Preparation of a chitosan-coated C₁₈-functionalized magnetite nanoparticle sorbent for extraction of phthalate ester compounds from environmental water samples

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Abstract Novel superparamagnetic chitosan-coated C₁₈-functionalized magnetite nanoparticles (MNPs) were successfully synthesized and applied as an effective sorbent for the preconcentration of several typical phthalate ester compounds from environmental water samples. The MNPs were 20 nm in diameter and had a high magnetic saturation value (52 emu g⁻¹), which endowed the sorbent with a large surface area and the convenience of isolation from water samples. Phthalate esters could be extracted by the interior octadecyl groups through hydrophobic interaction. The hydrophilic porous chitosan polymer coating promoted the dispersion of MNPs in water samples, and improved the anti-interference ability of the sorbent without influencing the adsorption of analytes. The main factors affecting the adsorption of phthalate esters, including the pH of the solution, humic acid, sample loading volume, adsorption time, and desorption conditions, were investigated and optimized. Under the conditions selected (pH 11, adsorption time 20 min, elution with 10 mL of acetonitrile, and concentration to 0.5 mL), concentration factors of 1,000

were achieved by extracting 500 mL of several environmental water samples with 0.1 g of MNP sorbent. The method detection limits obtained for di-*n*-propyl phthalate, di-*n*-butyl phthalate, dicyclohexyl phthalate, and di-*n*-octyl phthalate were 12.3, 18.7, 36.4, and 15.6 ng L⁻¹, respectively. The recoveries of spiked samples ranged from 60 to 100%, with a low relative standard deviation (1–8%), which indicated good method precision.

Keywords Chitosan-coated C₁₈-functionalized magnetite nanoparticles · Solid-phase extraction · Phthalate esters

Introduction

Phthalate esters, widely used as plasticizers and additives in many products, including plastics, pesticides, paints, and cosmetics, have spread all over the world owing to their huge production volume even though they are easily photodegraded or biodegraded by microorganisms [1]. Some of them can be accumulated in aquatic organisms [1] and have been regarded as endocrine disrupters and carcinogens [2], so many organizations, such as the European Union, the World Health Organization, and the US Environmental Protection Agency, have placed them on lists of priority pollutants [3]. But the determination of phthalate esters in environmental water samples is still a challenge because of their trace level [4] and interference of the complex matrix. Solid-phase extraction (SPE) is a routine method to preconcentrate trace phthalate esters in environmental samples [5–9] prior to high performance liquid chromatography (HPLC) analysis. SPE has many obvious advantages, such as high recovery, high concentration factor, low consumption of organic solvents, and convenience of operation. A reversed-phase C₁₈ SPE

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cartridge [5, 6], a Waters Oasis HLB SPE cartridge [7], and a polystyrene–divinylbenzene column [8, 9] have been used to enrich the targets from water samples. But the micron size of commercial sorbents may result in low extraction efficiency when ultratrace analytes are determined, and a long operating time is required when large volumes of water samples pass through the SPE column. Furthermore, the sorbents tend to be contaminated by natural organic matter (NOM) in environmental water samples. It is necessary to develop novel sorbents with high extraction efficiency and anti-interference ability.

Recently, there has been increasing interest in magnetic nanoparticles (MNPs) in various scientific fields [10–16]. MNPs with different sizes were synthesized [10, 13, 17, 18] and modified with metal, oxide, an organic group, a polymer, and even a biomacromolecule for various purposes [10–25]. Among them, MNP sorbents have been functionalized with special ligands by forming mixed hemimicelles [21–23] (temporary combination) or by covalent modification [17, 24, 25] (permanent combination) and used to extract target molecules from environmental water samples by many research groups. The MNP sorbents possess a large surface area and high adsorption performance owing to their nanosize, and can be quickly isolated from matrix solutions through an external magnetic field after adsorption of the target analytes. Thus, the difficulties of solid/liquid separation and the high back pressure encountered when water sample pass through an SPE column packed with nanosized adsorbents are avoided. However, the surfactant of mixed hemimicelles can be coeluted with target analytes from the sorbents, and can enter the following analysis system, which will contaminate the analysis system. On the other hand, MNPs with organic modification, especially for those below 50 nm, are difficult to disperse in water owing to their hydrophobicity. Furthermore, NOM in water samples with complex matrixes (e.g., humic acid) can also adhere onto the surface of the sorbents and influence the adsorption performance greatly. For these reasons, MNPs modified with an organic group are not suitable for SPE of ultratrace phthalate esters in complex water samples. A layer of hydrophilic porous polymer on the surface of hydrophobic MNPs may solve these problems.

In this research, Fe_3O_4 MNPs of 15 nm were synthesized by coprecipitation, and were modified with an octadecyl group on the surface by silanization, followed by coating a layer of hydrophilic chitosan–tripolyphosphate polymer on the surface. Thus, a novel type of MNP sorbent with an interior hydrophobic C_{18} group and an exterior hydrophilic chitosan polymer coating was obtained. This MNP sorbent had high extraction efficiency owing to the nanosize and the interior layer of the hydrophobic C_{18} group [25] and had the advantage of convenient operation. The exterior

hydrophilic chitosan polymer improved the dispersibility of the sorbent in aqueous solution. The porosity and basket-like structure of the chitosan–tripolyphosphate polymer [26] might prevent the NOM macromolecules in samples from entering the interior hydrophobic layer, while allowing the small phthalate ester molecules to pass through readily. Hence, extracting target compounds of trace level directly from complex environmental samples could be achieved.

Materials and methods

Reagents

Di-*n*-propyl phthalate (DPP), di-*n*-butyl phthalate (DBP), dicyclohexyl phthalate (DCP), and di-*n*-octyl phthalate (DOP) were obtained from Acros Organics (Morris Plains, NJ, USA). Standard stock solutions (10 mg L^{-1}) containing these compounds were prepared in methanol and stored in glass containers at 4°C . Working solutions were prepared daily by appropriate dilution of the stock solutions with methanol. Liquid chromatography grade methanol, ethanol, and acetonitrile were purchased from Merck (Darmstadt, Germany). Octadecyltriethoxysilane was obtained from Tokyo Chemical Industry (Tokyo, Japan). Chitosan (molecular weight 4.9×10^5 , degree of deacetylation 95%) was obtained from Dalian Xindie Chitin (Dalian, China). Sodium tripolyphosphate and humic acid were obtained from Sigma. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, sodium hydroxide, toluene, and hydrochloric acid were guaranteed-grade reagents (Beijing Chemicals, Beijing, China). Ultrapure water was prepared in the laboratory using a Milli-Q SP reagent water system from Millipore (Milford, MA, USA).

Chromatographic conditions

The detection of analytes was performed by using a liquid chromatography–spectrophotometry system. The HPLC equipment included two Dionex P680 HPLC pumps, an online-connected degasser, an SOR-100 solvent rack, a TCC-100 thermostated column compartment, and a Dionex PDA-100 photodiode-array detector. The separation conditions are described in the [electronic supplementary material](#).

Preparation of chitosan-coated $\text{Fe}_3\text{O}_4\text{--C}_{18}$ MNPs

The process of preparation of chitosan-coated $\text{Fe}_3\text{O}_4\text{--C}_{18}$ MNPs is shown in Fig. 1. Firstly, Fe_3O_4 MNPs were prepared by a chemical coprecipitation method [21]. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (5.2 g), $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (2.0 g), and 12 M HCl (0.85 mL) were dissolved in 25 mL of deionized water (degassed with nitrogen gas before use) to prepare a stock

Fig. 1 Synthesis of chitosan-coated Fe_3O_4 - C_{18} magnetic nanoparticles (MNPs)

solution. A 250-mL volume of 1.5 M NaOH solution was heated to 80 °C in a beaker. The stock solution was added dropwise to the NaOH solution under nitrogen gas protection and vigorous stirring. The mixture was stirred for 20 min and subsequently cooled to ambient temperature. After the reaction, the Fe_3O_4 MNPs precipitate obtained was separated from the reaction mixture by an external magnetic field, washed four times with 200 mL of deionized water, and vacuum-dried at 50 °C for 24 h for further use.

Next, Fe_3O_4 MNPs were functionalized with octadecyltriethoxysilane according to previous reported methods [24] with a minor modification. Briefly, 1.2 g of the dried Fe_3O_4 MNPs and 0.6 mL of octadecyltriethoxysilane were added to 60 mL of toluene under vigorous stirring. The mixture was then put into an autoclave and heated at 120 °C for 12 h in a furnace. The Fe_3O_4 - C_{18} MNPs were obtained after washing and drying.

Finally, chitosan-coated Fe_3O_4 - C_{18} MNPs were synthesized through ionotropic gelation [26]. Fe_3O_4 - C_{18} MNPs (0.8 g) were dispersed in 30 mL of chitosan solution (4 mg mL⁻¹) dissolved in 2% acetic acid. The suspension was mixed by ultrasonic irradiation for 30 min, and then 15 mL of sodium tripolyphosphate solution (0.5 mg mL⁻¹) was added, followed by mechanical stirring for another 30 min. The chitosan-coated Fe_3O_4 - C_{18} MNPs were collected from the reaction mixture by an external magnetic field. The product was washed several times with water and ethanol and dried at 50 °C in a vacuum oven.

Characterization of chitosan-coated Fe_3O_4 - C_{18} MNPs

The average particle size and morphology of the MNPs obtained were observed by using a Hitachi 8100 transmission electron microscope (Hitachi, Tokyo, Japan). X-ray diffraction measurements were performed with a PANalytical X'pert Pro diffractometer (PANalytical, Almelo, The Netherlands), using a monochromatized X-ray beam with nickel-filtered Cu

K α radiation with 4°min⁻¹ scan rate. A continuous scan mode was used to collect 2 θ data from 10° to 100°. The magnetization curves of the dried MNPs were recorded with a LDJ9600 magnetometer (LDJ Electronics, Troy, MI, USA) by changing H between +20,000 and -20,000 Oe at 25 °C. Fourier transform IR (FTIR) spectra of Fe_3O_4 MNPs, Fe_3O_4 - C_{18} MNPs and chitosan-coated Fe_3O_4 - C_{18} MNPs were recorded with KBr discs in the range 4000–400 cm⁻¹ using a Nicolet AVATAR 360 FTIR spectrometer (Nicolet Thermo, Waltham, MA, USA).

SPE procedure and sample loading

The SPE procedure consisted of three steps. First, 0.1 g of chitosan-coated Fe_3O_4 - C_{18} MNPs was dispersed in 500 mL of a filtered water sample by ultrasonic irradiation for 30 s and the pH was adjusted to about 11.0 with 1 M NaOH or HCl. Then, the mixture was placed in a beaker and allowed to equilibrate for 20 min to completely trap the target analytes. Second, a strong Nd-Fe-B magnet (150mm × 100mm × 20mm) was deposited at the bottom of the beaker to isolate the MNP sorbent from the suspension. After about 10 min, the suspension became limpid and the supernatant was decanted. Finally, the preconcentrated target analytes were eluted from the isolated sorbent with 10 mL of acetonitrile. The eluate was concentrated to 0.5 mL with a stream of nitrogen at 55 °C, and 20 μ L of this solution was injected into HPLC system for analysis. An illustration of the whole procedure of the application of chitosan-coated Fe_3O_4 - C_{18} MNPs as an SPE sorbent for enriching analytes is shown in Fig. 2. Predominant factors affecting the extraction efficiency of analytes were investigated with ultrapure water spiked with each analyte (2 ng mL⁻¹). The analytical performance of the method was also examined under the optimized conditions.

Water samples were obtained from different districts of Tangshan, Hebei Province, China. River water samples were

Fig. 2 Application of chitosan-coated $\text{Fe}_3\text{O}_4\text{-C}_{18}$ MNPs as a solid phase extraction sorbent for analysis. HPLC high-performance liquid chromatography

collected from Douhe River (Lubei district, Tangshan) in March 2009. Lake water samples were taken from Nanhu Lake in Fengnan district, Tangshan. Tap water samples were taken from the biochemistry laboratory of Hebei Polytechnic University in Lunan district, Tangshan. All samples were collected in methanol-rinsed and air-dried narrow-mouth glass bottles and filtered through 0.22- μm nylon membranes (Shanghai Institute of Pharmaceutical Industry, China) before use to remove suspended solids. The filtered samples were stored in glass containers at 4 °C until analysis. Under the optimized conditions, 500 mL of water sample or water sample spiked with analytes (0.5 and 5.0 ng mL^{-1}) was preconcentrated for sample analysis or a recovery test.

To eliminate the potential contamination of phthalate esters, all glassware, including samplers and containers, used in the study was washed with acetone at least three times, then rinsed with methanol three times, and dried at 120 °C for 4 h. The blanks of the entire SPE procedure were performed with ultrapure water following similar extraction and analysis procedures, and none of the target analytes were detected. The chromatogram of the blank of the procedure is shown in Fig. 6, chromatogram d.

Results and discussion

Chitosan-coated $\text{Fe}_3\text{O}_4\text{-C}_{18}$ MNPs

The size and shape of the naked Fe_3O_4 and chitosan-coated $\text{Fe}_3\text{O}_4\text{-C}_{18}$ MNPs are shown in Fig. 3a. The naked Fe_3O_4 MNPs are of uniform size, and the diameter is about 15 nm.

After modification with the C_{18} group and coating with chitosan (Fig. 3b), the MNPs, with better dispersion, had a typical core-shell structure of about 20 nm in diameter.

The vibrating sample magnetometer magnetization curves of Fe_3O_4 MNPs (Fig. S1, curve a) and chitosan-coated $\text{Fe}_3\text{O}_4\text{-C}_{18}$ MNPs (Fig. S1, curve b) both indicated typical superparamagnetic behavior, which was necessary for practical application. The chitosan polymer coating resulted in a decreased magnetic strength of the MNPs for the nonmagnetic shell. The saturation magnetization of chitosan-coated $\text{Fe}_3\text{O}_4\text{-C}_{18}$ MNPs was 52.2 emu g^{-1} , which was sufficient for magnetic separation with a conventional magnet.

Figure S3 shows the FTIR spectra of the naked Fe_3O_4 (Fig. S3, spectrum a), $\text{Fe}_3\text{O}_4\text{-C}_{18}$ MNPs (Fig. S3, spectrum b), and chitosan-coated $\text{Fe}_3\text{O}_4\text{-C}_{18}$ MNPs (Fig. S3, spectrum c). The peaks around 3,420 cm^{-1} in curves a–c related to the -OH group, and the peak at 564 cm^{-1} corresponds to an Fe-O group [27]. After modification with octadecyltriethoxysilane, characteristic bands of saturated C–H absorption at 2,851 and 2,921 cm^{-1} and of O–Si–C absorption at 1,623 cm^{-1} appeared [27] (Fig. S3, spectrum b). In the FTIR spectra of chitosan-coated $\text{Fe}_3\text{O}_4\text{-C}_{18}$ MNPs, the absorption band at 1,382 cm^{-1} could be assigned to -C-O stretching of the primary alcoholic group in chitosan [26]. The characteristic bands of saturated C–H absorption at 2,851 and 2,921 cm^{-1} could also be discerned, but the intensity of these peaks was much lower owing to the shielding effect of the chitosan coating. The presence of the P=O groups in chitosan–tripolyphosphate polymer was proved by the peak at 1,153 cm^{-1} . The broad

Fig. 3 Transmission electron microscope images of naked Fe₃O₄ (a) and chitosan-coated Fe₃O₄-C₁₈ MNPs (b)

adsorption peak near 3,300–3,500 cm⁻¹ was attributed to the stretching vibration of O–H, the extension vibration of N–H, and interhydrogen bonds of the polysaccharide [26]. These results revealed that chitosan–tripolyphosphate polymer was coated on the Fe₃O₄-C₁₈ MNPs successfully.

X-ray diffraction patterns of naked Fe₃O₄ and chitosan-coated Fe₃O₄-C₁₈ MNPs are shown in Fig. S2. Six characteristic peaks occur at 2θ of 30.1°, 35.5°, 43.1°, 53.4°, 57.0°, and 62.6° in both samples, which are marked by their indices [(220), (311), (400), (422), (511), and (440)] [27]. These reveal that pure Fe₃O₄, with a spinel structure, is the dominant phase in both samples and the functionalization of the C₁₈ group and the coating process with chitosan polymer did not change the crystalline phase of Fe₃O₄.

Effect of solution pH on SPE

The charge property of the surface of chitosan-coated Fe₃O₄-C₁₈ MNPs is a main factor affecting the aggregation

of the MNPs. It varies with the solution pH [26] and affects the surface area of the sorbent and the adsorption of target compounds. The influence of the solution pH on SPE of targets was investigated in the pH range from 3 to 11 under the following conditions: adsorption time, 30 min; MNP sorbent, 0.1 g; loading volume, 500 mL; eluent, acetonitrile, 15 mL and concentrated to 0.5 mL. The isoelectric point (pI) of the MNP sorbent was found to be at pH 6.9 (seen in Fig. S4). When the pH was above 9.0 or below 5.0, the MNPs tended to disperse in water solution owing to electrostatic repulsion [26], which increased the adsorption efficiency of the sorbent. However, in the pH range from 5.0 to 9.0, the charge density of the surface of chitosan-coated Fe₃O₄-C₁₈ MNPs was relatively low, leading to the increased aggregation tendency of the MNPs. Therefore, the recoveries of the analytes were higher under acidic or basic conditions than in neutral solution (seen in Fig. 4).

Effect of adsorption time on SPE

It takes some time for the adsorption of analytes on a sorbent, so a prolonged adsorption time may increase the recovery of analytes. The investigation of the influence of the adsorption time on the recoveries of analytes was carried out under the following conditions: MNP sorbent, 0.1 g; loading volume, 500 mL; pH 6; adsorption time, 0–90 min, eluent, acetonitrile, 15 mL and concentrated to 0.5 mL. The results are shown in Fig. S5. As can be seen from Fig. S5, 20 min was sufficient to achieve the maximum recoveries of all analytes; the recoveries of phthalate esters were above 95%, with the exception of DPP (75%). Therefore, 20 min was chosen as the optimal

Fig. 4 Effect of pH on the adsorption of di-*n*-propyl phthalate (DPP), di-*n*-butyl phthalate (DBP), dicyclohexyl phthalate (DCP), and di-*n*-octyl phthalate (DOP) onto chitosan-coated Fe₃O₄-C₁₈ MNPs obtained by extracting 500 mL of standard solutions spiked with 2 ng mL⁻¹ of each analyte. Adsorption time, 30 min; eluent, acetonitrile, 15 mL; MNP sorbent, 0.1 g

Fig. 5 Effect of humic acid on the adsorption of DPP, DBP, DCP, and DOP onto chitosan-coated $\text{Fe}_3\text{O}_4\text{-C}_{18}$ MNPs obtained by extracting 500 mL of standard solutions spiked with 2 ng mL^{-1} of each analyte at different pH. The concentration of humic acid was $50 \mu\text{g mL}^{-1}$. Adsorption time, 20 min; eluent, acetonitrile, 10 mL; MNP sorbent, 0.1 g

adsorption time for further studies. The MNPs were then isolated by using a strong Nd-Fe-B magnet. The superparamagnetism properties and the large saturation magnetization (52.6 emu g^{-1}) enabled them to be completely isolated in a short time (about 10 min). These results reveal that the use of chitosan-coated $\text{Fe}_3\text{O}_4\text{-C}_{18}$ MNPs could meet the need of rapid analysis.

Effect of desorption conditions on SPE

Both acetonitrile and methanol in different volumes were used to elute the analytes from the sorbent. The working conditions were as follow: MNP sorbent, 0.1 g, loading volume, 500 mL, pH 6; adsorption time, 20 min; concentration of the eluate to 0.5 mL. We found that the desorption ability of acetonitrile was superior to that of methanol. When methanol was used as the eluant, the recoveries of DPP, DCP, and DOP were less than 60% even when the methanol elution volume reached 13 mL. All analytes were quantitatively eluted from chitosan-coated $\text{Fe}_3\text{O}_4\text{-C}_{18}$

MNPs by using 10 mL of acetonitrile. Multiple elutions was found to be appropriate to completely desorb the analytes from the sorbent, and tripartite elution was necessary. Therefore, 10 mL of acetonitrile (2.5 mL every time and washed four times) was selected to ensure the complete elution of analytes for the further experiment.

Effect of solution loading volume on SPE

The effect of the sample volume on the enrichment of the analytes was studied with ultrapure water spiked with each analyte (2 ng mL^{-1}) under the following conditions: MNP sorbent, 0.1 g, loading volume 200–800 mL; pH 6; adsorption time, 20 min; eluent, acetonitrile, 10 mL and concentrated to 0.5 mL. The results are shown in Fig. S6. Under the above-mentioned optimal conditions, the recoveries of analytes were still above 95%, except for DPP (76%), as the sample volume was up to 500 mL. By concentrating the eluents (10 mL of acetonitrile solution) to 0.5 mL with nitrogen flow, we could easily achieve concentration factors of 1,000, which showed the high extraction efficiency of the chitosan-coated $\text{Fe}_3\text{O}_4\text{-C}_{18}$ MNP sorbent.

Influence of humic acid on SPE at different pH

Humic acid is the most common NOM in environmental water samples, and can adsorb many organic compounds owing to the skeleton of alkyl and aromatic units that attach to carboxylic acid, phenolic hydroxyl, and quinone functional groups [12]. It can also adsorb onto the surface of sorbents and thus contaminate the sorbents. Since the concentration of humic acid in natural water samples is in the range $0.2\text{--}50 \mu\text{g mL}^{-1}$ [12], $50 \mu\text{g mL}^{-1}$ of humic acid was added to each solution at different pH to investigate the anti-interference ability of the sorbent. The operating conditions was as follows: MNP sorbent, 0.1 g; loading volume, 500 mL; pH 3–11; adsorption time, 20 min; eluent, acetonitrile, 10 mL and concentrated to 0.5 mL. The results are shown in Fig. 5. The influence of humic acid on the extraction efficiency of phthalate esters was higher in acid and neutral solution than in alkali solution, especially for

Table 1 Analytical parameters of the proposed method

Analytes	Linearity range (ng mL^{-1})	Calibration equations	Correlation coefficient (r^2)	RSD (%) ($n=3$)	Limit of detection (ng L^{-1} , $S/N=3$)
DPP	0.1–10	$y = 0.8394x + 0.1241$	0.9983	6.867	12.3
DBP	0.1–10	$y = 0.6905x + 0.1999$	0.9981	6.976	18.7
DCP	0.1–10	$y = 1.032x - 0.0989$	0.9996	3.379	36.5
DOP	0.1–10	$y = 0.6453x + 0.1566$	0.9998	2.175	15.6

RSD relative standard deviation, S/N signal-to-noise ratio, DPP di-*n*-propyl phthalate, DBP di-*n*-butyl phthalate, DCP dicyclohexyl phthalate, DOP di-*n*-octyl phthalate

Table 2 Results of determination and recoveries of real water samples spiked with the target analytes extracted with chitosan-coated Fe₃O₄-C₁₈ magnetic nanoparticles

Water sample	Analytes	Detected ^a (ngmL ⁻¹)			Recovery ^b (%) ± RSD	
		Blank	0.5ngmL ⁻¹ spiked	5ngmL ⁻¹ spiked	0.5ngmL ⁻¹ spiked	5ngmL ⁻¹ spiked
Tap water	DPP	ND	0.444	3.89	89±3	78±2
	DBP	0.549	1.02	5.02	93±2	89±2
	DCP	ND	0.413	4.91	83±2	98±1
	DOP	<LOQ	0.502	4.71	95±1	94±2
Douhe River water	DPP	0.16	0.501	4.04	68±4	78±2
	DBP	0.755	1.11	5.32	72±6	91±5
	DCP	ND	0.502	4.6	94±2	92±1
	DOP	0.164	0.619	4.91	91±2	95±2
Nanhu Lake water	DPP	0.145	0.448	3.81	60±1	73±3
	DBP	0.635	1.04	5.64	81±6	100±2
	DCP	<LOQ	0.482	5.04	88±6	100±3
	DOP	0.149	0.575	4.66	85±8	90±4

ND not detected

^a Mean of three determinations^b Standard deviation for three determinations

DPP and DBP. Humic acid is negatively charged even at low solution pH. Therefore, at pH < pI, humic acid tended to be adsorbed by the oppositely charged chitosan coating and adhered on the surface of MNPs, which could block the pores of chitosan polymer. Humic acid would keep away from the chitosan-coated Fe₃O₄-C₁₈ MNPs at high pH owing to the electrostatic repulsion between the coating and humic acid. At pH 11, the recoveries of the analytes were higher than 95% (except DPP, 53%). This result implies that the chitosan polymer coating could increase the anti-interference ability of adsorbents at high pH, and the sorbent might be used to quantitatively extract phthalate esters from water samples with complex matrixes.

Analytical performance and analysis of environmental water samples

Calibration curves were obtained for four phthalate esters spiked at 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, and 10 ng mL⁻¹ in 500 mL of aqueous solution by using the peak area versus concentration. Each solution was determined three times according to the overall SPE procedure and the HPLC-UV analysis method mentioned earlier. The analytical performance of the method is shown in Table 1. The calibration curves were linear over the range 0.1–10 ng mL⁻¹, with correlation coefficients of more than 0.99. The limits of detection (LODs) of the analytes were all below 40 ng L⁻¹ (calculated as 3 times the standard deviation of six replicate runs of procedure blanks). The relative standard deviation of the method ranged from 2 to 7%, demonstrating good method precision.

To confirm the reliability of the method for the analysis of phthalate esters, it was applied to determine these analytes in some real water samples. The concentrations and recoveries obtained for the target compounds, expressed as the mean value (*n*=3), are listed in Table 2. In all water samples, the concentration of DBP was higher than that of the other phthalate esters. Low concentrations of phthalate ester

Fig. 6 HPLC-UV chromatograms of a Douhe River water sample pre-concentrated by chitosan-coated Fe₃O₄-C₁₈ MNP sorbent: **a** Douhe River water sample spiked with 5.0 ng mL⁻¹ of each compound; **b** Douhe River water sample spiked with 0.50 ng mL⁻¹ of each compound; **c** Douhe River water sample; and **d** blank with ultrapure water. 1 DPP, 2 DBP, 3 DCP, 4 DOP. Volume of water sample solution, 500 mL; adsorption time, 20 min; pH 11; eluent, acetonitrile, 10 mL; MNP sorbent, 0.1 g

compounds were found in Nanhu Lake water and Douhe River water samples, whereas almost no phthalate esters was detected in tap water, except for DBP. The recoveries of DPP, DBP, DCP, and DOP ranged between 60 and 92%, 66 and 102%, 81 and 103%, and 77 and 97% for the three water samples, with low relative standard deviation of determinations ranging from 1 to 6%. The HPLC-UV chromatograms of the Douhe River water sample and its spiked solutions are shown in Fig. 6.

Commercial reversed-phase C₁₈, Waters Oasis HLB, and polystyrene–divinylbenzene SPE cartridges are SPE cartridges commonly used to preconcentrate phthalate esters from environmental water samples as reported in the literature. The LODs obtained with C₁₈, HLB, and polystyrene–divinylbenzene cartridges were 10.0–100, 1.0, and 0.05–0.1 ng mL⁻¹, respectively [5–8]. Compared with these results, the LODs of the proposed method were increased by 10–100-fold with satisfactory recoveries. The preconcentration procedure was simplified greatly and plenty of time was saved. To pretreat 500 mL of water samples, only 40 min was required with MNP adsorbents, whereas at least 3 h was needed with conventional SPE columns. Therefore, we conclude that the MNP sorbent prepared in this work operates in an efficient manner under real-world conditions and its adsorption performance is superior to that of conventional SPE cartridges.

The stability and reuse feasibility of the MNP sorbent were investigated by reusing the MNP sorbent to extract analytes from water samples and their spiked solutions (0.50 ng mL⁻¹) within 2 months. After the MNP sorbent had been reused seven times, the decrease of the recoveries of all the analytes was lower than 7%, and the relative standard deviation ($n=7$) of the seven results was less than 12%. This result indicated that the sorbent was stable enough to be reused more than five times.

Conclusions

In this research, superparamagnetic chitosan-coated Fe₃O₄–C₁₈ MNPs (core–shell) were successfully synthesized and used for extraction of trace phthalate esters from large volumes of environmental water samples. The analytes could pass through the porous hydrophilic chitosan polymer coating and be adsorbed by the interior hydrophobic octadecyl groups of the sorbent. The nanosize of the granules endowed the sorbent with great adsorption ability, and the sorbent could be separated from the matrix solution easily owing to the superparamagnetic Fe₃O₄ core. Compared with the MNP–mixed hemimicelle systems of our previous work, extra reagent was not required, and the risk of contaminating the subsequent analysis system and the environment by surfactants was avoided. Furthermore, the

hydrophilic chitosan polymer coating promoted the dispersion of the Fe₃O₄–C₁₈ MNP sorbent in water samples, and improved the anti-interference of the sorbent. Therefore, we concluded that the chitosan-coated Fe₃O₄–C₁₈ MNP sorbent could extract phthalate esters quantitatively from large volumes of environmental water samples with complex matrixes, and this SPE method was proved to be viable.

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