

# Preparation of silica-magnetite nanoparticle mixed hemimicelle sorbents for extraction of several typical phenolic compounds from environmental water samples

Xiaoli Zhao, Yali Shi, Thanh Wang, Yaqi Cai\*, Guibin Jiang

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

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## Abstract

A novel type of superparamagnetic silica-coated ( $\text{Fe}_3\text{O}_4/\text{SiO}_2$  core/shell) magnetite nanoparticle modified by surfactants has been successfully synthesized and was applied as an effective sorbent material for the pre-concentration of several typical phenolic compounds (bisphenol A (BPA), 4-*tert*-octylphenol (4-OP) and 4-*n*-nonylphenol (4-NP)) from environmental water samples. Compared with pure magnetic particles, a thin and dense silica layer would protect the iron oxide core from leaching out in acidic conditions. In order to enhance their adsorptive tendency towards organic compounds, cetylpyridinium chloride (CPC) or cetyltrimethylammonium bromide (CTAB) were added, which adsorbed on the surface of the  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  nanoparticles ( $\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs) and formed mixed hemimicelles. Main factors affecting the adsolubilization of analytes were optimized and comparative study on the use of CPC and CTAB-coated  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs mixed hemimicelles-based SPE was also carried out. CPC-coated  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs system was selected due to lower elution volume required and more effective adsorption of the target compounds. Under selected conditions, concentration factor of 1600 was achieved by using this method to extract 800 mL of different environmental water samples. The detection limits obtained for BPA, 4-OP and 4-NP with HPLC-FLD were 7, 14, and 20 ng/L, respectively.

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**Keywords:** Silica-coated magnetite nanoparticles; Mixed hemimicelles; Solid-phase extraction; Phenolic compounds

## 1. Introduction

Magnetic carrier technology (MCT), first reported by Robinson et al. in 1973 [1], has become an increasingly popular tool in bioseparations, environmental and material science [2–5]. A distinct advantage of this technology is that magnetic materials can be readily isolated from sample solutions by the application of an external magnetic field. Generally, most of the dissolved environmental contaminants are nonmagnetic, and thus do not respond to magnetic field. Magnetic nanoparticles possess large surface areas and have unique magnetic properties. Selective removal of toxic target compounds from complex environmental matrices can be obtained when certain special functional lig-

ands with affinities for target molecules are bound onto these magnetic nanoparticles. To meet this requirement, the magnetic nanoparticles should be superparamagnetic, characterized with strong magnetic susceptibility and do not exhibit hysteresis, remanence and coercivity. However, pure magnetic particles suffer from some inherent limitations as they are prone to form aggregates, and alter magnetic properties in complex environmental and biological system. We also found that pure  $\text{Fe}_3\text{O}_4$  NPs were oxidized and easily lost their magnetism when pH was below 4.0 [6]. The above inherent limitations of  $\text{Fe}_3\text{O}_4$  NPs led us to develop a new extraction method using magnetic nanoparticles with a suitable protective coating.

There have been intense interests recently in the fabrication of core-shell particles. Silica has been considered as one of the most ideal materials for protecting  $\text{Fe}_3\text{O}_4$  NPs due to its reliable chemical stability, biocompatibility and versatility in surface modification [7]. It is anticipated that incorporating silica coating on a magnetic core could attain the advantage of silica and without sacrificing the unique magnetization

\* Corresponding author at: Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P.O. Box 2871, Beijing 100085, China.  
Tel.: +86 10 62849239; fax: +86 10 62849182.

E-mail address: [caiyaqi@rcees.ac.cn](mailto:caiyaqi@rcees.ac.cn) (Y. Cai).

characteristics of  $\text{Fe}_3\text{O}_4$ . Specifically, the inner magnetic  $\text{Fe}_3\text{O}_4$  core endues the nanoparticles with magnetic properties, while the outer silica shell shows high chemical stability and biocompatibility. Numerous reports have described the formation of magnetite/silica composite nanoparticles [2,8–13]. Zhao et al. [8] reported the fabrication of magnetic mesoporous core-shell nanomaterial of spherical morphology. Kim et al. [10] synthesized magnetite nanocrystals embedded in mesoporous silica spheres. Giersig et al. [12] assembled silica-coated magnetite nanoparticles by using a layer by layer self-assembly technique. However, most of the research works focus on the preparation of silica-coated magnetite nanoparticles and there is a lack of reports about its application in the fields of environmental monitoring.

Herein, we reported the preparation of superparamagnetic silica and its potential application in the pre-concentration of contaminations from environmental water samples. A thin and dense silica layer with a desired thickness was deposited on the surface of magnetic particles in order to protect the iron oxide core from leaching into the mother system under acidic conditions. Compared with nonmagnetic nanoparticles, the silica-magnetite nanoparticles can meet the need of rapid extraction of large volume samples by employing a strong external magnetic field.

Solid-phase extraction (SPE) is a routine extraction method for determining trace level contaminants in environmental samples. Recently, hemimicelles and admicelles, which are formed by the adsorption of ionic surfactants on mineral oxides such as alumina, silica, titanium dioxide and ferric oxyhydroxides, have been used as new and excellent sorbents for the SPE of organic compounds [14–24]. Some of the benefits obtained with the use of mixed hemimicelle sorbents are high extraction yields, easy elution of analytes and high breakthrough volumes. However, the applications of hemimicelles and admicelles based SPE reported in literatures were mainly based on ionic surfactants adsorbed onto micron-size particles. Since the micron-size particles have comparatively small surface areas, they may lead to relatively low extraction efficiency and concentration factor. If one combines the advantages of mixed hemimicelles and magnetic-silica nanoparticles to fabricate nanosized SPE adsorbents with high surface area, high chemical stability and good magnetic separability, a new kind of mixed hemimicelle nanosized SPE sorbent can be obtained.

In the present work, we successfully synthesized silica-coated magnetite ( $\text{Fe}_3\text{O}_4/\text{SiO}_2$  core/shell) nanoparticles and modified them by coating surfactants to enhance their adsorptive tendency towards organic compounds. A simple and reliable SPE sample pre-concentration method, based on MCT and the formation of mixed hemimicelles on silica-coated magnetic nanoparticles, was established. 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. Predominant factors influencing the synthesis of silica-coated magnetite nanoparticles and the formation of mixed hemimicelles were investigated. To the best of our knowledge, this is the first report of using silica-coated magnetic nanoparticles mixed hemimicelles-based SPE for the

pre-concentration of organic compounds from large volume of environmental water samples.

## 2. Experimental

### 2.1. Apparatus and reagents

All reagents were of analytical reagent-grade and were used as supplied. 4-OP and 4-NP were obtained from Tokyo Kasei Kogyo Co. LTD, Japan. BPA was obtained from Acros Organics, NJ, USA. Standard stock solutions (1000  $\mu\text{g/mL}$ ) containing these compounds were prepared by dissolving an appropriate amount of these compounds in methanol and stored under dark conditions at 4 °C. Working solutions were prepared daily by diluting the stock solutions with deionized water. The cationic surfactants, cetyltrimethylammonium bromide (CTAB) and cetylpyridinium chloride (CPC), were supplied by Beijing Chemical Reagents Company (Beijing, China). LC-grade methanol and acetonitrile were purchased from Merck (Darmstadt, Germany). Ferrous chloride ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ), ferric chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) and sodium silicate ( $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ ) were purchased from Beijing Chemicals Corporation (Beijing, China). Ultrapure water was prepared in the lab using a Milli-Q Advantage A10 reagent water system from Millipore (Milford, MA, USA).

Zeta potential measurements of  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs were performed with a Zetasizer 2000 apparatus (Malvern, United Kingdom). Magnetic properties were analyzed using a vibrating sample magnetometer (VSM, LDJ9600).

### 2.2. Preparation of silica-coated magnetite nanoparticle

$\text{Fe}_3\text{O}_4$  nanoparticles were prepared by chemical coprecipitation method [25]. 5.2 g of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , 2.0 g of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  and 0.85 mL of HCl (12 mol/L) were dissolved in 25 mL of deionized water (degassed with nitrogen gas before use) to prepare a stock solution. 250 mL of 1.5 mol/L NaOH solution was heated to 80 °C in a beaker. The stock solution was added dropwise under nitrogen gas protection and vigorous stirring using nonmagnetic stirrer. After the reaction, the obtained  $\text{Fe}_3\text{O}_4$  NPs precipitate was separated from the reaction medium by magnetic field, and washed with 200 mL deionized water four times.

$\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs were synthesized according to previous reported methods [2,26,27] with a minor modification. 1 M sodium silicate was added dropwise into the  $\text{Fe}_3\text{O}_4$  NPs suspension and the pH value of the mixture was adjusted to 6.0 by addition of 2 M HCl within 2 h. The mixture was stirred for 3 h after the addition. During the whole process, temperature was maintained at 80 °C and nitrogen gas was used to prevent the intrusion of oxygen. The molar ratio of  $\text{Fe}_3\text{O}_4$  to  $\text{SiO}_2$  was 1:4. Finally, the formed  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs were then thoroughly washed with deionized water and resuspended in 240 mL deionized water. The concentration of the generated nanoparticles suspension was estimated to be about 20 mg/mL. The diameter of this particle was in the range of 5–60 nm and most of the  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs were quasi-spherical in shape.

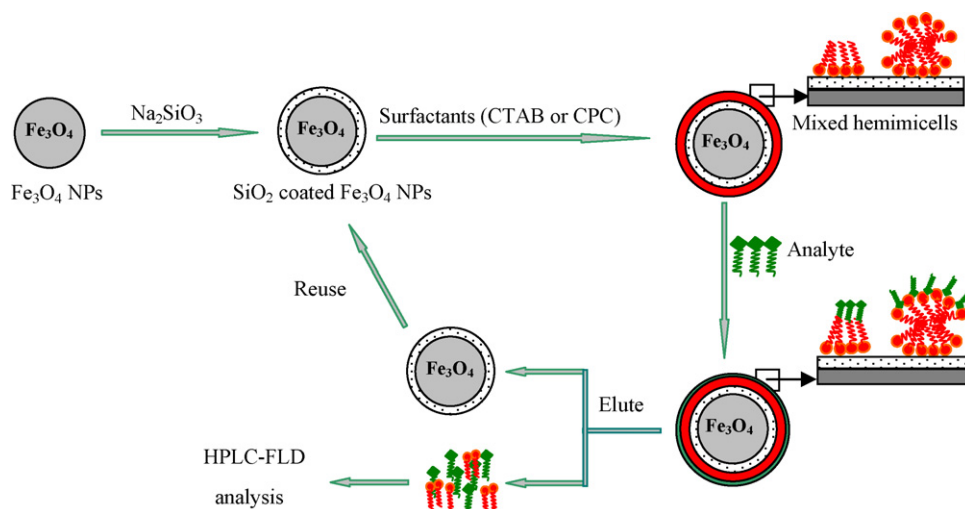


Fig. 1. Schematic illustration of the preparation of surfactants coated Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> NPs and its application for enrich analytes as SPE sorbents.

### 2.3. SPE procedure

The SPE procedure consists of three steps: firstly, 5 mL Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> NPs (20 mg/mL) and 5 mL CPC or CTAB solution (10 mg/mL) were added into 800 mL of filtered water sample and the pH was adjusted to about 7.0 with 1 M NaOH or HCl; secondly, to completely trap the target analytes, the mixture was placed in a beaker and allowed to equilibrate for 10 min. Furthermore, an Nd–Fe–B strong magnet (150 mm × 130 mm × 50 mm) was deposited at the bottom of the beaker and the surfactant coated Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> NPs were isolated from their suspension. After about 5 min, the suspension became limpid and was decanted. Finally, the preconcentrated target analytes were eluted from the isolated particles with acetonitrile (containing 1% acetic acid). The eluate was dried with a stream of nitrogen at 60 °C and dissolved in 0.5 mL acetonitrile, and 20 µL of this solution was injected into the HPLC system for analysis. Illustration of the whole procedure of the preparation of surfactants coated Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> NPs and its application as SPE sorbents for enriching analytes can be followed in Fig. 1.

### 2.4. Batch experiments

Following the similar SPE procedure, adsorption isotherms and predominant factor optimization were measured with batch experiments. 0.1 g Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> NPs were added to a series of 500 mL aqueous solutions. For zeta-potential experiments, the Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> NPs were added into  $1.0 \times 10^{-3}$  mol/L NaCl background electrolyte solution in the absence of target compounds. The Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> NPs were isolated by centrifugation, and the supernatant aqueous solution was used for the measurement of zeta potentials. To examine the effect of pH and obtain the isoelectric point (iep) for Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> NPs and native silica, the pH of the solution was adjusted with 1 M HCl and 1 M NaOH to designated values in the range of 1.8–10.0. For adsorption isotherm experiments; in the presence of BPA, 4-OP and 4-NP (2 µg/L), the Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> NPs were isolated by a magnet and the

amount of adsorbed analytes was determined using HPLC-FLD analysis.

### 2.5. Sample collection

All water samples were obtained from different districts of Beijing. Tap water samples were taken from our lab in Haidian District (Beijing), and a well water sample came from the campus of China Agricultural University. River water samples were collected from Jingmi Canal (Haidian District, Beijing) in July 2007. Influent domestic wastewater samples were collected from Gaobeidian wastewater treatment plants (Chaoyang District, Beijing). All samples were collected randomly and filtered through 0.22 µm nylon membranes (Shanghai Institute of Pharmaceutical Industry, China) before use in order to remove suspended solids. The filtered water samples were stored at 4 °C until analysis.

### 2.6. HPLC analysis and characterization

The three phenol compounds were separated and quantified by using a liquid chromatography-spectrophotometry system. The used HPLC equipment includes two DIONEX P680 HPLC pumps, an on-line connected degasser Solvent Rack SOR-100, a thermostated column compartment TCC-100, and a DIONEX RF 2000 fluorescence detector (FLD). A Diamonsil® C<sub>18</sub> column (250 mm × 4.6 mm; particle size, 5 µm) (Dikma Technologies, Beijing, China) was used as a separation column. Gradient separations for BPA, 4-OP and 4-NP were carried out using acetonitrile and acetonitrile–water (60:40, v/v) as the A and B solvents, respectively. The percentage of acetonitrile varied during the chromatographic run to give the following values at the specified times: 0% A at 0–3 min, linear gradient from 0–100% A in 12 min, keep 100% A at 15–17 min, and then linear gradient from 100–0% A in 3 min, keep for 2 min to equilibrate the column. The injection volume was 20 µL and the flow-rate was set at 1 mL/min. The fluorescence detector settings were as follows: 220 nm excitation and 315 nm emission.

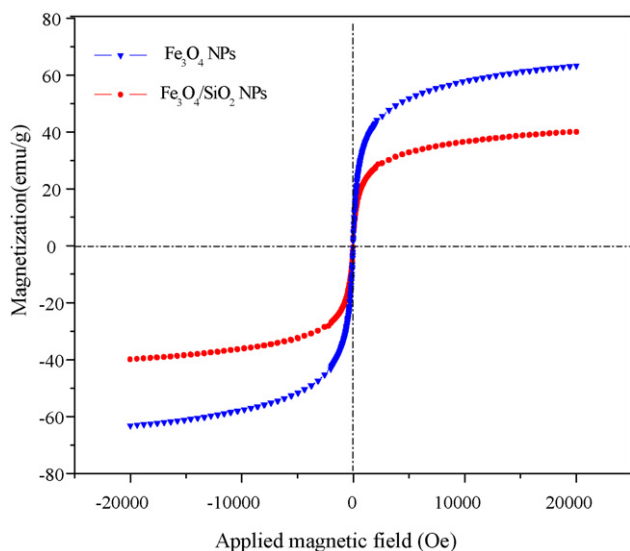


Fig. 2. VSM magnetization curves of  $\text{Fe}_3\text{O}_4$  NPs and  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs.

### 3. Results and discussion

#### 3.1. Characterization of $\text{Fe}_3\text{O}_4$ nanoparticles

##### 3.1.1. Magnetic properties

It is most important that the core/shell material should possess sufficient magnetic and superparamagnetism property for MCT practical application. Fig. 2 shows VSM magnetization curves of  $\text{Fe}_3\text{O}_4$  NPs and  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs at room temperature. Both of the magnetic nanoparticles without and with a coating of  $\text{SiO}_2$  exhibited typical superparamagnetic behavior due to not exhibiting hysteresis, remanence and coercivity. It is believed that the large saturation magnetization is a measure of the maximum magnetic strength [5]. The  $\text{SiO}_2$  shell results in the decrease in the magnetic strength of the core/shell nanoparticles due to the weight contribution from the non-magnetic  $\text{SiO}_2$ . The large saturation magnetization of  $\text{Fe}_3\text{O}_4$  NPs and  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs were 63.2 and 39.9 emu/g, which is sufficient for magnetic separation with a conventional magnet.

##### 3.1.2. Isoelectric point (iep)

The  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs were characterized by measuring the electrokinetics (more specifically, the zeta-potential) of the particles in aqueous solutions [2]. The iep for  $\text{Fe}_3\text{O}_4$  NPs and natural  $\text{SiO}_2$  were found to be at pH 6.5 and 3.0 (Fig. 3), which was consistent with the reported value [28,29]. In this case, the zeta-potential that responds to the suspension pH of the silica-coated magnetic nanoparticles approached to that of native silica. This finding confirmed that  $\text{Fe}_3\text{O}_4$  NPs was fully covered by silica which made the coated surface silica-like. To further confirm that the magnetite particles were indeed protected by silica coating, the coated particles were immersed in a 1 M hydrochloric acid solution. After 3 days immersion, only negligible amount of iron was leached out, indicating that a densely packed, robust silica layer was indeed formed.

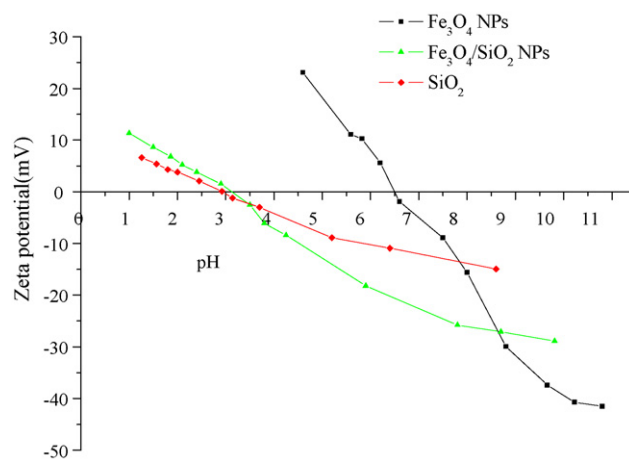


Fig. 3. Zeta-potential of  $\text{Fe}_3\text{O}_4$  NPs,  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs and native silica.

#### 3.2. Mixed hemimicelles-based SPE

##### 3.2.1. Zeta-potential Isotherm

The adsorption of surfactants can be demonstrated by the help of zeta potential isotherm. Specifically, the types of surfactant aggregates and the amount of surfactants that should be added to the samples can be easily inferred from the corresponding zeta-potential isotherm. The adsorption of surfactant on the surface of mineral oxides can be divided into three regions (hemimicelles, mixed hemimicelles, and admicelles). Consistent with three types of surfactant aggregates, the isotherms can be divided into three regions (Fig. 4). In the first region, the zeta potential of mineral oxides changed from negative to zero due to the fact that hemimicelles were gradually formed on the mineral oxide surfaces. Upon increasing the cationic surfactant concentration, admicelles were formed dominantly on the surface and the zeta-potential increases from zero to positive. When the concentration of CPC or CTAB was above critical micellar concentrations (CMC), aqueous surfactant micelles were in equilibrium with admicelles and the zeta potential of mineral oxide particles remained constant. However, the structure of the surfactant aggregates cannot be purely defined as monolayers (hemimicelles) or bilayers (admicelles); some studies have brought forward evidences of the formation of discrete surface aggregates [24].

##### 3.2.2. Effect of the amount of surfactant

The outer surface of hemimicelles is hydrophobic whereas that of admicelles is ionic, which provides different mechanisms for retention of organic compounds and are both suitable for the SPE method. In mixed hemimicelles phase, both hemimicelles and admicelles are formed in the surface of mineral oxides and the adsorption is driven by both hydrophobic interactions and electrostatic attraction. Consistent with Fig. 4, the ranges of 10–10 mg/0.1 g  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs for CPC and 10–90 mg/0.1 g  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs for CTAB were mixed hemimicelle regions (Fig. 5) and available for SPE. In the absence of surfactants, the proportion of target compounds that were adsorbed was very low. With the increasing amount of CPC or CTAB, the ratio of



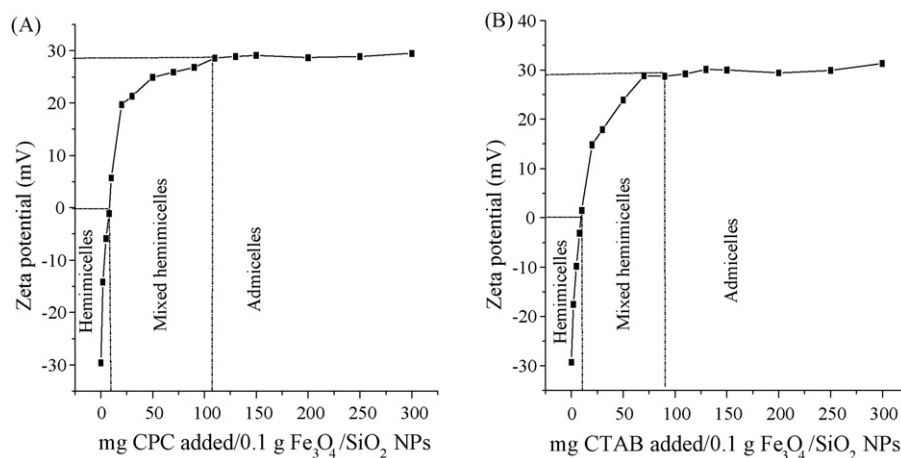


Fig. 4. Zeta-potential of  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs by adsorption of CPC (A) and CTAB (B) at pH 7.0.

adsorbed of BPA, 4-OP and 4-NP increased remarkably, while when surfactant concentrations were above CMC, the adsorption of analytes decreased gradually.

As can be seen from Fig. 5A and B, both CPC coated  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs system and CTAB coated  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs system can be successfully used for the SPE of BPA, 4-OP and 4-NP. In both systems, the retention of BPA was slightly lower due to lower hydrophobic properties compared to the other analytes, which indicated that strong hydrophobic interactions are the main mechanism for the adsolubilization of analytes.

The maximal adsorption of the target compounds obtained with the CPC coated  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs system (Fig. 5A) was slightly higher than that of CTAB coated  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs system (Fig. 5B). Furthermore, CPC was selected due to its higher solubility in polar solvent [17], which will facilitate analyte elution from the surface of  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs. Therefore, CPC coated  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs system was selected for further experiments.

### 3.2.3. Effect of the amount of nanoparticle sorbents

Compared to ordinary sorbents, nanoparticle sorbents have higher surface areas. Therefore, satisfactory results

can be achieved with fewer amounts of nanoparticle sorbents. The application of hemimicelles and admicelles based SPE method reported in literatures mainly use micron-size particle sorbents [15–23], which usually requires at least 0.5 g of sorbents. In this study, only 0.1 g  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs sorbents were enough for total adsolubilization of analytes in the optimal condition (Fig. 6). In the experiment process, the ratio of  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs and CPC added was kept constant (amount of CPC: $\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs = 1:2).

### 3.2.4. Effect of solution pH

The charge density of mineral oxide surface is a main factor affecting the adsolubilization of analytes and it varies strongly with pH. Thus, pH is a very important parameter for the adsorption of target compounds. In our previous work [6], we found that  $\text{Fe}_3\text{O}_4$  NPs were quickly oxidized when pH was below 4.0. In this study, a thin and dense silica layer prevented the  $\text{Fe}_3\text{O}_4$  from leaching into the mother system under acidic conditions; thus, this SPE method greatly extends the scope of application of magnetite nanoparticles.

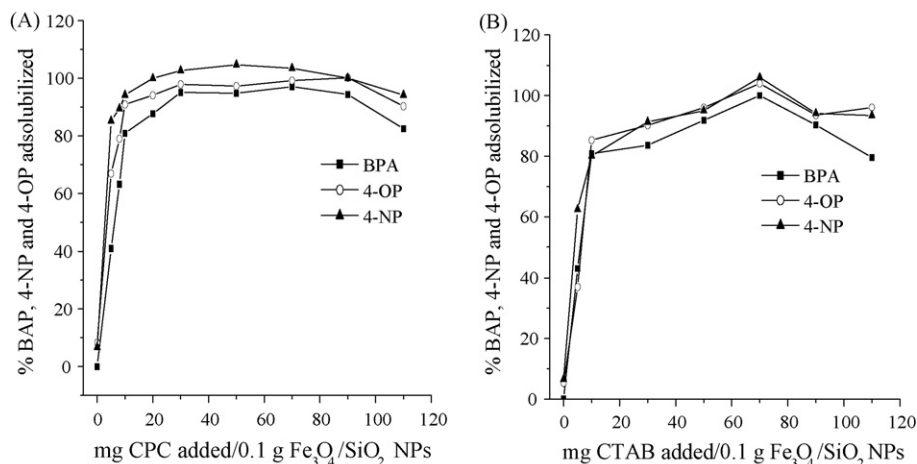


Fig. 5. Effect of the amount of (A) CPC and (B) CTAB on the adsolubilization of BPA, 4-OP and 4-NP. Performed in batch mode. Amount of mineral oxides: 0.1 g of  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs. pH: 7.0. Concentration of each analytes: 2 ng/mL.

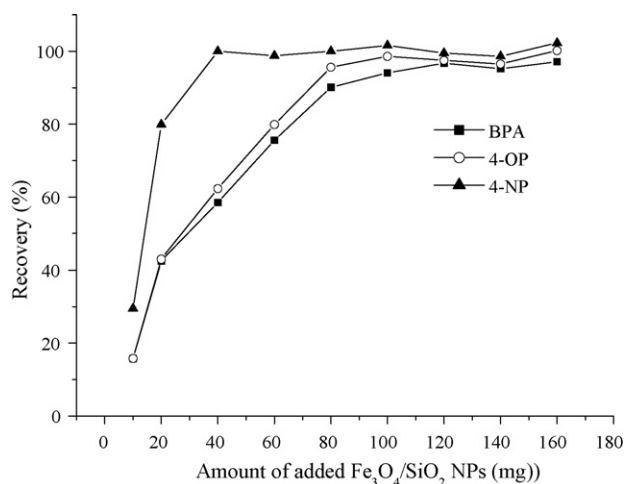


Fig. 6. Effect of the  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs amount on the adsolubilization of BPA, 4-OP and 4-NP. Performed in batch mode. pH: 7.0. Concentration of each analytes: 2 ng/mL.

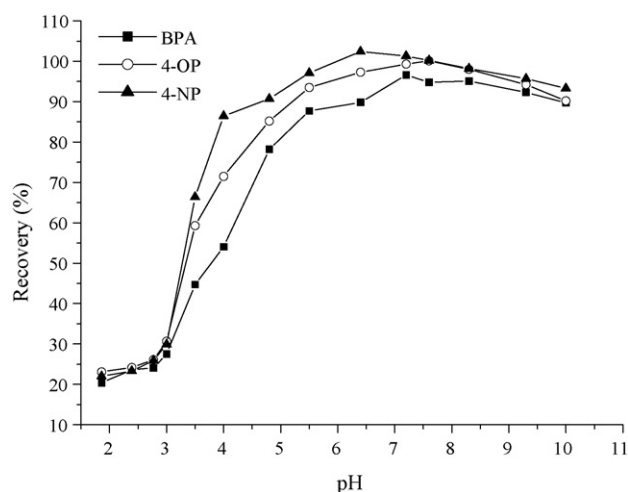


Fig. 7. Effect of pH on the adsorption of BPA, 4-OP and 4-NP onto mixed hemimicelles consisting of 50 mg CPC. Performed in batch mode. Concentration of each analytes: 2 ng/mL.

As can be seen from Fig. 7, the  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs do not exhibit any obvious adsorption of analytes when the pH value was between 1.8 and 3.0. With the increase in pH, the adsorption efficiency of the three analytes increased dramatically and reached maximum when the pH was above 6.5. This is mainly due to the fact that negative charges were favorable for the adsorption of cationic surfactants. When pH value was around its iep (the iep of  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs is about 3.3, Fig. 3) the charge density of  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs surface was very low. When the pH value was above iep, the  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs surface became negatively charged which gave rise to the strong electrostatic attraction between the CPC molecules and the charged  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs surface. We selected pH 7.0, at which a complete retention of BPA, 4-OP and 4-NP was observed, for further studies.

### 3.2.5. Standing and magnetic separating time

The use of  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs can meet the need of rapid analysis. As can be seen from Fig. 8, 10 min was sufficient to achieve

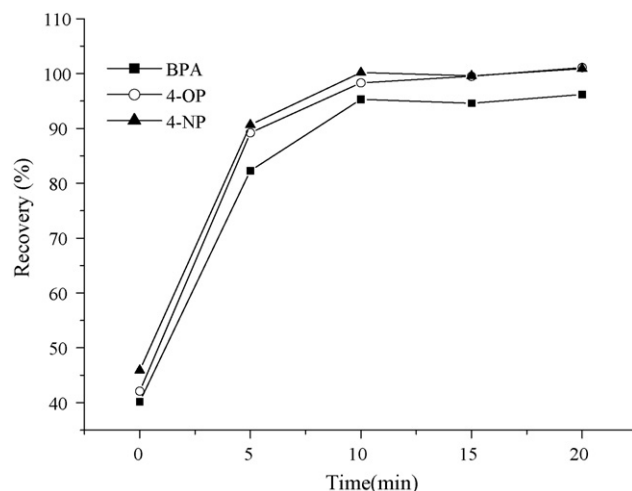


Fig. 8. Effect of standing time on the adsolubilization of BPA, 4-OP and 4-NP. Performed in batch mode. pH: 7.0. Amount of metal oxide: 0.1 g of  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs. Concentration of each analytes: 2 ng/mL.

complete adsorption. Recoveries of the three analytes were all above 98%.

In our experiments, CPC coated  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs possess superparamagnetism properties and large saturation magnetization (33.9 emu/g), which enables them to be completely isolated in a short amount of time (about 5 min) by a strong Nd–Fe–B magnet.

### 3.2.6. Desorption conditions

Organic solvents are known to disrupt mixed hemimicelles and were used to elute analytes from the CPC coated- $\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs. Desorption ability of acetonitrile containing 1% acetic acid was found to be superior to that without adding acetic acid. All analytes were quantitatively eluted from CPC mixed hemimicelles by using 3 mL of acetonitrile containing 1% acetic acid. This can be attributed to the fact that when the pH level was below or around its iep, charge density in  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs surface was weak and favorable for the disruption of mixed hemimicelles. Thus, 3 mL (1 mL every time and washed three times) acetonitrile (containing 1% acetic acid) was selected for desorption. In order to improve the recoveries,  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs were sonicated for 20 s during each desorption process.

### 3.2.7. Effect of solution volume

$\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs mixed hemimicelles SPE method based on MCT avoids the time-consuming column passing and filtration steps and shows great analytical potential in pre-concentration large volume water samples. The effect of sample volumes on the enrichment of the analytes is shown in Fig. 9. Under the optimal conditions selected above, the recoveries for the three analytes were still above 95% with sample volumes up to 800 mL.

### 3.3. Analytical performance

Calibration curves were run for three phenolic compounds in the range of 0.1–30 ng/mL (correlation coefficient  $r^2 > 0.999$ ). In this experiment, by enriching 800 mL aqueous solutions,

Table 1  
Analytical parameters of the proposed method

Analytes	Linearity range (ng mL <sup>-1</sup> )	Calibration equations	Correlation coefficient ( $r^2$ )	Detection limit <sup>a</sup> (ng L <sup>-1</sup> )
BPA	0.1–30	$y = 2.285x - 0.682$	0.9994	7
4-OP	0.1–30	$y = 1.406x - 0.250$	0.9997	14
4-NP	0.1–30	$y = 0.655x - 0.023$	0.9998	20

<sup>a</sup> The detection limits were calculated by using  $S/N = 3$ .

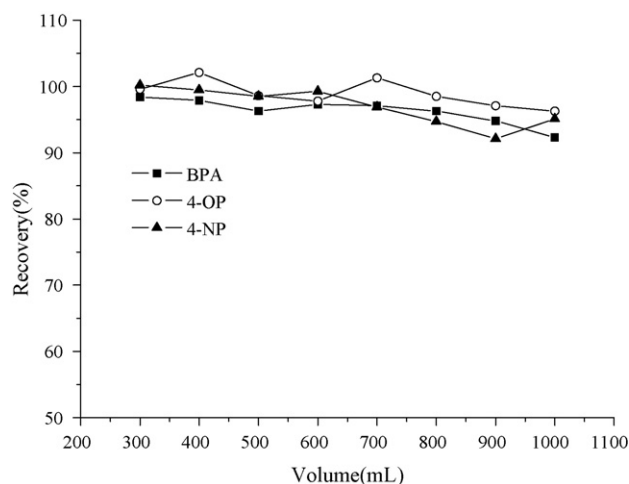


Fig. 9. Effect of volume of water sample solution on the adsorption of BPA, 4-OP and 4-NP. Performed in batch mode. pH: 7.0. Amount of metal oxide: 0.1 g of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> NPs (M3).

drying 3 mL desorption solution with a nitrogen flow and redissolving the target compounds into 0.5 mL acetonitrile, the pre-concentration factors achieved for BPA, 4-OP and 4-NP were 1600. With the overall SPE procedure and HPLC-FLD analysis method mentioned above, quantitative parameters such as linear range, correlation coefficient, detection limit were evaluated and the results were shown in Table 1. It can be seen that the present method has high sensitivity, wide linear range and good method precision. The limits

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

Water sample	Spiked <sup>a</sup> (ng/mL)	Detected (ng/mL)			Recovery (%) <sup>b</sup>		
		BPA	4-OP	4-NP	BPA	4-OP	4-NP
Tap water	0.00	nd <sup>c</sup>	nd	nd			
	0.20	0.192	0.188	0.194	96 ± 5	94 ± 3	97 ± 2
	0.50	0.477	0.496	0.511	96 ± 3	99 ± 1	102 ± 4
Ground water	0.00	nd	nd	nd			
	0.20	0.201	0.191	0.183	100 ± 4	96 ± 3	92 ± 5
	0.50	0.530	0.507	0.491	106 ± 4	102 ± 5	98 ± 2
Jingmi canal river	0.00	0.074	0.109	nd			
	0.20	0.246	0.277	0.157	86 ± 6	84 ± 3	79 ± 5
	0.50	0.530	0.544	0.473	91 ± 3	87 ± 2	95 ± 5
Gaobeidian wastewater	0.00	0.139	0.154	0.197			
	0.20	0.270	0.322	0.351	66 ± 5	84 ± 6	77 ± 5
	0.50	0.555	0.630	0.640	83 ± 2	90 ± 5	88 ± 3

<sup>a</sup> Mean of three determinations.

<sup>b</sup> Standard deviation for three determinations.

<sup>c</sup> Not detected.

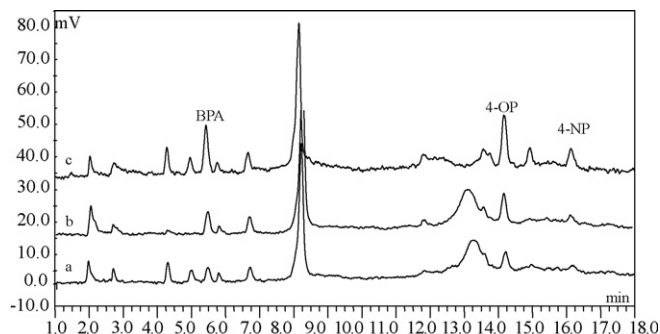


Fig. 10. Solid-phase extraction/LC-FLD chromatograms. (a) Gaobeidian wastewater sample, (b) Gaobeidian wastewater sample spiked with 0.20 ng/mL of each compound, and (c) Gaobeidian wastewater sample spiked with 0.50 ng/mL of each compound. Volume of water sample solution: 800 mL; volume of eluent: acetonitrile, 3 mL.

of detection were calculated by using signal-to-noise ratio of 3.

### 3.4. Analysis of environmental water samples

In order to validate the suitability of the developed method, it was applied to analyze the analytes in ground water and surface water samples. Low concentrations of the three phenolic compounds were found in Gaobeidian wastewater sample and trace levels of BPA and 4-NP were found in Jingmi canal river water. 800 mL of water samples spiked with 0.2 and 0.5 ng/mL of each analytes were extracted by the overall SPE procedure

mentioned above. Table 2 lists the recoveries and concentrations found for the target compounds, expressed as the mean value ( $n=3$ ). Recoveries of BPA, 4-OP and 4-NP ranged between 66–106%, 84–102% and 77–102% for the all four water samples and the relative standard deviation of recoveries ranged from 1 to 6%, demonstrating good method precision. Fig. 10 shows chromatograms for Gaobeidian wastewater samples and its spiked solution.

#### 4. Conclusions

In this research, superparamagnetic silica-coated magnetite ( $\text{Fe}_3\text{O}_4/\text{SiO}_2$  core/shell) nanoparticles have been successfully synthesized and modified by coating surfactants, and used for the pre-concentration of organic compounds from large volume of environmental water samples. Organic pollutants were entrapped on the surface of surfactants coated  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs and this SPE method were proved to be viable. Compared to traditional SPE method and our previous work [15], the favorable merits of this SPE method were 3-fold: (a) this material exhibits several desirable properties such as high chemical stability and dispersing ability. The synthesized particles were well protected by an inert silica coating, which greatly extends the scope of the application of magnetite nanoparticle based SPE methods. (b) The  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs possess the advantage of silica while without sacrificing magnetization characteristics of  $\text{Fe}_3\text{O}_4$  NPs. That is to say, the attributes of superparamagnetic properties and strong magnetization of the  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  NPs were favorable for MCT due to its unique superparamagnetic and strong magnetic properties. Furthermore, it avoids the time-consuming column passing and filtration operation and shows great analytical potential in pre-concentration large volume real water samples. (c) Satisfactory results can be achieved by using less amount nanoparticles sorbents than micron-size particle sorbents due to its higher surface areas. Furthermore, the presented SPE method combines the advantages of mixed hemimicelles and magnetic nanoparticles, which are expected to provide distinctive advantages such as high extraction yields, easy elution of analytes and high breakthrough volume.

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#### References

- [1] P.J. Robinson, P. Dunnill, M.D. Lilly, *Biotechnol. Bioeng.* 15 (1973) 603.
- [2] B.P. Wu, J.H. Zhu, Z.H. Xu, *Adv. Funct. Mater.* 14 (2004) 345.
- [3] T. Sen, A. Sebastianelli, L.J. Bruce, *J. Am. Chem. Soc.* 128 (2006) 7130.
- [4] D. Leun, A.K. Sengupta, *Environ. Sci. Technol.* 34 (2000) 3276.
- [5] C.J. Tan, Y.W. Tong, *Anal. Chem.* 79 (2007) 299.
- [6] X.L. Zhao, Y.L. Shi, Y.Q. Cai, S.F. Mou, *Environ. Sci. Technol.* 42 (2008) 1201.
- [7] Z.C. Zhang, L.M. Zhang, L. Chen, L.G. Chen, Q.H. Wan, *Biotechnol. Prog.* 22 (2006) 514.
- [8] W. Zhao, J.L. Gu, L.X. Zhang, H.R. Chen, J.L. Shi, *J. Am. Chem. Soc.* 127 (2005) 8916.
- [9] C.L. Chiang, C.S. Sung, C.Y. Chen, *J. Magn. Magn. Mater.* 305 (2006) 483.
- [10] J. Kim, J.E. Lee, J. Lee, J.H. Yu, B.C. Kim, K. An, Y. Hwang, C.H. Shin, J.G. Park, J. Kim, T. Hyeon, *J. Am. Chem. Soc.* 128 (2006) 688.
- [11] H.H. Yang, S.Q. Zhang, X.L. Chen, Z.X. Zhuang, J.G. Xu, X.R. Wang, *Anal. Chem.* 76 (2004) 1316.
- [12] M.A. Giersig, N.A. Kotov, L.M. Liz-Marzan, *Langmuir* 14 (1998) 6430.
- [13] Y.A. Barnakov, M.H. Yu, Z. Rosenzweig, *Langmuir* 21 (2005) 7524.
- [14] T.M. Holsen, E.R. Taylor, Y.C. Seo, P.R. Anderson, *Environ. Sci. Technol.* 25 (1991) 1585.
- [15] X.L. Zhao, J.D. Li, Y.L. Shi, Y.Q. Cai, S.F. Mou, G.B. Jiang, *J. Chromatogr. A* 1154 (2007) 52.
- [16] J.D. Li, Y.Q. Cai, Y.L. Shi, S.F. Mou, G.B. Jiang, *J. Chromatogr. A* 1139 (2007) 178.
- [17] L. Lunar, S. Rubio, D. Pérez-Bendito, *Analyst* 131 (2006) 835.
- [18] T. Saitoh, Y. Nakayama, M. Hiralde, *J. Chromatogr. A* 972 (2002) 205.
- [19] F. Merino, S. Rubio, D. Pérez-Bendito, *Anal. Chem.* 76 (2004) 3878.
- [20] M. Cantero, S. Rubio, D. Pérez-Bendito, *J. Chromatogr. A* 1067 (2005) 161.
- [21] M. Cantero, S. Rubio, D. Pérez-Bendito, *J. Chromatogr. A* 1046 (2004) 147.
- [22] F. Merino, S. Rubio, D. Pérez-Bendito, *Anal. Chem.* 75 (2003) 6799.
- [23] N. Luque, F. Merino, S. Rubio, D. Pérez-Bendito, *J. Chromatogr. A* 1094 (2005) 17.
- [24] R. Atkin, V.S.J. Craig, E.J. Wauless, S. Biggs, *Adv. Colloid Interface Sci.* 103 (2003) 219.
- [25] Z.F. Wang, H.S. Guo, Y.L. Yu, N.Y. He, *J. Magn. Magn. Mater.* 302 (2006) 397.
- [26] Z.Y. Lu, G. Wang, J.Q. Zhuang, W.S. Yang, *Colloids Surf. A: Physicochem. Eng. Aspects* 278 (2006) 140.
- [27] Z.Y. Ma, Y.P. Guan, H.Z. Liu, *J. Magn. Magn. Mater.* 301 (2006) 469.
- [28] Q. Wang, J.S. Jiang, Z.F. Gan, *Chem. Bull.* 3 (2006) 52.
- [29] A. Moral, M.D. Sicilia, S. Rubio, D. Pérez-Bendito, *J. Chromatogr. A* 1100 (2005) 8.