Magnetic solid-phase extraction of hydrophobic analytes in environmental samples by a surface hydrophilic carbon-ferromagnetic nanocomposite

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ABSTRACT

A new sorbent of carbon-ferromagnetic nanocomposite was proposed for the extraction of polycyclic aromatic hydrocarbons (PAHs) in environmental samples. The sorbent was specially designed with a hydrophobic sublayer and a hydrophilic surface, which endows the sorbent some unique features. The former shows high extraction capability for the PAHs and the latter provides benign compatibility with the sample matrix. The sorbent can be easily dispersed in aqueous solutions for extraction and no additional stirring or shaking was necessary to facilitate the dispersion, which may bring operational convenience especially for on-site sampling and extraction. Parameters affecting the extraction efficiency were investigated in detail. The optimal conditions were as follows: 10 mg of nanoparticles, 40 mmol/L of sodium chloride, 30 min of extraction time without shaking, hexane as the desorption solvent and 15 min as the desorption–sonication time. The results demonstrate that enrichment factors ranging from 35- to 133-fold were obtained for the analytes. The limits of detection and the limits of quantification are in the range of 0.015–0.335 ng/mL and 0.05–1.14 ng/mL, respectively. Finally, the new sorbent was successfully used for the extraction of PAHs in lake water samples.

1. Introduction

Environmental pollution is a significant issue that has drawn worldwide attention for decades [1–3]. Determination of the pollutants in environment is of primary importance for remediation. Currently, the most widely used methods for analyzing these pollutants are chromatographic techniques such as gas chromatography (GC) or high performance liquid chromatography. However, their sensitivity and selectivity are usually insufficient for direct determination of the pollutants at a very low concentration level in complex sample matrices. Therefore, prior to chromatographic analysis, a sample preparation step, which aims to enrich the target analytes and eliminate the possible matrix interference, is usually necessary.

In the past decades, sorbent-phase based sample preparation has gained considerable popularity [4–9]. Various types of sorbents have been developed to satisfy applications [10–12]. However, most of these sorbents are designed with the focus on their affinity for target analytes, but with little consideration on their compatibility with sample matrices. Unfortunately, in most cases, especially for environmental and biological samples, the matrices are aqueous or hydrophilic while the analytes are hydrophobic. Since the sorbents have little compatibility with the matrices, it may bring operational inconvenience or even be detrimental to the effectiveness of a sample preparation method. For example, when a solid-phase extraction (SPE) cartridge packed with octadecyl-bonded silica is used for aqueous samples, pre-equilibrium of the cartridge by water–organic solvent mixture is necessary to guarantee a good result.

In recent years magnetic nanoparticles as sorbents have aroused much interest [13–30]. Since they can be easily recovered by a magnet, the particles are generally directly dispersed in sample solutions to achieve extraction. It not only enhances the extraction efficiency by increasing the contact between analytes and the sorbents, but also overcomes problems with conventional SPE, such as eliminating packing the columns and avoiding time-consuming process of loading large-volume samples. However, in such a dispersive mode, the compatibility of sorbents with sample solutions is extremely important. Otherwise, the sorbents are apt to aggregate or float on aqueous solutions or adsorb onto the wall of vials, which would bring operational inconvenience. Design of sorbents having good affinity for analytes and being also compatible with sample matrix would be much appreciated.

In this work, a carbon-ferromagnetic nanocomposite containing a hydrophobic sublayer and a hydrophilic surface was fabricated and used in dispersive solid-phase extraction mode for the determination of hydrophobic polycyclic aromatic hydrocarbons

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(PAHs) in aqueous samples. The hydrophobic sublayer of the material adsorbed the PAHs efficiently while the hydrophilic surface provided benign compatibility with the aqueous matrices. Additionally, because of their magnetic property, after extraction, the nanoparticles were conveniently isolated from the sample solutions by a magnet for the following desorption and GC–mass spectrometric (MS) analysis.

2. Experimental

2.1. Chemicals and reagents

Analytical-grade ferrous chloride ($FeCl_2 \cdot 4H_2O$), polyvinyl alcohol (PVA), hydrogen peroxide (H_2O_2), sodium hydroxide (NaOH), glucose, methanol, hexane and acetonitrile were purchased from Shanghai Reagent Company (Shanghai, China). PAH standards (naphthalene (Nap), acenaphthylene (Acp), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), chrysene (Cry), benz[*a*]anthracene (BaA), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), indeno[*1,2,3-cd*]pyrene (InP), dibenz[*a,h*]anthracene (DBA), benzo[*g,h,i*]perylene (BPe)) were bought from Supelco (Bellefonte, PA, USA). Distilled water was from a quartz apparatus.

2.2. Synthesis and derivatization of ferromagnetic nanoparticles

The ferromagnetic nanoparticles were fabricated according to a previous report with a little modification [31]. In a three-necked round bottom flask, 90 mL of 0.24 mol/L $FeCl_2 \cdot 4H_2O$ was mixed with 120 mL of 5% PVA solution first. They were mechanically stirred for 10 min under a 50 °C water bath. To this mixture, 30 mL of 0.24 mol/L H_2O_2 was injected quickly. Afterwards, 240 mL of 1.5 mol/L NaOH solution was added with vigorous stirring. A black color solution was resulted immediately and the stirring was continued to age the product. Two hours later, the product was collected by a magnet and washed with plenty of water. Finally, it was dried and then calcinated at 330 °C for 3 h.

For synthesis of the carbon-ferromagnetic nanocomposite, 0.1 g of dried magnetic nanoparticles, 0.9 g of glucose and 10 mL of water were mixed for 30 min. Then they were put into an autoclave at 160 °C for 8 h. Afterwards the obtained particles were washed three times with water (100 mL) and dried before use.

2.3. Characterization of the nanoparticles

An X-650 (Hitachi, Tokyo, Japan) scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectroscopy (EDS) attachment was used for observation of the nanoparticles. Powder X-ray diffraction (XRD) was carried out on a Shimadzu Lab X-3000 (Kyoto, Japan) to investigate the internal array of the composite. Fourier transform infrared (FTIR) spectroscopic experiment was carried out on a Nicolet (Madison, WI, USA) Impact 420 apparatus. The water contact angle was determined on a DSA100 contact angle meter (Kruss, Hamburg, Germany). Nitrogen sorption experiment was carried out on a Beckman Coulter (Miami, FL, USA) SA 3100 Plus instrument. The surface area was calculated according to the BET (Brunauer–Emmett–Teller) equation at P_s/P_o (relative pressure) between 0.05 and 0.2. The pore volume and pore diameter were evaluated from the adsorption branch of the isotherm based on the BJH (Barrett–Joyner–Halenda) model.

2.4. Sample preparation

Stock solution (containing 10 μg/mL of each analyte) was prepared by diluting the standard PAH kit with methanol and was stored in the refrigerator. Water samples were prepared by spiking deionized water with analytes at a known concentration (25 ng/mL) to study the extraction performance under different conditions.

Genuine water samples collected from a local lake (Wuhan, China) were analyzed directly or after being spiked with the PAH standards at concentrations of 10 ng/mL or 25 ng/mL, respectively.

2.5. Extraction procedures

10 mg of the nanoparticles were put into a 25-mL vial. Then 20 mL of aqueous sample solution was added into the vial. As the very tiny nanoparticles show soft aggregation in their dry status, a short time sonication of 1 min was used to accelerate their dispersion in the solution. Then the mixture was shaken or kept still for 30 min. Subsequently, a magnet was attached to the outside bottom of the vial to isolate the particles. The sample solution was decanted. With the magnet kept in-situ, an aliquot of water (0.5 mL) was added into the vial to rinse the residue solution. Thereafter, the magnet was removed, and 100 μL of hexane was introduced to the vial to desorb the PAHs from the nanoparticles by sonication for 15 min. Finally, the magnet was again attached to the vial and the supernatant was collected into an Eppendorf tube by a pipettor for analysis.

2.6. GC–MS analysis

GC–MS analysis was carried out on a Shimadzu QP2010 system equipped with a RTX-5MS fused silica capillary column (30 m × 0.25 mm I.D., film thickness 0.25 μm) (Restek, Bellefonte, PA, USA). Helium was employed as the carrier gas at a flow rate of 1.7 mL/min. The injector temperature was set at 270 °C. The GC oven was initially held at 70 °C for 2 min and then increased to 190 °C at 15 °C/min. After being kept at 190 °C for 1 min, the oven was increased to 260 °C at 10 °C/min. Finally it was increased to 285 °C at 5 °C/min and held for 5 min. The GC/MS interface temperature was maintained at 300 °C. The solvent cut time was 6 min (to bypass the solvent peak). Selective ion monitoring mode was adopted for quantitative determination of the analytes. The masses monitored were as follows: 6–8 min, m/z 128, 129, 127, 102; 8–9.5 min, m/z 152, 153, 151, 154; 9.5–10.8 min, m/z 166, 165, 167, 139; 10.8–13 min, m/z 178, 176, 179, 152; 13–16 min, m/z 202, 203, 200, 101; 16–20 min, m/z 228, 226, 229, 227, 252; 20–23 min, m/z 253, 252, 250, 126; 23–28 min, m/z 276, 278, 277, 138.

3. Results and discussion

3.1. Consideration on the design of the sorbent

Though previous reports in magnetic SPE using water-immiscible sorbents have not raised any problems in extraction, in our studies, it is observed that extreme hydrophobic sorbents such as octadecyl modified Fe_3O_4 cannot be easily dispersed into aqueous solution. They are apt to float on the sample solution and adsorb onto wall of the vials. It is also found that the above problem can be minimized by adding salt or a small portion of organic solvent into the aqueous sample. Nevertheless, if a material, being characterized by a hydrophobic sublayer and a hydrophilic surface, is available, it has the potential to provide much better operational convenience and can enrich the sorbent categories for extraction.

3.2. Synthesis of the carbon-ferromagnetic nanocomposite

The ferromagnetic nanoparticles were prepared by a precipitation method. The NaOH solution was to induce the precipitation of Fe^{2+}. PVA was used as a dispenser to avoid or decrease conglomeration of the nanoparticles in the reaction process. H_2O_2 acted
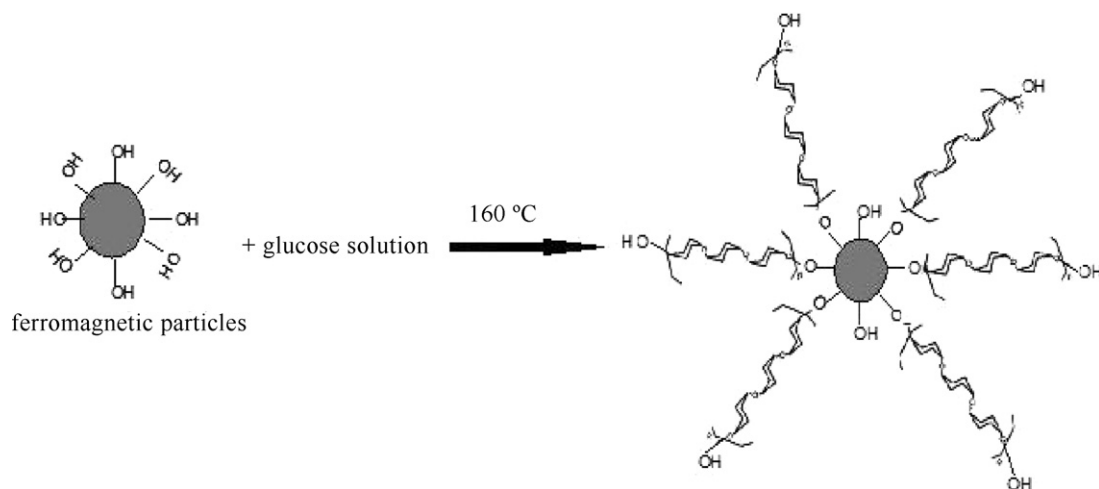
Fig. 1. The reaction and schematic structure of the carbon-Fe_3O_4 nanocomposite.

as an oxidization agent, which could oxidize Fe^{2+} to Fe^{3+}. The as-prepared particles show perfect paramagnetism to a permanent magnet. To understand the crystal structure of the particles, they were investigated by XRD analysis. The result demonstrates that the pattern of the particles agrees well with the standard pattern of Fe_3O_4, indicating the particles prepared are composed of Fe_3O_4 nanoarrays.

The aromatic reaction of glucose in near critical water condition has been previously reported [32,33]. The possible reaction mechanism in the process was studied in detail by Sakaki et al. [33]. It is found that, under critical conditions, glucose would be subject to dehydration, aromatization and carbonization process, which eventually leads to the formation of a carbonous material with hydrophobic, aromatic-like structure [32]. However, if the reaction takes place in aqueous media, because of the partial dehydration of the external functional moieties, the material would be enriched with hydroxyl groups on its surface (as shown in Fig. 1). In such a case, the material would possess a hydrophobic sublayer and a hydrophilic surface. The unique structure renders the material as a promising sorbent for environmental analysis. The former is applicable to extract hydrophobic analytes while the latter provides benign compatibility with aqueous sample solutions.

In this study, the Fe_3O_4 nanoparticles acted as cores for growing carbonous layers, which yielded carbon-Fe_3O_4 nanocomposite. The XRD pattern of this nanocomposite agrees well with that of the unmodified nanoparticles (as shown in Fig. 2), indicating the hydrothermal reaction process did not influence the magnetic arrays of the nanoparticles. By combining the magnetic Fe_3O_4 core and the carbonous layer, the particles can provide manipulative convenience as well as adsorption capability.

3.3. Characteristics of the carbon-ferromagnetic nanocomposite

The FTIR spectrum of the carbon-ferromagnetic nanocomposite is shown in Fig. 3. Adsorption peaks at wavelength of $3411 \, cm^{-1}$ and $1633 \, cm^{-1}$ were obviously found. The former was the stretching vibration of O–H groups and the latter was ascribed to the vibration of C=C. The results suggest the presence of both hydrophilic (O–H) and hydrophobic groups (C=C) in this material. The water contact angle of the material was measured to study the distribution of these functional groups. It demonstrates that the contact angle is less than 5°, which indicates the material possesses benign compatibility with aqueous phase. It can be concluded that hydrophilic O–H groups mainly exist on the surface of the nanocomposite, which is coherent with previous reports [32].

Fig. 4 displays the SEM image and EDS pattern of the nanocomposite. It can be observed from Fig. 4(a) that the particles are well dispersed and narrowly distributed. The approximate particle size is 70 nm. The EDS pattern shown in Fig. 4(b) reveals that the carbon layer has been successfully deposited onto the Fe_3O_4. The atom ratio of C:Fe:O is 55.2:29.67:15.13.

The nitrogen adsorption–desorption isotherm of the nanocomposite shows a capillary condensation at medium relative pressures, suggesting the pores in the nanocomposite are mainly in the mesoporous range. The surface area, pore volume and average pore size are $16 \, m^2/g$, $0.05 \, cm^3/g$ and 7.3 nm, respectively.
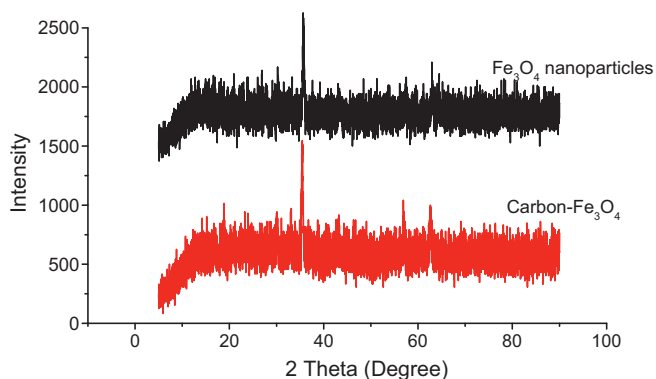

Fig. 2. The XRD patterns of the Fe_3O_4 and the carbon-Fe_3O_4 nanocomposite.
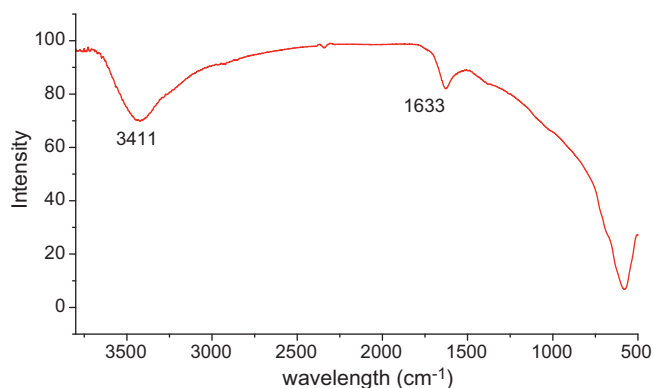

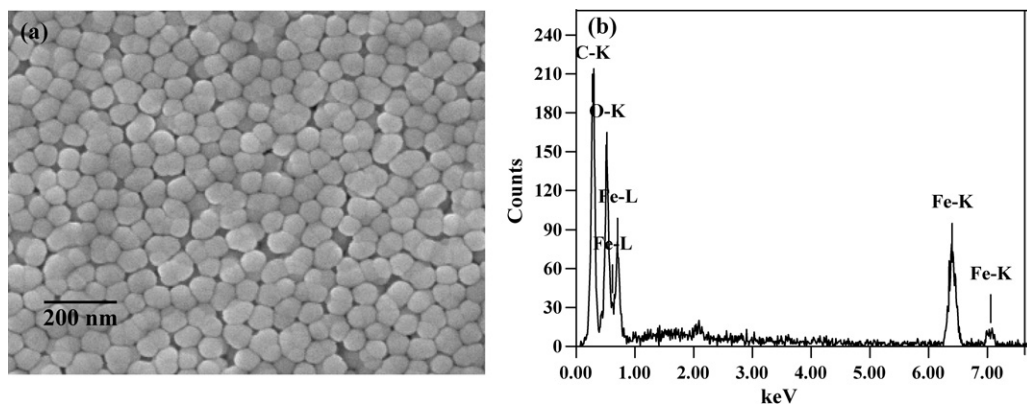**Fig. 3.** The FTIR spectrum of the carbon-ferromagnetic nanocomposite.

Fig. 4. The SEM image (a) and EDS spectrum (b) of the carbon-Fe$_3$O$_4$ nanocomposite.

3.4. Dispersion of the magnetic particles in aqueous solutions

Since the particles are very tiny, they tend to soft-aggregate in dry status. Considering this, to exhibit the extraction performance of the material fully, a short time of sonication (1 min) was used to accelerate their dispersion, when they were added into the solutions for extraction. Actually if the mixture was shaken for 5 min manually, comparable satisfac-

tory extraction performance was also achieved (the results are illustrated in Fig. 1S in the supplemental material.). The results demonstrate the particles can be easily dispersed into aqueous solution, which would be ascribed to the presence of –OH groups on the particles' surface. Nevertheless, since manual shaking is not a scientific method and cannot be quantitatively expressed, in this study, sonication was used alternatively.
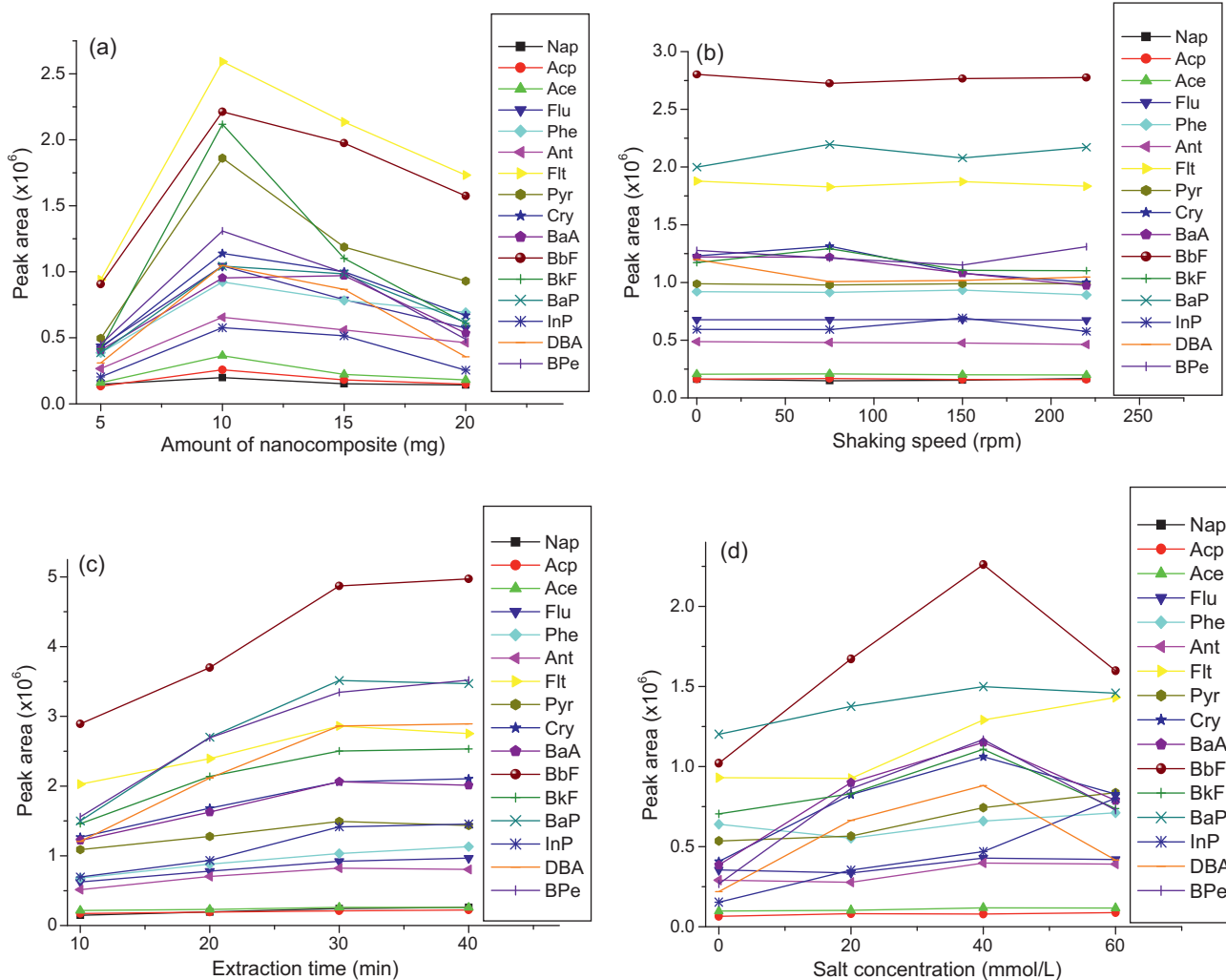

Fig. 5. The influence of several parameters on the extraction: (a) amount of nanocomposite, (b) shaking speed, (c) extraction time, (d) salt concentration.

Table 1
Linear range, regression data, limits of detection (LODs), limits of quantification (LOQs) and enrichment factors of PAHs of the proposed method.

Analytes	Linear range (ng/mL)	r^2	LOD (ng/mL)	LOQ (ng/mL)	RSD[a] (%, $n = 3$)	Enrichment factor[b]
Nap	2–80	0.9871	0.111	0.37	6.2	37
Acp	2–80	0.9997	0.324	1.09	5.8	35
Ace	2–80	0.9982	0.201	0.7	4.3	38
Flu	1–80	0.9879	0.061	0.21	4.9	41
Phe	1–80	0.9955	0.052	0.17	6.3	46
Ant	1–80	0.9917	0.065	0.22	6.1	42
Flt	0.5–80	0.9896	0.015	0.05	8.2	133
Pyr	0.5–80	0.9788	0.036	0.13	3.6	71
Cry	1–80	0.9966	0.048	0.17	7.1	37
BaA	1–80	0.9912	0.046	0.15	4.2	58
BbF	1–80	0.9875	0.040	0.15	5.4	78
BkF	1–80	0.9898	0.096	0.34	6.3	42
BaP	1–80	0.9891	0.068	0.24	6.1	44
InP	2–80	0.9939	0.105	0.35	9.1	39
DBA	2–80	0.9927	0.335	1.14	9.3	36
BPe	2–80	0.9968	0.188	0.64	7.2	38

[a] Calculated from the sample spiked at a LOQ level.
[b] Calculated from the sample spiked at a level of 25 ng/mL.

3.5. Optimization of the extraction process

Several parameters that may influence the extraction performance of the sorbent were optimized, including the nanoparticle amount, shaking speed, extraction time, desorption solvent, desorption time and salt addition.

Pure water samples spiked with the PAH standards were evaluated first. The amount of the nanoparticles was investigated from 5 to 20 mg. The results (as shown in Fig. 5(a)) demonstrate that, when the amount of the particles is 10 mg, highest analytical signals were obtained for all of the analytes. The shaking speed was studied in the range of 0–220 rpm. It is found from Fig. 5(b) that, at different shaking speeds, the chromatographic peak areas almost keep constant, indicating the shaking has little influence on the extraction of the analytes. The result should be ascribed to the hydrophilic surface of the sorbent, which guaranteed the good dispersion of the sorbent in the aqueous sample solutions. In such a case, no agitation was necessary to accelerate the diffusion of the analytes towards the sorbent. The extraction time was investigated from 10 to 40 min. The results shown in Fig. 5(c) demonstrates that, as the extraction time was increased up to 30 min, the analytical signals enhanced for all of the analytes; after 30 min, the signals flattened out. Therefore, 30 min was selected as the optimal extraction time. It is known that salt addition may influence the extraction performance of sorbents. In this study, 0–60 mmol/L of sodium chloride was separately added in the aqueous solutions for evaluation. It can be found from Fig. 5(d) that the extraction efficiency is the best in the presence of 40 mmol/L of sodium chloride.

Three solvents, hexane, methanol and acetonitrile, were investigated as the desorption solvents. The desorption capabilities of these solvents are compared in Fig. 6. It can be observed that, under the same extraction conditions, hexane shows the strongest signals for all of the PAHs, followed by acetonitrile and methanol. The desorption–sonication time was also studied. The results indicate that the peak areas of most of the PAHs increase with the increasing desorption time, up to 15 min. Therefore, the desorption time was set at 15 min.

Based on the above discussion, the optimal extraction conditions for the PAHs are 10 mg of nanoparticles, 40 mmol/L of sodium chloride, 30 min of extraction time without shaking, hexane as the desorption solvent and 15 min as the desorption–sonication time.

3.6. Method evaluation

A series of experiments with regard to the linearity, limit of detection (LOD), limit of quantification (LOQ), precision and enrichment factor were performed to validate the proposed method. The linearity was tested over a range of 0.5 and 80, 1 and 80, or 2 and 80 ng/mL, depending on the analytes. The calibration curves were obtained by plotting the mean peak area versus sample concentration. The results are listed in Table 1. All the analytes show good linearity with regression coefficients (r^2) ranging from 0.9788 to 0.9997. The enrichment factors are between 35 and 133. The LODs, calculated at a signal-to-noise of 3, range from 0.015 to 0.335 ng/mL. It is found that the enrichment factors of the particles towards the PAHs are not as good as the PDMS fibers in SPME, which may be ascribed to the desorption step in this magnetic-SPE for the desorption may dilute the enriched analytes. However, comparing with the LODs obtained by a previous magnetic-SPE method (0.8–36 μg/L) [15], in which octadecyl-derivatized Fe_3O_4 was used for the extraction of the PAHs, the results achieved in this method are much better. Moreover, since the sorbent is compatible with the sample solutions, the operation is much convenient and the extraction process is much simple (no shaking or stirring is necessary). The obtained LODs are acceptable and satisfactory for routine analysis of the PAHs. Obviously, the extraction of the PAHs can be regarded as an additional proof of the existence of a hydrophobic sublayer within the carbon-Fe_3O_4 nanocomposite.

The repeatability of the proposed method was also evaluated. The relative standard deviations (RSDs) for the PAHs are below 9.3%, illustrating the good repeatability achieved by the procedure.
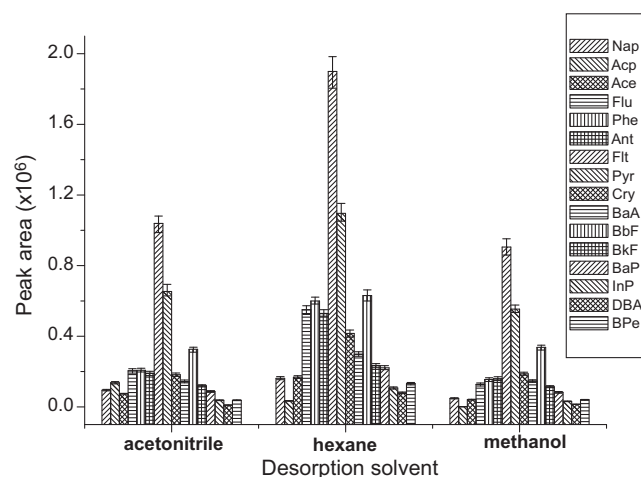

Fig. 6. The influence of different desorption solvents on the recovery of the PAHs.

Table 2
The PAHs in the lake water determined by the proposed method and by commercial PDMS fibers in SPME mode.

Analyte	Quantity[a] (ng/mL)	RSD[a] (%, $n = 3$)	Quantity[b] (ng/mL)	RSD[b] (%, $n = 3$)
Nap	4.59	8.1	4.73	5.4
Acp	1.63	7.5	1.78	6.3
Ace	1.98	5.7	1.72	5.3
Flu	2.34	7.4	2.28	7.6
Phe	1.22	8.9	1.45	3.9
Ant	0.71	6.6	0.78	7.2
Flt	1.02	5.8	1.13	4.8
Pyr	1.19	9.9	1.19	6.1
Cry	0.26	7.8	0.22	4.4
BaA	0.21	8.3	0.27	5.3
BbF	n.d.	–	n.d.	–
BkF	n.d.	–	n.d.	–
BaP	n.d.	–	n.d.	–
InP	n.d.	–	n.d.	–
DBA	n.d.	–	n.d.	–
BPe	n.d.	–	n.d.	–

n.d. = not detected.

[a] The results were determined by carbon-Fe_3O_4 sorbent in magnetic solid-phase extraction mode.

[b] The results were determined by commercial PDMS fiber in solid-phase microextraction mode.

3.7. Analysis of environmental water samples

To evaluate the applicability of the proposed method for genuine samples, water collected from a local lake was analyzed. The extraction was performed under the optimal conditions followed by GC–MS analysis.

To eliminate possible matrix effects, standard addition method was adopted for the quantitative determination of the PAHs. Three aliquots of the lake sample were analyzed in parallel, with RSDs less than 9.9%. The results are listed in Table 2. It can be observed that several PAHs were detected in these samples, indicating the procedure developed is suitable for environmental application. For comparison, the lake water was also analyzed by commercial PDMS fibers in SPME mode (the results are shown in Table 2). It can be found that the results obtained by two methods are quite similar, which is a testimony of the accuracy of the proposed method.

4. Conclusion

Magnetic solid-phase extraction based on a carbon-ferromagnetic nanocomposite sorbent was proposed. The sorbent features with a hydrophobic sublayer and a hydrophilic surface, which render it promising for extracting hydrophobic analytes in environmental samples. The hydrophilic surface provides benign compatibility with aqueous samples for the sorbent. It can be easily dispersed in aqueous solution and no additional stirring or shaking is necessary to facilitate the extraction.

The sorbent was evaluated by extracting polycyclic aromatic hydrocarbons (PAHs) in environmental samples. Under the optimized conditions, the limits of detection were in the low ng/mL range for the PAHs. Good linearity and repeatability were also achieved. In general, the study demonstrates that the carbon-ferromagnetic nanocomposite is a suitable sorbent for sample preparation, especially for environmental water samples.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2010.09.060.

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