Cetyltrimethylammonium Bromide-Coated Magnetic Nanoparticles for the Preconcentration of Phenolic Compounds from Environmental Water Samples

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S H I F E N   M O U

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The research presented in this paper investigates the adsorption of cation surfactants—cetyltrimethylammonium bromide (CTAB) and cetylpyridinium chloride (CPC)—onto magnetic nanoparticles and the application of this mixed hemimicelles solid-phase extraction (SPE) method for the preconcentration of several typical phenolic compounds—bisphenol A (BPA), 4-*tert*-octylphenol (4-OP), and 4-*n*-nonylphenol (4-NP)—from environmental water samples. In this novel SPE method, the charged surfactants CTAB and CPC form mixed hemimicelles on Fe_3O_4 nanoparticles (Fe_3O_4 NPs), which causes retention of analytes by strong hydrophobic and electrostatic interactions. The SPE method combines the advantages of mixed hemimicelles and magnetic nanoparticles. In order to provide guidelines for the mixed hemimicelles SPE method development, surfactant adsorption isotherms and ζ-potential isotherms were also investigated. The main factors affecting the adsolubilization of analytes, such as the amount of Fe_3O_4 NPs and surfactants, the type of surfactants, the solution pH, the sample loading volume, and the desorption conditions, were investigated and optimized. A concentration factor of 800 was achieved by the extraction of 800 mL of several environmental water samples using this SPE method. Under the selected conditions, detection limits obtained for BPA, 4-OP, and 4-NP were 12, 29, 34 ng/L, respectively. The accuracy of the method was evaluated by recovery measurements on spiked samples, and good recoveries (68–104%) with low relative standard deviations from 2 to 7% were achieved. The advantages of this new SPE method include high extraction yields, high breakthrough volumes, short analysis times, and easy preparation of sorbents. To the best of our knowledge, this is the first time that a mixed hemimicelles SPE method based on magnetic separation and nanoparticles has been used for the pretreatment of environmental water samples.

Introduction

In recent years, nanosized materials have attracted much interest in the research community due to their unique size and physical properties. These materials have been used in various scientific fields such as biotechnology, engineering, biomedical, environmental, and material science (*1–4*). Solid-phase extraction (SPE) is a routine extraction method for determining trace level contaminants in environmental samples. Many research groups, including ours (*5–10*), have explored the application of several nanosized SPE adsorbents such as nanoparticles (NPs) and nanotubes. Nanomaterials can offer several advantages over traditional SPE sorbents such as very high surface areas and a short diffusion route, which result in high extraction capacity, rapid extraction dynamics, and high extraction efficiencies. However, the use of nanomaterials with a sub-100 nm size range has some inherent limitations, especially when applied in the adsorption and separation of contaminations from large volumes of environment samples. When column dynamic extraction mode is used, the nanosized particles packed SPE column exhibits high backpressure, making it very difficult to adopt high flow rates; when the static batch mode is used, the nanosized SPE adsorbents often lead to a very low filtration rate.

Because of these disadvantages, it is necessary to develop new nanosized SPE methods that can be applied to preconcentrate and separate organic compounds from large volumes of environmental water samples. Recently, a unique magnetic carrier technology (MCT) has been reported by several research groups (*4, 11, 12*). A unique and attractive property of MCT is that magnetic nanoparticles can readily be isolated from sample solutions by the application of an external magnetic field. These particles are superparamagnetic, which means that they can readily be attracted by a magnet but do not retain magnetism after the field is removed. Therefore, suspended superparamagnetic particles tagged with organic contaminants can be removed from the matrix by applying a magnetic field, but they do not agglomerate after removal of the field. Hence, the particles may be reused or recycled. Magnetic nanoparticles are one of the most popular materials in analytical biochemistry, medicine, and biotechnology, and they have been increasingly applied to immobilizing proteins, enzymes, and other bioactive agents (*1, 12–18*). Magnetic nanoparticles offer several advantages over the traditional microsized sorbents; they possess not only high surface area, which can exhibit higher adsorption capacity for analytes, but also strong superparamagnetic properties which can meet the need of rapid extraction of large-volume samples by employing a strong external magnetic field. However, up to now, only a limited number of literatures have reported the use of MCT in the preconcentration of environmental samples (*19, 20*). In this paper, we will explore the possibility of Fe_3O_4 NPs to act as SPE sorbents for the preconcentration of trace level contaminants from large-volume environmental water samples.

Hemimicelles and admicelles, which are formed by the adsorption of ionic surfactants on mineral oxides such as alumina, silica, titanium dioxide, and ferric oxyhydroxides (*19*), have recently been used as novel sorbents for SPE of organic compounds with good results (*21–28*). Hemimicelles consist of monolayers of surfactants adsorbing with their headgroup down on an oppositely charged mineral oxide surface while the hydrocarbon tail-groups protrude into the solution. With more and more surfactants adsorbed onto the mineral oxide surface, after saturation of the oxide surface, the hydrophobic interactions between tails of surfactant hydrocarbon chains results in the formation of admicelles. In the phase, which is termed mixed hemimicelles, both

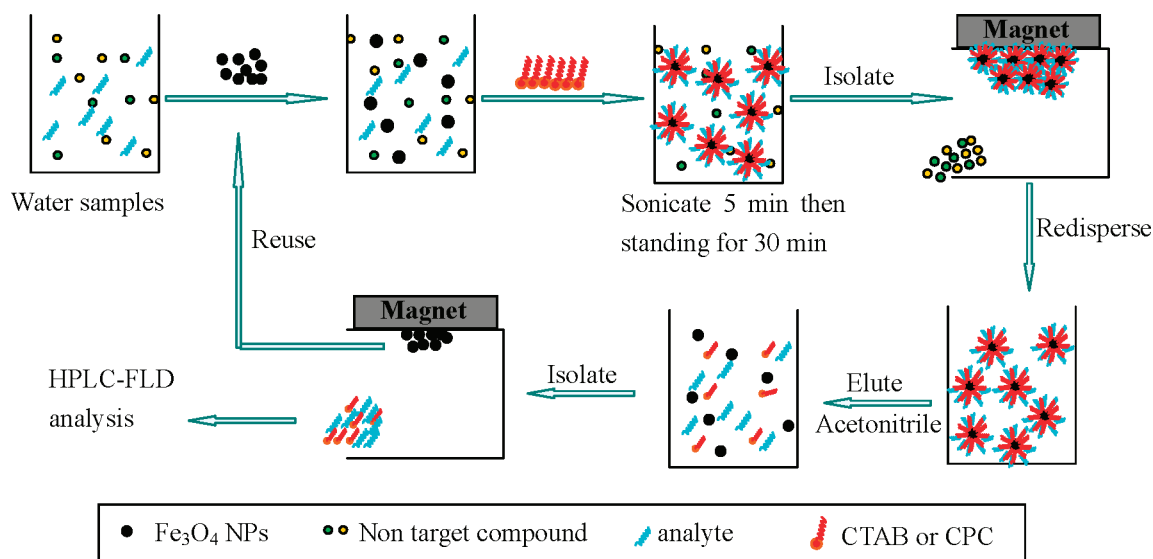* Corresponding author phone: (086) 010-62849239; fax: (086) 010-62849182; e-mail: caiyaqi@rcees.ac.cn.

FIGURE 1. Scheme illustrating the steps involved in extracting analytes from environmental water samples by using CTAB/ nanomagnets Fe₃O₄ sorbents. See key for identification of Fe₃O₄ NPs, nontarget compounds, analyte, and CTAB or CPC.
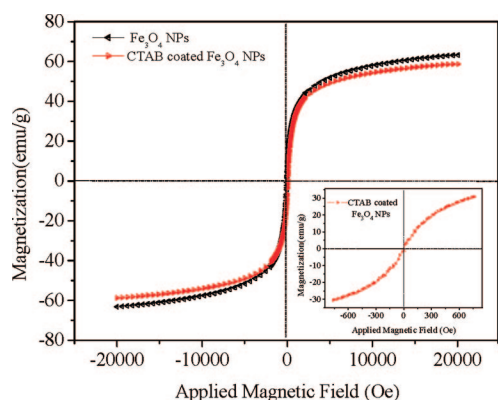

FIGURE 2. VSM magnetization curves of Fe₃O₄ NPs.

hemimicelles and admicelles are formed on the surface of mineral oxides, and the adsorption is driven by both hydrophobic interactions and electrostatic attraction. One of the main characteristics of these sorbents is their versatility. One feature is that the outer surface of hemimicelles is hydrophobic whereas that of admicelles is ionic, which provides different mechanisms for retention of organics. Another advantage is the large number of commercially available surfactants, hence both the degree of hydrophobicity and the charge of the sorbents can easily be modified according to the nature of the analytes. Other benefits obtained with the use of mixed hemimicelles sorbents are high extraction yields, easy elution of analytes, and high breakthrough volumes (27, 28).

To the best of our knowledge, hemimicelle and admicelle SPE methods based on magnetic nanoparticles adsorbing ionic surfactants have not yet been reported. If one combines the advantages of mixed hemimicelles and magnetic nanoparticles to fabricate nanosized SPE adsorbents with high surface area and magnetic separability, a new kind of mixed hemimicelle nanosized SPE adsorbents is obtained. This will not only extend the scope of application of mixed-hemimicelles-based SPE but will also offer several potential advantages for preconcentration of environmental water samples, such as high extraction capacity, rapid separation, easy elution of analytes, and simple and convenient procedures.

The aim of this work is to develop a simple and reliable SPE sample preconcentration method based on the formation of mixed hemimicelles on magnetic nanoparticles. To examine the feasibility of this approach, we selected three typical phenolic environmental estrogens—bisphenol A (BPA), 4-*tert*-octylphenol (4-OP), and 4-*n*-nonylphenol (4-NP)—as model compounds. Coupling this novel SPE technique with high-performance liquid chromatography separation and fluorescence detection, a highly selective SPE-HPLC-FLD analytical method was established. The reliability of this method was proven by the extraction and analysis of the three target compounds in environmental water samples. To our knowledge, this is the first report of using magnetic nanoparticles and mixed-hemimicelles-based SPE for the preconcentration of organic compounds from large-volume environmental water.

Experimental Section

Chemicals and Materials. All reagents were of analytical reagent grade and were used as supplied. 4-*tert*-Octylphenol (4-OP) and 4-*n*-nonylphenol (4-NP) were obtained from Tokyo Kasei Kogyo Co., LTD, Japan. Bisphenol A (BPA) and *N*-phenyl-naphthylamine (PN) were obtained from Acros Organics, NJ, USA. Ferric chloride (FeCl₃·6H₂O) and ferrous chloride (FeCl₂·4H₂O) were purchased from Beijing Chemicals Corporation (Beijing, China). Cetyltrimethylammonium bromide (CTAB) and cetylpyridinium chloride (CPC) were obtained from Shanghai Reagent Corporation (Shanghai, China). HPLC-grade acetonitrile and methanol were obtained from Merck (Darmstadt, Germany). Water used in all of the experiments was prepared using a compact ultrapure water system from Barnstead (Dubuque, IA, USA).

Preparation of Magnetic Nanoparticles. Fe₃O₄ NPs were prepared by the coprecipitation method (29). First, 5.2 g of FeCl₃·6H₂O, 2.0 g of FeCl₂·4H₂O, and 0.85 mL of HCl (12 mol/L) were dissolved in 25 mL of deionzed water that was degassed with nitrogen gas before use. Then, the resulting solution was added dropwise into 250 mL of 1.5 mol/L NaOH solution under vigorous stirring and nitrogen gas protection. After the reaction, the obtained precipitate was separated from the reaction medium by magnetic field, washed with 200 mL of deionzed water five times, and then resuspended in 220 mL of deionzed water. The concentration of the generated nanoparticle suspension was estimated to be about 10 mg/mL.

SPE Procedure. The SPE procedure using Fe₃O₄ NPs allowed rapid separation by a simple magnetic extraction method. First, 10 mL of Fe₃O₄ NPs solution (10 mg/mL) and a 5 mL solution containing CTAB (10 mg/mL) were added
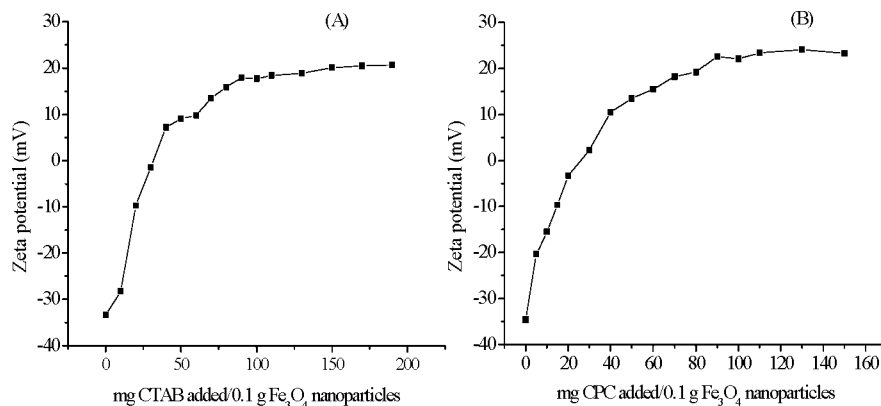
FIGURE 3. ζ-Potential of Fe_3O_4 NPs by adsorption of CTAB (A) and CPC (B) at pH 9.5.
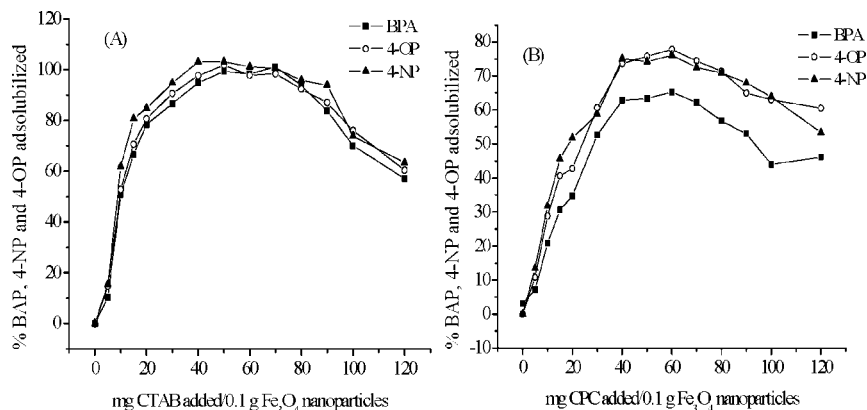

FIGURE 4. Effect of the amount of (A) CTAB and (B) CPC on the adsolubilization of BPA, 4-OP, and 4-NP. Operation in the batch mode. Amount of metal oxide: 0.1 g of Fe_3O_4NPs. pH: (A) 9.5 and (B) 9.0. Sample volume: 800 mL. Volume of acetonitrile: 6 mL. Concentration of each analyte: 2 ng/mL.

TABLE 1. Results of the Determination and Recoveries of Real Water Samples Spiked with Three Target Analytes

| water sample	spiked[a] (ng/mL)	detected (ng/mL)			recovery (%)[b]		
		BPA	4-OP	4-NP	BPA	4-OP	4-NP
tap water	0.00	nd[c]	nd	nd			
	0.50	0.488	0.479	0.492	97 ± 4	95 ± 6	98 ± 3
	2.00	1.970	1.949	1.806	99 ± 5	98 ± 4	90 ± 5
Jingmi canal river	0.00	nd	nd	nd			
	0.50	0.509	0.478	0.522	102 ± 5	96 ± 4	104 ± 6
	2.00	1.949	1.960	1.998	97 ± 5	98 ± 2	100 ± 3
groundwater	0.00	nd	nd	nd			
	0.50	0.510	0.455	0.451	102 ± 2	91 ± 7	90 ± 6
	2.00	1.954	1.856	1.781	97 ± 4	93 ± 5	89 ± 2
Xiaoqing river	0.00	0.124	nd	0.187			
	0.50	0.486	0.416	0.526	73 ± 6	83 ± 8	68 ± 6
	2.00	1.557	1.698	1.885	72 ± 3	85 ± 5	85 ± 2
Gaobeidian effluent	0.00	nd	nd	0.153			
	0.50	0.338	0.362	0.534	68 ± 4	72 ± 6	76 ± 3
	2.00	1.567	1.410	1.766	78 ± 2	70 ± 5	81 ± 7

[a] Mean of three determinations. [b] Standard deviation for three determinations. [c] Not detected.

into the 800 mL filtered water sample, the pH was adjusted to 9.5 with 1 M NaOH, and the mixture was sonicated for 5 min and placed for 30 min. Subsequently, an Nd-Fe-B strong magnet (150 × 130 × 50 mm) was deposited at the bottom of the beaker, and the CTAB-coated Fe_3O_4NPs were isolated from the solution. After about 5 min, the solution became limpid and was decanted. Finally, the preconcentrated target analytes were eluted from the isolated particles with acetonitrile. The eluate was dried with a stream of nitrogen at 60 °C and dissolved in 1 mL of methanol, and 20 μL of this solution was injected into the HPLC system for analysis. Illustration of the whole pretreatment procedure can be

followed in Figure 1. Detailed information on the optimization of the pretreatment method and the analysis method is provided in Supporting Information.

Results and Discussion

Magnetic Property of Fe_3O_4NPs. To enable practical application of MCT, it is most important that the sorbents should possess superparamagnetic properties. Figure 2 shows the hysteresis loops of Fe_3O_4 NPs and CTAB-coated Fe_3O_4 NPs at room temperature. Both the Fe_3O_4 NPs and CTAB-coated Fe_3O_4 NPs exhibited typical superparamagnetic behavior due to no hysteresis. The remanence and coercivity are zero,
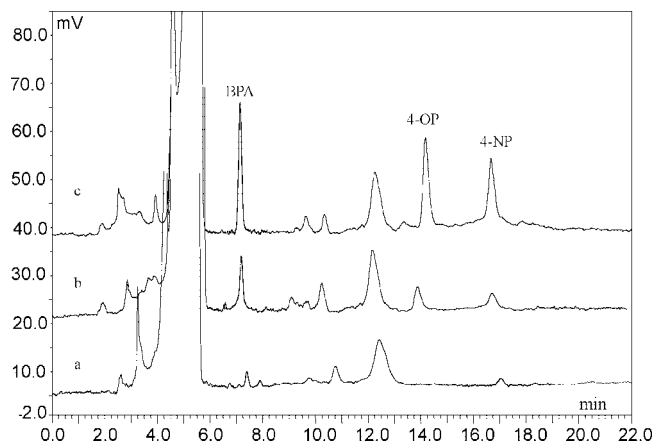
FIGURE 5. Solid-phase extraction/LC-FLD chromatograms: (a) Xiaoqing river water sample, (b) Xiaoqing river water sample spiked with 0.50 ng/mL of each compound, and (c) Xiaoqing river water sample spiked with 2.00 ng/mL of each compound. Volume of water sample solution: 800 mL; volume of eluent: acetonitrile, 6 mL.

illustrating that the particles respond magnetically to an external magnetic field, and redisperse rapidly when the magnetic field is removed. Another key parameter is the large saturation magnetization, which is a measure of the maximum magnetic strength (*30*). The large saturation magnetization is 58.7 emu/g for CTAB-coated Fe_3O_4 NPs; and compared with Fe_3O_4 NPs (63.2 emu/g), no significant difference can be distinguished. Their large saturation magnetization makes them very susceptible to magnetic fields, and solid and liquid phases separate easily. Therefore, the superparamagnetic properties were not significantly changed when the surfactants formed mixed hemimicelles on Fe_3O_4 NPs.

Spectroscopic Characteristics of CTAB-Coated Fe_3O_4 NPs. Spectroscopic evidence about CTAB or CPC mixed hemimicelles is available in the Supporting Information. FTIR spectroscopy and the emission spectrum have been employed to examine the surfaces and the solvent property of CTAB-coated Fe_3O_4 NPs, respectively.

ζ-Potential Isotherm. Knowledge of the adsorption isotherms of surfactants on mineral oxides is essential to knowing the regions where different aggregates form and to interpret the SPE of the target analytes (*31*). The ζ-potential isotherm is a useful tool for understanding the surface-charge characteristics and for optimizing the conditions of the SPE method. Figure 3 depicts the potential change of Fe_3O_4 NP suspensions by adsorptions of CTAB and CPC at pH 9.5. These isotherms are similar to those previously reported (*21*). Generally, the isotherms can be divided into three regions (hemimicelles, mixed hemimicelles, and admicelles) (*32*). In the first region (hemimicelles), the ζ-potential of Fe_3O_4 NPs at pH 9.5 (above the iep) is negative, and cationic surfactants are sparsely adsorbed onto the negatively charged Fe_3O_4 NP surface. The adsorption of surfactants is driven by both ionic surfactant–oxide electrostatic interactions and lateral hydrophobic interactions between the adsorbed surfactant monomers, which result in the formation of monolayers, hence the ζ-potential increases from negative to zero. In the second region (mixed hemimicelles), the hydrophobic interaction between hydrocarbon chains of surfactant molecules results in the formation of surfactant bilayers called admicelles. Herein, we must point out that the structure of the surfactant aggregates cannot purely be defined as a monolayer or bilayers; some studies have brought forward evidence of the formation of discrete surface aggregates (*32*). Because the outer surface of admicelles is positive, the ζ-potential increases from zero to positive. The amount of surfactants that should be added to the samples can be easily inferred from the corresponding ζ-potential isotherm. As shown in Figure 3, the ranges of 30–100 mg/0.1 g Fe_3O_4 NPs

for CTAB and 30–90 mg/0.1 g Fe_3O_4 NPs for CPC are mixed hemimicelles regions and available for SPE. At the end of the isotherm region, above the critical micellar concentrations (cmc), aqueous surfactant micelles are in equilibrium with admicelles, which causes a partition of analytes between both types of surfactant aggregates and prevents this isotherm region span to be used for SPE (*31*). In this region, the ζ-potential of mineral oxide particles remained constant.

Effect of the Amount of Surfactant. The effect of the surfactant amount on the adsolubilization of target compounds was studied in batch mode. As can been seen from Figure 4, analytes were hardly absorbed on the surface of Fe_3O_4 NPs in the absence of CTAB or CPC. However, in the mixed hemimicelles region, with the increasing amount of CTAB (pH = 9.5) and CPC (pH = 9.0), the percentage of adsorbed analytes increased remarkably. Consistent with Figure 3, maximum adsorption of the three target compounds is dependent on the amount of adsorbed surfactants and the charge density of the mineral oxide surface in a wide interval (30–100 mg for CTAB and 30–80 mg for CPC/0.1 g Fe_3O_4 NPs). For both CTAB and CPC, when surfactant concentrations were above the cmc, the adsorption percentage of analytes decreased due to the formation of micelles in the bulk aqueous solution, which led to a redistribution of the analytes into the solution.

Figure 4A,B also describes the differences in the adsolubilization capability of CTAB and CPC in the mixed hemimicelles region, where retention of analytes was governed by both hydrophobic and electrostatic interactions. The maximal adsorption of the target compounds was above 95% for the CTAB-coated–Fe_3O_4 NP system (Figure 4A), whereas the maximal adsorption for BPA, 4-OP, and 4-NP were 65%, 77%, and 76%, respectively, for the CPC-coated–Fe_3O_4 NP system (Figure 4B).

According to the above results, both CTAB- and CPC-coated–Fe_3O_4 NP systems can successfully be used for the SPE of the target compounds. The CTAB-coated–Fe_3O_4 NP (50 mg of CTAB/0.1 g Fe_3O_4 NPs) system was selected because the maximum adsorption percentage of the three typical phenolic compounds was higher than that of the CPC-coated–Fe_3O_4 NP system.

Desorption Conditions. Desorption of analytes from the CTAB-coated–Fe_3O_4 NPs was studied using different kinds of organic solvents (acetonitrile, methanol), which were known to rapidly and completely disrupt the mixed hemimicelles. We found that the surfactants were fully desorbed along with target compounds from the surface of Fe_3O_4 NPs. However, the presence of CTAB did not interfere with the analysis of the phenolic compounds due to the adoption of the highly selective FLD determination method. Desorption

ability of acetonitrile was found to be superior to that of methanol. Quantitative recoveries of analytes were observed with 6 mL (2 mL every time and washed three times) of acetonitrile. A higher volume of methanol (8 mL, 2 mL every time and washed four times) was required for complete desorption of the analytes. In order to achieve better recoveries, Fe_3O_4 NPs were sonicated for 20 s in each desorption process. We also found that Fe_3O_4 NPs were oxidized and lost their magnetism quickly when pH was below 4.0. Furthermore, some amount of nanoparticles even dissolved under this condition. Thus, 6 mL of acetonitrile was selected for the desorption step.

Effect of Solution Volume. The effect of solution volume was examined by preconcentrating different volumes (50–1000 mL) of aqueous solutions spiked with a constant mass of 1.0 μg of each analytes at pH 9.5. As shown in Figure S9 (Supporting Information), in the optimized experiment conditions mentioned above, when aqueous solution volume was up to 800 mL for BPA and 1000 mL for 4-OP and 4-NP, recoveries above 95% were obtained for the three analytes. By enriching 800 mL of aqueous solutions, drying 6 mL of desorption solution with a nitrogen flow, and redissolving the analytes in 1 mL of acetonitrile, the preconcentration factor achieved for BPA, 4-OP, and 4-NP was 800.

Analysis of Environmental Water Samples. The performance of the method was tested by analyzing river water, groundwater, and wastewater samples. Table 1 lists the recoveries and concentrations found for the target compounds, expressed as the mean value ($n = 3$), and the relative standard deviation of recoveries ranged from 2 to 7%. Among the five real environmental water samples, the three phenolic compounds were not detected in tap water, Jingmi canal river water, and groundwater samples. Only a trace level of BPA and 4-NP were found in wastewater and Xiaoqing river water samples. The results also indicated that the recoveries for the tap water, canal river water, and groundwater were very satisfactory, and were better than those of Xiaoqing river water and Gaobeidian wastewater treatment plants samples, mainly because the latter were much "dirtier". Recoveries of BPA, 4-OP, and 4-NP ranged between 68 and 102%, 70 and 98%, and 76 and 104% for all five water samples. Chromatograms of the Xiaoqing River water sample and its spiked solution are shown in Figure 5. Furthermore, the effect of humic acid was investigated, and the results showed that the recovery of the analytes was not significantly affected (Supporting Information).

Compared to our previous work (*21*), the present method also exhibited a fairly good analytical performance. In the present method, only a small amount of mineral oxide sorbent (0.1 g) and surfactants (50 mg) were used to extract analytes from 800 mL aqueous solutions. All these facts suggested that Fe_3O_4 NPs have great potential for the rapid enrichment of a large volume of real environmental water samples.

In this research, we combine the advantages of mixed hemimicelles and magnetic nanoparticles and developed a rapid and reliable SPE method to enrich organic compounds from a large volume of environmental water samples. Compared to previous SPE methods, the attractive merits of this SPE method was 3-fold: (a) Magnetic separation is a particular SPE method that avoids the time-consuming column passing and filtration operation and shows great analytical potential in preconcentration of large-volume real water samples. (b) Nanoparticle sorbents have higher surface areas; therefore, satisfactory results can be achieved by using a lesser amount of nanoparticle sorbents than micron-size particle sorbents. (c) The nanoparticle sorbents are easy to synthesize and simple to regenerate, which can meet the need of rapid analysis. Several other potential advantages obtained with the use of mixed hemimicelles sorbents include high extraction yields, easy elution of the analytes, and high

breakthrough volume. This research also greatly extends the scope of application for nanoparticles and mixed-hemimicelles-based SPE.

Supporting Information Available
Sample collection and HPLC analysis operating conditions; characterization of CTAB-coated Fe_3O_4 NPs including morphology of the nanoparticles, isoelectric point, solvent property, and IR spectra of CTAB-coated Fe_3O_4 NPs; effect of solution pH and the amount of Fe_3O_4NPs; effect of humic acid and standing time; and detailed analytical parameters and performances. This material is available free of charge via the Internet at http://pubs.acs.org.

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