



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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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 $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ 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 $\mu\text{g/L}$. 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 $\mu\text{g/L}$, 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 $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ was successfully applied for rapid extraction of trace amounts of PAEs in environmental water samples.

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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 amounts 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

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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 tailorabile chemistry [22,23]. Some MOFs have drawn special interest in analytical applications, such as Materials of Institut Lavoisier (MIL) [24,25], UiO-66 [26], $[\text{Cu}_3(\text{btc})_2]$ [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_3O_4 with ZIF-8 to produce $\text{Fe}_3\text{O}_4@\text{ZIF}-8$ 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 $\text{Fe}_3\text{O}_4/\text{ZIF}-8$ by doping polyacrylic acid functionalized Fe_3O_4 nanocrystals to ZIF-8 microsphere. And they also used the $\text{Fe}_3\text{O}_4/\text{ZIF}-8$ 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 $\text{Fe}_3\text{O}_4@\text{ZIF}-8$ 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 $\text{Fe}_3\text{O}_4@\text{ZIF}-8$ magnetic core–shell microspheres. The $\text{Fe}_3\text{O}_4@\text{ZIF}-8$ was synthesized by coating mercaptoacetic acids capped Fe_3O_4 nanoparticles with ZIF-8 at room temperature. Then, a simple MSPE method for enriching five PAEs was developed with the $\text{Fe}_3\text{O}_4@\text{ZIF}-8$ 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 $\text{Fe}_3\text{O}_4@\text{ZIF}-8$ 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 phthalate (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 $\text{Fe}_3\text{O}_4@\text{ZIF}-8$ magnetic core–shell microsphere was prepared in our laboratory. It was synthesized by coating mercaptoacetic acids (MAA) capped Fe_3O_4 nanoparticles with ZIF-8 at room temperature. The procedure for preparing $\text{Fe}_3\text{O}_4@\text{ZIF}-8$ 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 $\text{Cu K}\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$); 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 C₈ 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 $\text{Fe}_3\text{O}_4@\text{ZIF}-8$

Fig. 1(a) shows the transmission electron micrographs of the as-synthesized microspheres. It can be found that $\text{Fe}_3\text{O}_4@\text{ZIF}-8$ is composed of a Fe_3O_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_3O_4 , ZIF-8 and $\text{Fe}_3\text{O}_4@\text{ZIF}-8$. The band in the spectral region of

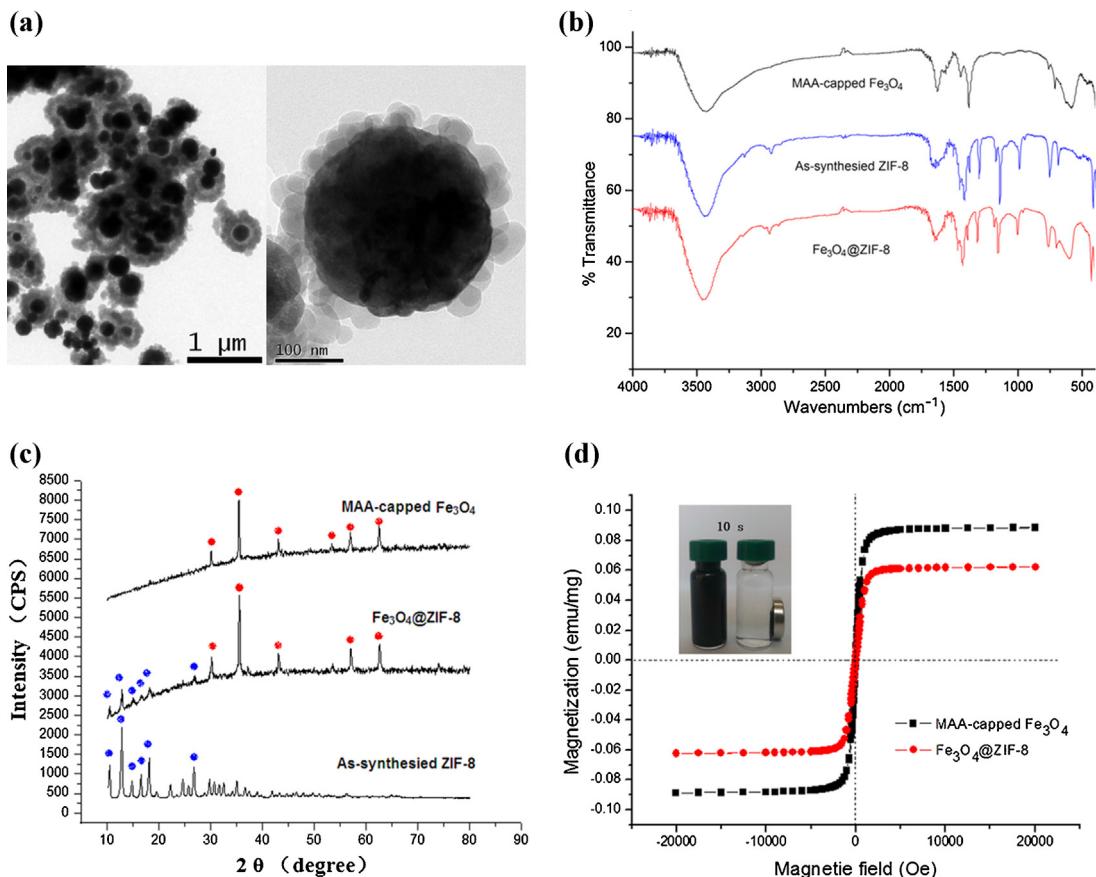


Fig. 1. The characterization of $\text{Fe}_3\text{O}_4@\text{ZIF}-8$ core-shell magnetic microspheres. (a) TEM micrograph of the $\text{Fe}_3\text{O}_4@\text{ZIF}-8$; (b) FT-IR spectra of MAA-capped Fe_3O_4 , ZIF-8 and $\text{Fe}_3\text{O}_4@\text{ZIF}-8$; (c) XRD spectra of MAA-capped Fe_3O_4 , ZIF-8 and $\text{Fe}_3\text{O}_4@\text{ZIF}-8$; (d) magnetic curves of MAA-capped Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{ZIF}-8$.

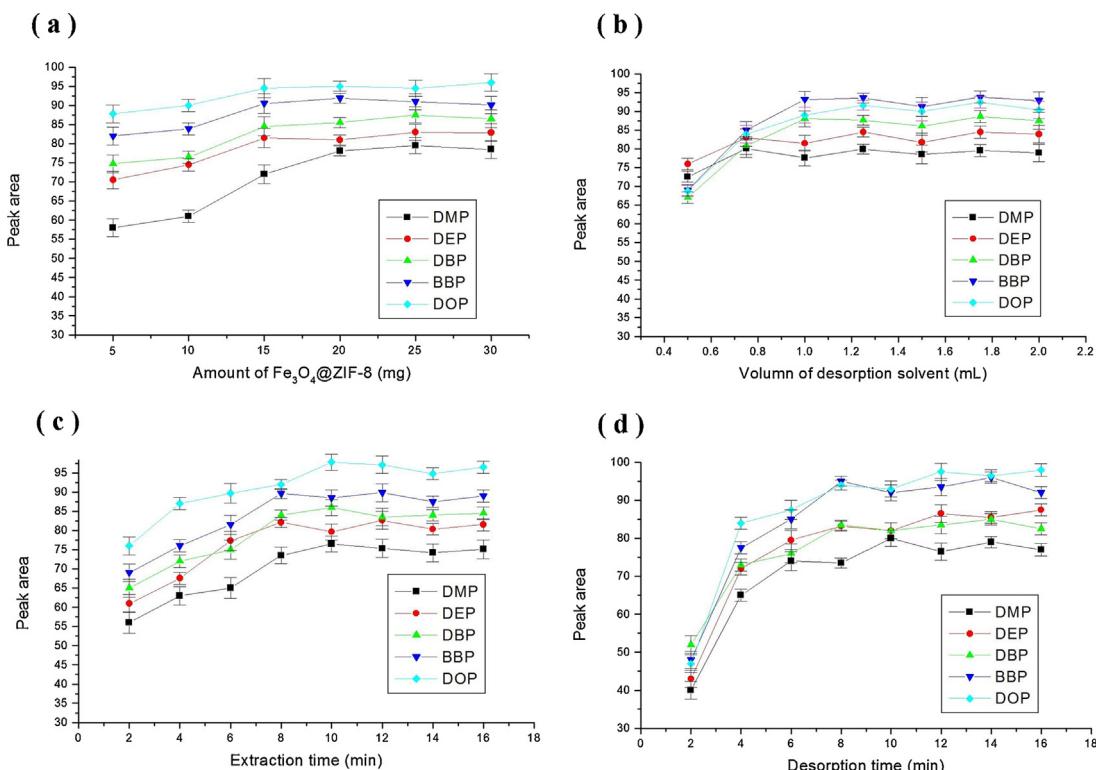


Fig. 2. Optimization of the MSPE conditions parameters. (a) Effect of the amount of $\text{Fe}_3\text{O}_4@\text{ZIF}-8$. (b) Effect of volume of desorption solvent. (c) Effect of the adsorption time. (d) Effect of desorption time.

Table 1

Calibration equations, LODs, LOQs, precision and accuracy data for the MSPE procedure.

Analytes	Linear range ($\mu\text{g/L}$)	Calibration equations ^a	Correlation coefficient (r)	LODs ($\mu\text{g/L}$)	LOQs ($\mu\text{g/L}$)	Recovery (%)			RSD (%)		
						1 $\mu\text{g/L}$	10 $\mu\text{g/L}$	100 $\mu\text{g/L}$	1 $\mu\text{g/L}$	10 $\mu\text{g/L}$	100 $\mu\text{g/L}$
DMP	1.0–100.0	$y = 112.907x - 0.06144$	0.9989	0.18	0.6	85.6	96.2	103.6	5.5	5.2	2.1
DEP	1.0–100.0	$y = 109.064x - 0.14866$	0.9992	0.24	0.8	89.3	90.8	95.4	4.4	4.3	4.7
DBP	1.0–100.0	$y = 154.250x - 0.07468$	0.9988	0.12	0.4	86.6	98.6	98.5	5.3	4.6	4.4
BBP	1.0–100.0	$y = 119.387x + 0.06761$	0.9988	0.14	0.5	93.8	92.3	96.4	4.7	3.3	3.7
DOP	1.0–100.0	$y = 222.094x - 0.03413$	0.9996	0.08	0.3	96.7	97.4	102.7	5.4	4.8	2.7

^a y : peak area of PAEs; x : the concentration of PAEs ($\mu\text{g/L}$).

580 cm^{-1} is assigned as Fe—O—Fe vibration of magnetite. In contrast to that of Fe_3O_4 , the spectra of $\text{Fe}_3\text{O}_4@\text{ZIF}-8$ show the additional adsorption bands which are connected with the structure of ZIF-8. For example, the absorption band in the 500–1350 cm^{-1} and 1350–1500 cm^{-1} are attributed to the bending and stretching of imidazole ring, respectively. X-ray diffraction shown in Fig. 1(c) detects the characteristic peaks of both MAA-capped Fe_3O_4 and ZIF-8 in $\text{Fe}_3\text{O}_4@\text{ZIF}-8$ core–shell microspheres. It indicates that ZIF-8 is well involved in the $\text{Fe}_3\text{O}_4@\text{ZIF}-8$ core–shell microspheres. The magnetic curves of MAA-capped Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{ZIF}-8$ are shown in Fig. 1(d), which is obtained by vibrating sample magnetometry within the field range of –20,000 to 20,000 Oe. As can be seen from Fig. 2(d), the magnetization saturation values of MAA-capped Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{ZIF}-8$ are about of 0.087 emu/mg and 0.060 emu/mg, respectively. The magnetic particles can be collected using a magnet within 10 s after dispersing in water, which indicates that $\text{Fe}_3\text{O}_4@\text{ZIF}-8$ core–shell magnetic microspheres are suitable for the MSPE.

3.2. Optimization of the MSPE conditions

The MSPE process was grouped into two steps: adsorption and desorption. In order to obtain the maximal extraction efficiency, several important parameters, including selection of desorption solvent, the amount of $\text{Fe}_3\text{O}_4@\text{ZIF}-8$, the volume of desorption solvent, adsorption time, desorption time, sample pH and reusability of the sorbent were investigated.

3.2.1. Selection of desorption solvent

The selection of the eluting solvent is quite important for the desorption procedure. PAEs may not be easily desorbed if the wrong sorbent is used, because they are relatively hydrophobic and have strong interaction with the sorbent. In this study, we selected

acetonitrile, methanol, chloroform and tetrahydrofuran as eluting solvent, and ZIF-8 is stable in the four organic solvents. The results indicated that methanol and chloroform gave equivalent desorption yields, which is about 1.1–1.3 times higher than those obtained with acetonitrile or tetrahydrofuran as desorption solvent. Comparing with the chloroform, methanol is less toxic and easy to handle. Hence, methanol was selected as the desorption solvent for further experiments.

3.2.2. Effect of the amount of $\text{Fe}_3\text{O}_4@\text{ZIF}-8$ and volume of desorption solvent

The effect of the amount of $\text{Fe}_3\text{O}_4@\text{ZIF}-8$ for this work is fairly significant. In this study, the amount of $\text{Fe}_3\text{O}_4@\text{ZIF}-8$ was estimated within the range of 5–30 mg. As can be seen from Fig. 2(a), the extraction efficiency of all PAEs kept on increasing when the amount of $\text{Fe}_3\text{O}_4@\text{ZIF}-8$ increased from 5 mg to 20 mg. As the amount of $\text{Fe}_3\text{O}_4@\text{ZIF}-8$ further increased after 20 mg, the extraction efficiency began to level off. So, 20 mg of $\text{Fe}_3\text{O}_4@\text{ZIF}-8$ was employed in the following experiments.

The volume of desorption solvent is another essential factor which affects the extraction efficiency of PAEs. Different volumes of desorption solvent were investigated. As is shown in Fig. 2(b), the maximum extraction efficiency of analytes was obtained when the volume of the desorption solvent was 1 mL. Therefore, 1 mL of desorption solvent was adopted.

3.2.3. Effect of the adsorption time and desorption time

In this experiment, adsorption time is also a necessary parameter for extraction efficiency. So the effect of adsorption time was investigated and the results are shown in Fig. 2(c). As is shown in Fig. 2(c), the extraction efficiency of all PAEs reached a maximum value when the adsorption time was 8 min. With adsorption time further increasing from 8 to 16 min, the extraction efficiency kept

Table 2

The contents of phthalate esters in real samples.

Real samples		DMP	RSD (%)	DEP	RSD (%)	DBP	RSD (%)	BBP	RSD (%)	DOP	RSD (%)
River water	Found ($\mu\text{g/mL}$)	nd		nd		0.020	2.7	0.060	2.2	0.010	2.3
	Recovery ^a (%)	92.9	4.5	96.6	3.7	99.3	3.8	99.4	3.7	96.8	3.4
	Recovery ^b (%)	96.1	4.7	89.7	3.1	97.5	4.1	96.1	2.6	103.2	4.3
	Recovery ^c (%)	97.8	5.8	95.1	4.2	98.7	3.4	98.5	4.3	99.7	3.5
Mineral water	Found ($\mu\text{g/mL}$)	nd									
	Recovery ^a (%)	93.0	5.1	84.6	2.8	86.6	4.3	95.4	2.7	94.5	4.3
	Recovery ^b (%)	103.5	2.4	87.7	3.1	89.0	3.2	97.8	3.6	96.5	5.1
	Recovery ^c (%)	97.8	4.2	101.0	3.5	94.1	2.1	101.5	3.4	103.0	4.2
Tap water	Found ($\mu\text{g/mL}$)	0.009	2.6	nd		nd		nd		0.005	2.8
	Recovery ^a (%)	94.9	3.8	88.4	4.1	89.3	3.1	96.0	4.2	97.8	3.5
	Recovery ^b (%)	96.0	3.8	93.6	3.3	95.1	3.2	89.5	2.7	92.6	3.2
	Recovery ^c (%)	99.7	5.5	93.3	2.9	97.9	3.8	104.5	2.4	89.8	4.1

nd means not detected.

^a 0.01 $\mu\text{g/mL}$.^b 0.05 $\mu\text{g/mL}$.^c 0.10 $\mu\text{g/mL}$.

Table 3

Comparison of the proposed method with previous methods for the determination of PAEs.

Analytes	Magnetic absorbent material	Analytical method	The ratio of material to sample	LODs	Adsorption time (min)	Desorption time (min)	References
DMP DEP DIBP DBP BBP DEHP DNOP	C ₁₈ -Fe ₃ O ₄ @mSiO ₂ microspheres	GC-MS	10 mg/10 mL	25–77 µg/L	10	10	[15]
DMP DEP DBP BBP DEHP DNOP	mag-graphene@mSiO ₂ -C ₁₈	GC-MS	20 mg/10 mL	0.1–10 µg/L	20	15	[16]
DMP DEP DIBP DBP BBP DEHP DNOP	Magnetic graphene	GC-MS	20 mg/10 mL	0.01–0.056 µg/L	15	15	[17]
DMP DEP DAP DPP	Three-dimensional graphene-based magnetic nanocomposite (3D-G-Fe ₃ O ₄)	HPLC-DAD	15 mg/150 mL	0.042–0.060 ng/mL	25	–	[18]
DAP DPP BBP DCP DEHP	Fe ₃ O ₄ @SiO ₂ -G	HPLC-UV	0.15 mg/mL	0.07–0.3 ng/mL	10	–	[19]
DEP DBP BBP DIOP DNOP	Magnetic dummy molecularly imprinted microspheres (MAG-MIM)	GC-FID	100 mg/10 mL	0.53–1.2 µg/L	10	5	[20]
DMP DEP BBP DBP DEHP	The diatomaceous earth-supported magnetite nanoparticles (DSMNPs)	HPLC-UV	25 mg/10 mL	0.5–5.0 ng/mL	8	–	[21]
DMP DEP DBP BBP DOP	Fe ₃ O ₄ @ZIF-8	HPLC-DAD	20 mg/20 mL	0.08–0.24 µg/L	8	8	This work

constant with no significant improvement. Therefore, 8 min was selected as the optimum adsorption time for the following work. With adsorption time fixed at 8 min, the effect of desorption time was investigated from 2 to 16 min. It can be seen from Fig. 2(d) that 8 min was enough to get the best extraction efficiency. Based on this observation, the optimum desorption time was pitched on 8 min.

3.2.4. Effect of the solvent pH

The charge property of the surface is a main factor affecting the aggregation of the magnetic nanoparticles. It might vary with solution pH and affect adsorption efficiencies of target compounds. In this work, the pH of the sample-extracting solution was investigated by adjusting the parameter with 0.15 M HCl or 0.15 M NaOH. The effect of pH on the extraction of PAEs was investigated in a pH range of 3–8. The results indicated that the extraction efficiency of PAEs exhibited no significant differences under different pH conditions. It can be attributed to the fact that the ZIF-8 coating is positively charged in a broad pH range of 2–10 [28]. In the tested pH range, the Fe₃O₄@ZIF-8 particles tended to disperse in water solution owing to electrostatic repulsion. Therefore, the pH of the sample-extracting solution was not controlled in the following experiments.

3.3. Analytical performance

A series of experiments regarding the analytical characteristics such as linearity, limits of detection (LODs), limits of quantification (LOQs), repeatability and accuracies were performed to validate the proposed method under the optimized working conditions (Table 1). As seen from Table 1, the proposed method exhibits good linearity in range of 1.0–100.0 µg/L with the correlation coefficients ≥ 0.9988 . The LODs ($S/N = 3$) of DMP, DEP, DBP, BBP, DOP are 0.18, 0.24, 0.12, 0.14 and 0.08 µg/L, respectively. The LOQs ($S/N = 10$) of the five analytes are 0.6, 0.8, 0.4, 0.5 and 0.3 µg/L, respectively. The intra-day precision and accuracy of the method were evaluated by assaying spiked water samples at three concentration levels (1, 10 and 100 µg/L) in the same day. The recoveries and relative standard deviations (RSDs) of precision are summarized in Table 1. Intra-day

precision values for the analytes are always less than 5.5%, and the accuracies are in the range of 85.6–103.6%.

3.4. Analysis of water samples

The developed MSPE-HPLC-DAD method was successfully applied to the analysis of PAEs in real water samples. The local river water, mineral water and tap water were analyzed. The calculated concentrations of PAEs are listed in Table 2, and the representative chromatogram of the tap water sample is shown in Fig. 3. In the tested tap water sample, DMP and DOP were detected and quantified; there are three PAEs were detected in the river sample; and no PAEs were found in the mineral water sample. The values of recoveries from the spiked samples ranged from 84.6% to 104.5%. All the results showed that the proposed method based on Fe₃O₄@ZIF-8 was feasible for the application in real water sample analysis.

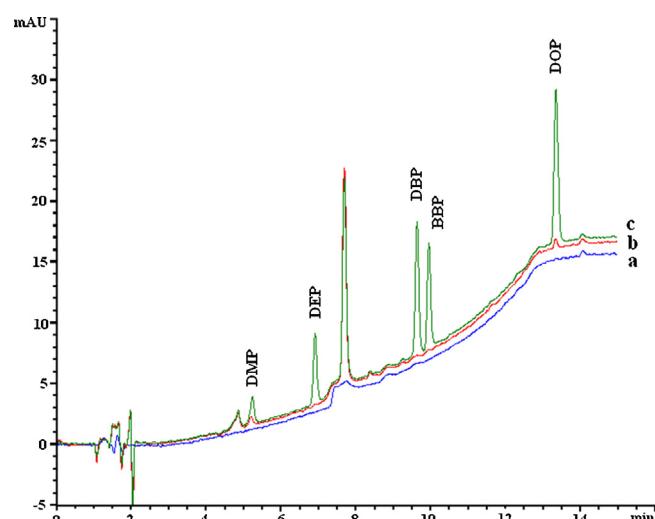


Fig. 3. The chromatograms for representative water samples. (a) Tap water; (b) tap water after MSPE; (c) the MSPE treated tap water with spiked standards.

3.5. Comparisons of this work with the reported MSPE methods

In order to further evaluate the advancement of the proposed method, it was compared with reported methods, and the characters and performance of these methods are shown in Table 3. As can be seen from Table 3, the kinds of analytes, absorbent, analytical method, the ratio of material to sample, adsorption time, desorption time, reusability of the magnetic adsorbent and LODs are summarized in detail. In these methods, the typical PAEs like DMP, DEP, DBP, BBP and DOP are likely to be selected for MSPE enrichment studies. In view of the convenience and easy-handling of magnetic separation, various materials have been used to develop MSPE method for enriching PAEs, such as mesoporous silica composites with modified interior pore-walls [15,16], graphene [17–19], dummy molecularly imprinted composites [20], the diatomaceous earth-supported composites [21] and MOFs. Remarkably, the proposed $\text{Fe}_3\text{O}_4@\text{ZIF}-8$ as well as $\text{C}_{18}-\text{Fe}_3\text{O}_4@\text{mSiO}_2$ possesses marvelous properties of restricted-access material, which could eliminate the influence of biological macromolecules on adsorption capacity (see Supplementary Materials). The amount of absorbent used in the proposed method (20 mg/20 mL) is less than those in most of previous methods [16,17,20,21]. The whole extraction was completed within 16 min with the proposed $\text{Fe}_3\text{O}_4@\text{ZIF}-8$ as sorbent. While extraction time in most previous method is about 15–35 min. The LODs values of the proposed method are lower than or equivalent to previous methods [15,16,18–21]. In addition, the reused times of $\text{Fe}_3\text{O}_4@\text{ZIF}-8$ in work is at least 10 times without significant loss of the sorption capacity (see Supplementary Materials). These results further demonstrate that the proposed method is rapid, sensitive, and efficient for the analysis of PAEs in water samples.

4. Conclusions

In this study, $\text{Fe}_3\text{O}_4@\text{ZIF}-8$ core–shell magnetic microspheres were successfully synthesized and used as sorbent for the MSPE of PAEs at trace levels in water samples. Combined with HPLC–DAD, the developed method displayed excellent sensitivity, ease of operational and satisfactory recovery and repeatability under optimized conditions. More importantly, the method was successfully applied to explore real environmental water samples. These results indicated that the $\text{Fe}_3\text{O}_4@\text{ZIF}-8$ core–shell magnetic microsphere would be a kind of hopeful MSPE material for trace analysis of pollutants in environmental water samples.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chroma.2015.07.068>

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