Barium alginate caged $\text{Fe}_3\text{O}_4@\text{C}_{18}$ magnetic nanoparticles for the pre-concentration of polycyclic aromatic hydrocarbons and phthalate esters from environmental water samples

Shengxiao Zhang, Hongyun Niu, Yaqi Cai*, Yali Shi

State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Science, Chinese Academy of Sciences, Beijing 100085, China

ARTICLE INFO

Article history:

Received 23 September 2009

Received in revised form 15 March 2010

Accepted 15 March 2010

Available online 23 March 2010

Keywords:

Magnetic nanoparticles

Barium alginate

Solid-phase extraction

Polycyclic aromatic hydrocarbons

Phthalate esters

ABSTRACT

The hydrophobic octadecyl (C_{18}) functionalized Fe_3O_4 magnetic nanoparticles ($\text{Fe}_3\text{O}_4@\text{C}_{18}$) were caged into hydrophilic barium alginate (Ba^{2+} -ALG) polymers to obtain a novel type of solid-phase extraction (SPE) sorbents, and the sorbents were applied to the pre-concentration of polycyclic aromatic hydrocarbons (PAHs) and phthalate esters (PAEs) pollutants from environmental water samples. The hydrophilicity of the Ba^{2+} -ALG cage enhances the dispersibility of sorbents in water samples, and the superparamagnetism of the Fe_3O_4 core facilitates magnetic separation. With the magnetic SPE technique based on the $\text{Fe}_3\text{O}_4@\text{C}_{18}@\text{Ba}^{2+}$ -ALG sorbents, it requires only 30 min to extract trace levels of analytes from 500 mL water samples. After the eluate is condensed to 0.5 mL, concentration factors for both phenanthrene and di-n-propyl-phthalate are over 500, while for other analytes are about 1000. The recoveries of target compounds are independent of salinity and solution pH under testing conditions. Under optimized conditions, the detection limits for phenanthrene, pyrene, benzo[a]anthracene, and benzo[a]pyrene are 5, 5, 3, and 2 ng L^{-1} , and for di-n-propyl-phthalate, di-n-butyl-phthalate, di-cyclohexyl-phthalate, and di-n-octyl-phthalate are 36, 59, 19, and 36 ng L^{-1} , respectively. The spiked recoveries of several real water samples for PAHs and PAEs are in the range of 72–108% with relative standard deviations varying from 1% to 9%, showing good accuracy of the method. The advantages of the new SPE method include high extraction efficiency, short analysis time and convenient extraction procedure. To the best of our knowledge, it is unprecedented that hydrophilic Ba^{2+} -ALG polymer caged $\text{Fe}_3\text{O}_4@\text{C}_{18}$ magnetic nanomaterial is used to extract organic pollutants from large volumes of water samples.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

To measure trace level contaminants in environmental water samples, pre-concentration is usually necessary before instrumental analysis. Some extraction methods, for example, liquid–liquid extraction, cloud point extraction, and solid-phase extraction (SPE), have been employed to extract organic pollutants. Among them SPE is the most popular one in environmental analysis for its high extraction efficiency, low consumption of organic solvents and easy operation. Nanomaterials, which possess nanosized diameter and large surface area, are being applied in numerous scientific fields [1–4]. In this regard many research groups have developed various types of nanosized SPE sorbents [5–12]. Compared with traditional SPE ones, these nanosized sorbents have high extraction efficiency with rapid extraction dynamics performance. However, the high

backpressure resulting from nanomaterial packed columns makes it difficult to adopt a high flow rate in column dynamic extraction mode or a high filtration rate in static batch mode.

In order to overcome such disadvantage, our groups have developed a novel SPE method based on mixed hemimicelle modified magnetic nanoparticles [11,12], where ionic surfactants are adsorbed on magnetic nanoparticles to form hemimicelle or admicelle. Surfactants coated magnetic nanoparticles are dispersed into solution to extract target compounds. The magnetic nanoparticles loaded with analytes are separated from solution rapidly and conveniently by using a magnet, and thus the target compounds can be eluted with a small amount of organic solvent for the subsequent determination with high-performance liquid chromatography (HPLC). This SPE method avoids a time-consuming step of water samples passing through SPE columns. However, there are still several issues in this magnetic SPE method: First, the formation of hemicelle/admicelles depends strongly on solution pH, and only under certain solution pH, can ionic surfactants be adsorbed on the surface of nanoparticles via electrostatic attraction; second, an appropriate amount of surfactants are required. Insufficient or overabundant surfactants will reduce the recover-

* Corresponding author at: Chinese Academy of Sciences, Research Center for Eco-Environmental Sciences, P.O. Box 2871, Beijing 100085, China.
Tel.: +86 010 62849239; fax: +86 010 62849182.

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

ies of analytes; third, the surfactants are co-eluted with target compounds, which may interfere with the subsequent HPLC analysis.

In recent years, a few researchers have studied the application of alkoxy-silanes modified magnetic nanoparticles in bio-separations and purification [13–15]. Bruce and Sen have prepared aminopropyl modified magnetite/silica core-shell nanoparticles, and investigated the efficiency of this material in the capture of single-stranded nucleic acids [14]. Hsiao et al. have reported the application of octadecyl (C_{18}) functionalized Fe_3O_4 nanoparticles to specifically trap phosphopeptides and nonphosphorylated peptides [15]. These successful studies have intrigued us to investigate the possibility of C_{18} functionalized Fe_3O_4 nanoparticles ($Fe_3O_4@C_{18}$) as SPE materials for pre-concentration of organic pollutants from large volumes of water samples. In the process of our study, we found that $Fe_3O_4@C_{18}$ were difficult to disperse in aqueous solution, which might be due to the surface hydrophobicity and nanoscaled size of the sorbents. The difficulty of dispersion made $Fe_3O_4@C_{18}$ unable to extract analytes from water samples, so hydrophilic modification without interfering adsorption was necessary.

Alginate is a polysaccharide that comprises homopolymeric and heteropolymeric chains of β -D-mannuronic and α -L-guluronic acids [16]. Bivalent cation, such as Ca^{2+} , Sr^{2+} , and Ba^{2+} can complex with the guluronic acid blocks of two neighboring alginate polymers, which yields the cross-linking of alginate polymers to form an extended gel network [17]. Fugetsu et al. have encapsulated multiwalled carbon nanotubes (MWCNTs) into cross-linked alginate microvesicles using Ba^{2+} as the bridging ion to form highly dispersed and biocompatible MWCNTs. Moreover, the polymer cage allows bidirectional diffusion of small molecules but restricts the access of large molecules [18,19]. Magnetite nanoparticles have also been encapsulated into calcium alginate for heavy metal removal from contaminated water [20,21]. So it is quite desirable to cage $Fe_3O_4@C_{18}$ into barium alginate (Ba^{2+} -ALG) polymers to enhance the dispersibility and stability of sorbents in aqueous solution. In the published studies, a special encapsulation system, electrostatic extrusion equipment which is unavailable in most laboratories, has been required to prepare cross-linked alginate microvesicle, and the size of the obtained magnetic bead is about hundreds of micron scale [18–21]. In this study, a $BaCl_2$ solution is dropped into a sodium alginate solution containing $Fe_3O_4@C_{18}$ under sonication and vigorous stirring. This method prevents alginate from being cross-linked to form large aggregation, and consequently allows the Ba^{2+} -ALG polymer to deposit onto the surface of $Fe_3O_4@C_{18}$ to form nanoscaled magnetite sorbents. To our knowledge, the SPE method based on hydrophilic Ba^{2+} -ALG modified $Fe_3O_4@C_{18}$ ($Fe_3O_4@C_{18}@Ba^{2+}$ -ALG) has not been reported.

In the present study, we reported the preparation of $Fe_3O_4@C_{18}@Ba^{2+}$ -ALG and their potential applications in the enrichment of organic contaminations from environmental water samples. To examine the feasibility of this approach, we selected four polycyclic aromatic hydrocarbons (PAHs) and four phthalate esters (PAEs) as model compounds. Coupling this novel SPE technique with HPLC separation and fluorescence or UV detection, a highly selective and sensitive SPE-HPLC analytical method was established.

2. Experimental

2.1. Chemicals and materials

All reagents used in the experiment were of analytical reagent grade and used without further purification. Phenanthrene (PHE),

pyrene (PYR), benzo[a]anthracene (BaA), and benzo[a]pyrene (BaP) were obtained from AccuStandard (New Haven, CT, USA). Di-n-propyl-phthalate (DPP), di-n-butyl-phthalate (DBP), dicyclohexyl-phthalate (DCP), and di-n-octyl-phthalate (DOP) were purchased from Acros Organics (Morris Plains, NJ, USA). Octadecyltriethoxysilane was supplied by Tokyo Chemical Industry Co. Ltd. (Tokyo, Japan). Ferric chloride ($FeCl_3 \cdot 6H_2O$) and ferrous chloride ($FeCl_2 \cdot 4H_2O$) were purchased from Beijing Chemicals Corporation (Beijing, China). Ultrapure water was prepared by using Milli-Q water purification system (Bedford, MA, USA).

2.2. Synthesis of Fe_3O_4 and $Fe_3O_4@C_{18}$ nanoparticles

Fe_3O_4 nanoparticles were prepared by a chemical coprecipitation method [11,22]. The synthesized Fe_3O_4 nanoparticles were rinsed with 50 mL of ethanol, and subsequently with 20 mL of anhydrous toluene twice, then dispersed into 80 mL of anhydrous toluene. After an addition of 1 mL of octadecyltriethoxysilane, the mixture was sonicated for 5 min and transferred in a PTFE-lined autoclave. The autoclave was heated for 12 h at 393 K. The crude $Fe_3O_4@C_{18}$ nanoparticles were washed several times with ethanol to remove toluene and impurities, and finally the products were dispersed into 100 mL of ethanol.

2.3. Preparation of $Fe_3O_4@C_{18}@Ba^{2+}$ -ALG

Half amount of the above synthesized $Fe_3O_4@C_{18}$ was dispersed into a sodium alginate solution (0.1%, 200 mL). Then a barium chloride solution (2%, 40 mL) was dropped into the mixture under sonication and vigorous stirring, and the reaction solution was aged for 30 min. The obtained sorbents were separated from solution by a powerful magnet and rinsed with deionized water for several times to remove impurities. The obtained $Fe_3O_4@C_{18}@Ba^{2+}$ -ALG sorbents were freeze-dried for use. The preparation procedure is illustrated in Fig. 1(a).

2.4. Characterization of sorbents

The morphology and particle size of the sorbents were studied with a transmission electron microscope (TEM) of H-7500 (Hitachi, Tokyo, Japan) operating at 80 kV accelerated voltage. UV-vis absorbance spectra were recorded on a Beckman DU 800 Spectrophotometer (Brea, CA, USA) in a wavelength range of 200–800 nm. Magnetic property was analyzed using a vibrating sample magnetometer (VSM, LDJ9600). IR spectra were recorded on a Nicolet Avatar 360 spectrometer (Nicolet Thermo, Waltham, MA, USA).

2.5. SPE procedure

The SPE procedure allowed rapid separation with a simple magnetic extraction method. First, 0.1 g of the $Fe_3O_4@C_{18}@Ba^{2+}$ -ALG sorbents was rinsed and activated in 5 mL of methanol, and then dispersed into a 500 mL aqueous sample. The mixture was sonicated for 1 min and stood still for 20 min. Subsequently, an Nd-Fe-B strong magnet was deposited at the bottom of the beaker and the sorbents were isolated from the solution. After about 5 min, the solution became clear and the supernatant was decanted. Finally, the pre-concentrated analytes were eluted from the isolated sorbents with acetonitrile. The eluate was dried with a stream of nitrogen at 333 K and the residue was dissolved in 0.5 mL of acetonitrile, and finally 20 μ L of aliquots were injected into the HPLC system for analysis. The whole pretreatment procedure is illustrated in Fig. 1(b).

Fig. 1. Schematic diagram of (a) the preparation of the $\text{Fe}_3\text{O}_4@C_{18}@Ba^{2+}$ -ALG sorbent, and (b) its application for enriching analytes as SPE sorbent.

2.6. HPLC analysis

PAHs and PAEs were separated and quantified by using an HPLC system (Dionex, Sunnyvale, CA, USA). The HPLC equipment included a Dionex P680 HPLC pump, a thermostated column compartment TCC-100, a Dionex RF 2000 fluorescence detector (FLD), and a PDA-100 photodiode array detector. The separation was conducted on a Diamonsil[®] C_{18} column (Dikma Technologies, Lake Forest, CA, USA, 250×4.6 mm; particle size, $5 \mu\text{m}$). The mobile phase for PAHs was water–acetonitrile (15:85), and the flow rate was 1 mL min^{-1} . PAHs were determined using a fluorescence detector, and its settings were as follows: 260 nm excitation, 392 nm emission for PHE, PYR, and BaA; 260 nm excitation, 432 nm emission for BaP. For PAEs, gradient separation carried out using water–acetonitrile (50:50) and acetonitrile as the A and B solvents, respectively, and the flow rate 1 mL min^{-1} . The linear gradient profile was as follows: B maintained at 40% in the first 15 min, 40–100% in 10 min, then held for 10 min, after that, the mobile phase returned to the initial conditions in 3 min. PAEs were quantified by a UV detector and the wavelength was set at 226 nm.

2.7. Sample collection

Snow samples were collected in our campus and melt at room temperature in February 2009, and tap water samples were taken from our laboratory in Haidian District (Beijing). River water samples were acquired from Xiaoqing River (Haidian District, Beijing). All samples were collected randomly and filtered through $0.45 \mu\text{m}$ 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. 2(a–c) shows the TEM images of Fe_3O_4 , $\text{Fe}_3\text{O}_4@C_{18}$ and $\text{Fe}_3\text{O}_4@C_{18}@Ba^{2+}$ -ALG, respectively. Fe_3O_4 nanoparticles appear quasi-spherical in shape with an average diameter of about 10 nm. Little or no difference is observed between Fe_3O_4 and $\text{Fe}_3\text{O}_4@C_{18}$, indicating that silanization has no obvious effect on the morphology of the support material. In Fig. 2(c),

Fig. 2. TEM images of (a) Fe₃O₄, (b) Fe₃O₄@C₁₈, and (c) Fe₃O₄@C₁₈@Ba²⁺-ALG. (d) UV-vis spectra of Fe₃O₄, Fe₃O₄@C₁₈, and Fe₃O₄@C₁₈@Ba²⁺-ALG.

Ba²⁺-ALG vesicles display as a light area surrounding the darker core of Fe₃O₄, revealing a core-shell structure of the Fe₃O₄@C₁₈@Ba²⁺-ALG sorbents. The Ba²⁺-ALG shell endows the surface hydrophilicity of the sorbents and ensures their dispersibility and stability in aqueous solution. Fig. 2(d) presents UV-vis spectra of Fe₃O₄, Fe₃O₄@C₁₈ and Fe₃O₄@C₁₈@Ba²⁺-ALG nanoparticles in methanol. There is no obvious difference between the absorbance of Fe₃O₄ and Fe₃O₄@C₁₈, agreeing well with the TEM image results. The reduction of absorbance for Fe₃O₄@C₁₈@Ba²⁺-ALG may result from the enhancement of particle size.

3.1.2. IR spectra

Fig. 3 displays IR spectra of Fe₃O₄, Fe₃O₄@C₁₈, and Fe₃O₄@C₁₈@Ba²⁺-ALG. All the spectra show a characteristic band of Fe₃O₄ at 580 cm⁻¹ [14]. The stretching vibrations of hydroxyl groups (OH) usually form a broad band region at 3100–3700 cm⁻¹ [21]. As shown in Fig. 4(b), after Fe₃O₄ nanoparticles are functionalized with C₁₈, the stretching vibration of hydroxyl groups disappears, while a C–H stretching vibrating band at 2920 and 2850 cm⁻¹ arises [13]. This indicates that the C₁₈ chain is successfully attached to the magnetic nanoparticles by reactions with the hydroxyl groups on the surface of Fe₃O₄. Once Fe₃O₄@C₁₈ are encapsulated into the Ba²⁺-ALG vesicles, the hydroxyl group absorption appears again, and a carboxylic group adsorption at 1413 and 1598 cm⁻¹ can also be observed [18,21]. These groups are introduced by the alginate polymer, indicating successful functionalization of alginate on the surface of the Fe₃O₄@C₁₈ nanoparticles.

3.1.3. Magnetic properties

Sufficient magnetic properties are necessary for practical applications of magnetic materials in aqueous solution. Fig. 4 shows VSM magnetization curves of Fe₃O₄, Fe₃O₄@C₁₈, and Fe₃O₄@C₁₈@Ba²⁺-ALG at room temperature. All the magnetic nanoparticles exhibit a typical superparamagnetic behavior due to no hysteresis, remanence or coercivity. Maximum saturation magnetizations of Fe₃O₄, Fe₃O₄@C₁₈, and Fe₃O₄@C₁₈@Ba²⁺-ALG are measured at 63.72, 62.59 and 49.31 emu g⁻¹, respectively. The decrease in the magnetic strength results from the nonmagnetic shell of C₁₈ and Ba²⁺-ALG. According to Ma's study, a saturation magnetization of

Fig. 3. IR spectra of (a) Fe₃O₄, (b) Fe₃O₄@C₁₈, and (c) Fe₃O₄@C₁₈@Ba²⁺-ALG.

Fig. 4. VSM magnetization curves of Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{C}_{18}$, and $\text{Fe}_3\text{O}_4@\text{C}_{18}@\text{Ba}^{2+}\text{-ALG}$.

16.3 emu g^{-1} is enough for magnetic separation from solution with a magnet [23]. The $\text{Fe}_3\text{O}_4@\text{C}_{18}@\text{Ba}^{2+}\text{-ALG}$ 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.

3.2. Optimization of extraction conditions

3.2.1. Effect of the amount of nanoparticle sorbents

In order to have satisfactory recoveries of target compounds, a certain amount of sorbents are required. In the traditional C_8 or C_{18} SPE method, SPE columns consist of about 0.4–0.9 g of sorbents [24–29], while in our study, only 0.1 g of the $\text{Fe}_3\text{O}_4@\text{C}_{18}@\text{Ba}^{2+}\text{-ALG}$ sorbents is enough for PAHs and PAEs to attain satisfactory results (Fig. 5). The recoveries of DPP and PHEN are relatively low (50–60%) because of their high solubility in water, and the recoveries of other target compounds are, however, over 80%. Nanoparticle sorbents have large surface area and high adsorption efficiency; therefore, satisfactory results can be achieved by using lower amount of nanoparticle sorbents than those used in traditional SPE sorbents.

3.2.2. Magnetic separation and equilibrium time

The $\text{Fe}_3\text{O}_4@\text{C}_{18}@\text{Ba}^{2+}\text{-ALG}$ sorbents possess superparamagnetism and large saturation magnetization, which make the sorbents completely isolated from solution within only about 5 min by a strong Nd–Fe–B magnet. In order to attain adsorption equilibrium, a certain standing time is required after the sorbents are dispersed into the solution. As shown in Fig. 6, the recoveries of PAEs and PAHs are all enhanced with an increased time, and the maximum recoveries of these analytes are obtained when the standing time is increased to 20 min. On one hand, the short diffusion route of nanosized sorbents results in rapid extraction dynamics. On the other hand, the polymer cage of $\text{Ba}^{2+}\text{-ALG}$ allows bidirectional diffusion of small molecules freely, so it will not interfere with the adsorption of target compounds. Generally, it takes only about 30 min to extract analytes from a 500 mL water sample with the magnetic SPE technique based on the $\text{Fe}_3\text{O}_4@\text{C}_{18}@\text{Ba}^{2+}\text{-ALG}$ sorbents. In comparison, 2–3 h are required to pretreat 500 mL environmental water samples by the traditional SPE column equipped with a vacuum pump.

3.2.3. Effect of salinity and pH

To investigate the effect of salinity on the recoveries of target compounds, NaNO_3 (0–50 mM) was added into solution. No obvi-

Fig. 5. Effect of the amount of sorbents on the recoveries of (a) PAHs, and (b) PAEs. Performed in batch mode. Sample volume: 500 mL. Volume of acetonitrile: 8 mL. Concentration of analytes: PAHs, 0.2 ng mL^{-1} ; PAEs, 1 ng mL^{-1} .

ous decrease was observed for the recoveries of analytes with the concentration of NaNO_3 in the range of 0–50 mM (data not shown). So the effect of salinity in real water samples on the recoveries of target compounds is negligible.

Solution pH plays an important role for adsorption of target compounds by affecting the existing form of target compounds and the charge species and density on the sorbents surface. PAEs and PAHs exist as neutral molecules under ordinary conditions, which may cause their adsorption unaffected by charges on the surface of the sorbents. The experimental results show that when the solution pH is in the range of 3–10, there is no obvious variation for the recoveries of PAEs and PAHs (data not shown).

The independence of the recoveries from salinity and pH may be due to two reasons: one is the stability of the sorbents under different conditions; the other is that hydrophobic interactions between C_{18} and analytes play a major role in adsorption. To confirm the stability of the sorbents, the UV–vis spectra of the $\text{Fe}_3\text{O}_4@\text{C}_{18}@\text{Ba}^{2+}\text{-ALG}$ sorbents under different salinity and pH are recorded (Fig. 7). Little or no obvious difference is observed for the position and intensity of absorption peaks, indicating good stability of the sorbents under different conditions. Compared with our group's previous studies based on mixed hemimicelles functionalized magnetic nanoparticles [11,12], which requires rigorous pH and appropriate amount of surfactants, the $\text{Fe}_3\text{O}_4@\text{C}_{18}@\text{Ba}^{2+}\text{-ALG}$ SPE system is more convenient and stable. Due to the independence of the recoveries from salinity and pH, the $\text{Fe}_3\text{O}_4@\text{C}_{18}@\text{Ba}^{2+}\text{-ALG}$

Fig. 6. Effect of standing time on the recoveries of (a) PAHs, and (b) PAEs. Performed in batch mode. Amount of adsorbent: 0.1 g. Sample volume: 500 mL. Concentration of analytes: PAHs, 0.2 ng mL⁻¹; PAEs, 1 ng mL⁻¹.

sorbents can be dispersed directly into water samples to extract target compounds without any loss of efficiency.

3.2.4. Effect of humic acid

In general, typical nonpolar pollutants such as PAHs may have great potentials to associate with humic acid [24,25]. To investigate the negative effect of humic acid on analytes adsorption, humic acid (0–20 mg L⁻¹) was added into water samples before the addition of sorbents. As shown in Fig. 8(a), with the increase of humic acid concentration, the extraction efficiency of DPP, DBP and DCP decreases slightly, while the extraction efficiency of DOP decreases by 30% as the humic acid concentration is increased to 20 mg L⁻¹, which may be because of the high hydrophobicity of DOP. Fig. 8(b) shows an obvious negative effect of humic acid on the recoveries of PAHs. The

Fig. 7. UV-vis spectra of Fe₃O₄@C₁₈@Ba²⁺-ALG under different (a) salinity, and (b) pH.

negative effect comes from the association of PAHs with humic acid [24,25]. Other researchers have also found similar negative effects of humic acid when C₈ or C₁₈ silica sorbents are used to extract PAHs and other organic compounds [24–28]. In surface water samples, the concentration of humic acid generally ranges from 1 to 5 mg L⁻¹ [25,29]. In this range, the recoveries of target compounds meet the requirement of analysis. For water samples with high concentration of dissolved organic carbon, it remains challenging to develop new effective sorbents or a SPE system to extract highly hydrophobic compounds.

3.2.5. Desorption conditions

Acetonitrile and methanol are used as solvents for the desorption of analytes from the Fe₃O₄@C₁₈@Ba²⁺-ALG sorbents. Results show that both acetonitrile and methanol are able to desorb

Table 1
Analytical parameters of the proposed method.

Analytes	Linearity range (ng mL ⁻¹)	Calibration equations	Correlation coefficient (r)	Detection limit ^a (ng L ⁻¹)
PHE	0.01–2	$y = 4.987x + 0.251$	0.9995	5
PYR	0.01–2	$y = 23.746x - 0.181$	0.9995	5
BaA	0.01–2	$y = 53.934x - 0.761$	0.9991	3
BaP	0.01–2	$y = 133.86x - 2.480$	0.9992	2
DPP	0.1–20	$y = 0.5296x + 0.1262$	0.9998	36
DBP	0.1–20	$y = 0.5384x + 0.0744$	0.9996	59
DCP	0.1–20	$y = 0.9442x - 0.0340$	0.9999	19
DOP	0.1–20	$y = 0.5684x + 0.1847$	0.9999	36

^a Detection limit calculated by using S/N = 3.

Fig. 8. Effect of humic acid on the extraction efficiencies of (a) PAHs and (b) PAEs. Performed in batch mode. Amount of adsorbent: 0.1 g. Sample volume: 500 mL. Concentration of analytes: PAHs, 0.2 ng mL⁻¹; PAEs, 1 ng mL⁻¹.

target compounds from the sorbents completely, whereas acetonitrile is more effective. Quantitative recoveries of analytes are observed with 8 mL (2 mL every time and washed four times) of acetonitrile. After an addition of the desorption solution, the vessel containing the sorbents was shaken vigorously for a few seconds. The mixture was set on a powerful magnet until the sorbents were separated from the solution, and the supernatant was transferred into a cuvette. After four cycles, the desorption solution was combined together and condensed. Compared with previous studies based on mixed hemimicelles SPE methods [9–12], where surfactants are co-eluted with target compounds, the eluate in this study is clean with little matrix disturbance because C₁₈ is grafted to the magnetic nanoparticle by covalent bonds and the Ba²⁺-ALG polymer does not dissolve in the desorption solution.

3.2.6. Reusability of the sorbents

In order to investigate the recycling of the nanoparticle sorbents, the Fe₃O₄@C₁₈@Ba²⁺-ALG sorbents used in SPE procedure were rinsed with 5 mL of acetonitrile twice before applied in the next SPE procedure. The recoveries of PAHs and PAEs are listed in Fig. 9. The sorbents can be reused eight times without much sacrifice of the recoveries of analytes.

3.3. Analytical performance

Under the above optimized conditions, calibration curves are established for PAEs and PAHs with the concentration in the range of 0.1–20 ng mL⁻¹ and 0.01–2 ng mL⁻¹, respectively. By extracting analytes from 500 mL spiked pure water samples and concentrating the eluate to 0.5 mL, the pre-concentration factors for PHE and DPP are over 500 due to their 50–60% recoveries, and for other analytes about 1000. Quantitative parameters such as linear range, correlation coefficient, detection limit are evaluated and the results are summarized in Table 1. It suggests that the present method has high sensitivity, wide linear range and good precision. Calibration curves of the analytes exhibit good linearity with correlation coefficient $r > 0.999$ in the study range. The detection limits, which are

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

Water sample	Tap water			Snow water			River water		
Spiked ^a (ng mL ⁻¹)	0	0.05	0.5	0	0.05	0.5	0	0.05	0.5
Detected (ng mL ⁻¹)									
PHE	0.098	0.1498	0.585	0.694	0.749	1.194	0.023	0.066	0.454
PYR	0.012	0.0608	0.529	0.156	0.193	0.627	0.013	0.059	0.472
BaA	nd ^b	0.0497	0.487	0.077	0.120	0.495	0.011	0.058	0.444
BaP	nd	0.0372	0.411	0.01	0.053	0.459	nd	0.046	0.405
Recovery (%) ^c									
PHE		102.7 ± 5	97.3 ± 2		108.3 ± 6	100 ± 8		86.0 ± 6	86.2 ± 5
PYR		97.6 ± 3	103.4 ± 7		93.6 ± 2	94.2 ± 3		92.0 ± 2	91.8 ± 3
BaA		99.4 ± 6	97.4 ± 1		86.0 ± 4	84.0 ± 3		94.0 ± 1	86.6 ± 6
BaP		74.4 ± 5	82.2 ± 6		86.0 ± 5	89.8 ± 1		92.0 ± 4	81.0 ± 8
Spiked ^a (ng mL ⁻¹)	0	0.5	5	0	0.5	5	0	0.5	5
Detected (ng mL ⁻¹)									
DPP	0.133	0.641	5.23	0.272	0.754	4.84	0.254	0.679	3.97
DBP	nd	0.519	5.01	0.371	0.789	4.87	0.205	0.668	4.81
DCP	nd	0.542	4.70	nd	0.530	4.82	nd	0.563	4.77
DOP	nd	0.535	4.86	nd	0.504	4.98	0.034	0.446	3.64
Recovery (%) ^c									
DPP		101.6 ± 1	101.9 ± 2		96.4 ± 3	91.4 ± 5		85.0 ± 6	74.3 ± 9
DBP		103.8 ± 3	100.2 ± 4		83.6 ± 9	90.0 ± 8		92.6 ± 4	92.1 ± 2
DCP		108.4 ± 7	94.0 ± 7		106.0 ± 3	96.4 ± 3		112.6 ± 8	95.4 ± 1
DOP		107.0 ± 4	97.2 ± 7		100.8 ± 1	99.6 ± 2		82.4 ± 6	72.1 ± 8

^a Mean of three determinations.

^b Not detected.

^c Standard deviation for three determinations.

Fig. 9. Effect of recycling times on the recoveries of (a) PAHs and (b) PAEs. Amount of sorbents: 0.1 g. Sample volume: 500 mL. Concentration of analytes: PAHs, 0.2 ng mL⁻¹; PAEs, 1 ng mL⁻¹.

calculated by using a signal-to-noise ratio of 3, for PHE, PYR, BaA, and BaP are 5, 5, 3, and 2 ng L⁻¹, and for DPP, DBP, DCP, and DOP are 36, 59, 19, and 36 ng L⁻¹, respectively.

3.4. Analysis of environmental water samples

To test the method, it was applied to analyze tap water, snow water, and river water samples. Table 2 summarizes the recoveries and concentrations of the target compounds in the real water samples, expressed as mean value ($n=3$), and the relative standard deviation (RSD) of recoveries ranging from 1% to 9%. Among three environmental water samples, four PAHs are all detected in the snow water sample and the concentrations are in a relatively high level, meanwhile trace levels of PHE, PYR and BaA are found in the river water sample. One to three PAEs analytes are detected in all water samples, and the concentrations are in the level of 10⁻¹ ng mL⁻¹. The results also indicate that the recoveries of spiked environmental water samples are very satisfactory. The recoveries of PAHs range from 74% to 108%, and those of PAEs 72–112%. Chromatograms of PAHs in the snow water sample and PAEs in the river water sample and their corresponding spiked solutions are shown in Fig. 10(A and B), respectively.

Compared to previous studies from our groups, the present method shows a fairly good analytical performance. In this study, only 0.1 g of sorbents is enough to extract target compounds from a 500 mL aqueous solution. There is no need to adjust solution pH or add other additives because the functionalized C₁₈ is an available layer to extract analytes. All these results suggest that this SPE method is convenient for the rapid enrichment of

Fig. 10. (A) Solid-phase extraction/LC-FLD chromatograms. (a) Snow water sample; (b) snow water spiked with 0.05 ng mL⁻¹, and (c) snow water spiked with 0.5 ng mL⁻¹. (B) Solid-phase extraction/LC-UV chromatograms. (a) Xiaoqing river water sample, (b) Xiaoqing river water spiked with 0.5 ng mL⁻¹, and (c) Xiaoqing river water spiked with 5 ng mL⁻¹.

organic pollutants from large volumes of environmental water samples.

4. Conclusions

In this study, magnetic nanoparticles were successfully functionalized with C₁₈ groups and then caged into Ba²⁺-ALG polymers to improve their hydrophilicity and dispersibility in aqueous solution. The obtained materials were developed as magnetic SPE sorbents to extract organic compounds from large volumes of environmental water samples. Compared with previous SPE methods, this SPE method have following merits: (a) After adsorption of analytes from water samples, the sorbents can be collected conveniently and rapidly with a magnet for elution due to superparamagnetism of materials, which avoids the time-consuming column passing or filtration operation. (b) Nanoparticle sorbents possess high adsorption capacity and rapid adsorption rates, so low amount of sorbents and short equilibrium time are required to extract analytes from large volumes of water samples. (c) The recoveries of target compounds are independent of salinity and solution pH. Therefore, there is no need to adjust solution pH or add other additives before extraction. (d) The cage of Ba²⁺-ALG allows target compounds with small molecular weight diffuse bidirectionally, but restricts the access of humic acid and colloid because of electrostatic repulsion and size exclusion, which protect the sorbents from being damaged or stuffed during real water sample analysis. This study has not only proposed a rapid and convenient SPE method to extract organic compounds from large volumes of

water samples, but also extended the scope of application of SPE based on C₁₈ functionalized magnetic nanoparticles.

Acknowledgments

This work was jointly supported by National Basic Research Program of China (2009CB421605); National High Technology Research and Development Program of China (2007AA06A407, 2009AA061603); the National Natural Science Foundation of China (20877079, 20907061, 20921063).

References

- [1] B. Raguse, E. Chow, C.S. Barton, L. Wieczorek, *Anal. Chem.* 79 (2007) 7333–7339.
- [2] H.H. Yang, S.Q. Zhang, X.L. Chen, Z.X. Zhuang, J.G. Xu, X.R. Wang, *Anal. Chem.* 76 (2004) 1316–1321.
- [3] M. Liong, J. Lu, M. Kovochich, T. Xia, S.G. Ruehm, A.E. Nel, F. Tamanoi, J.I. Zink, *ACS Nano* 2 (2007) 889–896.
- [4] C.T. Yavuz, J.T. Mayo, W.W. Yu, A. Prakash, J.C. Falkner, S. Yean, L. Cong, H.J. Shipley, A. Kan, M. Tomson, D. Natelson, V.L. Colvin, *Science* 314 (2006) 964–967.
- [5] Y.Q. Cai, G.B. Jiang, J.Y. Liu, Q.X. Zhou, *Anal. Chem.* 75 (2003) 2517–2521.
- [6] Y.Q. Cai, G.B. Jiang, J.Y. Liu, Q.X. Zhou, *Anal. Chim. Acta* 494 (2003) 149–156.
- [7] Y.Q. Cai, Y.E. Cai, S.F. Mou, Y.Q. Lu, *J. Chromatogr. A* 1081 (2005) 245–247.
- [8] H.Y. Wang, A.D. Campiglia, *Anal. Chem.* 80 (2008) 8202–8209.
- [9] H.Y. Niu, Y.Q. Cai, Y.L. Shi, F.S. Wei, S.F. Mou, G.B. Jiang, *J. Chromatogr. A* 1172 (2007) 113–120.
- [10] L. Sun, C.Z. Zhang, L.G. Chen, J. Liu, H.Y. Jin, H.Y. Xu, L. Ding, *Anal. Chim. Acta* 638 (2009) 162–168.
- [11] X.L. Zhao, Y.L. Shi, Y.Q. Cai, S.F. Mou, *Environ. Sci. Technol.* 42 (2008) 1201–1206.
- [12] X.L. Zhao, Y.L. Shi, T. Wang, Y.Q. Cai, G.B. Jiang, *J. Chromatogr. A* 1188 (2008) 140–147.
- [13] H.Y. Shen, Y. Zhu, X.E. Wen, Y.M. Zhuang, *Anal. Bioanal. Chem.* 387 (2007) 2227–2237.
- [14] I.J. Bruce, T. Sen, *Langmuir* 21 (2005) 7029–7035.
- [15] H.H. Hsiao, H.Y. Hsieh, C.C. Chou, S.Y. Lin, A.H.J. Wang, K.H. Khoo, *J. Proteome Res.* 6 (2007) 1313–1324.
- [16] Y. Jodra, F. Mijangos, *Environ. Sci. Technol.* 37 (2003) 4362–4367.
- [17] K.L. Chen, S.E. Mylon, M. Elimelech, *Environ. Sci. Technol.* 40 (2006) 1516–1523.
- [18] B. Fugetsu, S. Satoh, T. Shiba, T. Mizutani, Y.B. Lin, N. Terui, Y. Nodasaka, K. Sasa, K. Shimizu, *Environ. Sci. Technol.* 38 (2004) 6890–6896.
- [19] B. Fugetsu, S. Satoh, A. Iles, K. Tanaka, N. Nishi, F. Watari, *Analyst* 129 (2004) 565–566.
- [20] S.F. Lim, J.P. Chen, *Appl. Surf. Sci.* 253 (2007) 5772–5775.
- [21] S.F. Lim, Y.M. Zheng, S.W. Zou, J.P. Chen, *Environ. Sci. Technol.* 42 (2008) 2551–2556.
- [22] Z.F. Wang, H.S. Guo, Y.L. Yu, N.Y. He, *J. Magn. Magn. Mater.* 302 (2006) 397–404.
- [23] Z.Y. Ma, Y.P. Guan, H.Z. Liu, *J. Polym. Sci. Polym. Chem.* 43 (2005) 3433–3439.
- [24] N.Q. Li, H.K. Lee, *Anal. Chem.* 72 (2000) 5272–5279.
- [25] N.Q. Li, H.K. Lee, *J. Chromatogr. A* 921 (2001) 255–263.
- [26] W.E. Johnson, N.J. Fendinger, J.R. Plimmer, *Anal. Chem.* 63 (1991) 1510–1513.
- [27] B. Jiménez, J.C. Moltó, G. Font, *Chromatographia* 41 (1995) 318–324.
- [28] P. Bonifazi, E. Pierini, F. Bruner, *Chromatographia* 44 (1997) 595–600.
- [29] D.A. Hinckley, T.F. Bldleman, *Environ. Sci. Technol.* 23 (1989) 995–1000.