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n-Octadecylphosphonic acid grafted mesoporous magnetic nanoparticle: Preparation, characterization, and application in magnetic solid-phase extraction

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ABSTRACT

A new sorbent for magnetic solid-phase extraction, n-octadecylphosphonic acid modified mesoporous magnetic nano particles (OPA/MMNPs), was easily prepared via a two-step strategy. MMNPs were synthesized by a solvent-thermal process, and then OPA was grafted onto the surface of MMNPs via the strong Lewis acid/base interaction. The resultant material was characterized by transmission electron microscopy, tensionmeter, Fourier-transform infrared spectroscopy, vibrating sample magnetometry, elemental analysis, and nitrogen adsorption analysis. The results demonstrated that the particles exhibited mesoporous structure, superparamagnetic (57 emu/g) and extremely hydrophobic (water contact angle of 136°) properties. To evaluate the extraction performance of the resultant sorbent, polycyclic aromatic hydrocarbons (PAHs) were chosen as model analytes. The extraction conditions were optimized. Based on these, a rapid, convenient and efficient method for the determination of PAHs in water samples was established by combination of magnetic solid-phase extraction and gas chromatography–mass spectroscopy. The linearity range of proposed method was 0.2–100 μg/L with correlation coefficients (R^2) of 0.9726–0.9970. The intra- and inter-day relative standard deviations (RSDs) were less than 17.6%. Batch-to-batch reproducibility was acceptable with RSD values less than 12.1%.

1. Introduction

In recent years magnetic solid-phase extraction (MSPE) has attracted much interest in sample preparation [1–3]. It adopts magnetic particles as sorbents, which endow some unique features in extraction. For instance, after extraction, the magnetic particles can be readily isolated from sample matrix by a magnet. Compared with isolation of conventional sorbents by filtration or centrifugation, magnetic isolation is obviously much more convenient, economic and efficient. Additionally, in MSPE, the sorbents are universally dispersed into sample solution to achieve extraction. In such a dispersive mode, the contact area between the sorbents and the analytes is large enough to ensure a fast mass transfer, which is beneficial to guarantee high extraction efficiency of this method. Moreover, MSPE is suitable for direct analysis of samples containing particles or microorganisms, which are widely existing in environmental or biological matrices and may arouse blockage and lead to extraction failure on conventional SPE cartridges. All of these merits render MSPE a promising technique for sample preparation.

The sorbent is the kernel of MSPE. Hitherto, nano-Fe_3O_4 has been the most widely used sorbent in MSPE because of its super paramagnetism, high magnetic saturation, and simple preparation process. To afford desirable property for extracting various analytes, nano-Fe_3O_4 should be subject to proper surface modification prior to MSPE. Silane reaction makes the modification possible. For instance, cetyl trimethylammonium bromide derivatized Fe_3O_4 for phenols [4,5], β-cyclodextrin modified Fe_3O_4 for bisphenol A [6], core-shell structure Fe_3O_4@Ta_2O_5 microspheres for phosphopeptides [7], mercaptophenylboronic acid-functionalized Fe_3O_4@C@Au for glycopeptides and glycoproteins [8], Zr^{4+}-phosphate functionalized magnetic Fe_3O_4@C microspheres for phosphopeptides [9], γ-mercaptopropyl modified Fe_3O_4 for metal ions, chitosan-coated Fe_3O_4 for perfluorinated compounds [10], and poly(divinylbenzene-co-methacrylic acid)-coated Fe_3O_4 for estrogenic endocrine disrupting chemicals [11]. Among all surface modifications, hydrophobic modification of Fe_3O_4 has been extensively studied because of its wide application in both environmental analysis and proteomics field. For example, Fe_3O_4 was derivatized with octadecyl moieties to extract polycyclic aromatic hydrocarbons from environmental samples [12], Fe_3O_4-C18 nano-magnetic composite materials were applied for cleanup and enrichment of organophosphorous pesticides [13], Fe_3O_4@SiO_2@PMMA has been used to extract trace peptides

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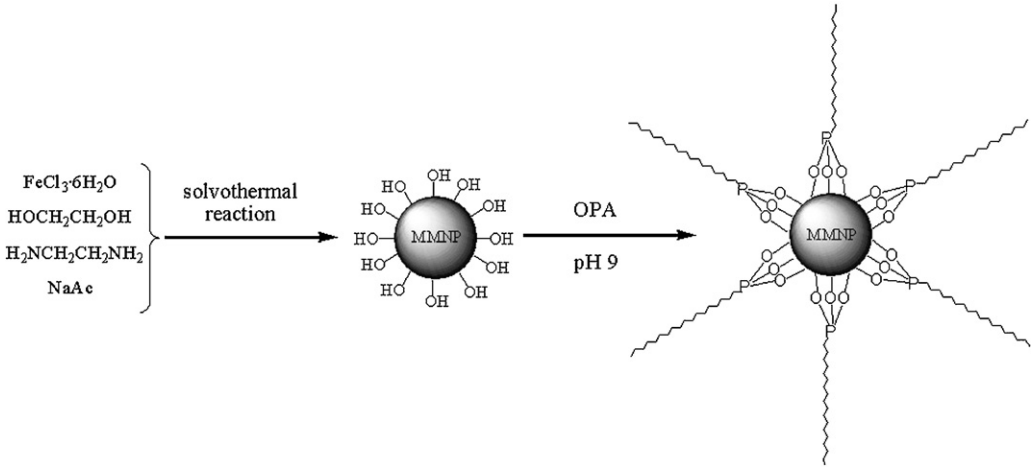

Fig. 1. Preparation scheme of OPA/MMNPs.

and proteins [14], and C8-functionalized magnetic carbonaceous polysaccharide microspheres have been applied to enrich peptides [15]. Silane reaction is the most conventional method. However, direct silane bonds on metal oxides other than silica are not stable and apt to hydrolysis in water or water-organic solutions [16]. To solve this problem, coating Fe_3O_4 particles with silica or polysaccharide layer prior to silanization is an alternative method [12,17]. Nevertheless, the whole process is a little tedious and troublesome.

As an effort to develop the convenient surface modification method, in this work, a new approach of n-octadecylphosphonic acid (OPA) modification strategy was proposed. OPA is a type of surfactant that can be strongly bonded onto the metal oxide surface via Lewis acid/base interaction, which has been successfully used to modify ZrO_2, TiO_2, MgO–ZrO_2, and so on [16,18–22]. Compared with conventional modification method by silanization, the OPA modification is simply carried out in mild aqueous conditions and is reported to yield a much stable product with higher surface coverage [16,23]. Therefore, OPA was proposed to functionalize mesoporous Fe_3O_4 nanoparticles by this simple strategy (the product was called as OPA/mesoporous magnetic nano particles (OPA/MMNPs)). It provides a new route for modification of magnetic nanoparticles. Since a variety of phosphonate compounds are available, magnetic nanoparticles are ready to be enriched with various functional moieties, via such a simple method, to cater for applications, which is beneficial for the development of MSPE. To verify the extraction performance of OPA/MMNPs, they were investigated to extract polycyclic aromatic hydrocarbons (PAHs), which are ubiquitous and priority pollutants, from environmental water samples.

2. Experimental

2.1. Reagents and materials

Ethyl acetate (HPLC grade) and n-hexane (HPLC grade) were obtained from CNW technologies GmbH (Dusseldorf, Germany). Methanol, ethylene glycol (EG), isopropanol, acetone, ethylene diamine (ED), tetrahydrofuran (THF), ferric chloride ($FeCl_3·6H_2O$), sodium acetate (NaAc) and sodium hydroxide (NaOH) were purchased from Sinopharm Chemical Reagent (Shanghai, China). OPA was synthesized according to a previous Ref. [19].

PAHs standard solution, anthracene-d10 (internal standard (I.S.), 0.2 mg/mL in CH_2Cl_2) and chrysene-d12 (I.S., 4 mg/mL in CH_2Cl_2) were bought from J&K Chemical Ltd. The PAHs standard solution contains naphthalene (NAPH), acenaphthylene (ACY), acenaphthene (ACP), fluorene (FLU), phenanthrene (PHEN), anthracene (ANTH), fluoranthene (FLT), pyrene (PYR), chrysene (CHRY), benzo[a]anthracene (BaA), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (INPY), dibenzo[a,h]anthracene (DiahA) and benzo[g,h,i]perylene (BghiP), each at 0.2 mg/mL in n-hexane/methylene dichloride (1/1, v/v). Diphenyl (I.S.) was bought from Sinopharm Chemical Reagent (Shanghai, China). The PAHs stock solution was prepared in methanol at a concentration of 0.5 μg/mL. The I.S. stock solution was prepared in methanol at the concentrations of 0.2 μg/mL for diphenyl and 1 μg/mL for anthracene-d10 and chrysene-d12, respectively. All the stock solutions were kept at 4 °C in darkness.

Tap water, lake water and hospital sewage were used for real sample investigation. Tap water was taken from a lab tap after flowing for 10 min. Lake water sample was collected from the East Lake in Wuhan. Hospital sewage was obtained from the sewer exit pipe of Zhongnan hospital (Wuhan, China). All the water samples were filtered through a 0.45 μm membrane and stored in brown bottles at 4 °C in the refrigerator.

2.2. Preparation of OPA/MMNPs

The preparation scheme of OPA/MMNPs is depicted in Fig. 1. MMNPs were synthesized via a solvothermal process according to Wang's method [3]. Briefly, $FeCl_3·6H_2O$ (5.0 g) was dissolved in EG (100 mL). Then NaAc (15.0 g) and ED (50 mL) were added to the solution. After being vigorously stirred for 30 min, the homogeneous mixture was sealed in a teflon-lined stainless-steel autoclave (200 mL). The autoclave was heated to 200 °C and maintained for 8 h, and then allowed to cool down to room temperature. The product was magnetically collected and washed with water/ethanol for several times and vacuum-dried at 60 °C for 6 h.

The resultant MMNPs were modified with OPA as follows. The OPA solution was prepared by dissolving OPA (1.0 g) in 50 mL mixture of H_2O:THF (1/1, v/v), and then was adjusted to a pH of 9 with NaOH solution. Then MMNPs (5.0 g) were added into the solution. The mixture was refluxed at 80 °C for 12 h. The final product was magnetically collected and washed by water/ethanol/acetone/n-hexane successively and repeatedly, then vacuum-dried at 60 °C for 6 h.

2.3. Instrumentation and analytical conditions

TEM images were obtained from JEM-100CXII transmission electron microscope (TEM, JEOL, Japan). The water contact angle was determined by X100 tensionmeter (KRUSS, German). Fourier-

Table 1
The qualitative and quantitative ions for the analysis of PAHs.

Analyte	Qualitative ions	Quantitative ion
ACY	152, 151	152
ACP	154, 153, 152	153
FLU	165, 166, 167	166
PHEN	176, 178, 179	178
ANTH	176, 178, 179	178
FLT	200, 202, 203	202
PYR	200, 202, 203	202
BaA	226, 228, 229	228
CHRY	226, 228, 229	228
BbF	250, 252, 253	252
BkF	250, 252, 253	252
BaP	250, 252, 253	252
INPY	276, 277, 278	276
DiahA	276, 277, 278	278
BghiP	276, 277, 278	276
Diphenyl (I.S.)	152	152
Anthracene-d10 (I.S.)	188	188
Chrysene-d12 (I.S.)	240	240

transform infrared spectroscopy (FT-IR) spectra were obtained from AVATAR 360 instrument (Thermo, USA). Magnetic data of the samples were characterized by a PPMS-9 vibrating sample magnetometer (QUANTOM, USA). Elemental analysis was performed on an Elementar VarioEL III elemental analyzer (Hanau, Germany). Nitrogen sorption experiments were carried out at 77 K using JW-BK surface area and pore size analyzer (JWGB Sci. & Tech., Beijing, China).

The gas chromatography–mass spectroscopy (GC–MS) analysis was performed on a Shimadzu GC–MS QP2010plus which is equipped with an AOC-20i+s autosampler (Kyoto, Japan). The GC separation was achieved on a Rxi^{TM}-5ms column (30 m × 0.25 mm × 0.25 μm) (Rescek, USA). The oven temperature was held at 70 °C for 2.0 min, then increased to 190 °C at a rate of 15 °C/min and held for 1.0 min, then increased to 260 °C at a rate of 10 °C/min and to 285 °C at a rate of 5 °C/min. Finally it was held at 285 °C for another 10.0 min. The injection volume was 1.0 μL in splitless mode. Helium (purity ≥ 99.999%) was used as carrier gas at a flow rate of 1.2 mL/min. The temperatures of injection port, detector and interface were held at 290 °C, 220 °C and 280 °C, respectively. Selective ion monitoring (SIM) mode was adopted for the quantitative analysis. The information on retention time, qualitative and quantitative ions for each PAH is listed in Table 1.

2.4. Extraction procedure

OPA/MMNPs (50 mg) were placed in a 15-mL vial and activated with 2 mL of acetone and distilled water, respectively, in sequence. Then 10 mL of spiked PAHs solution was added into the vial. The solution was vortexed fiercely for 1 min to form a dispersive solution. Then an external magnet was attached to the outside bottom of the vial and the OPA/MMNPs were gathered to the bottom of the vial. The supernatant was discarded and the PAHs absorbed on OPA/MMNPs were eluted with 0.5 mL desorption solvent (isopropanol/n-hexane (1/4, v/v)) by fierce vortex for 1 min. The desorption solution was collected and dehydrated with 100 mg anhydrous magnesium sulfate, and filtered through a 0.22-μm membrane. Finally, 1 μL of the desorption solution was injected into GC–MS instrument for analysis.

3. Results and discussion

3.1. Characterization of materials

To confirm the porous structure, MMNPs were characterized by N_2 adsorption/desorption. We found that the MMNPs possessed type IV isotherms and H3 hysteresis loops (as shown in Fig. 2a) which is consistent with Wang's result [3]. From the pore size distribution in Fig. 2b, the pores in the MMNPs were mainly in the mesoporous range.

Fig. 3 shows the TEM images of MMNPs and OPA/MMNPs. MMNPs were nearly monodispersed and sphere-like, with a mean diameter of about 65 nm (Fig. 3a). There were no obvious morphological differences between OPA/MMNPs (Fig. 3b) and MMNPs (Fig. 3a), suggesting that the grafted OPA layer is very thin.

In order to confirm the successful graft of OPA onto the MMNPs, FT-IR spectrometry and element analysis were performed. Fig. 4 shows the FT-IR spectra of MMNPs (a), OPA/MMNPs (b) and OPA (c). Compared with the spectra of OPA, the presence of OPA component in OPA/MMNPs could be proven by the peaks at 2854 cm^{-1} and 2925 cm^{-1} corresponding to the symmetric and asymmetric stretching vibrations of $-CH_2-$ and $-CH_3$ groups of the alkyl chains on OPA, respectively. Fig. 4 (b) also shows that the P=O (1231 cm^{-1}) and P–O–H (949 cm^{-1}) characteristic peaks are absent in the spectrum of OPA/MMNPs. It suggests that OPA was bonded onto the MMNPs via three symmetric P–O–Fe bonds, which is consistent with previous results [18,24,25]. In addition, the element contents of C and H of OPA/MMNPs were measured to be 0.55 wt.% and

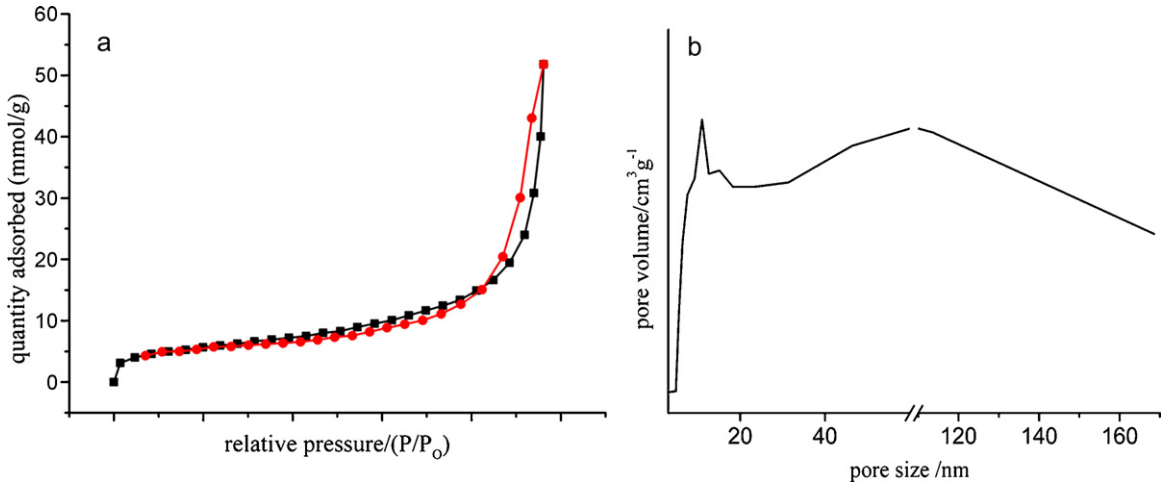

Fig. 2. N_2 adsorption/desorption isotherms (a) and BJH pore size distribution curve (b) of MMNPs.

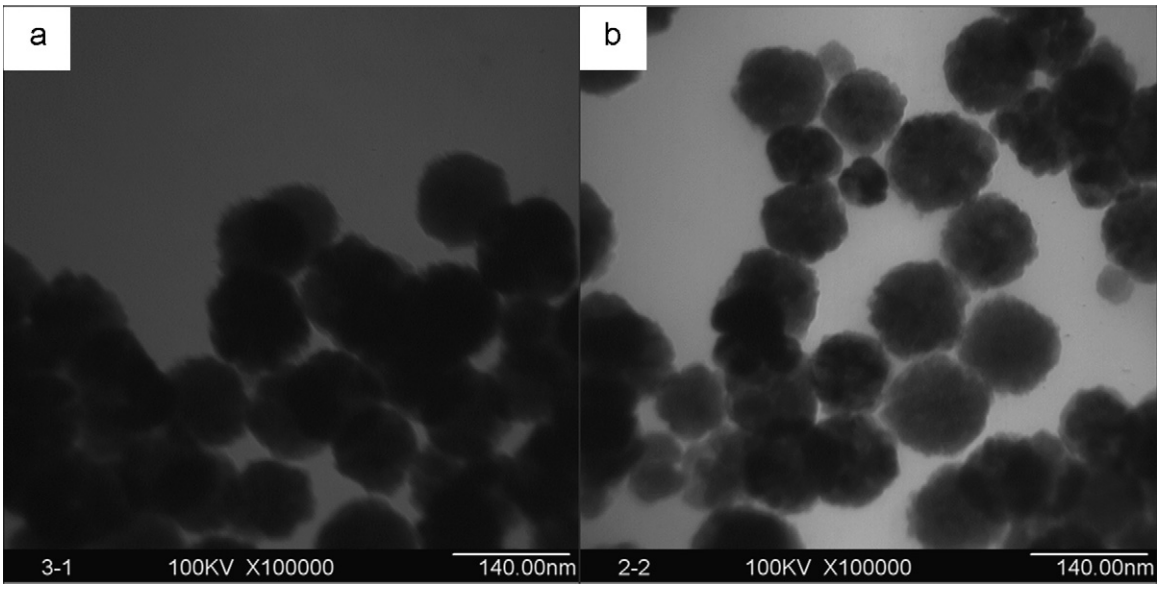

Fig. 3. TEM images of OPA/MMNPs (a) and MMNPs (b).

0.68 wt.%, respectively, which further verified the existence of OPA on the particles.

The hydrophobicity of OPA/MMNPs and MMNPs was tested by water contact angle measurement. Water drop on MMNPs tablet was found to immediately spread out, suggesting that MMNPs were highly hydrophilic (data not shown). By contrast, the contact angle of OPA/MMNPs was up to 136° (Fig. 5), suggesting that OPA/MMNPs are hydrophobic. These results further confirmed the successful graft of OPA onto the MMNPs.

The magnetic properties of OPA/MMNPs and MMNPs were investigated by a vibrating sample magnetometer. As shown in Fig. 6, both curves had no magnetic hysteresis loops. The saturation magnetization values of MMNPs and OPA/MMNPs were 63 emu/g and 57 emu/g, respectively. The results indicated the as-prepared MMNPs were super paramagnetic and the magnetic property was not significantly changed after OPA grafting. Because of the relatively high saturation magnetization values, the particles could be rapidly and efficiently separated from matrix solutions by an external magnet (taking OPA/MMNPs as an example in Fig. 7).

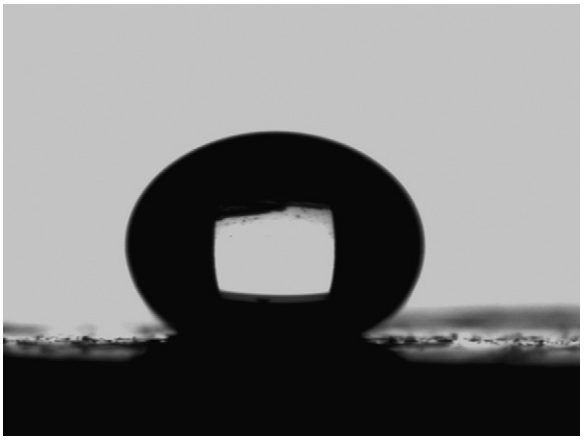

Fig. 5. Optical image of water droplets on the surface of OPA/MMNPs tablet.

4. Optimization of MSPE conditions

To achieve the optimal extraction efficiency of PAHs, various conditions such as amount of the sorbent, salt concentration,

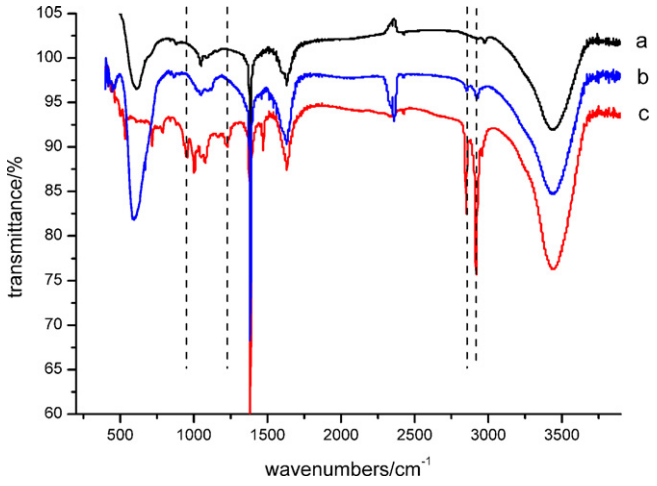

Fig. 4. FTIR spectra of MMNPs (a), OPA/MMNPs (b) and OPA (c).

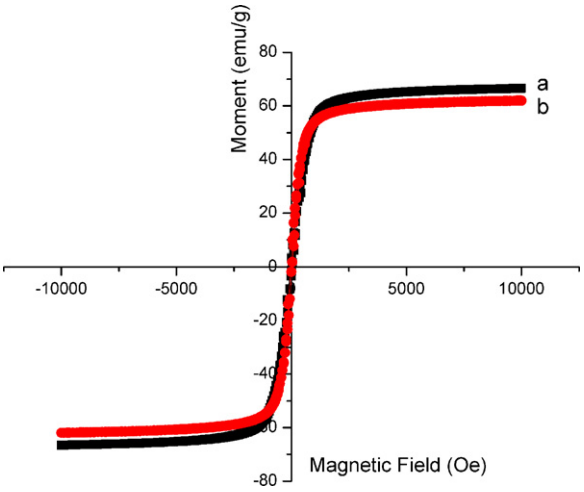

Fig. 6. Room-temperature magnetization curves of MMNPs (a) and OPA/MMNPs (b).

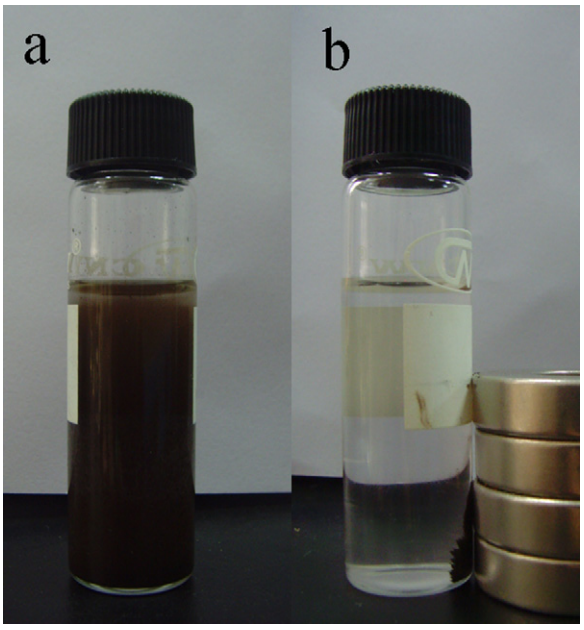

Fig. 7. OPA/MMNPs dispersed in matrix solution (a) and OPA/MMNPs collected by a magnet (b).

methanol content in matrix solution, extraction time and desorption time, desorption solvent were optimized.

To evaluate the effect of the sorbent amount on extraction efficiency, 10 mg, 25 mg, 50 mg and 75 mg of OPA/MMNPs were investigated. As shown in Fig. 8a, the sorbent amount had little effect on the recoveries of less-volatile PAHs with more than four benzene rings; as for the volatile 2–3 ring PAHs, the recoveries achieved by 50 mg magnetic sorbent was much higher than that of by 10 mg and 20 mg sorbent, but almost the same as by 75 mg. Thus 50 mg was employed in the following experiments.

To reduce PAHs adsorption on the glass vials (named as "wall effect" [26,27]), varying amount of methanol was added to the matrix solution. Fig. 8b shows the effect of methanol content on the extraction efficiency. With the increasing methanol content, volatile 2–3 ring PAHs were found to decline in recoveries, while less-volatile PAHs with more than 4 rings increased. This phenomenon could be explained by the fact that the solubility of PAHs would change slightly when methanol was added to water samples [26,27]. Overall, the moderate methanol content (10%) was suitable for our investigations.

The effect of ionic strength was investigated by adding NaCl to the matrix solution in the range from 0 mM to 50 mM. It was found that the recoveries decreased slightly with the increase of salt amount (Fig. 8c). This result could be explained by the "oil effect" [26,28]. The addition of salt into the matrix solution would reduce the interaction between PAHs and OPA/MMNPs, which led to poor extraction efficiency. So no salt was added in the following experiments.

The extraction time investigations were conducted by increasing the vortex time from 1 min to 10 min. It was found that extraction time had no significant influence on extraction efficiency. Therefore extraction time was fixed at 1 min. Also, we found that 1 min was enough to elute PAHs from the sorbents.

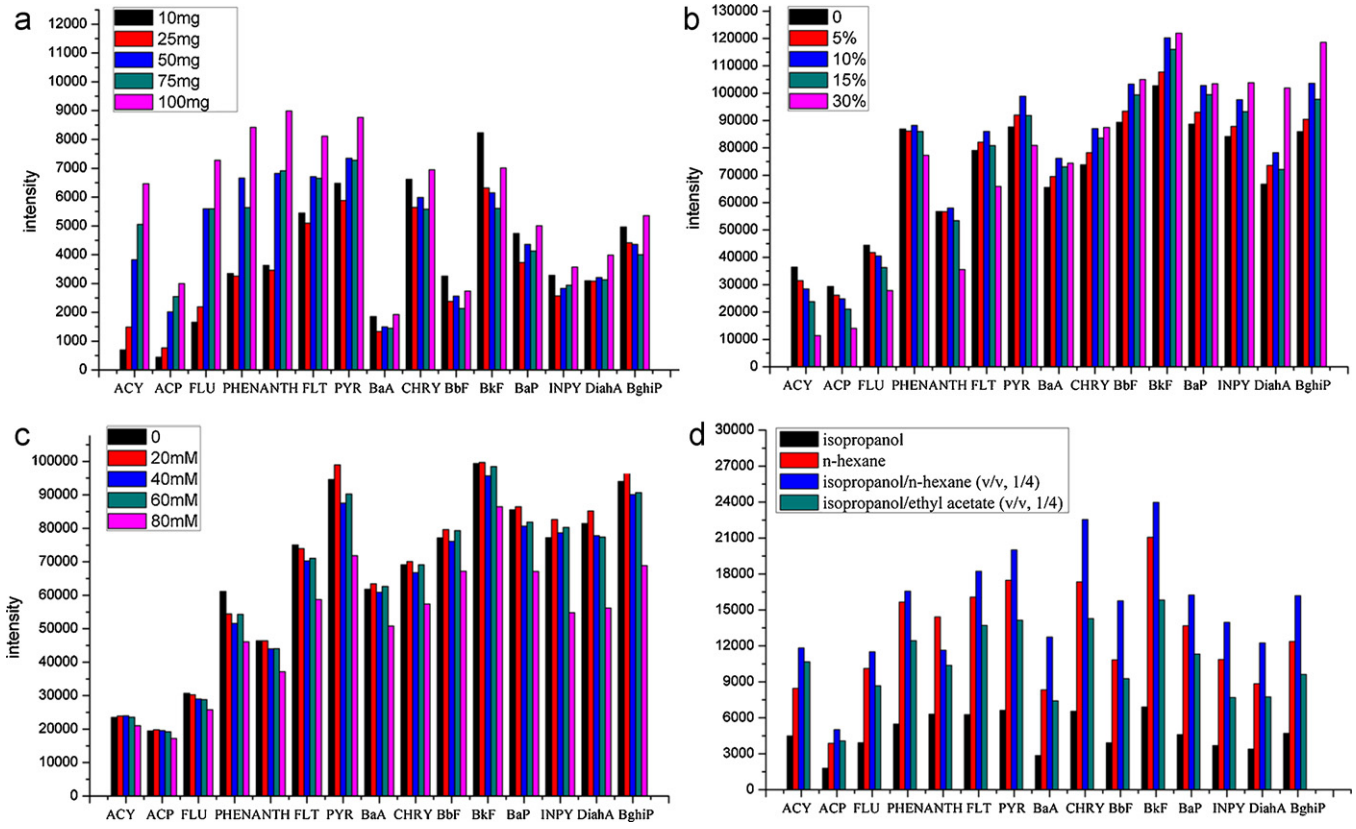

Fig. 8. Effect of the amount of the sorbent on extraction performance. Sample: 10 mL 2 μg/L spiked PAHs in aqueous sample, extraction time: 5 min, desorption solvent: 1 mL n-hexane, desorption time: 5 min (a). Effect of addition of organic solvent. 50 mg adsorbents, sample: 10 mL 4 μg/L spiked PAHs in aqueous sample, extraction and desorption time: 1 min, desorption solvent: 0.5 mL isopropanol/n-hexane(v/v, 1/4) (b). Effect of salt addition. 50 mg adsorbents, sample: 10 mL 4 μg/L spiked PAHs in water/methanol (v/v, 9/1), extraction and desorption time: 1 min, desorption solvent: 0.5 mL isopropanol/n-hexane (v/v, 1/4), added salt: NaCl (c). Effect of the desorption solvent. 50 mg sorbent, sample: 10 mL 4 μg/L spiked PAHs in aqueous sample, extraction time: 5 min, volume of desorption solvent: 1 mL, desorption time: 5 min (d).

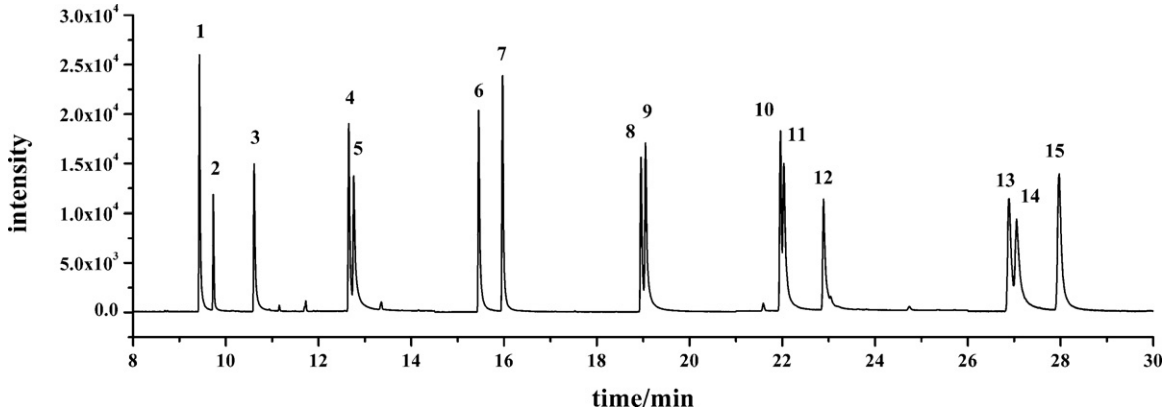

Fig. 9. Chromatogram of 15 PAHs standard mixture at a concentration of 80 μg/L. Peak identification: (1) ACY, (2) ACP, (3) FLU, (4) PHEN, (5) ANTH, (6) FLT, (7) PYR, (8) CHRY, (9) BaA, (10) BbF, (11) BkF, (12) BaP, (13) INPY, (14) DiahA, (15) BghiP.

The effect of desorption solvent was investigated by selection of n-hexane, isopropanol, binary solvents isopropanol/n-hexane (1/4, v/v) and isopropanol/ethyl acetate (1/4, v/v). The results are depicted in Fig. 8d. The isopropanol:n-hexane (1/4, v/v) exhibited the highest analytical signal. Therefore, this solvent mixture was used as the optimal desorption solvent.

On the basis of the above-described discussion, the optimal extraction conditions were 50 mg OPA/MNP, analytes in methanol/water (1/9, v/v) as the sample solution, 1 min for both extraction and desorption, isopropanol/n-hexane (1/4, v/v) as the desorption solvent. No salt was added to the sample solution.

4.1. Analytical performance

Under the optimized conditions, PAHs were quantitatively analyzed using diphenyl, anthracene-d10 and chrysene-d12 as I.S. A chromatogram for the separation of 15 PAH standard mixture is shown in Fig. 9. The calibrations were obtained by plotting peak areas versus concentrations. The sample solutions were spiked with stock solution to get final concentrations of PAHs at 0.2 μg/L, 0.5 μg/L, 1 μg/L, 2 μg/L, 5 μg/L, 10 μg/L, 20 μg/L, and 50 μg/L, 100 μg/L. As shown in Table 2, satisfactory correlation coefficients for fifteen compounds were obtained. The limits of detection (LODs) and limits of quantification (LOQs) were calculated at concentrations at which signal-to-noise ratios were equal to 3 and 10, respectively. LODs and LOQs data of PAHs are in the range of 14.1–70.0 ng/L and 46.9–233.2 ng/L, respectively. Compared with several previously reported materials or methods applied to analyze PAHs, as shown in Table 3, OPA/MMNPs show better extraction sensitivity than most of them.

The reproducibility of the method was determined by the intra-day and inter-day precisions. Six extractions of a mixture sample solution over a day gave the intra-day RSDs, and the inter-day RSDs were determined by extracting a mixture sample solution that had been independently prepared for continuous three days. The results are summarized in Table 4. Acceptable precision was obtained with RSD values less than 18.7% (as shown in Table 3).

4.2. Reproducibility of OPA/MMNPs

For sorbent-phase based extraction, the reproducibility has been a tackling problem concerning different batches of sorbent materials used. In the present study, the batch-to-batch reproducibilities of the OPA/MMNPs were investigated. Three batches of OPA/MMNPs prepared under the same conditions were used for the extraction of PAHs. Table 5 presents RSD values of fifteen PAHs with these sorbents. The RSDs were less than 12.1%, indicating that laboratory-prepared adsorbents, OPA/MMNPs, possessed acceptable reproducibility.

4.3. Analysis of real samples

After the method was established, it was applied to analyze three kinds of water samples including tap water, lake water and hospital sewage. All these samples were analyzed in triple replicates. The results are outlined in Table 6. One of samples (lake water) was found in the existence of PHEN, at a concentration of 0.94 μg/L.

Table 2
Calibration curves, LOD and LOQ data of the PAHs in aqueous samples.

Analytes	Concentration range (μg/L)	Regression line			LOD (ng/L)	LOQ (ng/L)
		Slope	Intercept	R^2 value		
ACY	0.2–100	0.1769	16.4	54.7	16.4	54.7
ACP	0.2–100	0.0739	34.1	113.6	34.1	113.6
FLU	0.2–100	0.2087	33.4	111.2	33.4	111.2
PHEN	0.2–100	0.4239	52.2	174.0	52.2	174.0
ANTH	0.2–100	0.2999	70.0	233.2	70.0	233.2
FLT	0.2–100	0.4099	16.0	53.5	16.0	53.5
PYR	0.2–100	0.6743	14.1	46.9	14.1	46.9
BaA	0.2–100	0.4627	15.4	51.4	15.4	51.4
CHRY	0.2–100	0.2357	16.5	54.9	16.5	54.9
BbF	0.2–100	0.3094	50.9	169.6	50.9	169.6
BkF	0.2–100	0.2854	57.5	191.7	57.5	191.7
BaP	0.2–100	0.2951	64.4	214.8	64.4	214.8
INPY	0.2–100	0.2971	41.5	138.3	41.5	138.3
DiahA	0.2–100	0.2537	55.2	184.0	55.2	184.0
BghiP	0.2–100	0.2870	53.0	176.8	53.0	176.8

Table 3
Comparison of different materials applied to extract PAHs.

Matrix	Extraction technique	Characteristics	LOD		Instrumental analysis	Ref.
Sea and estuarine water	Stir bar sorptive extraction	Commercial stir bar (twisters supplied by Gerstel)	ACY: 1.3 ng/L	BaA: 0.2 ng/L	GC–MS	[27]
			ACP: 0.3 ng/L FLU: 0.2 ng/L PHEN: 1.4 ng/L ANTH: 0.9 ng/L FLT: 0.4 ng/L PYR: 0.05 ng/L	CHRY: 0.1 ng/L BbF: 0.5 ng/ BkF: 0.5 ng/L BaP: 0.4 ng/L DiahA: 0.1 ng/L BghiP: 0.2 ng/L		
Aqueous samples	MSPE	Octadecyl functionlized monodisperse magnetic ferrite microspheres	ACY: 2.8 μg/L	CHRY: 4.9 μg/L	GC–MS	[12]
			ACP: 4.1 μg/L FLU: 1.6 μg/L PHEN: 3.4 μg/L ANTH: 4.2 μg/L FLT: 3.9 μg/L PYR: 5.1 μg/L BaA: 5.8 μg/L	BbF: 3.5 μg/L BkF: 3.6 μg/L BaP: 5.6 μg/L INPY: 36 μg/L DiahA: 7.6 μg/L BghiP: 7.9 μg/L		
Tea samples	Stir bar sorptive extraction	10-mm-long stir bars coated with a 0.5 mm film thick layer of PDMS	ACP: 3.7 ng/L	CHRY: 2.8 ng/L	HPLC-FLD	[26]
			FLU: 0.2 ng/L PHEN: 8.9 ng/L ANTH: 1.3 ng/L FLT: 0.1 ng/L PYR: 0.5 ng/L BaA: 0.9 ng/L	BbF: 2.4 ng/L BkF: 0.7 ng/L BaP: 1.2 ng/L INPY: 3.5 ng/L DiahA: 2.5 ng/L BghiP: 2.3 ng/L		
Tap water, hospital sewage, river water	MSPE	OPA/MMNPs	ACY: 16.4 ng/L ACP: 34.1 ng/L FLU: 33.4 ng/L PHEN: 52.2 ng/L ANTH: 70.0 ng/L FLT: 16.0 ng/L PYR: 14.1 ng/L BaA: 15.4 ng/L	CHRY: 16.5 ng/L BbF: 50.9 ng/L BkF: 57.5 ng/L BaP: 64.4 ng/L INPY: 41.5 ng/L DiahA: 55.2 ng/L BghiP: 53.0 ng/L	GC–MS	This work

Table 4
Method precisions at three different concentrations of the PAHs in aqueous samples.

Analytes	Intra-day precision (RSD, $n = 6$)			Inter-day precision (RSD, $n = 3$)		
	1 μg/L	10 μg/L	50 μg/L	1 μg/L	10 μg/L	50 μg/L
ACY	3.1	3.2	4.1	12.8	6.7	4.7
ACP	6.0	3.0	4.2	7.3	3.3	3.6
FLU	9.7	4.1	4.6	18.7	7.6	7.5
PHEN	6.7	4.6	6.0	17.6	11.3	8.3
ANTH	3.6	2.1	1.4	11.5	4.0	3.8
FLT	2.8	2.8	3.0	8.8	3.2	2.5
PYR	4.6	5.0	7.9	13.4	4.7	6.7
BaA	4.2	3.3	4.6	4.3	3.7	5.0
CHRY	4.3	4.3	3.2	12.6	5.8	3.4
BbF	4.4	3.4	3.3	4.2	3.2	4.3
BkF	2.8	4.4	3.3	4.1	4.2	5.8
BaP	4.2	3.7	3.5	4.5	3.6	3.8
INPY	3.7	3.5	2.9	4.9	4.5	5.0
DiahA	2.9	3.6	5.2	14.4	13.9	14.7
BghiP	3.4	3.4	4.4	8.4	12.5	14.3

Table 5
The RSD values of the extracted PAHs[a] with three different batches of OPA/MMNPs.

Analytes	ACY	ACP	FLU	PHEN	ANTH
Batch-to-batch reproducibility (RSD, $n=3$)	4.8	4.2	6.0	8.7	4.8
Analytes	FLT	PYR	BaA	CHRY	BbF
Batch-to-batch reproducibility (RSD, $n=3$)	5.5	12.1	8.0	3.8	4.8
Analytes	BkF	BaP	INPY	DiahA	BghiP
Batch-to-batch reproducibility (RSD, $n=3$)	4.9	5.8	7.3	8.4	8.3

[a] Sample solution was spiked at a concentration of 10 ng/L.

Table 6
Recoveries, precisions and concentrations of PAHs in the analysis of real samples.[a]

Analytes	Tap water		Lake water		Hospital sewage	
	Concentration (μg/L)	Recovery (%, RSD %, $n=3$)	Concentration (μg/L)	Recovery (%, RSD %, $n=3$)	Concentration (μg/L)	Recovery (%, RSD %, $n=3$)
ACY	Nd[b]	85.0 (4.7)	Nd	74.4 (3.5)	Nd	76.7 (3.1)
ACP	Nd	97.2 (4.5)	Nd	83.0 (3.6)	Nd	89.1 (4.5)
FLU	Nd	82.2 (3.8)	Nd	61.9 (4.1)	Nd	61.9 (6.3)
PHEN	Nd	77.0 (4.4)	0.94	53.5 (5.7)	Nd	54.2 (5.0)
ANTH	Nd	90.2 (1.6)	Nd	83.6 (3.5)	Nd	87.5 (3.4)
FLT	Nd	99.2 (1.2)	Nd	89.8 (2.7)	Nd	91.2 (3.6)
PYR	Nd	119.1(4.8)	Nd	97.1 (7.2)	Nd	90.9 (2.1)
BaA	Nd	104.2(2.6)	Nd	93.3 (2.2)	Nd	94.1 (3.8)
CHRY	Nd	96.1 (2.9)	Nd	88.8 (2.9)	Nd	90.8 (3.1)
BbF	Nd	97.9 (1.6)	Nd	90.7 (2.8)	Nd	94.5 (3.5)
BkF	Nd	101.9(2.1)	Nd	96.5 (0.8)	Nd	96.1 (2.6)
BaP	Nd	93.8 (2.5)	Nd	87.3 (1.9)	Nd	89.9 (3.8)
INPY	Nd	80.7 (1.5)	Nd	73.5 (5.3)	Nd	73.9 (8.1)
DiahA	Nd	108.8(1.7)	Nd	103.5(7.6)	Nd	91.6(11.7)
BghiP	Nd	105.3(2.1)	Nd	98.0 (4.6)	Nd	90.5 (9.3)

[a] Tap water, lake water and hospital sewage are all spiked at 10 ng/mL.
[b] Nd, not detected.

5. Conclusion

In this study, we proposed an easy method to prepare a magnetic material, the OPA modified mesoporous magnetite nanoparticles (OPA/MMNPs). OPA was directly grafted onto MMNPs using one-step reaction based on Lewis acid/base interaction. The novel magnetic material showed nano and mesoporous structures, superparamagnetic and excellent hydrophobic properties. Combined with GC–MS, a rapid, convenient and efficient method for the determination of PAHs in water samples was established successfully. The linearity ranges were 0.2–100 μg/L, with the inter- and intra-day precisions less than 17.6%. Moreover, OPA/MMNPs exhibited a good batch-to-batch reproducibility, with RSDs less than 12.1%. With these remarkable features, OPA/MMNPs should have great potential for the extraction of other hydrophobic analytes from water samples.

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