

Novel Uniform Fe₃O₄ Hollow Spheres for Magnetic Solid-phase Extraction of Polycyclic Aromatic Hydrocarbons

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A novel magnetic absorbent based on Fe₃O₄ hollow nanospheres was developed for polycyclic aromatic hydrocarbons (PAHs) extraction. Fe₃O₄ hollow nanospheres were prepared by a one-pot facile solvothermal method and its structural properties were characterized by scanning electron microscope (SEM) and analyzer transmission electron microscopy (TEM). It was the first time to use hollow nanospheres which possess high special surface area for magnetic solid-phase extraction (MSPE). The extraction condition of Fe₃O₄ hollow nanospheres and its performance for PAHs was systematically investigated. Besides, its extraction performance also compared with bare Fe₃O₄ nanoparticles. The results indicated the structure with hollow and spherical Fe₃O₄ perform better enrichment ability than that with solid and amorphous ones. The developed MSPE coupled with HPLC method shows good linearity (0.1 – 5 ng/mL) and low detection limits (2.5 – 10 pg/mL) for six PAHs. It also has been executed for the analysis of environmental samples, with recoveries in the range of 84.6 – 97.8%.

Keywords Fe₃O₄ hollow nanospheres, magnetic solid-phase extraction, high-performance liquid chromatography, polycyclic aromatic hydrocarbons

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) containing several aromatic rings are mainly formed by the pyrolysis, dehydrogenation, and incomplete combustion of organic material.^{1,2} Many PAHs have been found to have toxic, carcinogenic, and mutagenic properties.^{3–5} Due to their ubiquitous presence and potential to cause adverse human health effects, it is essential to develop a sensitive analytical method to detect PAHs in the environment.

High-performance liquid chromatography (HPLC) coupled with fluorescence detection (FLD) has been widely used for the separation and determination of PAHs.^{6–10} Due to their trace amounts together with the complexity of the matrices, a sample preparation method is generally required before instrumental analysis. Solid-phase extraction (SPE) is one of the established and popular methods for sample enrichment due to its high extraction efficiency.^{11–13} However, it still has some drawbacks such as time-consuming due to the tedious operation procedures, relatively expensive of consumption, and sometimes limited by the sample volume.¹⁴ To deal with these drawbacks, magnetic solid-phase extraction (MSPE) has attracted much attention since the sorbent can be easily separated from the sample solution using an external magnetic field without the need of additional centrifugation or filtration.^{15–17} Besides, own to the large specific surface area of magnetic nanoparticles, it results

in relatively higher extraction capacity and detection sensitivity.^{18,19}

The iron oxides magnetite (Fe₃O₄) are by far the most commonly used magnetic materials in sample preparation because of the simple procedures of fabrication, their superparamagnetic character and low toxicity.¹⁶ Naked magnetic nanoparticles Fe₃O₄ tend to aggregate and do not possess selectivity toward target analytes.²⁰ In order to enhance their stability and selectivity toward the target analytes, various functionalized magnetic Fe₃O₄ nanoparticles such as carbon materials,²¹ inorganic silica materials,²² organic polymers,²³ surfactants,²⁴ ionic liquids²⁵ and metal-organic frameworks²⁶ coated nanoparticles have been prepared and used as sorbents in MSPE technique. For example, Amiri *et al.* prepared polyfuran modified magnetite nanoparticles (PFu/Fe₃O₄) which were used as adsorbents for the MSPE of the polycyclic aromatic hydrocarbons.²⁷ Moreover, Capriotti *et al.* applied polydopamine-coated magnetic nanoparticles for isolation and enrichment of trogenic compounds followed by liquid chromatography-tandem mass spectrometry determination.²⁸ In all the reported literatures for MSPE, Fe₃O₄ nanoparticles were almost all prepared by chemical coprecipitation method. The prepared Fe₃O₄ nanoparticles are amorphous and irregular with solid inside. These kind of magnetic nanoparticles possess the limited surface area and its modification amount by other materials are also restricted. Therefore, developing novel spherical Fe₃O₄ nanoparticles consisting of large surface area is highly desired.

In this work, novel Fe₃O₄ hollow nanospheres were prepared by one-pot solvothermal method and were first used as sorbents for PAHs extraction in water and soil samples by HPLC-FLD. Compared with our previous work concerning in-tube solid

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phase microextraction based on layer-by-layer assembled graphene²⁹ and MOFs³⁰ as sorbents, Fe₃O₄ hollow nanospheres exhibit excellent stability and can be recycled after washing with solvents. The synthesized Fe₃O₄ hollow nanospheres not only possess large surface area but also hollow inside which make the analytes easily access to the inside further enhancing the sorption capacity and the interaction between analytes and nanospheres. Their structures were characterized by scanning electron microscope (SEM) and analyzer transmission electron microscopy (TEM). The extraction conditions were systematically optimized. The extraction performance of Fe₃O₄ hollow nanospheres towards PAHs was also compared with the naked solid Fe₃O₄ nanoparticles, which reveal the excellent extraction efficiency of prepared Fe₃O₄ hollow nanospheres. Herein, the Fe₃O₄ hollow nanospheres were first applied as the sorbents for MSPE and the results showed good potential for extraction based on modified Fe₃O₄ hollow nanospheres.

Experimental

Chemicals and instruments

Six polycyclic aromatic hydrocarbons (PAHs) standards including fluoranthene (FLU), pyrene (PYR), benz[a]anthracene (B[a]AN), benzo[a]fluorathene (B[a]FL), benzo[a]pyrene (B[a]PY), and dibenz[a,h]anthracene (D[a,h]AN) were purchased from Sigma-Aldrich (MO, USA). Acetonitrile and isopropanol were HPLC grade and purchased from Tedia (OH, USA). Fe(NO₃)₃·9H₂O and glycerol obtained from Shenshi Chemical Reagent and Instrumental Company (Wuhan, China) were of analytical grade. Deionized water was purified by a Milli-Q system (MA, USA).

All the experiments were carried out on Dionex UltiMate 3000 HPLC system (USA), equipped with UltiMate LPG-3400SD pump, WPS-3000 autosampler, TCC-3x00(RS) column compartment, FLD-3x00(RS) detector. Data collection was performed on Dionex Chromeleon software. The morphology and surface characteristics of the prepared Fe₃O₄ hollow nanospheres were characterized with a field-emission scanning electron microscope (SEM, FEI, Nova NanoSEM 450), transmission electron microscopy (TEM, TECNAI G2 20 U-Twin instrument, Netherlands) and surface area and pore size analyzer (Micromeritics ASAP 2020, USA).

Sample preparation

Six PAHs standards including FLU (3.0 mg), PYR (3.0 mg), B[a]AN (3.0 mg), B[a]FL (3.0 mg), B[a]PY (3.0 mg) and D[a,h]AN (3.0 mg) were weighed accurately, and dissolved with acetonitrile (5 mL), respectively, to obtain six PAHs standard solution with both concentration of 600 µg/mL. PAHs mixed stock solutions (100 µg/mL) were prepared by mixing equal amount of above solution and were stored at 4°C in a refrigerator. PAHs stock solutions were diluted to certain concentrations with acetonitrile step-by-step to obtain standard solutions for further use. Solutions for condition optimization of SPME were prepared by 200 µL of PAHs standard solution (100 ng/mL) diluted into 20 mL water containing 200 µL acetonitrile.

Water and soil samples were used to prove the feasibility of this method in real environmental samples. Fe₃O₄ hollow nanospheres were dispersed in tap water including 2% acetonitrile for extraction. Soil samples were obtained from the side of the road. Then, it was dried at 60°C in an oven overnight and grounded into small particles. After that, the soil (10.0 g) were weighed accurately and mixed with 30 mL acetonitrile for

extraction. The above solution was sonicated for 3 h and the supernatant was collected after filtering. At last, the supernatant was concentrated by rotary evaporation and redissolved with 1 mL acetonitrile to obtain soil sample solution. 200 µL soil sample solution and 200 µL acetonitrile were diluted with water into 20 mL for extraction. Before extraction, all the tap water and soil samples were filtered with 0.22 µm membrane filter.

For recovery test, 20 mL water was spiked 40 µL of 100 ng/mL PAHs standard solution (0.2 ng six PAHs respectively per mL of water) and 10 g soil sample was spiked 40 µL of 100 ng/mL PAHs standard solution (0.4 ng six PAHs respectively per gram of soil). The two real samples were preconditioned as above procedures.

Preparation of Fe₃O₄ hollow nanospheres and Fe₃O₄ nanoparticles

Fe₃O₄ hollow nanospheres were prepared by a one-pot facile solvothermal method using Fe(NO₃)₃·9H₂O as the iron source, and glycerol, isopropyl alcohol together with a small amount of water as a solvent.³¹ The detailed procedures are as follows. Firstly, 0.5 mmol of Fe(NO₃)₃·9H₂O and 7.5 mL of glycerol were added into a 100-mL Teflon container pre-filled with 52.5 mL of isopropanol. After stirring for 10 min, 1 mL of deionized water was added into the above solution. After stirring for another 10 min, the container was then transferred to stainless steel autoclave and kept in an electrical oven at 190°C for 12 h. After cooling to room temperature naturally, the precipitate was separated by centrifugation, washed with ultrapure water and ethanol several times, and dried in an oven at 60°C overnight. Finally, the as-obtained Fe-glycerate precursor was then annealed at 350°C in argon flow for 3 h with a slow heating rate of 2°C min⁻¹. After that, the products were collected and obtained the Fe₃O₄ hollow nanospheres.

Bare Fe₃O₄ nanoparticles were prepared by chemical co-precipitation method.²⁵ Typically, 0.40 g of FeCl₂·4H₂O, 1.04 g of FeCl₃·6H₂O and 170 µL of concentrated hydrochloric acid were dissolved in 5 mL of deionized water. The resultant solution was added dropwise into 50 mL of 1.5 M NaOH solution at 80°C under vigorous stirring in a nitrogen atmosphere. After the reaction, the black product was separated using a magnet and washed with 50 mL deionized water several times, and further dried under the vacuum condition to obtain bare Fe₃O₄ nanoparticles.

Procedures of MSPE and HPLC separation

The MSPE procedures for PAHs by Fe₃O₄ hollow nanospheres are as follows. Firstly, 5 mg of Fe₃O₄ hollow nanospheres was added into 20 mL of sample solution containing 100 ng/mL of the PAHs (200 µL) in a glass vial. The mixture was then ultrasonicated for 1 min and kept still for 30 min for extraction. After the extraction, the Fe₃O₄ hollow nanospheres with bound PAHs were separated using an external magnet and the supernatant was decanted. In order to desorption of PAHs from the sorbent, 400 µL of acetonitrile were added and sonicated for 1 min. After the magnetic separation, the desorbed solution was filtered for HPLC analysis. The extraction procedures on bare Fe₃O₄ nanoparticles were the same as Fe₃O₄ hollow nanospheres.

The chromatographic separation was performed on Dikma Platisil C18 column (25 × 4.6 mm i.d., 5 µm particle size). The temperature of HPLC separation was set at 30°C and the injection volume was 20 µL. A mobile phase of acetonitrile-water (85:15, v/v) was employed at a flow rate of 1 mL/min. The detection wavelength was set at 300 nm for exiting wavelength and 440 nm for emission wavelength.

Results and Discussion

Characterization of Fe_3O_4 hollow nanospheres

The size and the morphology of the prepared Fe_3O_4 hollow nanospheres were characterized by field-emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). The FESEM image shows that the as-prepared material is integrated and uniform with an average diameter of about 800 nm (Figs. 1a and 1b). The high-magnification FESEM indicates that the hollow nanospheres are constructed by a large amount of radially standing nanosheets with an interconnected structure. The hollow structure and the radially standing nanosheets should facilitate the extraction in both outer and inner surface.

Representative TEM images (Fig. 1c) further confirm the well-defined hollow structure with a shell thickness of around 80 nm. High-resolution TEM (HRTEM) image of particles (Fig. 1d) also reveals that the shell of Fe_3O_4 nanospheres are actually consisted of many tiny monocrystalline nanoparticles, in which the interplanar spacing between the lattice fringes are 0.258 nm (311). Furthermore, the thin shell possesses unique mesoporous structure, this leads to an enhanced diffusion for the solution and facile mass transportations, and thus enhances extraction performance.

The hierarchical hollow structure of Fe_3O_4 nanospheres was further characterized by N_2 specific surface area measurements and pore size analysis. The Brunauer-Emmett-Teller (BET) specific surface areas of Fe_3O_4 nanospheres were measured to be $67.1 \text{ m}^2/\text{g}$ (Fig. 2a), which is much higher than that of bare Fe_3O_4 nanoparticles ($29.9 \text{ m}^2/\text{g}$) (Figs. 2c and 2d). The pore size distributions exhibit a majority of mesopores with width from 2 to 5 nm (Fig. 2b) for Fe_3O_4 nanospheres, which is consistent with the HRTEM image.

Optimization of extraction condition

In this study, FLU, PYR, B[a]AN, B[a]FL, B[a]PY and D[a,h]AN were selected as target analytes to evaluate MSPE efficiency of the prepared Fe_3O_4 hollow nanospheres. In order to obtain the optimum extraction efficiency of the proposed method, the main affecting parameters such as the amount of Fe_3O_4 hollow nanospheres, extraction time, desorption time, pH value and acetonitrile concentration of sample solution were

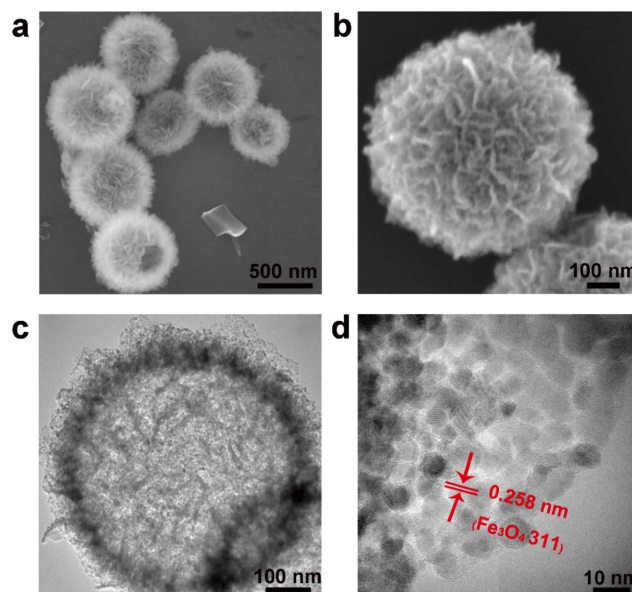


Fig. 1 (a), (b) High-resolution FESEM images of as-prepared Fe_3O_4 hollow nanospheres, (c) TEM image of the Fe_3O_4 hollow nanospheres, and (d) HRTEM image of the Fe_3O_4 hollow nanosphere.

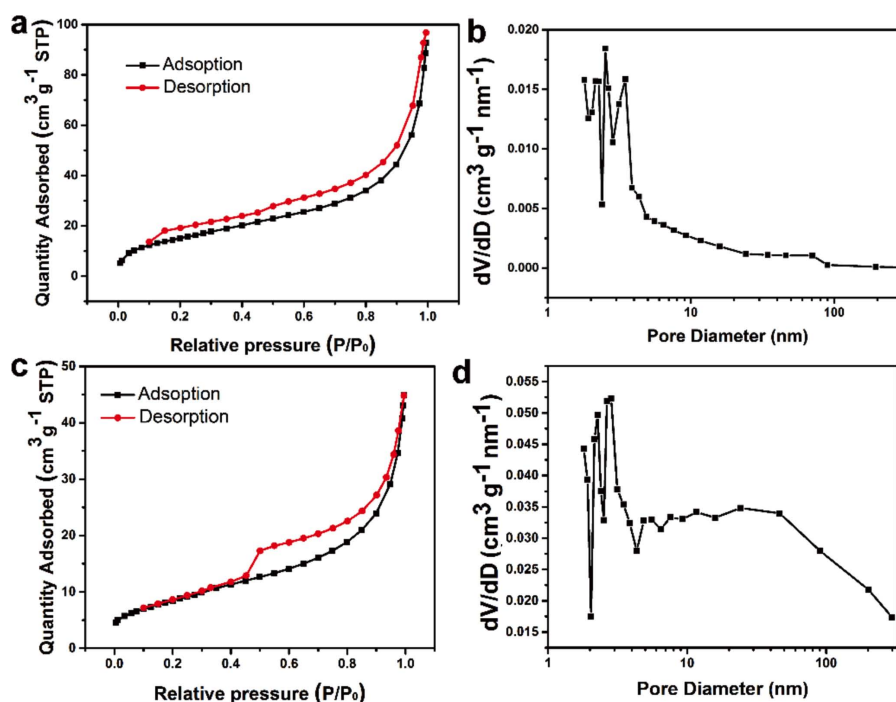


Fig. 2 (a) Nitrogen adsorption/desorption isotherms of Fe_3O_4 hollow nanospheres and (b) accordant pore-size distributions. (c) Nitrogen adsorption/desorption isotherms of bare Fe_3O_4 nanoparticles and (d) accordant pore-size distributions.

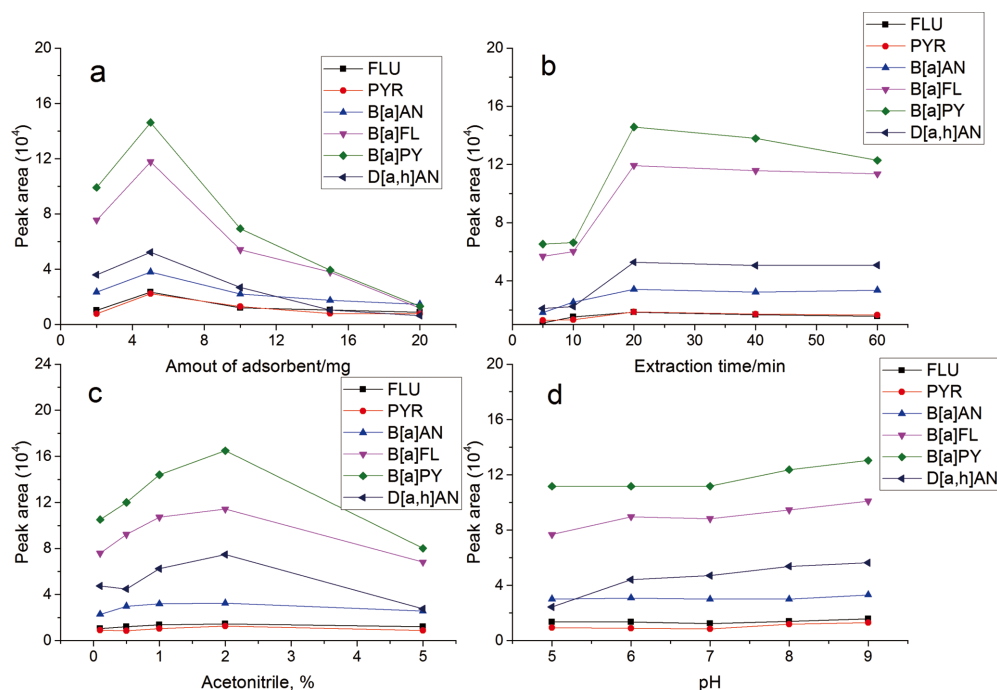


Fig. 3 Influences of adsorbent amount (a), extraction time (b), acetonitrile content (c), and pH value (d) on extraction efficiency by MSPE-HPLC. Standard PAH solution: 1 ng/mL.

systematically investigated with a PAH standard solution of 1 ng/mL to achieve good peak shape and sensitivity.

To obtain the optimum amount of adsorbent for the extraction, the amounts of Fe_3O_4 hollow nanospheres varied from 2 to 20 mg were investigated, while the extraction time was set as 20 min, the desorption time was 2 min by ultrasonic. The results shown in Fig. 3a reveal that 5 mg adsorbent is enough for the PAHs extraction. When the amount was over 5 mg, the peak area was decrease, because larger volume of solvent were needed to a better desorption of PAHs and the analytes could be diluted by excessive solvent. Thus, 5 mg Fe_3O_4 hollow nanospheres was chosen to be the optimized dosage.

Extraction time was important to provide the sufficient contact between sorbents and analytes, which was investigated ranging from 5 to 60 min to achieve the best extraction efficiency with the shortest analysis time. The results were shown in Fig. 3b. The peak area of PAHs was increased with extraction time from 5 to 20 min, after that it remained almost constant, therefore, the extraction time of 20 min was selected for further studies. Variety of desorption time (0.5, 1, 2, 5, and 10 min) were also studied to obtain the best desorption effect. The results illustrated that 2 min was sufficient to elute the PAHs from the prepared Fe_3O_4 hollow nanospheres. The rapid adsorption and desorption processes might result from the excellent dispersity and large specific surface area of Fe_3O_4 hollow nanospheres.

Since PAHs are highly hydrophobic, a small amount of acetonitrile was added to extraction solution to facilitate their solubility.³² The influence of acetonitrile content on extraction performance was also studied. As shown in Fig. 3c, increase of acetonitrile content from 0 to 2% resulted in the increase of chromatographic peak area of PAHs. The peak area of six PAHs were decreased when the acetonitrile content was above 2%. It might be due to the PAHs partly distributed in acetonitrile in the course of absorption. Therefore, acetonitrile content of 2% in sample solution was chosen for extraction.

The pH of sample solution affecting the charge of some

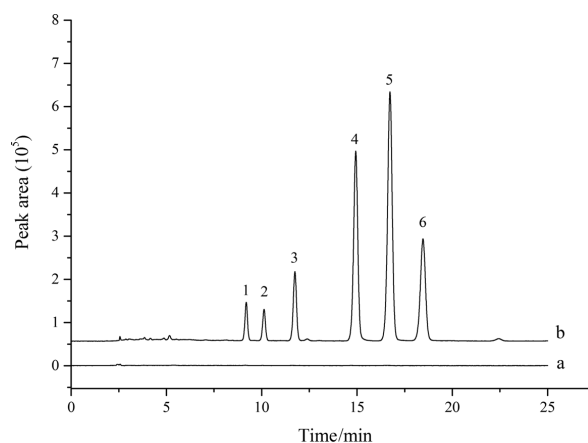


Fig. 4 Chromatograms of six PAHs standard solutions before extraction (a) and after extraction (b) by Fe_3O_4 hollow nanospheres. Extraction condition: 20 mL of 1 ng/mL PAH aqueous solution (containing 5 mg adsorbent and 2% acetonitrile), 20 min of extraction time and 2 min of desorption time. Peak identification: 1, FLU; 2, PYR; 3, B[a]AN; 4, B[a]FL; 5, B[a]PY and 6, D[a,h]AN.

analytes and sorbents plays an important role in extraction.³³ Its influence was investigated in the range of pH 5.0–9.0 with 10 mM phosphate buffers. As can be seen in Fig. 3d, no significant variation for the peak area of six PAHs was observed between those pH values. PAHs perform as electrically neutral under ordinary conditions. Therefore, the pH of sample solution had no significant influence on PAHs extraction efficiency. Besides, it could be inferred that the Fe_3O_4 hollow nanospheres used for MSPE stably exist in weak acidic or alkaline environment. To simplify sample preparation process, we use deionized water to dilute sample solution for extraction in further studies.

Table 1 Characteristic data by MSPE-HPLC for PAHs determination

Analyte	Linearity		LOD/ pg mL ⁻¹	RSD, % (n = 5)		EF
	Regression equation	R		Intra-day	Inter-day	
FLU	$Y = 8181X + 1028$	0.9975	10	1.8	3.6	155
PYR	$Y = 4250X + 2280$	0.9982	5	2.1	4.1	160
B[a]AN	$Y = 20530X + 343$	0.9956	10	2.7	3.6	312
B[a]FL	$Y = 58993X + 528$	0.9937	3	2.7	3.5	343
B[a]PY	$Y = 73737X + 100$	0.9922	2.5	3.8	4.2	227
D[a,h]AN	$Y = 26203X + 518$	0.9903	5	4.6	6.3	155

Analytical performance

Under optimum conditions, the chromatograms of six PAHs standard solution (1 ng/mL) before extraction (a) and after extraction (b) by Fe₃O₄ hollow nanospheres were shown in Fig. 4. The six PAHs standard solution were not detected by direct injection, while can be well detected by MSPE, illustrating the high extraction capability of Fe₃O₄ hollow nanospheres.

The proposed method of MSPE was developed for quantitative determination of PAHs. The enrichment factors (EFs) and the quantitative parameters are listed in Table 1. The EF was calculated as the formula:^{34,35}

$$EF = \frac{C_1}{C_0}$$

where C_1 and C_0 are the concentration of the PAHs in the settled phase and in the aqueous samples before extraction, respectively. C_1 was obtained from the calibration graph of direct injection standard solution in methanol. All six PAHs possess good linearity in a wide linear region, with determination coefficient (R) higher than 0.99 for six PAHs. The low limits of detection (LODs) ($S/N = 3$) can reach 10 pg/mL for FLU and B[a]AN, 5 pg/mL for PYR and D[a,h]AN, 3 pg/mL for B[a]FL, and 2.5 pg/mL for B[a]PY, respectively. The precision of the analytical method was investigated using five replicate experiments with 20 mL sample solution, and the relative standard deviation (RSD) of below 6.3% was obtained.

Regeneration is another important indicator to evaluate the performance of magnetic sorbent. The Fe₃O₄ hollow nanospheres were recycled after being washed with acetonitrile and deionized water and dried in vacuum at 70°C for 12 h. There were no significant differences on peak area of six PAHs by using recycled nanospheres. The good reusability reveals that the Fe₃O₄ hollow nanospheres possess excellent stability during the extraction procedure.

Applications in environmental samples

The proposed MSPE-HPLC method was applied to determine PAHs in environmental samples, including tap water and soil samples. No residues of the PAHs were found in the tap water, while five PAHs was detected and quantified in soil sample after extraction. Figure 5 shows the chromatograms of PAHs in soil sample before (a) and after (b) extraction. The contents were calculated and listed in Table 2. To determine the recoveries of this method, the tap water and soil samples were spiked with 4 ng/mL of each analyte. As a result, the recoveries were calculated to be 93.5 – 97.8% for tap water and 84.6 – 94.2% for soil sample, respectively (Table 2), indicating a good accuracy of the proposed method.

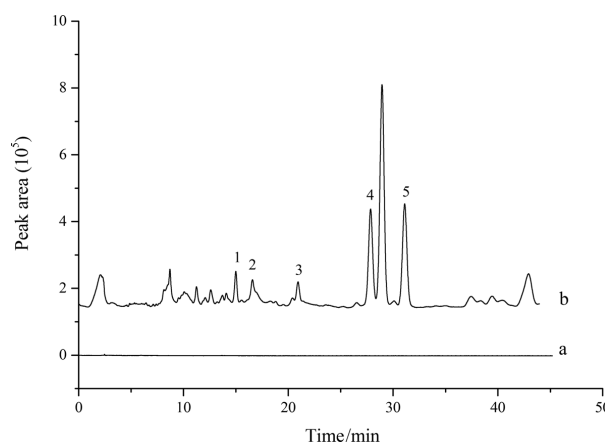


Fig. 5 Chromatograms of six PAHs in soil sample before extraction (a) and after extraction (b) by Fe₃O₄ hollow nanospheres. Extraction condition and peak identification is the same as Fig. 3.

Table 2 Recoveries for the determination of PAHs in tap water and soil samples

Analyte	Tap water		Soil	
	Content/ng g ⁻¹	Recovery, %	Content/ng g ⁻¹	Recovery, %
FLU	nd	96.9	1.56	90.5
PYR	nd	97.8	2.84	88.7
B[a]AN	nd	95.2	2.36	94.2
B[a]FL	nd	97.7	10.3	89.3
B[a]PY	nd	96.5	10.7	87.5
D[a,h]AN	nd	93.5	nd	84.6

Comparison extraction performance of Fe₃O₄ hollow nanospheres with bare Fe₃O₄ nanoparticles

In this study, we also prepared bare Fe₃O₄ nanoparticles by chemical co-precipitation method for comparison. The PAHs extraction by bare Fe₃O₄ nanoparticles was done under optimum condition. The chromatograms of PAHs extraction by bare Fe₃O₄ nanoparticles (a) and Fe₃O₄ hollow nanospheres (b) were shown in Fig. 6. As revealed in Fig. 6, the extraction performance of Fe₃O₄ hollow nanospheres was much better than that of bare Fe₃O₄ nanoparticles. The results were mostly attributed to high porosity and specific surface area of hollow structural Fe₃O₄ nanospheres.

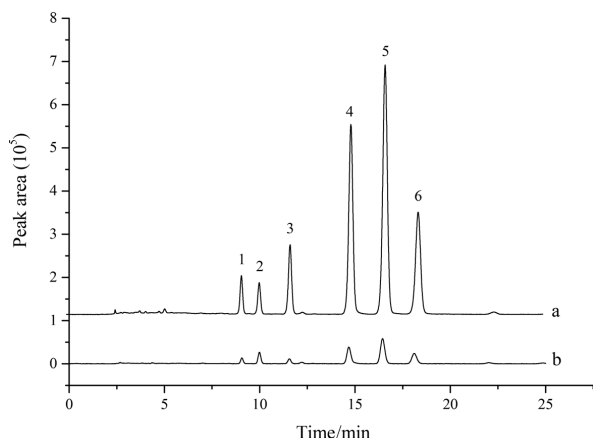


Fig. 6 Comparative chromatograms of six PAHs after extraction by Fe_3O_4 hollow nanospheres (a) and bare Fe_3O_4 nanoparticles (b). Extraction condition and peak identification is the same as Fig. 3.

Table 3 Comparison of Fe_3O_4 hollow nanospheres-based MSPE with other material-based MSPE methods

Method	Sorbents	Limit of detection/ pg mL^{-1}
This method	Fe_3O_4 hollow nanospheres	2.5 – 10
HPLC-DAD ³⁶	MNP@CN/IL	400 – 590
GC-FID ³⁷	Fe_3O_4 @PPy/CNT	30 – 100
HPLC-FLD ³⁸	Fe_3O_4 -TBCD nanoparticles	0.3 – 1.2
GC-MS ³⁹	Fe_3O_4 -diphenyl nanoparticles	0.04 – 0.39

Comparison of Fe_3O_4 hollow nanospheres-based MSPE with other material-based MSPE methods

Sensitivity is an important parameter for detecting trace amount of pollutants in real samples. Therefore, the proposed method was also compared with other material-based MSPE method which was recently employed for PAHs determination. As shown in Table 3, the LOD of this method was significantly lower than those of cyano-ionic liquid functionalized Fe_3O_4 nanoparticles by HPLC-DAD and Fe_3O_4 @PPy/CNT nanocomposites by GC-FID.^{36,37} However, compared with GC-MS and modified magnetic nanoparticles with HPLC-FLD,^{38,39} the LOD for PAHs on those methods was lower than that on prepared Fe_3O_4 hollow nanospheres. It might result from the Fe_3O_4 hollow nanospheres without any modification, which provide less interactions between absorbents and PAHs. Therefore, in our future work, we will focus on the modification of Fe_3O_4 hollow nanospheres and its application in sample preparation.

Conclusions

In this study, Fe_3O_4 hollow nanospheres were prepared and first used as absorbent for PAHs enrichment by MSPE. It was a significant improvement in MSPE by using hollow nanospheres instead of nanoparticles which dramatically enhance the porosity and specific surface area. Compared with bare Fe_3O_4 nanoparticles, the extraction performance of prepared Fe_3O_4 hollow nanospheres was greatly increased. The proposed method was also successfully used in PAHs analysis of environmental sample. This work reveals the tremendous

application potentials of Fe_3O_4 hollow nanospheres in magnetic extraction. Our further work will focus on the modification of Fe_3O_4 hollow nanospheres for extraction towards wide range of analytes.

Acknowledgements

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