Preparation of carbon coated Fe₃O₄ nanoparticles and their application for solid-phase extraction of polycyclic aromatic hydrocarbons from environmental water samples

Shengxiao Zhang^{a,b}, Hongyun Niu^a, Zhengjun Hu^a, Yaqi Cai^{a,*}, Yali Shi^a

^a State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P. O. Box 2871, Beijing 100085, China

^b School of Chemistry and Materials Science, Ludong University, Yantai 264025, China

ARTICLE INFO

Article history:

Received 1 April 2010

Received in revised form 17 May 2010

Accepted 19 May 2010

Available online 31 May 2010

Keywords:

Fe₃O₄ nanoparticle

Carbon

Solid-phase extraction

Polycyclic aromatic hydrocarbons

ABSTRACT

The carbon coated Fe₃O₄ nanoparticles (Fe₃O₄/C) were synthesized by a simple hydrothermal reaction and applied as solid-phase extraction (SPE) sorbents to extract trace polycyclic aromatic hydrocarbons (PAHs) from environmental water samples. The Fe₃O₄/C sorbents possess high adsorption capacity and extraction efficiency due to strong adsorption ability of carbon materials and large surface area of nanoparticles, and only 50 mg of sorbents are required to extract PAHs from 1000 mL water samples. The adsorption attains equilibrium rapidly and analytes are eluted with acetonitrile readily. Salinity and solution pH have no obvious effect on the recoveries of PAHs, which avoids fussy adjustment to water sample before extraction. Under optimized conditions, the detection limits of PAHs are in the range of 0.2–0.6 ng L⁻¹. The accuracy of the method was evaluated by the recoveries of spiked samples. Good recoveries (76–110%) with low relative standard deviations from 0.8% to 9.7% are achieved. This new SPE method provides several advantages, such as high extraction efficiency, high breakthrough volumes, convenient extraction procedure, and short analysis times. To our knowledge, this is the first time that Fe₃O₄/C nanoparticles are used for the pretreatment of environmental water samples.

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1. Introduction

Recently many research groups, including ours, have developed various nanomaterials for sample extraction in biological and chemical analysis [1–6]. Compared with traditional solid-phase extraction (SPE) sorbents, nanomaterials possess large surface area and short diffusion route, which may result in high extraction efficiency and rapid extraction dynamics. However, there are some unavoidable difficulties when nanomaterials are applied to extract target compounds from large volumes of water samples. If column dynamic extraction mode is used, it consumes plenty of time for water samples passing through nanoparticle packed SPE columns due to the high backpressure. When static batch mode is used, centrifugal separation is inapplicable for large volumes of samples, and filtration will encounter the same problem as column dynamic extraction mode.

In order to overcome these disadvantages, various magnetic nanoparticle SPE sorbents have been developed in recent years [7–21]. We have developed a novel SPE method based on mixed

hemimicelle modified magnetic nanoparticles [7–9]. Under certain solution pH, ionic surfactants are adsorbed on magnetic nanoparticles to form hemimicelle and admicelle. Surfactants coated magnetic nanoparticles are dispersed into solution to adsorb target compounds. In order to obtain surfactant-free eluate, Ballesteros-Gómez and Rubio have prepared hemimicelles of alkyl carboxylates chemisorbing onto magnetic nanoparticles and applied them for the extraction of carcinogenic polycyclic aromatic hydrocarbons (PAHs) in environmental water samples [11]. In SPE methods based on magnetic nanoparticles, functionalized magnetic nanomaterials are dispersed into samples to adsorb target compounds, then the sorbents are collected rapidly and conveniently with a magnet and the adsorbed analytes are eluted with solvent, which avoid time-consuming operation of samples passing through the column. Effective though these SPE methods are, there are some drawbacks existed, such as excessively complex preparation procedure, expensive reagents, low extraction efficiency, strong dependence on certain extraction condition, and co-eluted compounds that interfere with determination of analytes. New magnetic nanoparticle SPE sorbents with simple preparation process, low price and high adsorption efficiency should be developed for environmental analysis.

Carbon materials, including graphitized carbon black, porous graphitic carbon and activated carbon, possess strong adsorption

* Corresponding author. Tel.: +86 010 62849239; fax: +86 010 62849182.

E-mail address: caiyaqi@rcees.ac.cn (Y. Cai).

ability, but they may encounter with desorption problem due to irreversible adsorption of some analytes when they are applied as SPE sorbents [22,23]. If a thin layer of hydrophilic carbon material is covered onto the surface of magnetic nanoparticles to form carbon coated Fe_3O_4 nanoparticles ($\text{Fe}_3\text{O}_4/\text{C}$) SPE sorbents, the desorption problem should be overcome. Moreover, the nanosized $\text{Fe}_3\text{O}_4/\text{C}$ SPE sorbents combine strong adsorption ability of carbon materials, superparamagnetism of magnetic materials, and high surface area of nanomaterials.

To coat uniform ZrO_2 , TiO_2 and Al_2O_3 on single magnetic microsphere for selective enrichment and determination of phosphopeptides, Li et al. [24–26] have coated Fe_3O_4 microspheres with hydrophilic carbon by hydrothermal reaction to prepare core-shell-structured $\text{Fe}_3\text{O}_4/\text{C}$, which not only endows Fe_3O_4 microspheres with better dispersibility and stability than the as-synthesized Fe_3O_4 microspheres, but also significantly enhances the affinity between the microspheres and the prehydrolyzed metal salts of isopropoxide. Liu et al. [27] have synthesized carbon coated magnetite nanorods as anode materials for lithium-ion batteries, and the $\text{Fe}_3\text{O}_4/\text{C}$ nanorods demonstrate better performance than commercial graphite anode. Carbon-encapsulated magnetic nanoparticles are also synthesized by a carbon arc plasma route and applied as separable and mobile sorbents of heavy metal ions from aqueous solutions [28,29]. Wang et al. [30] have prepared $\text{Fe}_3\text{O}_4/\text{C}$ nanocompositions with the average diameter in the range of 100–200 nm which have good surface properties and can be modified by biomolecule. Successful though these preparation methods are, these previous reported $\text{Fe}_3\text{O}_4/\text{C}$ particles are all over 100 nm in diameters. These relative large particles may lack of some properties of nanomaterials, for example, large surface area and short diffusion route. To the best of our knowledge, there is no report about preparation of $\text{Fe}_3\text{O}_4/\text{C}$ nanoparticles with diameters below 20 nm, and there is lack of report about the application of $\text{Fe}_3\text{O}_4/\text{C}$ nanoparticles as SPE sorbents for environmental analysis.

Herein, we reported the preparation and characterization of $\text{Fe}_3\text{O}_4/\text{C}$ nanoparticles and their potential application in preconcentration pollutants from environmental water samples. To examine the feasibility of this method, we selected seven representative PAHs as model compounds. Extraction conditions including amount of nanoparticle sorbents, equilibrium time, salinity, solution pH, humic acid, and desorption conditions were optimized. Coupling this novel SPE technique with high performance liquid chromatography (HPLC) separation and fluorescence detection (FLD), a highly selective and sensitive SPE-HPLC-FLD analytical method was established. To our knowledge, this is the first report of using $\text{Fe}_3\text{O}_4/\text{C}$ nanoparticles for enrichment of pollutants from large volumes of environmental water samples.

2. Experimental

2.1. Chemicals and materials

All reagents used in the experiment were of analytical reagent grade and used without further purification. Phenanthrene (PhA), fluoranthene (FluA), pyrene (Pyr), benzo(a)anthracene (BaA), benzo[b]fluoranthene (BaF), benzo(a)pyrene (BaP), and benzo[g,h,i]perylene (BghiP) were obtained from AccuStandard (New Haven, USA). Ferric chloride ($\text{FeCl}_3 \cdot 4\text{H}_2\text{O}$) and ferrous chloride ($\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$) were purchased from Beijing Chemicals Corporation (Beijing, China). Glucose was supplied by Beijing Hongxing Chemicals Corporation. HPLC-grade acetonitrile were obtained from Fisher Scientific Corporation (Fair Lawn, NJ, USA). Ultrapure water was prepared using Milli-Q water purification system (Bedford, MA, USA).

Fig. 1. Schematics of (a) the preparation of $\text{Fe}_3\text{O}_4/\text{C}$ nanoparticles, and (b) their application for enriching analytes as SPE sorbents.

2.2. Preparation of Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{C}$ nanoparticles

The preparation of Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{C}$ nanoparticles follows the reported method with minor modification [30], and the detailed procedure is described below. $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (2 g) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (5.2 g) were dissolved into 25 mL deoxygenated water followed by adding 0.85 mL of concentrated hydrochloric acid. The resulting solution was dropped into 250 mL of 1.5 M NaOH solution under vigorous stirring and N_2 protection at 353 K. The obtained magnetic nanoparticles were separated from solution by a powerful magnet and rinsed with 200 mL deionized water for three times. Finally the products were dispersed into 110 mL deionized water to get 20 mg mL^{-1} suspension of Fe_3O_4 nanoparticles.

The $\text{Fe}_3\text{O}_4/\text{C}$ nanoparticles were synthesized by a simple hydrothermal reaction, 0.4 g of Fe_3O_4 nanoparticles was rinsed with deionized water and ethanol for several times in sequence, then dispersed into 80 mL glucose solution (0.5 M), and the mixture was sonicated for 20 min and transferred in a polytetrafluoroethylene-lined autoclave. The autoclave was heated for 4 h at 453 K. After reaction, the $\text{Fe}_3\text{O}_4/\text{C}$ nanoparticles were isolated with a magnet and washed with deionized water and ethanol. The final products were dispersed into 67 mL deionized water to get 10 mg mL^{-1} $\text{Fe}_3\text{O}_4/\text{C}$ suspension. Illustration of the preparation procedure is shown in Fig. 1a.

2.3. Characterization of sorbents

The morphology and particle size of the sorbents were studied using a transmission electron microscope (TEM) of H-7500 (Hitachi, Japan) operating at 80 kV accelerated voltage. The specific surface areas of sorbents were determined by the Brunauer–Emmett–Teller method with N_2 gas (ASAP2000V3.01A; Micromeritics, Norcross, GA). Energy-dispersive spectroscopy (EDS) was performed by S-3000N (Hitachi, Japan). The X-ray diffraction (XRD) pattern was collected by a PANalytical X'pert Pro diffractometer. Magnetic property was analyzed using a vibrating sample magnetometer (VSM, LDJ9600). Fourier transform infrared (FT-IR) spectra were taken in KBr pressed pellets on a NEXUS 670 FT-IR Spectrometer (Nicolet Thermo, USA).

Fig. 2. TEM images of (a) Fe₃O₄, and (b) Fe₃O₄/C nanoparticle; and EDS spectrum of (c) Fe₃O₄, and (d) Fe₃O₄/C nanoparticle.

2.4. SPE procedure

First, 50 mg of the Fe₃O₄/C sorbents was dispersed into a 1000 mL filtered water sample. The mixture was stirred vigorously for 20 s to make the sorbents dispersed uniformly in solution. Subsequently, an Nd–Fe–B strong magnet was deposited at the bottom of the beaker to separate the sorbents from the solution. After about 30 min, the solution became limpid and the supernatant was decanted. Finally, the adsorbed target compounds were eluted from the sorbents with 8 mL of acetonitrile. The eluate was dried with a stream of N₂ at 333 K and the residue was dissolved in 1 mL of acetonitrile, and finally 20 µL of this solution was injected into the HPLC system for analysis. The whole pretreatment procedure is illustrated in Fig. 1b.

2.5. HPLC analysis

PAHs were separated and quantified using a HPLC system (DIONEX, USA). The HPLC equipment included a DIONEX P680 HPLC pump, a thermostated column compartment TCC-100, a DIONEX RF 2000 fluorescence detector. The separation was conducted on a Diamonsil® C₁₈ column (250 mm × 4.6 mm; particle size, 5 µm). Gradient separation carried out using water–acetonitrile (50:50) and acetonitrile as A and B solvents, respectively, and the flow rate was 1 mL min^{−1}. The linear gradient profile was as follows: B maintained at 80% in the first 15 min, and then linear gradient to 100% in 2 min and maintained for 3 min, after that,

mobile phase was returned to initial conditions in 2 min. The PAHs were determined using a fluorescence detector, and the time-programmed excitation/emission wavelengths were as following: 0 min, 252/370 nm; 7 min, 280/460 nm; 8 min, 270/390 nm; 11 min, 260/432 nm; 13.5 min, 290/410 nm; 22 min, 252/370 nm.

2.6. Sample collection

All water samples were obtained from different districts of Beijing. Rain water sample was collected in our campus in June 2009, and tap water sample was taken from our lab in Haidian District (Beijing). River water sample was acquired from Hucheng river (Haidian District, Beijing). Effluent wastewater sample was supplied by Gaobeidian wastewater treatment plants (Chaoyang District, Beijing). All samples were collected randomly and filtered through 0.45 µm membranes to remove suspended particles. The filtered water samples were analyzed within 24 h.

3. Results and discussion

3.1. Characterization of sorbents

3.1.1. Particle size and morphology

Fig. 2a and b shows the TEM images of Fe₃O₄ and Fe₃O₄/C. The synthesized Fe₃O₄ magnetic nanoparticles are quasi-spherical in shape, and have nearly uniform distribution of particle size with an average diameter of about 10 nm. In Fig. 2b, the carbon shell can be

Fig. 3. (a) VSM magnetization curves, (b) X-ray diffraction patterns, and (c) IR spectra of Fe₃O₄ and Fe₃O₄/C nanoparticle.

observed as a light area surrounding dark core of Fe₃O₄, revealing a core/shell structure of Fe₃O₄/C nanoparticles. The carbon shell endows Fe₃O₄/C sorbents strong adsorbability.

3.1.2. Element analysis

The EDS spectra of Fe₃O₄ and Fe₃O₄/C are shown in Fig. 2c and d. A small carbon peak is observed in the spectrum of Fe₃O₄ nanoparticles. There are two possible for the appearance of the small amount of carbon in Fe₃O₄. One is the introduced impurity by the reagents during the preparation of Fe₃O₄. Second, during sample preparation for EDS analysis, ethanol is used as dispersive solvent, the residual ethanol may be another possible carbon source. As shown in Fig. 2d, the spectrum of Fe₃O₄/C indicates that the surface molar ratio of carbon and iron are 54.4% and 13.8%, respectively, which demonstrates that carbon materials are successfully coated onto the surface of Fe₃O₄ nanoparticles.

3.1.3. Magnetic properties

Sufficient magnetic properties are necessary for practical applications of magnetic materials in aqueous solution. Fig. 3a shows VSM curves of Fe₃O₄ and Fe₃O₄/C at room temperature. Both Fe₃O₄ and Fe₃O₄/C nanoparticles exhibit typical superparamagnetic behavior due to no hysteresis, remanence and coercivity. The maximal saturation magnetizations of Fe₃O₄ and Fe₃O₄/C nanoparticles are 59.87 and 43.75 emu g⁻¹, respectively. The decrease of maximal saturation magnetizations of Fe₃O₄/C results from the nonmagnetic carbon shell. Ma et al. have reported that a saturation magnetization of 16.3 emu g⁻¹ is sufficient for magnetic separation with a magnet [31]. Thus, the Fe₃O₄/C sorbents loaded with analytes are readily separated from solution with a magnet due to their

superparamagnetism and large saturation magnetization. Once the external magnetic field is taken away, these sorbents can redisperse rapidly.

3.1.4. FT-IR spectra

FT-IR is employed to examine the surface groups of the as-synthesized Fe₃O₄ and Fe₃O₄/C nanoparticles. In Fig. 3b, the peak at 580 cm⁻¹ in the spectra of Fe₃O₄ and Fe₃O₄/C is ascribed to the characteristic band of Fe₃O₄ [13]. The bands at 1700 and 1616 cm⁻¹ in the spectrum of Fe₃O₄/C are associated with the C=O vibration and C=C vibration, respectively, indicating the carbonization of glucose during hydrothermal reaction [24,26]. The peaks at 1000–1300 cm⁻¹ are attributed to the C–OH stretching and O–H bending vibrations [26], and the broad band region at 3100–3700 cm⁻¹ results from the stretching vibrations of O–H [32]. The presence of carboxyl groups and hydroxyl groups endow Fe₃O₄/C nanoparticles with hydrophilic surface, thus these nanoparticles can disperse stably in solution for practical application. The hydrophilic surface decreases the irreversible adsorption of analytes on the sorbents, which overcomes the desorption problem of carbon materials to a certain extent.

3.1.5. Crystal phase analysis

The crystal phase of Fe₃O₄ and Fe₃O₄/C were investigated by XRD. As shown in Fig. 3c, there is no obvious difference between Fe₃O₄ and Fe₃O₄/C nanoparticles, and they match well with that of cubic crystalline magnetite. The result indicates that the coated carbon layer is amorphous and the crystal phase of Fe₃O₄ nanoparticle is not changed during coating process.

Fig. 4. Effect of the amount of Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{C}$ sorbents on the extraction efficiencies of PAHs. Operation in the batch mode. Sample volume: 500 mL; volume of acetonitrile: 8 mL; and concentration of each analyte: 0.4 ng mL^{-1} .

3.1.6. Surface area

The specific surface area of Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{C}$ are 111, and $71 \text{ m}^2 \text{ g}^{-1}$, respectively. The decrease of surface area may result from the increase of particle diameter due to the encapsulation shell of carbon layer and partly aggregation of particles during encapsulation process.

3.2. Optimization of extraction conditions

3.2.1. Effect of amount of nanoparticle sorbents

To obtain the maximum recoveries of target analytes, the amount of the adsorbents is optimized by varying $\text{Fe}_3\text{O}_4/\text{C}$ sorbents from 0 to 100 mg. Fig. 4 shows that 40 mg of $\text{Fe}_3\text{O}_4/\text{C}$ sorbents are sufficient to extract PAHs from 500 mL of water sample. However, if the pure Fe_3O_4 nanoparticles are applied as sorbents, the recoveries of target compounds are all below 20% even when the sorbents are up to 100 mg. This result indicates that it is the carbon layer that responsible for the effective adsorption of PAHs on the magnetic $\text{Fe}_3\text{O}_4/\text{C}$ sorbents. The required dosage of $\text{Fe}_3\text{O}_4/\text{C}$ sorbents is not only far less than some traditional SPE sorbents, such as graphitized carbon blacks, C_8 or C_{18} bonded silica [22,33–36], but also less than previous reported nanomaterial SPE sorbents [1–3,5,7–11,15], which may result from the large surface areas of $\text{Fe}_3\text{O}_4/\text{C}$ sorbents and strong adsorption ability of carbon materials. In the following experiment, 50 mg $\text{Fe}_3\text{O}_4/\text{C}$ nanoparticle sorbents are applied to assure complete adsorption of analytes.

3.2.2. Desorption conditions

Organic solvents are known to be effective for desorption of organic analytes from sorbents. Desorption of PAHs from $\text{Fe}_3\text{O}_4/\text{C}$ sorbents was studied using acetonitrile and methanol. In order to achieve better recoveries, $\text{Fe}_3\text{O}_4/\text{C}$ nanoparticle sorbents were sonicated for 20 s in desorption solvents. The results show that acetonitrile is superior to methanol for analyte desorption. The recoveries of target compounds are over 80% with 8 mL acetonitrile as desorption solvents. However, if equal volume of methanol is applied as desorption solvents, the recoveries of PAHs are below 60%. Thus, 8 mL acetonitrile is recommended for desorption. When traditional carbon materials are applied as SPE sorbents, they usually encounter desorption problems [22]. If the carbon materials are coated onto the surface of nanomaterials to form nanoparticle sorbents, the problem have been overcome for the hydrophilic carbon layer avoiding the irreversible adsorption of analytes effectively.

3.2.3. Magnetic separation and equilibrium time

Although $\text{Fe}_3\text{O}_4/\text{C}$ sorbents possess superparamagnetism and large saturation magnetization, the magnetic separation is still difficult due to their high dispersibility and the electrostatic repulsion among the carboxyl groups on the surface of sorbents. In order to assist magnetic separation, 2 mL NaCl solution (1 M) was added into the solution to provide counterion. After the vessel was placed on a powerful magnet, the sorbents could be completely isolated within 30 min.

Generally, sufficient contact time is required to attain adsorption equilibrium for target compounds on sorbents. Results show that there is no obvious fluctuation for the recoveries of target compounds when the standing time is changed from 0 to 120 min, indicating that analytes are completely adsorbed onto the $\text{Fe}_3\text{O}_4/\text{C}$ sorbents within a very short time. The rapid extraction dynamics of PAHs on $\text{Fe}_3\text{O}_4/\text{C}$ can be attributed to the short diffusion route of nanosized sorbents. Magnetic separation and rapid adsorption, which avoid the time-consuming step of column passing, make this new SPE method timesaving and feasible in operation.

3.2.4. Effect of salinity and pH

To investigate the effect of salinity on the recoveries of target compounds, sodium chloride (NaCl) was applied to adjust the salinity of solution. Results show that the effect of salinity on recoveries of target compounds is negligible with the concentration of NaCl ranging from 1 to 400 mM.

Since the charge species and density on the surface of sorbents usually change with the variation of solution pH, the adsorption of analytes on $\text{Fe}_3\text{O}_4/\text{C}$ may be affected by solution pH. The effect of solution pH on the extraction of PAHs was investigated by adjusting pH from 3 to 10. No obvious variations for the recoveries of PAHs are observed in the whole pH range. PAHs exist as neutral molecules under ordinary conditions, therefore their adsorptions are not affected by the charges on the surface of the sorbents. Compared with our group's previous studies based on mixed hemimicelles coated nanomaterials [5,7–9], which require rigorous pH and appropriate amount of surfactants, the $\text{Fe}_3\text{O}_4/\text{C}$ SPE method is more convenient and stable. Due to the unobvious effect of salinity and solution pH on extraction efficiency, this method avoids fussy adjustment before extraction when the $\text{Fe}_3\text{O}_4/\text{C}$ nanoparticles are applied as SPE sorbents for environmental water samples analysis.

3.2.5. Effect of solution volume

The $\text{Fe}_3\text{O}_4/\text{C}$ SPE method based on magnetic separation technique avoids the time-consuming step of column loading or pressure filtration and possesses great potential in pretreatment of large volumes of water samples. To test the effect of solution volume on extraction efficiency of PAHs, the sample volume was varied from 200 to 1000 mL, and the amount of each spiked analyte was fixed at $0.2 \mu\text{g}$. As shown in Fig. 5a, the recoveries of all the analytes do not decrease with sample volume increasing from 200 to 1000 mL. The high breakthrough volume is attributed to large surface area and strong adsorption ability of $\text{Fe}_3\text{O}_4/\text{C}$ sorbents. By extracting analytes from 1000 mL aqueous solution and condensing desorption solution to 1 mL, the preconcentration factors, which are calculated from the ratio of PAHs concentration in the final condensed solution to that in the initial sample solution, for PhA, FluA, Pyr, BaA, BaF, BaP, and BghiP are 1017, 906, 896, 892, 862, 816 and 757, respectively.

3.2.6. Effect of humic acid

The presence of natural organic matter (NOM) will interfere with the determination of target compounds in environmental water sample. We investigated the effect of humic acid, a typical NOM, on extraction efficiency of PAHs. Fig. 5b indicates that

Fig. 5. Effect of (a) volume of water samples, and (b) concentration of humic acid on the recoveries of PAHs. Operation in batch mode. Amount of sorbents: 50 mg; volume of acetonitrile: 8 mL; and amount of each analyte: 0.2 μ g.

the extraction efficiency of PAHs decreases slightly (below 10%) except for BghiP (about 20%) with the concentrations of humic acid increasing from 0 to 40 mg L^{-1} . This negative effect may result from the association of PAHs with humic acid [33,34], and the $\text{Fe}_3\text{O}_4/\text{C}$ sorbents cannot adsorb PAHs associated with humic acid due to the electrostatic repulsion between sorbents and humic acid. When traditional SPE sorbents are applied for extraction of PAHs and other organic compounds, the negative effect of humic acid is comparative or more serious [33–36]. For most environmental water samples, in which the concentration of humic acid is in the range of 1–5 mg L^{-1} [34,35], the recoveries of PAHs can meet the requirement of analysis.

3.2.7. Reusability of the $\text{Fe}_3\text{O}_4/\text{C}$ sorbents

In order to investigate the recycling of the nanoparticle sorbents, the $\text{Fe}_3\text{O}_4/\text{C}$ sorbents used in SPE procedure were rinsed with 5 mL of acetonitrile twice before application in the next one. The recov-

Fig. 6. Effect of recycling times on the recoveries of PAHs. Amount of sorbents: 50 mg; sample volume: 500 mL; and concentration of each analyte: 0.4 ng mL^{-1} .

eries of PAHs are listed in Fig. 6. After six times of recycling, there is no obvious decrease or increase for the recoveries of analytes. The results indicate that the $\text{Fe}_3\text{O}_4/\text{C}$ sorbents are stable as well as no carryover of analytes during SPE procedure, showing good reusability.

3.3. Analytical performance

With the overall SPE procedure and HPLC–FLD analysis, calibration curves were established for PAHs in the range of 0.01–1 ng mL^{-1} . In this experiment, the preconcentration factors achieved for PAHs are 1000 through extracting analytes from 1000 mL aqueous solution and concentrating 8 mL desorption solution to 1 mL. Quantitative parameters including linear range, correlation coefficient, and detection limit are shown in Table 1. It can be seen that the present method has high sensitivity and wide linear range. The correlation coefficients (R^2) are above 0.999 for each analyte, exhibiting good linearity in the studied range. The detection limits, which are calculated using signal-to-noise ratio of 3, are in the range of 0.2–0.6 ng L^{-1} .

3.4. Analysis of environmental water samples

The performance of this novel SPE method was validated by analyzing tap water, rain water, river water and wastewater samples. Three PAHs including PhA, BaP and BghiP are detected in rain water sample, and their concentrations are 0.102, 0.010 and 0.018 ng mL^{-1} , respectively. In wastewater sample PhA with concentration of 0.023 ng mL^{-1} is found. Water samples spiked with 0.05 and 0.5 ng mL^{-1} of each analyte were determined through the overall SPE procedure mentioned above. The concentrations and recoveries of analytes in the spiked water samples, expressed as mean value ($n=3$), and the relative standard deviation (RSD) of recoveries are shown in Table 2. Recoveries of analytes are in the

Table 1
Analytical parameters of the proposed method.

Analytes	Linearity range (ng mL^{-1})	Calibration equations	Correlation coefficient (R^2)	Detection limit ^a (ng L^{-1})
PhA	0.01–1	$y = 15.88x + 0.420$	0.9998	0.2
FluA	0.01–1	$y = 9.64x + 0.012$	0.9999	0.6
Pyr	0.01–1	$y = 15.80x + 0.024$	0.9999	0.4
BaA	0.01–1	$y = 33.91x - 0.045$	0.9999	0.2
BbF	0.01–1	$y = 20.08x - 0.066$	0.9999	0.5
BaP	0.01–1	$y = 71.02x - 0.279$	0.9999	0.2
BghiP	0.01–1	$y = 23.08x - 0.175$	0.9999	0.5

^a Detection limits are calculated using $S/N=3$.

Table 2
Results of determination and recoveries of real water samples spiked with seven target analytes.

Water sample	Spiked (ng/mL)	Detected ^a (ng mL ⁻¹)							Recovery (%) ^b						
		PhA	FluA	Pyr	BaA	BbF	BaP	BghiP	PhA	FluA	Pyr	BaA	BbF	BaP	BghiP
Tap water	0.00	nd ^c	nd	nd	nd	nd	nd	nd	110 ± 4.4	108 ± 2.5	96 ± 3.4	96 ± 1.6	94 ± 0.8	94 ± 1.9	92 ± 0.9
	0.05	0.055	0.054	0.048	0.048	0.047	0.047	0.046	99 ± 3.4	94 ± 2.8	92 ± 2.8	90 ± 2.4	88 ± 2.0	87 ± 0.8	88 ± 3.6
	0.5	0.495	0.468	0.460	0.452	0.438	0.433	0.440	84 ± 9.7	92 ± 1.7	92 ± 1.8	98 ± 1.0	98 ± 1.8	88 ± 1.4	86 ± 0.8
Rain water	0.00	0.102	nd	nd	nd	nd	0.010	0.018	89 ± 1.0	93 ± 1.1	95 ± 0.9	96 ± 1.1	97 ± 0.9	95 ± 1.5	94 ± 1.8
	0.05	0.144	0.046	0.046	0.049	0.049	0.054	0.061	88 ± 4.1	90 ± 3.7	96 ± 3.1	98 ± 3.8	98 ± 5.3	98 ± 5.5	102 ± 4.7
	0.5	0.545	0.467	0.474	0.479	0.484	0.485	0.489	77 ± 4.8	87 ± 3.4	91 ± 3.7	93 ± 3.2	96 ± 3.0	96 ± 3.4	98 ± 5.2
River water	0.00	nd	nd	nd	nd	nd	nd	nd	86 ± 8.4	90 ± 8.4	90 ± 7.6	96 ± 7.0	98 ± 5.5	98 ± 6.2	102 ± 5.9
	0.05	0.044	0.045	0.048	0.049	0.049	0.049	0.051	76 ± 3.8	85 ± 1.7	86 ± 1.6	89 ± 1.5	92 ± 2.5	91 ± 2.5	93 ± 4.7
	0.5	0.383	0.436	0.456	0.466	0.480	0.481	0.492	86 ± 8.4	90 ± 8.4	90 ± 7.6	96 ± 7.0	98 ± 5.5	98 ± 6.2	102 ± 5.9
Wastewater	0.00	0.023	nd	nd	nd	nd	nd	nd	76 ± 3.8	85 ± 1.7	86 ± 1.6	89 ± 1.5	92 ± 2.5	91 ± 2.5	93 ± 4.7
	0.05	0.066	0.045	0.045	0.048	0.049	0.049	0.051	86 ± 8.4	90 ± 8.4	90 ± 7.6	96 ± 7.0	98 ± 5.5	98 ± 6.2	102 ± 5.9
	0.5	0.401	0.426	0.432	0.445	0.462	0.457	0.464	76 ± 3.8	85 ± 1.7	86 ± 1.6	89 ± 1.5	92 ± 2.5	91 ± 2.5	93 ± 4.7

^a Mean of three determinations.^b Standard deviation for three determinations.^c Not detected. **Fig. 7.** Solid-phase extraction/HPLC-FLD chromatograms. (a) Rain water sample, (b) rain water sample spiked with 0.05 ng mL⁻¹ of each analyte, and (c) rain water sample spiked with 0.5 ng mL⁻¹ of each analyte. Volume of water sample: 1000 mL; and volume of eluent: acetonitrile, 8 mL.

range of 76–110% for all the spiked water samples and the RSD of recoveries ranges from 0.9% to 9.7%, indicating satisfactory recoveries and good method precision. Fig. 7 shows chromatograms of rain water sample and its spiked solution. The present method exhibits a fairly good performance in environmental water sample analysis. All these facts suggest that the Fe₃O₄/C sorbents have great potential for the rapid enrichment of organic pollutants from large volumes of environmental water samples.

4. Conclusions

In this research, superparamagnetic Fe₃O₄/C sorbents were successfully synthesized and applied for enrichment of PAHs from large volumes of environmental water samples. Compared with traditional SPE methods, this SPE method have following merits: (a) superparamagnetic Fe₃O₄/C sorbents can be dispersed directly in water samples to extract analytes, then collected and eluted under the help of a magnet, which avoids time-consuming column passing or filtration operation. (b) The Fe₃O₄/C sorbents combine the advantages of nanoparticle and carbon material. Large surface area of nanomaterial and strong adsorption ability of carbon material result in high adsorption capacity and extraction efficiency to target compounds, therefore, satisfactory results are achieved using lower amount of Fe₃O₄/C nanoparticle sorbents than common sorbents. (c) The recoveries of target compounds are not interfered by salinity and solution pH, which avoids fussy adjustment to samples. (d) The synthesis method is simple, and the reagents are nontoxic. The obtained Fe₃O₄/C sorbents are environmental friendly, and no poisonous substances are introduced into water samples during SPE. This research has not only developed a rapid and convenient SPE method for extraction of PAHs from large volumes of water samples, but also extended the scope of application of magnetic SPE technology.

Acknowledgments

This work was jointly supported by National Basic Research Program of China (2009CB421605), National High Technology Research and Development Program of China (2007AA06A407), and the National Natural Science Foundation of China (20877079, 20907061, 20921063).

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