Determination of phthalate esters in environmental water by magnetic Zeolitic Imidazolate Framework-8 solid-phase extraction coupled with high-performance liquid chromatography

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ARTICLE INFO

ABSTRACT

In this study, the magnetic Zeolitic Imidazolate Framework-8 (ZIF-8) microspheres were successfully synthesized and applied as an effective sorbent for preconcentration of several typical phthalate esters (PAEs) from environmental water samples. Firstly, the solvothermal treatment method was used for preparation of Fe_3O_4 nanoparticles. Then, mercaptoacetic acid (MAA) was served as the functionalized chemical to modify Fe_3O_4 nanoparticles. The Fe_3O_4@ZIF-8 core–shell microspheres were synthesized through coating the MAA-capped Fe_3O_4 nanoparticles with ZIF-8. By coupling magnetic solid-phase extraction (MSPE) with high-performance liquid chromatography (HPLC), a reliable, sensitive and cost-effective method for simultaneous determination of five main PAEs including dimethyl phthalate (DMP), diethyl phthalate (DEP), di-*n*-butyl phthalate (DBP), benzyl butyl phthalate (BBP), and dioctyl phthalate (DOP) was developed. Good linearity was observed in the range of 1.0–100.0 μg/L. The limits of detection (S/N = 3) and limits of quantification (S/N = 10) were in the range of 0.08–0.24 and 0.3–0.8 μg/L, respectively. The relative standard deviations were less than 5.5% and the accuracies of the method for the PAEs were in the range from 85.6% to 103.6%. Finally, the Fe_3O_4@ZIF-8 was successfully applied for rapid extraction of trace amounts of PAEs in environmental water samples.

1. Introduction

Phthalate esters (PAEs) are widely used as polymer additives in the manufacture of plastics, rubber, building materials, medical devices, children's toys, as well as cosmetics to improve their flexibility. It is estimated that the global consumption of PAEs in plastics industry is more than 18 billion pounds each year, and these PAEs would be released from the above-mentioned products and find a way to various environmental matrices [1]. Due to the accumulation of PAEs in natural waters, it causes wide distribution within surface water systems, for example, rivers, lakes, and ground waters [2]. Several studies have shown that PAEs can produce effects similar to those of estrogens, causing feminization of male infants and disturbances in genital development and testes maturation. In animals, PAEs have shown teratogenic, carcinogenic, reproductive and developmental effects [3,4]. Therefore, the establishment of effective methods for the determination of trace PAEs is necessary.

Nowadays, various pretreatment techniques followed by chromatographic analysis have been developed to extract PAEs from different samples, such as solid-phase extraction (SPE) [5], solid-phase microextraction (SPME) [6], classical liquid–liquid extraction (LLE) [7] and dispersive liquid–liquid microextraction (DLLME) [8–10]. SPE often suffers from plugging of the cartridge and consumption of large of toxic solvents at the desorption step. SPME fibers are relatively expensive, generally fragile, and have a limited lifetime. The classical LLE is time-consuming, promotes loss of target analytes, and requires consumption of large amounts of hazardous organic solvents. DLLME has gained considerable applicability in analysis of PAEs with advantages of being economical, effective, and solvent-minimized [11]. Moreover, Lee's group has recently developed a completely automated procedure for PAEs analysis by combining de-emulsification DLLME and GC/MS, which

opens up an innovative way to expand the convenience and applicability of DLLME [12]. Additionally, the magnetic solid-phase extraction (MSPE) based on various magnetic nanoparticles became more and more popular in recent years [13,14]. Due to the simple mechanism of magnetic separation, MSPE also showed great potential applications in preconcentration and separations of PAEs [15–21].

Metal-organic frameworks (MOFs) typically are characterized by large internal surface areas, uniform but tunable cavities and tailorable chemistry [22,23]. Some MOFs have drawn special interest in analytical applications, such as Materials of Institut Lavoisier (MIL) [24,25], UiO-66 [26], [Cu$_3$(btc)$_2$] [27], as well as Zeolitic Imidazolate Framework-8 (ZIF-8) [28–31]. Thereinto, ZIF-8 has permanent porosity, hydrophobic property and open metal sites, and especially it is very stable in water samples [22]. It has been employed as SPE sorbent for enriching trace amount of compounds from aqueous samples by many researchers. Ge and Lee used ZIF-8 as a sorbent for μ-SPE of six polycyclic aromatic hydrocarbons from environmental water samples for the first time [23]. Jiang et al. [28] used ZIF-8 for fast adsorption and removal of benzotriazoles from aqueous solution. Yang et al. [29] utilized ZIF-8 for on-line SPE of tetracyclines in water and milk samples. Wang et al. [30] used ZIF-8 as sorbent for μ-SPE of estrogens in environmental water samples. However, only a few ZIF-8 related magnetic materials have been reported for now [31–34]. Zhang et al. coated polystyrolsulfon acid functionalized Fe$_3$O$_4$ with ZIF-8 to produce Fe$_3$O$_4$@ZIF-8 magnetic microspheres. They used this material as catalyst for Knoevenagel condensation reaction of benzaldehyde and ethyl cyanoacetate, which was easily loaded/unloaded into/out a capillary microreactor with the help of an external magnetic field [31]. Pang et al. prepared Fe$_3$O$_4$/ZIF-8 by doping polyacrylic acid functionalized Fe$_3$O$_4$ nanocrystals to ZIF-8 microsphere. And they also used the Fe$_3$O$_4$/ZIF-8 for catalytic application of Knoevenagel condensation reaction [32]. Both of the above works were carried out for catalysis purpose instead of MSPE application. Also, Lan et al. prepared a kind of magnetic molecularly imprinted polymer microsphere with Fe$_3$O$_4$@ZIF-8 as the intimal carrier for enrichment of estrogens from food samples. In their work, the molecularly imprinted polymer was the main sorbent for analytes, and ZIF-8 only served as an interlayer carrier for structure and auxiliary factor for adsorption [33]. Recently, Lin et al. [34] reported that ZIF-8 coated magnetic nanocomposites were used for enrichment and direct detection of small molecules by negative-ion matrix-assisted laser desorption/Ionization time-of-flight mass spectrometry (MALDI-TOF-MS) for the first time.

In our work, we developed a simple and facile synthetic strategy to prepare Fe$_3$O$_4$@ZIF-8 magnetic core–shell microspheres. The Fe$_3$O$_4$@ZIF-8 was synthesized by coating mercaptoacetic acids capped Fe$_3$O$_4$ nanoparticles with ZIF-8 at room temperature. Then, a simple MSPE method for enriching five PAEs was developed with the Fe$_3$O$_4$@ZIF-8 core–shell magnetic microspheres as sorbent. The proposed MSPE procedure is shown in Fig. S1 (Supplementary Materials). Compared with previous reported extraction methods, this proposed method based on Fe$_3$O$_4$@ZIF-8 is a simpler, more rapid, and more cost-effective method for extraction of PAEs. Finally, this method was successfully applied in determination of five typical PAEs in environmental water samples.

2. Experimental

2.1. Materials and chemicals

Standard mixtures of five PAEs containing dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-butyl phthalate (DBP), benzyl butyl phthalat (BBP), and dioctyl phthalate (DOP) were purchased from Aladdin Industrial Corporation (Shanghai, China). HPLC grade methanol, acetonitrile and toluene were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Deionized water was obtained from a Milli-Q water purification system.

The Fe$_3$O$_4$@ZIF-8 magnetic core–shell microsphere was prepared in our laboratory. It was synthesized by coating mercaptoacetic acids (MAA) capped Fe$_3$O$_4$ nanoparticles with ZIF-8 at room temperature. The procedure for preparing Fe$_3$O$_4$@ZIF-8 is elaborated in Supplementary Materials.

2.2. Instrumentation

Infrared absorption spectra were conducted on NEXUS-470 Fourier transform infrared (FT-IR) spectrometer made in Thermo Nicolet Corporation (America). X-ray powder diffraction (XRD) measurements were performed on a Rigaku MiniFlex 600 diffractometer (Rigaku, Tokyo, Japan) with Cu K$_\alpha$ radiation ($\lambda = 0.15418$ nm); a scanning rate of 5 deg/min was applied to record the patterns in the 2θ range of 10–80°. Transmission electron micrographs (TEM) were given by FEI Tecnai G20 (America). Magnetic curves were obtained by Magnetic Property Measurement System XL 7 (MPMS-XL-7) (America).

The PAEs were separated and determined using an Agilent 1100 series high-performance liquid chromatography (HPLC) system equipped with a diode array detection (DAD) and an analytical reversed-phase C$_8$ column (5 μm, 4.6 mm × 150 mm) (America). Mobile phase A: 5% acetonitrile in water; mobile phase B: acetonitrile. Linear gradient elution program: 0–15 min, 70–0% A; flow rate: 1.0 mL/min. Injection volume: 20 μL. The column temperature: 25 °C. The DAD detection wavelength: 254 nm.

2.3. Sample preparation

River water, tap water and bottled mineral water samples were collected from the local river, Water Supply Company and supermarket, respectively. The water samples were stored at room temperature in glass bottle and filtered through a 0.22 μm Millipore cellulose membrane immediately after sampling, stored in clean glass bottle, and analyzed within one day.

2.4. Procedure of MSPE

20 mL of the standard solution or sample solution and a certain amount of magnetic microspheres were successively added to a 50 mL glass centrifuge tube, and the microspheres were homogeneously diffused in the mixed solution for 8 min under sonication. Then, an external magnet was placed beside the tube to hold the magnetic composites which had already extracted analytes. With the sorbent remained in the tube, the water was dumped from the tube. Subsequently, 1 mL of methanol was added to the tube as an eluent to desorb the analytes under ultrasonication for 8 min. After the magnetic microspheres were collected by magnetic separation, the obtained extract was dried with a stream of nitrogen at 55 °C. And then 100 μL of methanol was added to the centrifuge tube to dissolve the residue. The resolved solution was injected into the HPLC for analysis.

3. Results and discussion

3.1. Characterization of Fe$_3$O$_4$@ZIF-8

Fig. 1(a) shows the transmission electron micrographs of the as-synthesized microspheres. It can be found that Fe$_3$O$_4$@ZIF-8 is composed of a Fe$_3$O$_4$ core and a ZIF-8 shell. Fig. 1(b) shows the FT-IR spectroscopies of the synthesized microspheres, which are applied to characterize the chemical structure of MAA-capped Fe$_3$O$_4$, ZIF-8 and Fe$_3$O$_4$@ZIF-8. The band in the spectral region of