environmental Protection Agency (US EPA) has listed PAEs as priority contaminants [7,8]. In 2011, a variety of food contamination cases due to the addition of cloudy agents and emulsifiers in food processing were reported by different media in Taiwan. Many foods, including some beverages, were heavily contaminated with PAEs, such as DEP, DEHP and DBP. Recent incidents involving contamination of white liquor with plasticizers in China emerged in November 2012, and an unacceptable amount of plasticizers were found in Jiugui white liquor produced in Hunan Province. The intensive use of PAEs and their pollutions of the environments have become a more and more serious problem worldwide and a major public health concern. Therefore, the measurement of these compounds in drinking water and food is urgently required for environmental impact and risk assessment. Unfortunately, the relatively low concentration level of PAEs and the complex matrix of real samples make it very difficult to measure these compounds. Therefore, a selective, sensitive, rapid and efficient method for sample preparation and enrichment is needed.

Up to now, various pretreatment techniques have been attempted to extract PAEs from different samples, such as liquid–liquid extraction (LLE) [9,10], solid–phase extraction (SPE) [11,12], solid–phase microextraction (SPME) [13,14] and dispersive liquid–liquid microextraction (DLLME) [15]. SPE has been the most widely used separation technique in the past decades, however, the

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ordinary SPE process is expensive and time-consuming due to the limited rate of diffusion and mass transfer of analytes in the bulk sorbents packed in a cartridge. Furthermore, solid particles may cause a blockage of cartridges and lead to extraction failure. Magnetic solid–phase extraction (MSPE), which has attracted considerable attention in sample preparation in recent years [16–19], is a new mode of SPE based on the adsorption of magnetic particles. In MSPE, the powder magnetic adsorbents need not be packed into an SPE cartridge, but instead are universally dispersed into the sample solution to achieve extraction. Because of this dispersive mode, MSPE not only enhances the extraction efficiency by increasing the interfacial area between the solid adsorbent and the sample solution [20], but also overcomes problems that occur with conventional SPE. Additionally, the adsorbed analytes can be easily eluted from the adsorbent with only a small amount of the appropriate solvent or mixed solvents. All of these merits render MSPE a promising technique for sample preparation [21].

Considerable attention has been paid to magnetic adsorbents due to the development of MSPE. Fe_3O_4 nanoparticles are the most popular owing to their low cost and low toxicity. For analytical purposes, Fe_3O_4 nanoparticles have been modified and functionalized by different materials. Among them, carbon is the most commonly used owing to its ease of functionalization and its stability [22]. Examples of modifications of magnetic nanoparticles designed for the analysis of specific compounds include the synthesis of magnetic graphitic carbon nitride nanocomposites (g-C_3N_4) for the solid–phase extraction of PAEs in water samples [23]; analysis of PAEs in environmental water by magnetic graphene solid–phase extraction coupled with gas chromatography–mass spectrometry [24]; fabrication of magnetic microsphere-confined graphene ($Fe_3O_4@SiO_2$–G) for the extraction of PAHs from environmental water samples coupled with high performance liquid chromatography–fluorescence analysis [25]; and determination of the trace leaching PAEs in water by magnetic solid phase extraction based on magnetic multi-walled carbon nanotubes followed by GC–MS/MS [26]. Due to the complexity of real samples, the magnetic adsorbents typically did not recognize the specific targets effectively. Therefore, during the analysis of actual samples, other substances disturbed the separation of target molecules.

Molecular imprinting technology (MIT) has already become a highly accepted tool for the synthesis of tailor-made recognition materials with cavities that can selectively recognize target molecules [27,28]. However, molecularly imprinted polymers (MIPs) prepared via the conventional technique have several disadvantages, such as a heterogeneous distribution of the binding sites and embedding of most binding sites [29–32]. To resolve these problems, researchers have made efforts to prepare the MIP film on a solid-support substrate using a surface imprinting technique, which can provide an alternative way to improve the mass transfer and reduce the permanent entrapment of the template. Carbon materials, such as graphene oxide [33], multiwalled carbon nanotubes [34,35] and carbon microspheres [36,37] have been widely used in surface-imprinting processes in previous studies. Recently, our group has successfully synthesized yolk–shell magnetic mesoporous carbon–surface molecularly imprinted polymer microspheres ($Fe_3O_4@void@C$–MIPs) based on $Fe_3O_4@void@C$ as a new carbon solid-support substrate [38]. The study shows that the $Fe_3O_4@void@C$–MIPs have several advantages, such as large surface areas, high adsorption capacity, specific recognition, and fast magnetic response. The results of experiments with the $Fe_3O_4@void@C$–MIPs demonstrate that these microspheres are desirable magnetic adsorbents for the separation and enrichment of PAEs in real samples.

In this work, we report potential applications of $Fe_3O_4@void@C$–MIPs as magnetic solid–phase adsorbents for the extraction and enrichment of PAEs from environmental water and beverage samples. To examine the feasibility of this approach, five phthalate esters were selected as model compounds. The magnetic solid–phase extraction procedure was investigated systematically. Coupling this novel magnetic molecularly imprinted solid–phase extraction (MMIP–SPE) technique with GC–MS, a highly selective and sensitive $Fe_3O_4@void@C$–MIPs–SPE–GC/MS (MMIP–SPE–GC/MS) analytical method was established and was applied to the analysis of real samples.

2. Experimental

2.1. Materials and chemicals

The standards of six phthalate esters, including diethyl phthalate (DEP), dibutyl phthalate (DBP), benzyl butyl phthalate (BBP), diethylhexyl phthalate (DEHP), dioctyl phthalate (DNOP), and diisononyl phthalate (DINP) were obtained from Aladdin Reagent Corp. (China). Methacrylic acid (MAA, 98%) was purified by distillation under vacuum. Ethylene glycol dimethacrylate (EGDMA, 98%), azobisisobutyronitrile (AIBN, chemical grade), ammonium hydroxide (28%), methanol, ethanol, ethylene glycol, tetraethoxysilane (TEOS, 99%), resorcinol, formaldehyde (37.0–40.0%), trisodium citrate (Na_3Cit), anhydrous $FeCl_3$, sodium acetate (NaAc), hydrochloric acid (HCl), sodium hydroxide (NaOH), and hydrogen peroxide (H_2O_2, 30%) were of analytical grade and purchased from Sinopharm Shanghai Chemical Corp. (China). Doubly distilled water obtained from a laboratory purification system was used throughout the experiments.

2.2. Instrumentation and analytical conditions

Transmission electron microscopy (TEM) images were collected using a JEOL 2010 electron microscope operated at 200 kV. Gas chromatography–mass spectrometry (GC–MS) were performed using an Agilent 5975C with an HP-5 ms capillary column (30 m × 250 μm × 0.25 μm) and quadrupole mass spectrometers. The split/splitless injector was set to 250 °C, and 1 μL of sample was injected without split. High purity helium (99.999%) was used as the carrier gas (1.2 mL/min). The temperature program was as follows: initial 120 °C, hold 0.5 min, rate 20 °C/min to 280 °C, and hold 3.5 min

2.3. Synthesis of $Fe_3O_4@void@C$–MIPs and $Fe_3O_4@SiO_2@C$–MIPs

The $Fe_3O_4@void@C$–MIPs were synthesized according to the procedure described in our previous study but with some modifications [38]. (1) 0.35 g of resorcinol and 4.0 mL of 28% $NH_3 \cdot H_2O$ were added to a 250 mL flask that contained 0.25 g of Fe_3O_4, 150 mL of ethanol, and 50 mL of H_2O. The mixture was mechanically stirred for 1 h at 30 °C. Next, 0.5 mL of formaldehyde solution and 0.72 mL of TEOS were added dropwise. Then the mixture was stirred at 30 °C and 80 °C for 5 h and 12 h respectively. The resultant solid product was washed and dried at 60 °C for 12 h. After that, the obtained $Fe_3O_4@$polymer nanospheres were heated under a N_2 atmosphere to 600 °C and were maintained at 600 °C for 3 h (denoted as $Fe_3O_4@SiO_2@C$). (2) The $Fe_3O_4@void@C$ was acquired by corroding $Fe_3O_4@SiO_2@C$ with saturated NaOH at room temperature. Next, 0.2 g of $Fe_3O_4@void@C$ was added into 20 mL of 20% H_2O_2 and the mixture was kept at 40 °C for 3 h under magnetic stirring. The products were washed with distilled water until neutral and labeled $Fe_3O_4@void@C$–COOH. (3) Finally, 0.5 g of $Fe_3O_4@void@C$–COOH, 1 mmol DINP and 4 mmol MAA were dissolved in 50 mL of chloroform and ultrasonicated for 30 min, followed by the addition of 20 mmol EGDMA and 60 mg of AIBN. Next, the solution was ultrasonicated for 10 min and purged with