



Preparation of Fe₃O₄@C@PANI magnetic microspheres for the extraction and analysis of phenolic compounds in water samples by gas chromatography–mass spectrometry

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ABSTRACT

In this work, core–shell structure Fe₃O₄@C@polyaniline magnetic microspheres were synthesized using simple hydrothermal reactions. The carbon-coated magnetic microspheres (Fe₃O₄@C) were first synthesized by a hydrothermal reaction, and then aniline was polymerized on the magnetic core via another hydrothermal reaction. Then, the obtained Fe₃O₄@C@polyaniline magnetic microspheres were applied as magnetic adsorbents for the extraction of aromatic molecules due to π – π interactions between polyaniline shell and aromatic compounds. In our study, five kinds of phenols including phenol, 2,4-dichlorophenol (DCP), 2,4,5-trichlorophenol (TCP), pentachlorophenol (PCP) and bisphenol A (BPA) were selected as the model analytes to verify the extraction ability of Fe₃O₄@C@PANI microspheres. After derivatization, the phenols were detected using gas chromatography–mass spectrometry (GC–MS). The dominant parameters affecting enrichment efficiency were investigated and optimized. Under the optimal conditions, the proposed method was evaluated, and applied to the analysis of phenols in real water samples. The results demonstrated that our proposed method based on Fe₃O₄@C@polyaniline magnetic microspheres had good linearity ($r^2 > 0.991$), and limits of quantification (2.52–29.7 ng/mL), high repeatability (RSD < 13.1%) and good recovery (85.3–110.6%).

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1. Introduction

Nowadays, synthesis and application of functionalized magnetic particles have caused great interest [1,2]. The development and application of magnetic separation techniques have been as a hot topic. Magnetic materials are always synthesized based on a magnetic magnetite (Fe₃O₄) or maghemite (γ -Fe₂O₃) core, which are afterwards modified with different compounds to form various configurations [2,3], such as the conventional core–shell structure. Due to their magnetic properties, magnetic particles are easy to retrieve from matrices with a magnetic field, which makes sample pretreatment fast, simple, as well as highly effective. As a result of that, magnetic materials have been applied successfully and widely in sample pretreatment, especially in biochemistry at early period, such as cell image, drug delivery, and biomolecule detection [4–8]. Magnetic particles have turned to be used as the adsorbents in solid-phase extraction since 1999, when Safarikova and Safarik

reported the new separation method called magnetic solid-phase extraction [9].

As one of the most widely used magnetic particles, naked Fe₃O₄ particles have good solubility in water. However, they are easy to aggregate and cannot adsorb analytes effectively due to the simplicity of its surface. So they are usually modified with different functional groups to prevent aggregation and extend their application. These functional groups include silica, metal oxides, polymers and so on [10–14]. Our group has achieved much success in synthesis of core–shell structure Fe₃O₄@metal oxides and the application of the magnetic materials to bio-separation [15–19]. Recently, we successfully synthesized a new magnetic particle of Fe₃O₄@SiO₂@PMMA and applied to the enrichment of peptides and proteins [20]. Apart from extraction and separation of biomolecules, we have started to pay more attention on the extraction of small molecules from environmental matrices using functionalized magnetic materials [21].

Among these modified functional groups, conducting polymers are one of the most attractive compounds due to their versatile properties especially the electric conductivity [22–24]. Many synthetic methods about magnetic particles modified with dif-

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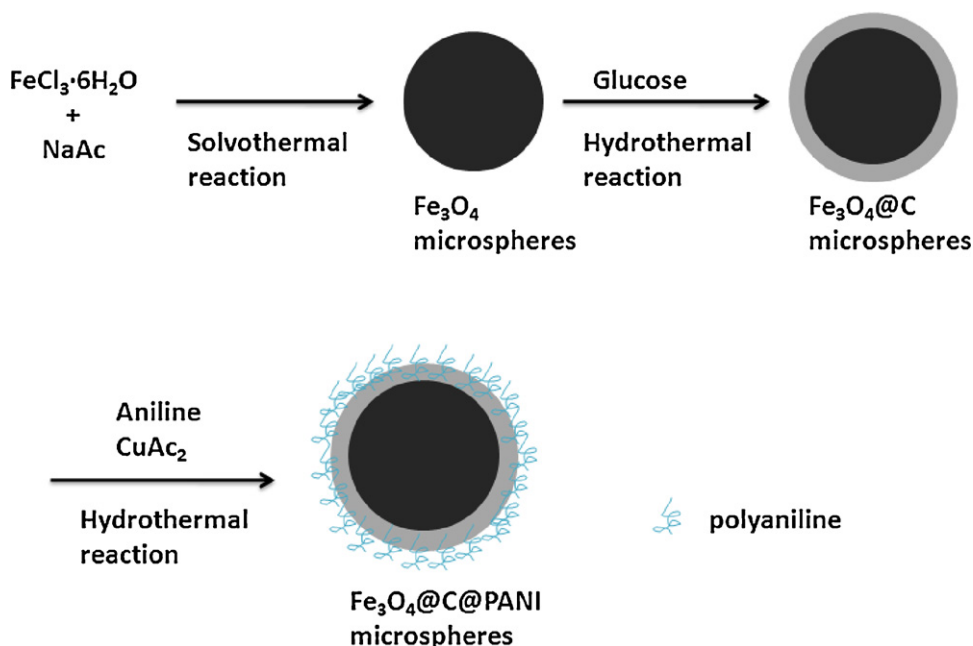


Fig. 1. Synthetic steps of Fe₃O₄@C@PANI microspheres.

ferent kinds of conducting polymers have been reported, such as polypyrrole, polystyrene and poly (N-isopropylacrylamide) [25–28]. Among these polymers, polyaniline (PANI) is studied most because it has advantages of hydrophilic, environmental stability and also oxidation- or protonation-adjustable electro-optical properties [29,30]. In addition, the large benzene ring system contributes to the remarkable interaction with aromatic compounds by π - π interaction [31]. Due to these superiorities, polyaniline has exceptional potentiality in solid-phase extraction from water sample. Up to now, many works have been published to synthesize polyaniline-coated magnetic particles. Wan et al. reported chemical polymerization method to synthesize polyaniline magnetic nanoparticles [32,33]. Deng et al. synthesized a core-shell structure of Fe₃O₄@PANI nanoparticles via in situ polymerization and dodecylbenzene sulfonic acid sodium (NaDS) was used as surfactants in the procedure [34]. Lu et al. introduced aniline dimer-COOH to assist the preparation of well dispersed Fe₃O₄@PANI nanoparticles [30,35]. However, these polymerization procedures were always tedious, and took very long time, which limited their real application in extraction and separation.

In this work, we developed a facile method to synthesize polyaniline-coated magnetic particles. First, according to our previous method [36], Fe₃O₄@C microspheres were synthesized by a hydrothermal reaction. Then aniline was polymerized on the Fe₃O₄@C microspheres to form a core-shell structure via another hydrothermal reaction. Finally, to demonstrate that Fe₃O₄@C@polyaniline magnetic microspheres have the extraction ability of aromatic compounds, five kinds of phenolic compounds were selected as the model analytes. Phenolic compounds are a kind of common environmental contaminants, among which bisphenol A is an important monomer in the production of polycarbonate plastics, and it can probably be found in environmental water sample [37]. Many other methods have been reported to detect phenolic compounds from water sample [38–42]. In this study, we selected five kinds of phenolic compounds as the model analytes, and the Fe₃O₄@C@PANI particles were successfully applied in the extraction and detection of phenolic compounds from real water sample, which showed that the Fe₃O₄@C@PANI microspheres have great application potential in the extraction of aromatic compounds from water systems.

2. Experimental

2.1. Chemicals and reagents

Phenolic compounds were purchased from Dr. Ehrenstorfer (Augsburg, Germany). Copper(II) acetate (CuAc₂) was from Alfa Aesar (Ward Hill, MA). Bis-(trimethylsilyl)-trifluoroacetamide (BSTFA) with 1% trimethyl chlorosilane (TMCS) was purchased from Fluka (Buchs, Switzerland). Deionized water was purified by a Milli-Q system (Milford, MA, USA). All other chemicals and reagents were the highest grade and commercially available. Phenolic stock solution was prepared by dissolving five phenols in methanol at a concentration of 10 μ g/mL and was stored at 4 °C for following usage.

2.2. Synthesis of Fe₃O₄ and Fe₃O₄@C

As the scheme of the synthesis approach shows (Fig. 1), Fe₃O₄ microspheres were first synthesized according to the previous method [36,43]. 1.35 g FeCl₃·6H₂O and 75 mL glycol were added in a dry beaker, and the solution was under stirring until it turned to be transparent. Then 3.6 g sodium acetate (NaAc) was added in the solution. After NaAc was dissolved totally, the mixture was transferred to an autoclave, ultrasonicated for 5 min, and then heated at 200 °C for 16 h. The obtained particles were washed with deionized water and ethanol for several times and dried at 50 °C for 24 h.

In the following step, 0.4 g Fe₃O₄ microspheres were treated by 0.1 M HNO₃ followed by ultrasonicated for 10 min, and washed with deionized water. Then, the microspheres were introduced in 80 mL glucose aqueous solution (0.5 M), and dispersed under ultrasonic for 5 min. Next, the mixture was transferred to an autoclave and heated at 180 °C for 6 h. When it was cooled to room temperature, the Fe₃O₄@C microspheres were isolated with a bar of magnet, and washed with deionized water and ethanol successively. Finally, the obtained microspheres were dried at 50 °C for the following work.

2.3. Synthesis of Fe₃O₄@C@PANI microspheres

The synthetic method of Fe₃O₄@C@PANI microspheres was conducted according to the previously reported method with some

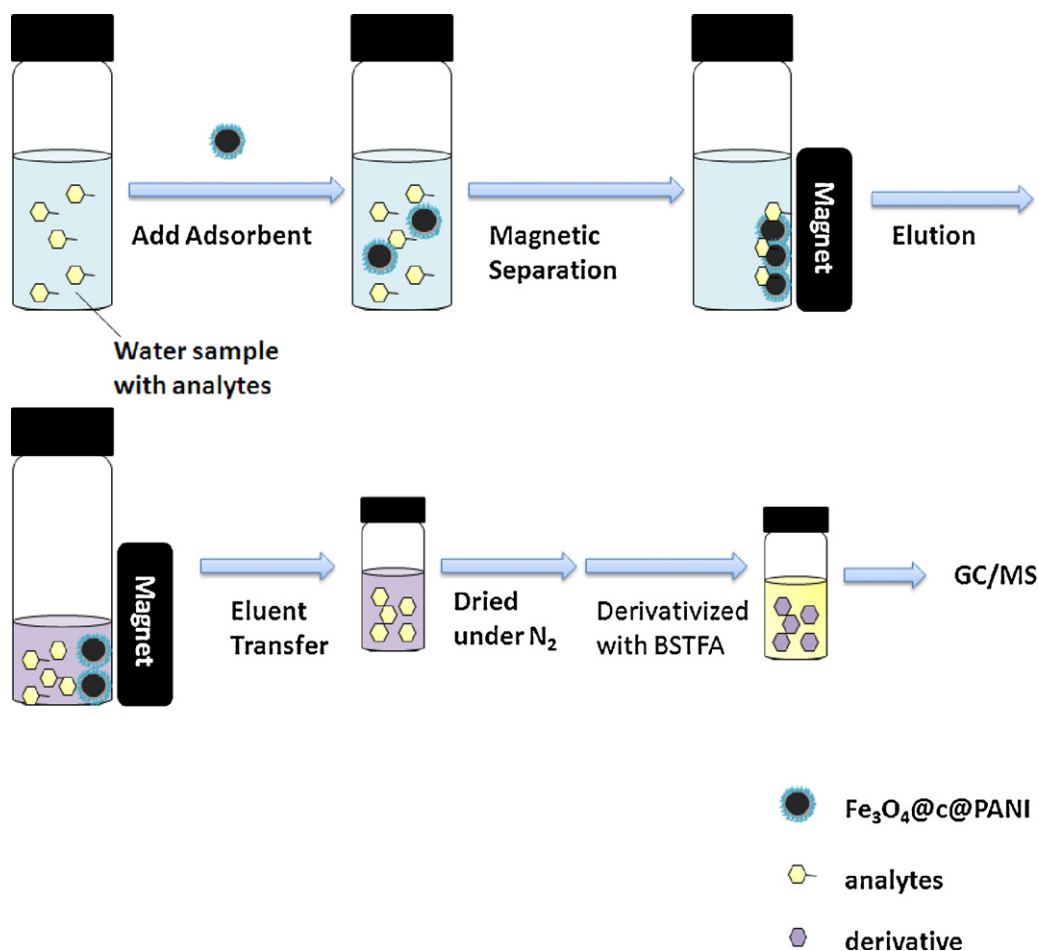


Fig. 2. Procedure of magnetic solid phase extraction of water sample.

modification [44]. In Tan's work [44], a template-free method was proposed to synthesize mono-dispersed polyaniline microspheres. We introduced this method with some modification and made the polymerization occurred on the surface of magnetic particles. The procedure was as follows: 0.2396 g CuAc_2 and 85.6 μL aniline were first dissolved in 16 mL and 64 mL deionized water, respectively (the deionized water needed to be bubbled with N_2 for at least 30 min in advance). Then both of the two solutions were transferred into an autoclave, and 50 mg $\text{Fe}_3\text{O}_4\text{@C}$ particles were added in at the same time. The mixture was then heated at 180 °C for 4 h. The obtained microspheres were washed with water and ethanol, and dried at 50 °C for 24 h.

2.4. Characterization of $\text{Fe}_3\text{O}_4\text{@C@PANI}$ particles

The size and structure of $\text{Fe}_3\text{O}_4\text{@C@PANI}$ microspheres were characterized by JEOL JSM-6500F scanning electron microscope (SEM) and JEOL JEM-2010 transmission electronic microscopy (TEM). Powder X-ray diffraction (XRD) patterns were conducted by Bruker D4 X-ray diffractometer with Ni-filtered Cu $\text{K}\alpha$ radiation (40 kV, 40 mA). The success of forming and coating of polyaniline was proved by Fourier-transform infrared (FT-IR) spectra, which were collected on a Nicolet Fourier spectrophotometer using KBr pellets (USA).

2.5. Gas chromatography–mass spectrometry instrumental

In this work, gas chromatography–mass spectrometry (GC–MS) was introduced to determine the analytes. The GC–MS instrument

was HP6890/5973, and the column was HP-5MS (30 m \times 250 μm , 0.25 μm). Helium (99.999%) was used as carrier gas with a flow rate of 1.0 mL/min. The temperature of injection was set to 250 °C, and 1 μL sample was injected at a splitless mode. The temperature programming was set as followings: the initial temperature was 60 °C, holding for 3 min; and it was heated up to 280 °C at a rate of 10 °C/min, holding for 5 min at the final temperature. All the analytes were detected in selected ion mode (SIM), and the characteristic ions for each analyte are shown in Table 1.

2.6. Procedure of magnetic solid phase extraction coupled with gas chromatography–mass spectrometry (MSPE–GC–MS)

In the proposed extraction procedure (Fig. 2), 40 mg $\text{Fe}_3\text{O}_4\text{@C@PANI}$ was used to extract the analytes from 10 mL spiked water samples at a concentration of 100 ng/mL. The extraction process lasted 20 min to ensure a large amount of analytes adsorbed on the solid phase, and then the magnetic adsorbents were attracted by a magnetic field to be removed from water. In order to elute the adsorbed analytes, 1 mL ethyl acetate was added

Table 1
The retention time and characteristic ion of the analytes.

Compound	Characteristic ion (m/z)	Retention time (min)
Phenol	151, 166	7.24
DCP	93, 219	10.66
TCP	217, 253	11.75
PCP	93, 323	14.70
BPA	357, 372	16.80

in the vial followed by an ultrasonic oscillation of 5 min. After elution, 400 μL solutions were taken out, introduced to a 4 mL vial and was dried under N_2 . Then the analytes were derivatized with 100 μL BSTFA by a microwave reaction under 300 W for 10 min. After that, 1 μL derivative was injected in GC–MS to analyze.

2.7. Sample collection and analysis

Tap water sample was collected from our laboratory and the waste water was collected from the river in Yangpu District, Shanghai, which were both stored at 4 $^\circ\text{C}$ and analyzed within one day. No special treatment was taken before analysis.

3. Results and discussion

3.1. Characterization of $\text{Fe}_3\text{O}_4@\text{C@PANI}$ microspheres

In this work, polyaniline-coated magnetic particles were synthesized by a facile hydrothermal method. In this approach, aniline was polymerized on magnetic $\text{Fe}_3\text{O}_4@\text{C}$ microspheres with the presence of small amount of CuAc_2 as an initiator, and the polymerization procedure only took 4 h via a hydrothermal reaction without any templates. So, unlike other synthetic method, this novel synthetic approach was very fast and simple. In the following work, characterizations of the synthesized $\text{Fe}_3\text{O}_4@\text{C@PANI}$ microspheres were carried out by electron microscopy, X-ray diffraction (XRD) and infrared spectra (IR).

The morphology of $\text{Fe}_3\text{O}_4@\text{C@PANI}$ microspheres was conducted by SEM and TEM images. The SEM image shown in Fig. 3a suggests that the particles formed a sphere-like shape with a rough surface. These microspheres appeared to be well-distributed with an average diameter of about 200 nm. From TEM image in Fig. 3b, it was found that a distinguished core-shell structure was formed. The light-colored layers of C and PANI were successful coated on the black core of magnetic Fe_3O_4 microspheres, and the thin coating layer had a thickness about 30 nm. The XRD patterns in Fig. 4 show that $\text{Fe}_3\text{O}_4@\text{C@PANI}$, $\text{Fe}_3\text{O}_4@\text{C}$ and Fe_3O_4 microspheres had similar locations of diffraction peak, which were in good agreement with the previous report [30], so that the synthesized $\text{Fe}_3\text{O}_4@\text{C}$ and $\text{Fe}_3\text{O}_4@\text{C@PANI}$ microspheres had same crystal structure as naked Fe_3O_4 particles.

In addition, the infrared spectra of Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{C}$ and $\text{Fe}_3\text{O}_4@\text{C@PANI}$ microspheres (Fig. 5) demonstrated the successful functionalization of forming and coating of polyaniline on the magnetic core. First, the most intense signal at 570 cm^{-1} was Fe–O stretching of Fe_3O_4 [45], and the bonds at 1700 and 1606 cm^{-1} illustrated the successful coating of carbon on magnetite. For the spectra of $\text{Fe}_3\text{O}_4@\text{C@PANI}$ the broad peak from 3400 cm^{-1} to 3500 cm^{-1} was observed as N–H stretching. Then, the bonds at 1592 cm^{-1} and 1488 cm^{-1} were assigned to quinoid ring and benzene ring, respectively. The bonds at 1296 cm^{-1} and 1387 cm^{-1} were related to C–N stretching absorptions and $-\text{CH}_3$ -substituted group, respectively [46,47]. What is more, the bands around 433 cm^{-1} were probably associated with the o-substituted aromatic rings [44]. Therefore, we considered that the magnetic cores were successfully coated by polyaniline.

3.2. Application of $\text{Fe}_3\text{O}_4@\text{C@PANI}$ microspheres to the extraction of phenolic compounds in water sample

The polyaniline coating of $\text{Fe}_3\text{O}_4@\text{C@PANI}$ microspheres has large conjugated systems of benzene rings, so it is easy to capture aromatic compounds due to π – π interaction. In this work, we selected five common phenolic contaminants (phenol, DCP, TCP, PCP and BPA) to verify the extraction ability of $\text{Fe}_3\text{O}_4@\text{C@PANI}$ microspheres. At first, the dominant extraction parameters were

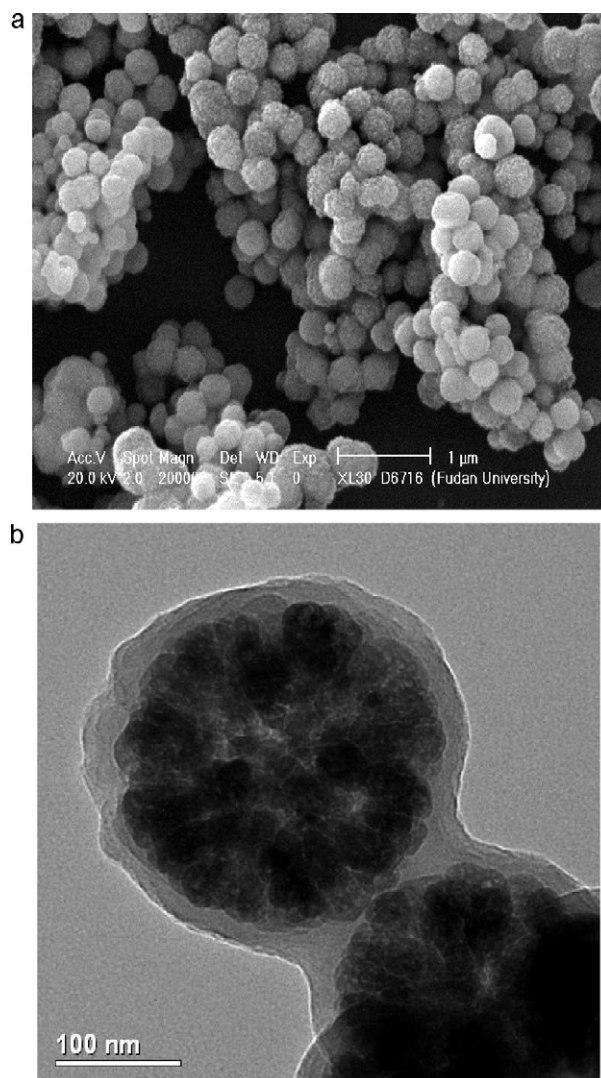


Fig. 3. SEM (a) and TEM (b) images of $\text{Fe}_3\text{O}_4@\text{C@PANI}$.

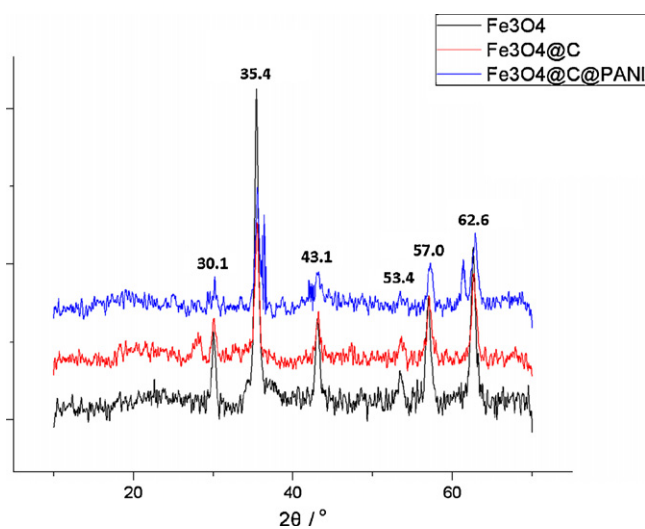


Fig. 4. XRD patterns of Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{C}$ and $\text{Fe}_3\text{O}_4@\text{C@PANI}$.

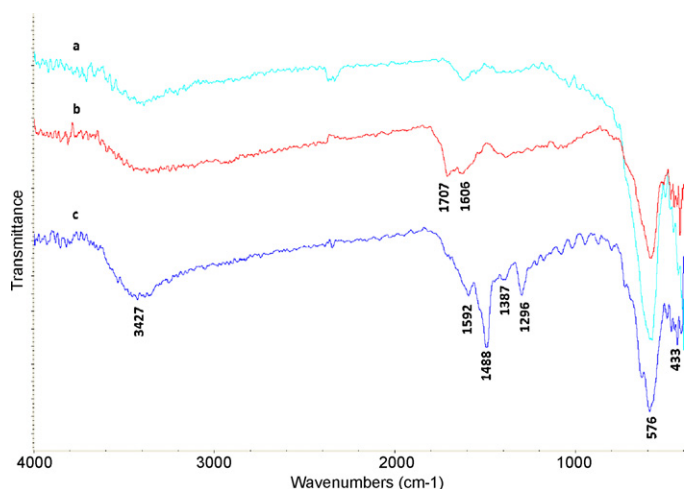


Fig. 5. The FTIR spectra of Fe₃O₄ (a), Fe₃O₄@C (b) and Fe₃O₄@C@PANI (c).

optimized, including organic solvent, amounts of adsorbents, extraction time and pH of water sample.

3.2.1. Organic solvent selection

Organic solvent is one of the most important factors which influenced the extraction procedure directly, and the extraction efficiency strongly relies on the different properties of eluents, so we worked first on the solvent selection. In this study, three kinds of organic solvents were chosen to compare their eluting efficiency, which were methanol, chloroform and ethyl acetate. As seen from Fig. 6, the experiment results show that the extraction efficiency changed a lot for different analytes and eluents. First, methanol had best eluting results of BPA obviously, but its eluting abilities of phenol, DCP and TCP were the least of all. In a similar way, chloroform also had lower eluting efficiency of both DCP and TCP, and it was even difficult to determine these two analytes when the concentration was lowered. It was very likely caused by the hydrophilic differences among analytes and eluents. Among these three solvents, methanol had the highest polarity, so it could elute more polar analytes, such as BPA, while for ethyl acetate, although it eluted less BPA than methanol, it eluted much more of phenol, DCP and TCP compared with methanol and chloroform, so that these analytes could be detected at a considerable lower concentration. Therefore, we sacrificed some efficiency benefit of BPA and selected ethyl acetate as eluent in the following work.

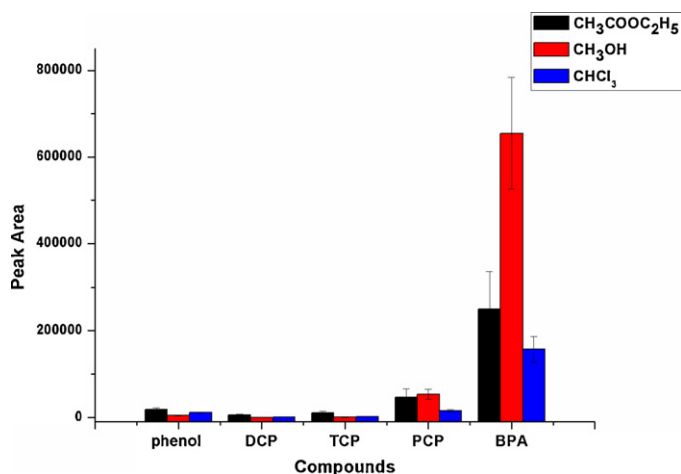


Fig. 6. Comparison of the eluting abilities of different organic solvent.

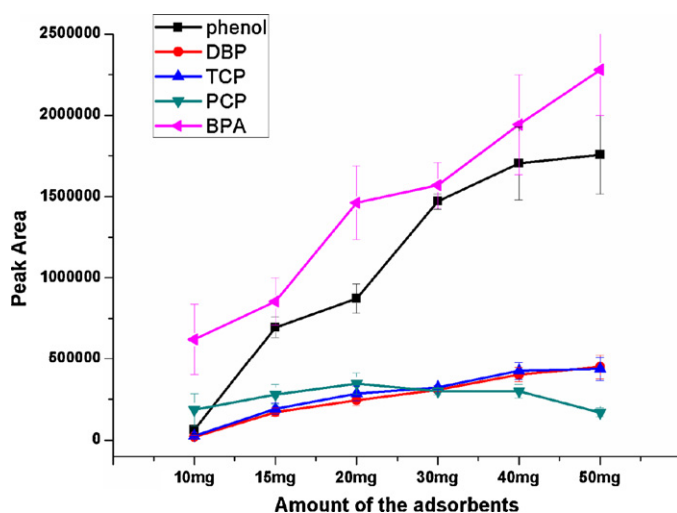


Fig. 7. The different effects on the extraction efficiency of different amounts of adsorbents.

3.2.2. Amounts of Fe₃O₄@C@PANI particles

The effect of the amounts of adsorbents on the extraction efficiency was investigated. The enrichment experiments of the five analytes in water samples were performed using different amounts (from 10 mg to 50 mg) of the synthesized materials. As results shown in Fig. 7, the extraction efficiency increased gradually when more adsorbents were used. However, due to the different properties of each analyte, the extraction equilibriums were achieved with different amounts of the particles. For PCP, 20 mg particles could largely extract it, and 40 mg particles were needed to ensure the fully extraction of phenol. What is more, the extraction efficiency of BPA still slightly increased even when the amount of adsorbent reached 50 mg. So, taking all factors into consideration, we selected 40 mg as the optimal amount.

3.2.3. Adsorption time

The influence of adsorption time was studied by preconcentration of analytes with spiked distilled water sample (100 ng/mL), and the extraction times were 10, 20, 30 and 45 min. Due to good dispersibility of polyaniline in water, the particles could disperse in aqueous phase easily and totally with slight vibration, instead of aggregation in a short time. As a result of that, as seen from Fig. 8, all the curves turned to be flattened out when the extraction time reached 20 min, which showed that the system achieved extraction

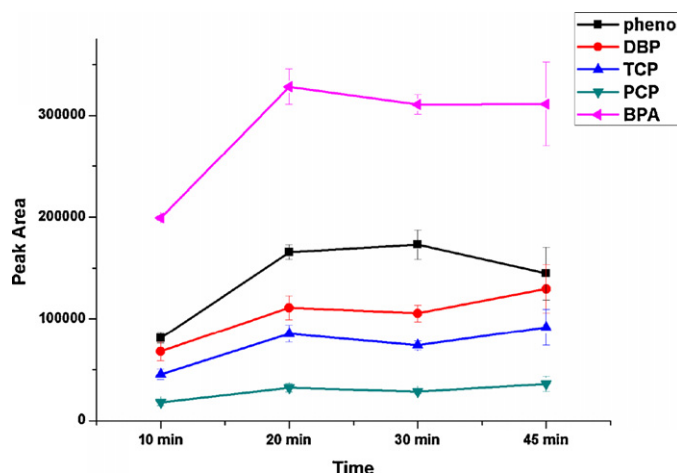


Fig. 8. The Influence of different extraction time on the adsorption of phenols.

Table 2
The validation data of MSPE-GC-MS procedure.

Compound	Calibration equation	r^2	Linearity range (ng/mL)	RSD (%) ($n=3$)		LOD (ng/mL)	LOQ (ng/mL)	Recovery (%)	RSD of recovery (%)
				Interday	Intraday				
Phenol	$y=3036x+11912$	0.992	5–200	5.9	10.6	2.13	7.10	90.0	5.0
DCP	$y=1835x+740.5$	0.998	10–200	8.7	7.7	5.55	18.5	87.7	8.9
TCP	$y=2065x+2337$	0.998	10–200	13.1	15.8	7.58	25.2	98.0	8.3
PCP	$y=1038x+1065$	0.991	5–200	5.7	12.2	3.22	10.7	103.1	5.5
BPA	$y=5914x+21752$	0.998	1–200	10.9	11.2	0.89	2.97	103.2	9.8

balance after 20 min. Virtually, there was no obvious change on PCP from 10 min to 45 min, compared with the noteworthy increase of BPA from 10 min to 20 min. In a word, it was sufficient to get plentiful analytes extracted during a moderate time of 20 min, which was therefore chosen as the best adsorption time.

3.2.4. Influence of pH value of solution

The pH value of the solution could change the superficial charge distribution of polyaniline, which would influence the adsorption capacity of polyaniline. To investigate the effect of pH, we adjusted the solution pH by adding hydrochloric acid or NaOH solution from acidic to basic, including pH values of 2, 5, 7, 9 and 12. The results are shown in Fig. 9. We found that, at higher solution pH (pH = 12), the extraction efficiency dropped apparently. Under this pH condition, the polyaniline coating became deprotonated, so that Coulombic repulsion between polyaniline coating and negatively charged phenolates probably hinder the interaction between each other. Moreover, for BPA only, the best adsorption efficiency was achieved at pH 7, while for the other analytes, there was no notable change when pH was below 10. Therefore, there was no need to adjust pH value before analyzing general water sample.

3.3. Method evaluation

A series of experiments were conducted to further validate our proposed method, such as linearity, reproducibility, limit of detection (LOD), and limit of quantification (LOQ). All the parallel experiments were repeated three times and the results are tabulated in Table 2. Calibration curves were conducted by analyzing 10 mL distilled water spiked with different analytes in the range from 1 ng/mL to 200 ng/mL (1, 5, 10, 50, 100 and 200 ng/mL). The relative standard deviations (r^2) of these curves were all above 0.991. Reproducibility of inter- and intra-day was carried out to analyze spiked water sample (100 ng/mL), and the RSD values of intra-day were slightly larger than those of inter-day. The detection and quantification limits were calculated on the basis of $S/N=3$

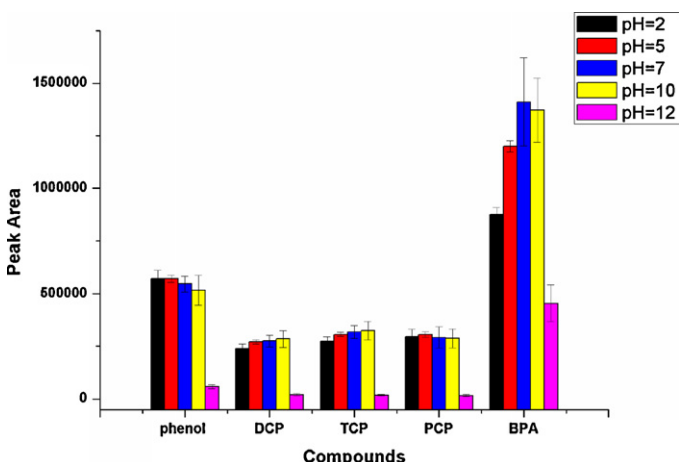


Fig. 9. The effect of solution pH on the adsorption efficiency.

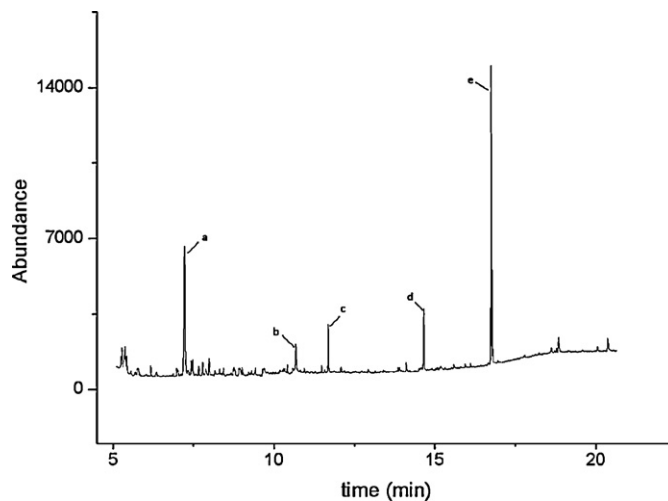


Fig. 10. The chromatogram of spiked tap water sample. (a: phenol; b: DCP; c: TCP; d: PCP; e: BPA).

and $S/N=10$, with the values from 0.89 to 7.58 ng/mL and from 2.52 to 29.7 ng/mL, respectively. Compared other conventional SPE method [48,49], our procedure had equivalent abilities to analyze phenolic compounds from water sample, and these results showed that our method had good linear range, low detection limits and high reproducibility, which could be further introduced to the real water sample analysis.

3.4. Analysis of real water samples

To further verify our proposed method, tap water and river water sample were collected to be analyzed. Since none of the five kinds of phenols were detected in non-spiked tap water sample, spiked tap water samples were analyzed to calculate the recoveries of the five phenolic compounds. Fig. 10 shows the chromatogram of the spiked water sample, and the recoveries of the analytes are listed in Table 2. The results demonstrated that all the recoveries were in the ranges of 85.3–110.6%, with a relative standard deviation ranging from 5.0 to 9.8%. What is more, river water sample was also analyzed and three kinds of phenolic compounds were detected, except for DCP and TCP. The concentrations of the detected three compounds are tabulated in Table 3. All the results illustrated that the $Fe_3O_4@C@PANI$ magnetic microspheres have

Table 3
The concentrations of phenolic compounds in waste water sample obtained after MSPE-GC-MS procedure.

Compound	Concentration (ng/mL)
Phenol	8.15
DCP	ND
TCP	ND
PCP	11.67
BPA	7.94

ND: not detected.

potential application in the analysis of phenolic compounds from water sample.

4. Conclusions

In this work, a facile approach was successfully introduced to synthesize $\text{Fe}_3\text{O}_4@\text{C}@\text{PANI}$ magnetic microspheres. First, $\text{Fe}_3\text{O}_4@\text{C}$ magnetic microspheres were synthesized, and then aniline was polymerized and coated on this magnetic core in the presence of CuAc_2 . In this procedure, all the reactions were solvothermal or hydrothermal reactions, which were simple, fast, low-cost, solvent-free and easy to realize in large-scale production. Finally, the $\text{Fe}_3\text{O}_4@\text{C}@\text{PANI}$ magnetic microspheres were successfully applied to the preconcentration of phenols from water sample. We also obtained low limits of detection, good linearity and recovery, which indicated that our $\text{Fe}_3\text{O}_4@\text{C}@\text{PANI}$ magnetic microspheres had a considerable potential use in sample preparation of water sample.

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