Preparation of polydopamine coated Fe₃O₄ nanoparticles and their application for enrichment of polycyclic aromatic hydrocarbons from environmental water samples

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ABSTRACT

Core/shell structured magnetic Fe₃O₄/polydopamine (Fe₃O₄/PDA) nanoparticles have been successfully synthesized and developed as a magnetic solid-phase extraction (SPE) adsorbent in dispersion mode for the determination of trace polycyclic aromatic hydrocarbons (PAHs) in environmental samples. The Fe₃O₄/PDA synthetic procedure is simple and involves no organic solvents. Only 20 mg of Fe₃O₄/PDA adsorbents are required to extract PAHs from 500 mL water samples. The adsorption attains equilibrium rapidly and analysts are eluted with acetonitrile readily. The extraction efficiency is not influenced by salt concentrations up to 300 mM and pH values over the range 4–11. Under optimized conditions, the detection limits of PAHs are in the range of 0.5–1.9 ng L⁻¹. The accuracy of the method is evaluated by the recoveries of PAHs from environmental samples. Good recoveries (76.4–107%) with low relative standard deviations from 1.0% to 9.7% are achieved. Comparison study shows that the recoveries of target PAHs are low when they are extracted using traditional SPE method even with the addition of methanol or tetrabutylammonium bromide surfactants in water samples, suggesting great application potential of magnetic SPE method to preconcentrate highly hydrophobic contaminants (such as PAHs) from large volume of water samples. This new SPE method provides several advantages, such as simplicity, low environmental impact, high extraction efficiency, high breakthrough volumes, convenient extraction procedure, and short analysis time.

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1. Introduction

Nowadays, magnetic solid-phase extraction (MSPE), a novel SPE method, has been developed based on the use of magnetic nanoparticles since its high extraction efficiency and rapid extraction kinetics [1–20]. The magnetic adsorbents are usually devised on the basis of Fe₃O₄ nanoparticles. Due to the highly hydrophilic property of Fe₃O₄, a layer of hydrophobic coat or adlayer such as hemimicelles/admicelles of ionic surfactant or alkyl carboxylates groups [2–6], phenyl or C₁₈ groups [7–13], carbon [14–16], or polymers [17–20], must be immobilized on the surface of Fe₃O₄ MNPs, which involves toxic reagents or high temperature, and multiple,

complicated procedures. With regard to MSPE method established with mixed hemimicelle modified magnetic nanoparticles, the extraction efficiency is strongly dependent on certain extraction condition and the adsorbed ionic surfactant is coeluted with targets, which interferes with determination of analytes. Therefore, new magnetic adsorbents with simple and green preparation process, low price and high adsorption efficiency should be developed for environmental analysis.

Commonly known as a neurotransmitter, dopamine is a small-molecule mimic of the adhesive proteins. Recently, Messersmith reported a simple but versatile surface modification approach in which self-polymerization of dopamine at weak alkaline pH produced an adherent polydopamine (PDA) coating on a wide variety of materials [21]. The advantage of PDA modification lies in its easy, convenience and substantial-independence [22]. A conjugate of dopamine and bisphosphonate can be anchored to Fe₃O₄ nanoparticles for collection of uranyl ion and easy recovery from solution by magnetic field [23]. Zhou et al. developed a facile approach for

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imprinting protein based on self-polymerization of dopamine in the presence of template protein on the Fe_3O_4 nanoparticles surface [24]. These studies indicate that dopamine has the potential to modify Fe_3O_4 nanoparticles directly and the formed nanomaterials can be used as adsorbents. The use of PDA as affinity material for organic pollutants has several significant advantages, including biocompatibility, dispersibility in water, multifunctional groups (amino and catechol groups), and providing π – π stacking interaction to targets.

Herein, we reported the preparation, characterization and application of Fe_3O_4 /PDA nanoparticles as SPE adsorbents. The aim of this study was to develop a novel SPE adsorbents preparation method and investigate the extraction performance of the synthesized adsorbents to targets from large volume of water samples. Polycyclic aromatic hydrocarbons (PAHs), well-known environmental pollutants with two or more fused aromatic rings, are selected as model compounds. Since there are abundant phenyls on the PDA coats, the Fe_3O_4 /PDA nanoparticles are expected to offer strong adsorption affinity to PAHs due to their π – π stacking interaction. Parameters affecting the extraction efficiency were investigated in detail, including amount of adsorbents, equilibrium time, salinity, solution pH, solution volume and desorption conditions. Coupling this novel SPE technique with high performance liquid chromatography (HPLC)–fluorescence detection (FLD), a highly sensitive SPE–HPLC–FLD analytical method for PAHs was established.

2. Experimental

2.1. Chemicals and materials

All chemicals used in the experiment were of analytical grade and used without further purification. 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). Dopamine and tetrabutylammonium bromide were supplied by J&K Chemical Ltd. (China). Fluoranthene (FluA), pyrene (Pyr), benz[a]anthracene (BaA), benzo[b]fluoranthene (BbF), benzo[a]pyrene (BaP), and benzo[g,h,i]perylene (BghiP) were obtained from AccuStandard (New Haven, USA). HPLC-grade acetonitrile and methanol were obtained from Fisher Scientific Corporation (Fair Lawn, NJ, USA). Ultrapure water was prepared using Milli-Q water purification system (Bedford, MA, USA).

2.2. Preparation of Fe_3O_4 and Fe_3O_4 /PDA magnetic nanoparticles

The magnetic Fe_3O_4 nanoparticles were prepared by the chemical coprecipitation method [2], 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 three times. Finally the products were dispersed into 110 mL deionized water to get 20 mg mL^{-1} suspension of Fe_3O_4 nanoparticles.

Fe_3O_4 nanoparticles (400 mg) were dispersed in 200 mL Tris buffer (10 mM , $\text{pH } 8.5$), then dopamine was added, and the mixture solution was mechanically stirred for 12 h at room temperature. After reaction, the Fe_3O_4 /PDA nanoparticles were isolated with a magnet and washed with deionized water. The final products were dispersed into 100 mL deionized water to get 4 mg mL^{-1} Fe_3O_4 /PDA suspension.

2.3. Characterization of adsorbents

The morphology and particle size of Fe_3O_4 /PDA were studied using a transmission electron microscope (TEM) of H-7500 (Hitachi, Japan) operating at 80 kV accelerated voltage. The specific surface areas of adsorbents were determined by the BET method with N_2 gas (ASAP2000V3.01A; Micromeritics, Norcross, GA). 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).

2.4. Magnetic SPE procedure

First, 20 mg of Fe_3O_4 /PDA adsorbents were dispersed into 500 mL filtered water samples containing trace level of target compounds. The mixture was stirred vigorously for 20 s so that the adsorbents can disperse uniformly in solution. Subsequently, an Nd–Fe–B strong magnet was deposited at the bottom of the beaker and the adsorbents were isolated from solution. After about 30 min , the solution became clear and the supernatant was decanted. Finally, the adsorbed target compounds were eluted from the adsorbents with 8 mL of acetonitrile. The eluants were concentrated to 0.2 – 0.3 mL with a stream of N_2 at 333 K and then diluted to 0.5 mL with acetonitrile. Twenty microlitres of this solution was injected into the HPLC system for analysis.

2.5. HPLC analysis

PAHs were separated and quantified using an HPLC system (Dionex, USA). The HPLC equipment included a Dionex P680 HPLC pump, a thermostated column compartment TCC-100, and a Dionex RF 2000 fluorescence detector. The separation was conducted on a Diamonsil C_{18} column ($250 \text{ mm} \times 4.6 \text{ mm}$; particle size, $5 \mu\text{m}$). Gradient separation was carried out using water–acetonitrile ($50:50$) and acetonitrile as A and B solvents, respectively. 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 increased 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 , $252/370 \text{ nm}$; 7 min , $280/460 \text{ nm}$; 8 min , $270/390 \text{ nm}$; 11 min , $260/432 \text{ nm}$; 13.5 min , $290/410 \text{ nm}$; 22 min , $252/370 \text{ nm}$.

2.6. Water samples

Four types of environmental water samples, namely tap water sample, river water sample, influent water and effluent water sample, were selected for investigation. Tap water sample was taken from our lab. River water sample was collected from Qinghe River. Influent water and effluent water samples were supplied by Qinghe River wastewater treatment plants. Before use, all samples were filtered through $0.45 \mu\text{m}$ membranes to remove suspended particles. To decrease the adsorption of PAHs on nylon membranes during filtration, tetrabutylammonium bromide (TBABr) surfactants with a concentration of 50 mg L^{-1} were spiked into water samples before filtration [6]. Then the filtered samples were stored in brown glasses at 4°C in the refrigerator.

3. Results and discussion

3.1. Characterization of adsorbents

The TEM image of Fe_3O_4 /PDA in Fig. 1a shows that an obvious PDA coat (about 5 – 8 nm -in-thickness) is immobilized on the

Fig. 1. TEM image of Fe₃O₄/PDA (a), VSM magnetization curves (b) and FTIR spectra (c) of Fe₃O₄ and Fe₃O₄/PDA.

surface of Fe₃O₄ nanoparticles, revealing the core/shell structure of Fe₃O₄/PDA. The specific surface area of Fe₃O₄ and Fe₃O₄/PDA are 111 and 84 m² g⁻¹, respectively. The decrease of surface areas may result from the increase of particle diameter due to the encapsulation shell of polydopamine layer and partly aggregation of particles during encapsulation process.

Sufficient magnetic properties are important for practical applications of magnetic materials in aqueous solution. In the VSM magnetization curves of Fe₃O₄ and Fe₃O₄/PDA nanoparticles, there is no hysteresis, and the remanence and coercivity is negligible, indicating the superparamagnetism of these nanomaterials (Fig. 1b). The maximal saturation magnetizations of Fe₃O₄ and Fe₃O₄/PDA nanoparticles are 61 and 45 emu g⁻¹, respectively. Thus, the Fe₃O₄/PDA adsorbents loaded with analytes are readily separated from solution with a magnet due to their superparamagnetism and large saturation magnetization.

FT-IR is employed to examine the surface composition of the synthesized Fe₃O₄ and Fe₃O₄/PDA nanoparticles. In the spectrum of bare Fe₃O₄ (Fig. 1c), the strong peak at 575 cm⁻¹ is related to the vibration of the Fe–O function group and the peaks at 1628 and 3441 cm⁻¹ are corresponding to the surface-adsorbed water and hydroxyl groups. New peaks at ~1250 cm⁻¹, ~1500 cm⁻¹ and ~1600 cm⁻¹ in the spectrum of PDA modified Fe₃O₄ MNPs derive from the aromatic rings in the PDA polymer. The peak at ~3400 cm⁻¹ of Fe₃O₄/PDA NPs is broader than that of Fe₃O₄ NPs, which results from the overlapping of hydroxyls, water adsorbed in PDA polymer and amines of PDA. The adsorption peaks at 2923 cm⁻¹, 2920 cm⁻¹ are ascribed to the bending vibration or stretching vibration of –CH₂ and –CH₃ species. A weak adsorbance at ~1710 cm⁻¹ can be indicative of esters formed by reaction of the hydroxyl groups of Fe₃O₄ with catechol hydroxyl groups of PDA [25]. These results suggest that PDA polymer is successfully

immobilized on the surface of Fe₃O₄ NPs via both physical and chemical adsorption.

3.2. Optimization of extraction conditions

3.2.1. Effect of Fe₃O₄/PDA amount

To achieve good extraction performance of Fe₃O₄/PDA adsorbents toward the targets, the amount of Fe₃O₄/PDA was investigated from 0 mg to 80 mg to enrich trace level of PAHs from 500 mL of water samples. As shown in Fig. 2a, the recoveries of these PAHs increased rapidly when the adsorbent amount enhanced from 0 mg to 5 mg, and then enhanced slightly as the adsorbent amount was in the range of 10–80 mg, indicating the remarkable enrichment ability of adsorbents to PAHs. In our previous study, we found that bare Fe₃O₄ nanoparticles exhibited limited extraction ability to PAHs, and the recoveries of PAHs were below 20% even when the amount of adsorbents was up to 100 mg [14]. We concluded that the excellent enrichment ability of Fe₃O₄/PDA to PAHs resulted from the PDA coat. In the following experiment 20 mg of Fe₃O₄/PDA was employed, which was fairly lower than the amount of commercial or previously reported nanomaterial SPE adsorbents used to enrich PAHs [5,6,13,14,17,18,26–28].

3.2.2. Desorption condition

Acetonitrile and methanol were studied as elutant to desorb PAHs from Fe₃O₄/PDA adsorbents. In order to obtain better recoveries, Fe₃O₄/PDA nanoparticle adsorbents with adsorbed PAHs were sonicated for 10 s in desorption solvents. The results showed that acetonitrile was superior to methanol for analyte desorption. The highest recoveries of six PAHs were observed as 8 mL acetonitrile was used as desorption solvents. However, if equal volume of methanol was applied as desorption solvents, the recoveries of

Fig. 2. Effect of amount (a), extraction time (b), ionic strength (c) and pH (d) on the extraction efficiency of PAHs pretreated with $\text{Fe}_3\text{O}_4/\text{PDA}$ adsorbents.

PAHs were below 70%. Thus, 8 mL acetonitrile was recommended for desorption.

3.2.3. Magnetic separation and equilibrium time

Since the superparamagnetism property and large saturation magnetization of $\text{Fe}_3\text{O}_4/\text{PDA}$, the adsorbents could completely separate from 500 mL aqueous solution within 5–10 min as the vessel was placed on a powerful magnet. In the magnetic SPE method, sufficient contact time is necessary for the analytes to attain adsorption equilibrium on adsorbent. We investigated the effect of extraction time on PAHs recoveries by varying the standing time in the range of 0–120 min before phase separation. As a result (Fig. 2b), most of the targets were captured by $\text{Fe}_3\text{O}_4/\text{PDA}$ in the moment $\text{Fe}_3\text{O}_4/\text{PDA}$ was dispersed in water samples. After contact for 5 min, the maximum recoveries for all targets were obtained, indicating that the adsorption equilibrium was reached within 5 min. The rapid extraction dynamics of PAHs on $\text{Fe}_3\text{O}_4/\text{PDA}$ might be attributed to the short diffusion route of nanosized adsorbents.

3.2.4. Effect of ionic strength and pH

The effect of ionic strength on PAHs recoveries was examined by adjusting the salinity of solution with NaCl in the range of 0–300 mM. The results indicated that the extraction efficiency of PAHs was independent of the ionic strength (Fig. 2c). We investigated the effect of solution pH on the recoveries of PAHs as the solution pH was ranged in 4–11. Fig. 2d shows that the recoveries of targets almost remained constant in the whole pH range. This result suggested the perfect stability of $\text{Fe}_3\text{O}_4/\text{PDA}$ adsorbents in both acid and alkaline solution.

3.2.5. Effect of solution volume

In environmental water samples, the concentrations of targets are usually much lower than the detection limit of analytical instruments. It is generally necessary to enrich target analytes from large

volume of water samples to get a high preconcentration factor. Fortunately, the magnetic SPE technique avoids the time-consuming step of column loading or pressure filtration and exhibits great potential in pretreatment of large volumes of water samples. To investigate the effect of sample volume on PAHs recoveries, the volume of water sample was changed from 200 mL to 1000 mL with the spiked concentration of each analyte fixed at 10 ng. The recoveries of all the analytes remained unchanged as sample volume increased from 200 to 1000 mL. Since the eluate was concentrated to 0.5 mL, the preconcentration factor of 1600–2000 for six PAHs could be achieved when they were extracted from 1000 mL of water samples with $\text{Fe}_3\text{O}_4/\text{PDA}$ adsorbents. The high extraction ability of $\text{Fe}_3\text{O}_4/\text{PDA}$ adsorbents to PAHs was caused by their large surface areas and strong adsorption ability of PDA coat.

3.3. Analytical performance

Under the optimal conditions, calibration curves were established for analytes in the range of 5.0–200 ng L^{-1} . The calibration runs of each analyte were 14 times ($n = 14$). Quantitative parameters including linear range, correlation coefficient, relative standard deviation (R.S.D.), and limit of detection are listed in Table 1. It can be seen that the present method has wide linear range and good method precision. All the PAHs exhibited good linearities with the correlation coefficients (R) > 0.990 in the studied range. The detection limits of all analytes were calculated from Eqs. (1)–(3) based on type I and II errors [29,30]

$$x_d(p, q) = \frac{w_0 \Delta(p, q) \sigma}{\beta} \quad (1)$$

$$w_0 \equiv \frac{1}{r} + \frac{1}{n} + \frac{\bar{x}}{Q_{xx}} \quad (2)$$

Table 1
Analytical parameters of the proposed method.

Analytes	Linearity range (ng L ⁻¹)	Calibration equations	Correlation coefficient (R)	R.S.D. (n = 14)	Detection limit ^a (ng L ⁻¹)
FluA	5–200	$y = 0.9521x + 5.4378$	0.996	2.55	1.46
Pyr	5–200	$y = 0.967x + 4.659$	0.995	3.42	1.92
BaA	5–200	$y = 0.9452x + 2.2673$	0.990	2.17	1.22
BbF	5–200	$y = 0.9398x + 0.9901$	0.999	8.83	0.510
BaP	5–200	$y = 0.9725x + 0.4613$	0.996	3.12	1.74
BghiP	5–200	$y = 0.9315x + 1.6074$	0.993	9.11	0.530

^a Detection limits are calculated based on type I error and type II error, $r = 1$, $p = 0.01$, $q = 0.01$.

Table 2
Results of determination and recoveries of real water samples spikes with six analytes.

Sample	Analytes	Concentration detected in water sample (ng L ⁻¹)	Detected (ng L ⁻¹) ^a	Recovery (%)	RSD (% n = 3)
Tap water	FluA	nd ^b	18.0	90.0	4.13
	Pyr	nd	16.0	80.0	6.92
	BaA	nd	16.3	81.5	4.25
	BbF	nd	19.3	96.5	2.37
	BaP	nd	19.4	97.0	3.43
	BghiP	nd	20.5	103	2.72
River water	FluA	nd	17.7	88.5	9.71
	Pyr	nd	19.8	99.0	1.94
	BaA	nd	18.1	90.5	7.02
	BbF	nd	19.5	97.5	5.01
	BaP	nd	20.0	100	6.50
	BghiP	nd	19.7	98.5	4.93
Influent water	FluA	4.73	16.7	83.5	1.87
	Pyr	nd	17.1	85.5	1.49
	BaA	nd	17.1	85.5	1.06
	BbF	nd	21.5	108	3.80
	BaP	nd	17.5	87.5	3.33
	BghiP	nd	18.7	93.5	2.05
Effluent water	FluA	1.75	19.3	96.5	4.03
	Pyr	nd	20.4	102	3.82
	BaA	nd	17.8	89.0	7.93
	BbF	0.82	18.8	94.0	5.20
	BaP	nd	19.2	101	2.47
	BghiP	nd	20.8	104	8.15

^a Mean of three determination.

^b Not detected.

$$Q_{xx} = \sum_{j=1}^m n_j (x_j - \bar{x})^2 \quad (3)$$

where β represents the slope of the straight-line calibration, σ is the measurement error variance estimated from several replicate observations ($n = 14$) at concentration of 10 ng L⁻¹. With the fixed p (false positive error rate, 0.01), q (false negative error rate, 0.01), $r (=1)$ and known model parameters, the detection limits of all analytes were ranged in 0.510–1.92 ng L⁻¹.

3.4. Analysis of environmental water samples

To demonstrate the applicability and reliability of developed method, it was applied to the analysis of real water samples

Table 3
Recoveries of PAHs extracted with commercial C₁₈ SPE columns.

Analytes	Recoveries (R.S.D.)	
	Additives	
	TBABr (50 mg L ⁻¹)	10% Methanol
FluA	83.6 (10.3%)	104 (7.94%)
Pyr	98.6 (11.2%)	101 (8.98%)
BaA	98.1 (4.86%)	98 (12.3%)
BbF	40.1 (12.9%)	12.2 (9.90%)
BaP	29.9 (3.83%)	21.0 (11.1%)
BghiP	34.1 (3.68%)	12.5 (11.4%)

including tap water, river water, influent water and effluent water. Table 2 shows the recoveries and concentrations of the target compounds in real water samples, expressed as mean value ($n = 3$), and the relative standard deviation of recoveries ranged from 1.06% to 9.71%. FluA was detected in influent water and effluent water and the concentrations were 4.73 and 1.75 ng L⁻¹, respectively. In effluent water sample, BbF with concentration of 0.820 ng L⁻¹ was found. The recoveries of spiked solution (in the level of 20 ng L⁻¹)

Fig. 3. Solid-phase extraction/HPLC–FLD chromatograms of PAHs in real water samples. (a) Qinghe River water sample, (b) Qinghe River water sample was spiked at 20 ng L⁻¹ for each of PAHs, peaks: 1, FluA; 2, Pyr; 3, BaA; 4, BbF; 5, BaP; 6, BghiP.

Table 4

Comparison of analytical performances of the proposed method with those in literature.

Sorbent	Detection technique	Sorbent amount	Loading volume (mL)	Recoveries (%)	Detection limit (ng L ⁻¹)
Fe ₃ O ₄ /PDA (this work)	HPLC–FLD	20 mg	500	76–103	0.510–1.92
Supelclean ENVI-18 [26]	HPLC–FLD	1.0 g	1000	63–99	0.52–1.2
Carbon coated Fe ₃ O ₄ MNPs [14]	HPLC–FLD	50 mg	1000	76–110	0.2–0.6
Supelco ENVI-18 SPE cartridges [27]	HPLC–FLD	1.0 g	800	50–111	0.8–1.6
Phosphatidylcholine bilayer coated Fe ₃ O ₄ [18]	HPLC–FLD	100 mg	500	89–115	0.2–0.6
100-PDMS fiber [28]	HPLC–FLD	–	250	–	3.0–37
C ₁₄ carboxylic Fe ₃ O ₄ MNPs [6]	HPLC–FLD	200 mg	350	85–94	0.1–0.25
C ₁₆ mimBr–Fe ₃ O ₄ MNPs [5]	HPLC–FLD	80 mg	300	76–105	0.33–8.3
Octadecylphosphonic Fe ₃ O ₄ MNPs [17]	GC–MS	50 mg	10	87.3–119	14.1–53.0
Fe ₃ O ₄ –C ₁₈ MNPs [13]	GC–MS	50 mg	40	70–91	3900–7600

for all the samples were satisfactory and ranged in 80.0–108%. Fig. 3 shows chromatograms of PAHs in river water sample and its spiked solution.

In a comparison study, the extraction performance of commercial SPE cartridges (Agela CleanertTMC18) to the target PAHs from 500 mL of simulated water samples (the concentration of each PAH is 20 ng L⁻¹) were also investigated. After loading of water samples, the cartridges were dried and 10 mL of dichloromethane was used to elute PAHs from the cartridge. The eluate was concentrated to 1 mL under 45 °C with a nitrogen stream before analysis by GC–MS. The results showed that the target PAHs was hardly recovered when they were extracted with C₁₈ cartridges without the addition of additives. To decrease the adsorption of PAHs to containers and collecting tubes, methanol (10%) or TBABr surfactants (50 mg L⁻¹) were added into the water samples. With the addition of methanol, the recoveries of FluA, Pyr and BaA enhanced to about 100%, but the recoveries of BbF, BaP and BghiP were lower than 20%. In the presence of TBABr, the recoveries of BbF, BaP and BghiP increased but still were lower than 50%, indicating the strong adsorption ability of PAHs to containers (Table 3). As a result, none of PAHs were detected in natural waters using the traditional SPE method. This study suggests that MSPE method based on magnetic nanoparticles has great application potential to pre-concentrate highly hydrophobic contaminants (such as PAHs) from large volume of water samples.

The extraction efficiencies of Fe₃O₄/PDA adsorbents to target PAHs were also compared with commercial RP-C₁₈ [26,27], 100-PDMS solid-phase microextraction fiber [28], various functionalized Fe₃O₄ MNPs including C₁₄ carboxylic MNPs [6], ionic liquid-coated MNPs [5], carbon coated MNPs [14], octadecylphosphonic MNPs [17,18] and Fe₃O₄–C₁₈ MNPs [13] reported in literature. The adsorbent amount, loading volume, detection limits and recoveries obtained with different materials are listed in Table 4. Generally, due to their high adsorption ability and large specific surface areas, less amount of nanomaterials are required to efficiently preconcentrate trace targets from larger volume of water samples with satisfactory recoveries than the micro-sized adsorbents. Since even 20 mg of Fe₃O₄/PDA adsorbents can enrich low level of PAHs from 500 mL of water samples, we conclude that Fe₃O₄/PDA adsorbents possessed stronger adsorption ability to PAHs than other nanosized adsorbents. The detection limits obtained in this study was comparable with those in other studies achieved using the same HPLC–FLD detection technique. The abundant phenyls in the thick PDA coat can provide potent π – π stacking interaction and hydrophobic interaction to PAHs, which is the main reason for the high preconcentration performance of Fe₃O₄/PDA adsorbents to PAHs. Furthermore, the enrichment procedure was simplified greatly by using magnetic separation technology and the time consuming in conventional SPE procedure was shortened. Therefore, Fe₃O₄/PDA magnetic adsorbent is suitable for the pre-concentration of trace PAHs from complex environmental water samples with large volume and the proposed method is reliable.

4. Conclusions

In this study we proposed a simple method to prepare a novel magnetic material, polydopamine modified Fe₃O₄ magnetic nanoparticles. The polydopamine was directly grafted onto Fe₃O₄ using one step self-polymerization reaction. The obtained Fe₃O₄/PDA adsorbents are environmental friendly, and no poisonous substances are introduced into water samples during SPE. The adsorbents show a large surface area and strong superparamagnetism. Polydopamine layer provides a high extraction efficiency of the adsorbent to PAHs. Equilibrium time, solution pH and high ionic strength have little influence in the extraction, which avoid the adjustment of samples. Satisfactory results can be achieved by using small amount of nanoparticles adsorbents. Combined with HPLC–FLD, a rapid, convenient and matrix-independent method for the determination of PAHs in water samples was established successfully.

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