

Extraction of Phthalate Esters in Environmental Water Samples Using Layered-Carbon Magnetic Hybrid Material as Adsorbent Followed by Their Determination with HPLC

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Received June 13, 2012, Accepted July 13, 2012

In this paper, a layered-carbon-Fe₃O₄ (LC-Fe₃O₄) hybrid material was synthesized through a facile one-pot solvothermal method and used as the adsorbent for the preconcentration of some phthalate esters (dimethyl phthalate, diethyl phthalate, diallyl phthalate, diisobutyl phthalate and benzyl butyl phthalate) in water samples. The effects of the adsorbent dosage, extraction time, the solution pH and salinity on the adsorption of the phthalate esters (PAEs) were investigated. The magnetic nanocomposite adsorbent could remove and enrich the PAEs from water samples efficiently. After the adsorption, the analytes were desorbed and then determined by high performance liquid chromatography-ultraviolet detection. Under the optimum conditions, the enrichment factors of the method for the analytes were in the range from 161 to 180. A linear response with peak area as the quantification signal was observed in the concentration range from 0.5 to 100 ng mL⁻¹. The limits of detection (*S/N* = 3) of the method were between 0.08 and 0.1 ng mL⁻¹. The method was suitable for the determination of trace phthalate esters in environmental water samples.

Key Words : Adsorption, Determination, High performance liquid chromatography, Magnetic layered-carbon nanocomposite, Phthalate esters

Introduction

Phthalate esters (PAEs), as a group of industrial chemicals, are widely used in consumer products as solvent, additives and plasticizers. They can make the plastic flexible through weak secondary molecular interactions with polymer chains to improve flexibility, workability and durability of the polymeric materials.¹ Each year, about 2 million tons of PAEs are produced all over the world. Since they are only physically bound to the polymers, they can be released easily from products to migrate into environment and consequently to pollute water, soil, air and food products.² Nowadays, due to their massive use and persistent character, PAEs are considered as ubiquitous environmental pollutants. The United States Environmental Protection Agency (US EPA) has listed PAEs as the priority contaminants.³ The intensive use of PAEs and their pollutions have become a serious problem worldwide and also a major public health concern. Therefore, the removal of PAEs from wastewater and the determination of trace levels of PAEs in environmental samples are especially desirable.

Trace analysis of the analytes in environmental samples generally requires a sample pretreatment step to isolate and enrich the target analytes before an instrumental analysis. Up to now, various sample pretreatment techniques have been developed to extract PAEs from different samples, such as liquid-liquid extraction (LLE),^{4,5} solid-phase extraction (SPE),⁶⁻⁹ liquid-phase microextraction (LPME),^{10,11} solid-phase microextraction (SPME),¹²⁻¹⁵ single-drop microextr-

action (SDME),¹⁶ dispersive liquid-liquid microextraction (DLLME),¹⁷⁻²⁰ hollow fiber-based liquid-phase microextraction (HF-LPME),²¹ accelerated solvent extraction (ASE)²² and liquid-phase microextraction based on the solidification of a floating organic microdrop (LPME-SFO).²³ Among them, LLE and SPE are the most commonly used techniques for environmental analysis. SPE procedures are considered superior to LLE for their simplicity and less consumption of organic solvents. However, SPE is still tedious, time-consuming and relatively expensive. Recently, a lot of research works have been oriented towards the development of more efficient, economical and miniaturized sample preparation methods. As a result, a new mode for SPE, based on the use of magnetic or magnetically modified adsorbents called magnetic solid-phase extraction (MSPE) has been developed.²⁴ Compared with traditional adsorbents, a distinct advantage of MSPE is that the magnetic adsorbents can be readily isolated from sample solutions by the application of an external magnetic field without the need of column passing operations and additional centrifugation or filtration procedures. In recent years, the study on nanoscale magnetic materials as the adsorbents has been made extensively.²⁵⁻³¹ Nanosized magnetic materials are superparamagnetic; they can be attracted by a magnet but do not retain magnetism after the magnetic field is removed. So, the magnetic nanoparticles tagged with organic contaminants can be separated from the matrix by applying a magnetic field, and they do not agglomerate after the removal of the magnetic field. To date, much attention has been paid to the preparation of

different kinds of magnetic nanoparticles. Recently, alginate-polymer-caged C_{18} -functionalized magnetic titanate nanotubes,³² barium alginate caged Fe_3O_4 - C_{18} magnetic nanoparticles³³ and polypyrrole-coated magnetic particles³⁴ have been prepared for the extraction of PAEs in water samples.

Carbon nanoparticles, due to their extremely large surface area, excellent adsorption capacity, unique mechanical, thermal and optical properties, have attracted tremendous attention and found many valuable applications in adsorption, catalysis, electronics, nanomaterials and nanotechnology. Carbon nanoparticle materials have been successfully used as adsorbent in SPE and SPME for trapping or separation of some organic compounds.³⁵ As a novel nanomaterial, single and multi-layered-carbon nano-materials have sparked researcher's remarkable interest in recent years.³⁶⁻³⁸ The introduction of magnetic properties into layered-carbon will combine the high adsorption capacity of the layered-carbon and the separation convenience of the magnetic materials.

In the present work, layered-carbon- Fe_3O_4 (LC- Fe_3O_4) hybrid material was synthesized through a facile one-pot solvothermal method and the potential applications of LC- Fe_3O_4 for the removal and enrichment of some PAEs from water samples were explored. Five PAEs including dimethyl phthalate (DMP), diethyl phthalate (DEP), diallyl phthalate (DAP), diisobutyl phthalate (DIBP) and benzyl butyl phthalate (BBP) were selected as model compounds. After the adsorption, the analytes were desorbed and then analyzed by high performance liquid chromatography (HPLC) with ultraviolet (UV) detection.

Experimental

Reagents and Materials. Graphite powder (50 meshes) was purchased from Boaxin Chemical Reagents Company (Baoding, China). Standards of the PAEs (DMP, DEP, DAP, DIBP and BBP) were purchased from Aladdin-Reagent (Shanghai, China). Ammonium ferrous sulfate and ammonium ferric sulfate were obtained from Chengxin Chemical Reagents Company (Baoding, China). Acetonitrile, acetone, hydrochloric acid (HCl), sodium hydroxide (NaOH), and all other reagents were purchased from Beijing Chemical Reagents Company (Beijing, China). The water used throughout the work was double-distilled on a SZ-93 automatic double-distiller purchased from Shanghai Yarong Biochemistry Instrumental Factory (Shanghai, China).

A mixture stock solution containing each of DMP, DEP, DAP, DIBP and BBP at $50.0 \mu\text{g mL}^{-1}$ was prepared in methanol. A series of standard solutions were prepared by mixing an appropriate amount of the stock solution with double-distilled water in a 10 mL volumetric flask. All the standard solutions were stored at 4°C and protected from light.

River water was collected from Yimu River (Baoding, China); reservoir water was collected from Wangkuai reservoir (Baoding, China); sea water was collected from Rushan (Shandong, China).

Apparatus. HPLC was carried out on a LC-20AT liquid chromatography (Shimadzu, Japan) with two LC-20AT VP

pumps and a SPD-20A UV/vis detector. A CenturySil C_{18} -EPS column ($250 \text{ mm} \times 4.6 \text{ mm I.D.}$, $5.0 \mu\text{m}$) from Dalian Johnsson Separation Science Technology Corporation (Dalian, China) was used for separations. The mobile phase was a mixture of acetonitrile-water (65:35 v/v) at a flow rate of 1.0 mL min^{-1} . The UV monitoring wavelength for all the analytes was set at 225 nm.

X-ray diffraction (XRD) measurements were carried out using a Rigaku D/max-rB diffractometer (Rigaku, Tokyo, Japan) with $\text{Cu K}\alpha$ radiation (40 kV, 60 mA).

The size and morphology of the magnetic nanoparticles were observed by transmission electron microscopy (TEM) using a JEOL model JEM-2011(HR) at 200 kV. The sample for TEM analysis was obtained by dipping a holey grid to nanoparticles-dispersed ethanol solution and evaporated in air at room temperature.

Synthesis of LC- Fe_3O_4 . Oxide-form of layered carbon (OLC) was prepared from natural graphite powders by a modified Ma's method.³⁶ Firstly, 180 mL H_2SO_4 (95%) and 20 mL H_3PO_4 (85%) were added into a 500 mL flask, and then 3.0 g graphite powder was added under vigorous stirring. After the graphite powder was well dispersed, 18 g KMnO_4 was gradually added under stirring. The reaction was then heated to 50°C and stirred for 12 h. Secondly, the reaction mixture was poured onto about 400 mL ice. Then, 30 mL of 30% H_2O_2 was added to the mixture. Finally, the mixture was filtered and washed first with 5% HCl aqueous solution to remove metal ions and then with water until the pH became 7, then OLC was obtained.

The synthesis of the LC- Fe_3O_4 hybrid material was carried out in a solvothermal system using FeCl_3 as iron source and ethylene glycol as the reducing agent. OLC (400 mg) was ultrasonicated in 60 mL ethylene glycol for 1 h to produce a clear solution. Then, 0.65 g FeCl_3 was added into the solution and ultrasonicated for 10 min. After that, 2.6 g NaAc was added with vigorous stirring for 20 min. The mixture was sealed in a Teflon-lined stainless steel autoclave and maintained at 200°C for 8 h, and then cooled to room temperature. The black product (LC- Fe_3O_4) was rinsed with ethanol for several times, and dried in vacuum.

MSPE Procedure. The MSPE procedures for the adsorption of the five PAEs from environmental water samples are as follows. Firstly, 36 mg LC- Fe_3O_4 was added into 300 mL of water sample. To completely trap the analytes, the mixture was shaken on a slow-moving platform shaker for 10 min. Secondly, a magnet was deposited at the bottom of the beaker and the LC- Fe_3O_4 was isolated from the solution. A few minutes later, the solution became limpid and the supernatant was decanted. Then the residual solution and LC- Fe_3O_4 was totally transferred to a 10 mL centrifuge tube. The LC- Fe_3O_4 was aggregated again by positioning a magnet to the outside of the tube wall so that the residual solution could be completely removed by pipette. Finally, the adsorbed analytes were desorbed from the isolated particles with 0.5 mL acetone by vortex for 10 s. After positioning a magnet to the outside of the centrifuge tube, the supernatant solution was collected using a micropipette. The same

desorption procedures were repeated another two times. The desorption solutions were combined together and 20.0 μL was injected into the HPLC system for analysis. Peak area was used as the quantification signal.

Results and Discussion

Characterization of the Magnetic Layered-Carbon Nanoparticles. The typical TEM images of the LC and LC-Fe₃O₄ are shown in Figure 1(a) and 1(b), respectively. As can be seen from Figure 1(a), LC consisted of randomly aggregated and crumpled sheets to form a disordered solid. It is clear that these LC are basically transparent and no large graphitic crystallites are observed. Figure 1(b) shows that iron oxide nanoparticles were successfully coated on the surface of the LC to form a LC-Fe₃O₄ nanocomposite and the size of Fe₃O₄ particles ranges from 20 to 50 nm. The results indicated that the combination between Fe₃O₄ nanoparticles and LC was almost perfect in the solvothermal system.

Figure 2 shows the XRD patterns of LC-Fe₃O₄. A broad peak at $2\theta = 26^\circ$ was observed, which corresponds to the (002) reflection of layered-carbon. Except for the diffraction peak at 26° , all the significant diffraction peaks of the LC-Fe₃O₄ sample matched well with data from the JCPDS card (19-0629) for Fe₃O₄ (the diffraction angles at 2θ : 30.2° , 35.6° , 43.3° , 53.7° , 57.3° and 62.8° can be assigned to (220), (311), (400), (422), (511) and (440) of the crystal planes of Fe₃O₄).

Optimization of Adsorption Conditions. In order to

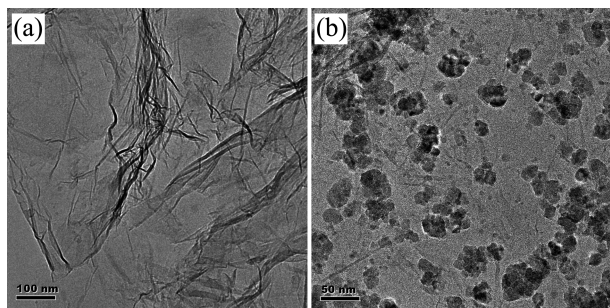


Figure 1. TEM image of LC (a) and LC-Fe₃O₄ composite (b).

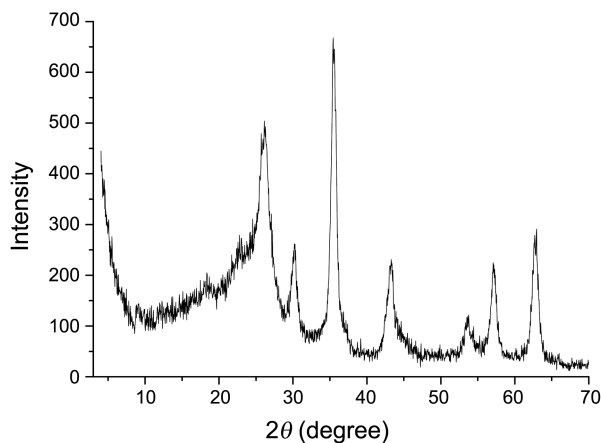


Figure 2. X-ray diffraction pattern of the LC-Fe₃O₄.

select the optimum MSPE conditions for the extraction of the PAEs, 300.0 mL double-distilled water spiked with 10.0 ng mL⁻¹ each of the five PAEs was used to study the extraction performance of the MSPE under different experimental conditions. The recovery was measured as the ratio between the amount of the analytes in the final desorption solution and their corresponding initial amount in the spiked aqueous sample. All the experiments were performed in triplicate and the mean results obtained were used for the optimization of extraction condition.

Effect of LC-Fe₃O₄ Dosage: In order to choose the optimum dosage of the adsorbent (LC-Fe₃O₄) for the adsorption of the PAEs, the concentrations of the LC-Fe₃O₄ were investigated in the range from 0.03 to 0.15 mg mL⁻¹. Figure 3 shows that the adsorption of DAP, DIBP and BBP could reach the maximum plateau when the concentration of LC-Fe₃O₄ was increased to 0.09 mg mL⁻¹ while the maximum adsorption efficiencies of DMP and DEP were achieved when the concentration of LC-Fe₃O₄ was increased to 0.12 mg mL⁻¹. Therefore, 0.12 mg mL⁻¹ LC-Fe₃O₄ was used in the following experiments. Compared with common adsorbents, LC-Fe₃O₄ nanoparticle has a higher surface area and therefore, only a small amount of the nanoparticle sorbent was required to achieve a satisfactory result.

Extracting Time: In MSPE process, the extraction time is one of the prime factors that influence the extraction efficiency. The effect of the extraction time on the extraction efficiency of the PAEs was investigated. As shown in Figure 4, when the extraction time was increased to 10 min, the extraction recoveries for all the analytes reached their maxima, indicating that the extraction equilibrium could be achieved in a short time. Therefore, the extraction time of 10 min was selected.

Influence of Sample Solution pH and Salinity: In this study, the effect of sample solution pH was investigated in the range between 2.0 and 12.0. The experimental results showed that the adsorption efficiency was almost not changed when the pH of the sample solution was changed. The reason for this could be that the PAEs exist as neutral mole-

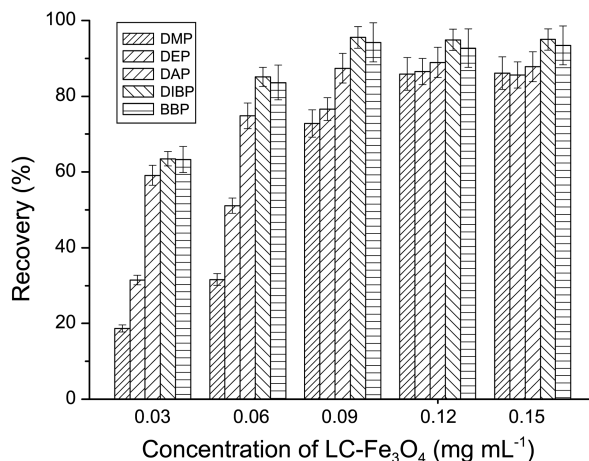


Figure 3. Effect of LC-Fe₃O₄ dosage on the adsorption efficiency for the PAEs.

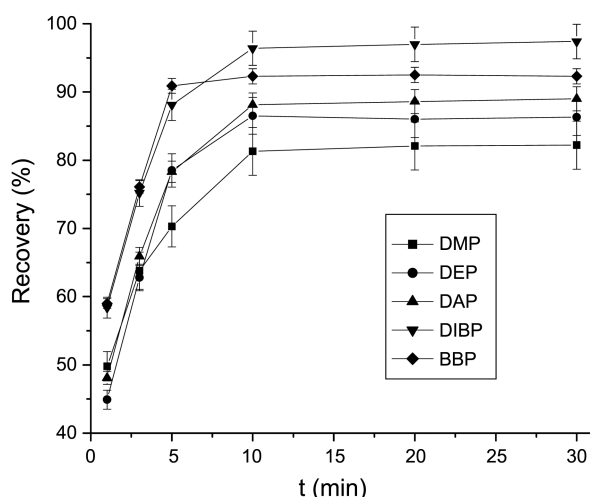


Figure 4. Effect of adsorption time on the adsorption efficiency for the PAEs by LC-Fe₃O₄ nanocomposite.

cules under ordinary conditions and are likely not to be influenced by the change of the sample solution pH. Considering that the pH of the studied water samples was in the neutral range, there is no need to adjust the sample solution pH. However, because the iron oxide nanoparticles on carbon materials would be partly dissolved when the solution pH is 2, it is recommended that the pH of the sample solution be adjusted to about 7 when the sample solution pH is too low.

In most cases, the addition of salt can decrease the solubility of organic analytes (salting-out effect) and increase the distribution constant. However, it can also increase the viscosity of the solution, which will reduce the adsorption capability and the diffusion coefficient. In this study, the effect of sample salinity on the adsorption efficiency of the analytes was investigated by changing the NaCl concentration in the solution to 1.0%, 2.0%, 5.0%, 10.0% and 15.0% (w/v), respectively. The results showed that the addition of NaCl had a negligible effect on the adsorption efficiency of the analytes within the concentration range investigated. Therefore, no addition of salt to the sample solution was selected.

Desorption Conditions: The analytes adsorbed on the LC-Fe₃O₄ particles should be desorbed completely for their further sensitive HPLC-UV analysis. In this work, acetonitrile, methanol and acetone were tried as the desorption solvent for the desorption of the analytes from the magnetic adsorbents. The results showed that the desorption power of acetone was much stronger than either methanol or acetonitrile. Thus, acetone was selected as the desorption solvent. The influence of the acetone volume on the desorption efficiency of the analytes was also investigated. It was found that the quantitative desorption of the analytes were achieved with 1.5 mL (0.5 mL each time and three times) of acetone.

Analytical Performance. To investigate the performance of the method for the determination of the PAEs in water samples, several parameters including linear range (LR), correlation coefficients (*r*) and limits of detection (LODs) were evaluated under the above-optimized conditions and

Table 1. Analytical performance data for the PAEs by the MSPE technique

PAEs	LR (ng mL ⁻¹)	<i>r</i>	RSD (%) (<i>n</i> = 6)	<i>EF</i>	LOD (ng mL ⁻¹)
DMP	0.5-100.0	0.9977	4.3	161	0.08
DEP	0.5-100.0	0.9987	3.8	170	0.1
DAP	0.5-100.0	0.9995	2.6	169	0.1
DIBP	0.5-100.0	0.9993	3.1	180	0.08
BBP	0.5-100.0	0.9991	3.2	177	0.08

LR: linear range. *EF*: enrichment factors.

the results are summarized in Table 1. For the establishment of the calibration curve, a series of standard solutions containing each of the PAEs at seven concentration levels of 0.5, 1.0, 5.0, 10.0, 20.0, 50.0 and 100.0 ng mL⁻¹ were prepared. A linear response for the peak area was observed in the concentration range of 0.5-100.0 ng mL⁻¹ of the PAEs with the *r* ranging from 0.9977 to 0.9995. The LODs (*S/N* = 3) ranged between 0.08 and 0.1 ng mL⁻¹ for the PAEs. The enrichment factors (*EF*), defined as the ratio between the analyte concentration in 1.5 mL acetone and the initial analyte concentration in the aqueous samples, were in the range between 161 and 180. To evaluate the precision of the method, the repeatability study was carried out by performing six parallel experiments at the concentration of 20.0 ng mL⁻¹ each of the PAEs. The resultant repeatabilities expressed as the relative standard deviations (RSDs) varied from 2.6% to 4.3%. The above results suggest that the present method has a high sensitivity, wide linear range and good precision.

Analysis of Environmental Water Samples. In order to test the applicability of the developed method, the method was applied to analyze the PAEs in different environmental water samples, including reservoir, river and sea water samples. The results are shown in Table 2. No residues of the PAEs were detected in either sea or reservoir water samples and only a low concentration of DAP (0.52 ng mL⁻¹) and DIBP (0.86 ng mL⁻¹) was found in river water sample. To test the accuracy of the method, the recoveries of the method

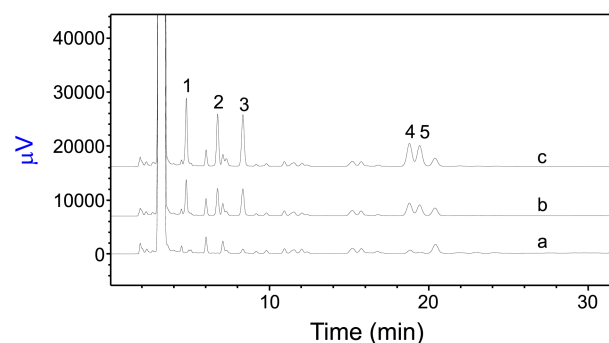


Figure 5. The typical chromatograms of blank river water sample (a) and the blank sample spiked with PAEs at each concentration of 5.0 ng mL⁻¹ (b) and 10.0 ng mL⁻¹ (c). The UV detection wavelength: 225 nm. Peak identification: (1) DMP, (2) DEP, (3) DAP, (4) DIBP, and (5) BBP.

Table 2. Recoveries obtained in the determination of the PAEs in spiked water samples

PAEs	Spiked (ng mL ⁻¹)	Sea water (<i>n</i> = 5)			River water (<i>n</i> = 5)			Reservoir water (<i>n</i> = 5)		
		Found (ng mL ⁻¹)	R ^b (%)	RSD (%)	Found (ng mL ⁻¹)	R ^b (%)	RSD (%)	Found (ng mL ⁻¹)	R ^b (%)	RSD (%)
DMP	0.0	nd ^a			nd ^a			nd ^a		
	5.0	4.43	88.6	3.1	4.40	88.0	3.7	4.51	90.2	2.9
	10.0	9.12	91.2	2.8	9.35	93.5	2.9	8.84	88.4	3.2
DEP	0.0	nd ^a			nd ^a			nd ^a		
	5.0	4.45	89.0	3.2	4.58	91.6	4.2	4.61	92.2	2.2
	10.0	9.83	98.3	3.1	10.05	100.5	2.4	9.73	97.3	4.4
DAP	0.0	nd ^a			0.52			nd ^a		
	5.0	4.63	92.6	4.3	5.31	95.8	4.1	4.41	88.2	3.4
	10.0	10.47	104.7	3.6	10.27	97.5	3.4	9.02	90.2	4.1
DIBP	0.0	nd ^a			0.86			nd ^a		
	5.0	4.68	93.6	3.3	5.42	91.2	2.9	4.78	95.6	4.6
	10.0	9.98	99.8	4.2	10.94	100.8	4.3	10.13	101.3	4.5
BBP	0.0	nd ^a			nd ^a			nd ^a		
	5.0	4.57	91.4	3.7	5.17	103.4	3.6	4.58	91.6	4.8
	10.0	8.78	87.8	4.0	9.25	92.5	4.1	8.85	88.5	2.7

^and: not detected. ^bR: recovery of the method.

were investigated by determining the PAEs in spiked water samples at two concentration levels (5.0 and 10.0 ng mL⁻¹). As a result, the recoveries for the PAEs fell in the range from 88.0% to 104.7%, which showed that the method was suitable for the analysis of the PAEs in real water samples. The typical chromatograms of the PAEs for the river water samples are shown in Figure 5.

Comparison with Other Extraction Methods. The performance of the developed MSPE method was compared with other reported sample preparation methods such as SPE,^{6,7,9} SPME,^{11,12} LPME,^{10,21,23} DLLME^{17,19,20} and

MSPE^{32-34,39,40} from the viewpoint of LOD, RSD, linearity and extraction time. The comparison results are shown in Table 3. In comparison with DLLME and IL-DLLME, although a relatively long extraction time was required for the current method, no toxic extraction solvents were used in MSPE. Compared with the other methods, less time was needed in the magnetic extracting process.

Magnetic adsorbents can make separation process easier and faster without the need of additional centrifugation or filtration procedures and also can avoid the time-consuming column passing operations encountered in SPE. Therefore, it

Table 3. Comparison of presented method with other microextraction techniques

Methods	Sample	Linearity (ng mL ⁻¹)	LOD (ng mL ⁻¹)	Extraction time (min)	RSD (%)	References
SPE-HPLC-UV	water	2.0-100	0.18-0.86	-	-	6
SPE-GC-MS	soybean milk	500-1000	13-22	-	1.82-10.11	7
SPE-HPLC-UV	water	0.6-50	0.12-0.17	-	4.1-5.9	9
LPME-HPLC-UV	landfill leachates	5-50000	1.2-2.2	40	3.2-7.4	10
SFO-LPME-GC-MS	water	0.05-100	0.02-0.05	25	5.5-7.7	23
SPME-GC-MS	waters	0.08-8	0.002-0.103	20	3.4-16	11
SPME-GC-MS	bottled water	0.1-20	0.003-0.085	60	0.78-17.24	12
DLLME-HPLC-UV	water	50-600	10.6-28.5	5	7.8-15	17
IL-DLLME-HPLC-UV	water	2-100	0.68-1.36	3	2.2-3.7	20
IL-DLLME-HPLC-UV	water	1-100	0.23-0.47	40	2.2-5.9	19
HF-LPME-GC-MS	water	0.02-10	0.005-0.1	20	4-11	21
MSPE-HPLC-FLD	water	0.06-10	0.011-0.046	40	0.3-11	32
MSPE-HPLC-UV	water	0.1-20	0.019-0.059	20	1-9	33
MSPE-GC/MS	water	0.1-100	0.006-0.068	15	3.4-11.7	34
MSPE-GC/MS	beverages water	0.2-50	0.005-0.038	3	< 14.6	39
MSPE-HPLC-UV	water	0.1-10	0.012-0.036	20	1-8	40
MSPE-HPLC-UV	water	0.5-100	0.08-0.1	10	2.6-4.3	This method

FLD: fluorescence detector.

was much easier to deal with large volume samples to obtain high sensitivity. Therefore, the MSPE method is indeed simple, rapid, efficient, easy to use and environment-friendly. Different magnetic materials, such as alginate-polymer-caged C₁₈-functionalized magnetic titanate nanotubes,³² barium alginate caged Fe₃O₄-C₁₈ magnetic nanoparticles,³³ polypyrrole-coated magnetic particles,³⁴ magnetic carbon nanotubes (CNTs)³⁹ and chitosan-coated C₁₈-functionalized magnetite nanoparticle,⁴⁰ had been used for the MSPE of some PAEs in water and beverage samples with excellent results. Compared with the reported MSPE methods, less time was needed for the current process, which indicated a high extraction efficiency of the LC-based magnetic nanocomposite for the PAEs.

Conclusions

In this research, a LC-based magnetic nanocomposite was studied as the adsorbent for the adsorption of some PAEs in water samples. The magnetic nanocomposite adsorbent could remove and enrich the PAEs from water samples efficiently. Its main advantage is that as a MSPE adsorbent, it could be easily and quickly isolated from water samples with an external magnetic field and the MSPE process could avoid the time-consuming column passing or filtration operations often encountered in common SPE. The results indicated that the developed method was fast, efficient, easy to operate, sensitive and environmentally friendly for the preconcentration of trace levels of the PAEs in water samples.

Acknowledgments. Financial support from the National Natural Science Foundation of China (No. 31171698) is gratefully acknowledged.

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