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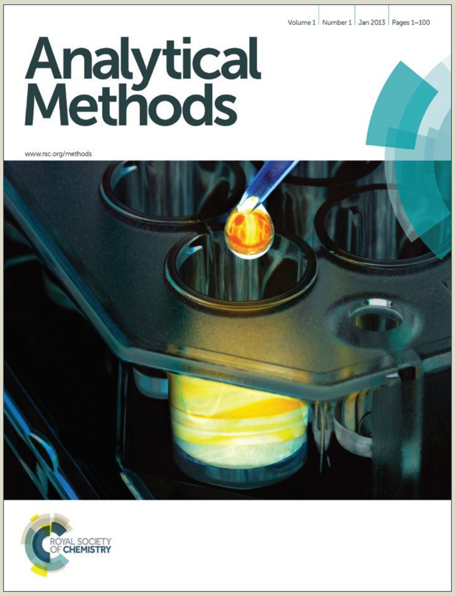

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Analysis of bisphenols in environmental water using polydopamine coated magnetic Fe_3O_4 as magnetic solid phase extraction materials coupled with high-performance liquid chromatography

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Abstract

In this work, polydopamine coated magnetic Fe_3O_4 composites were synthesized via a simple solvothermal reaction and self-polymerization of dopamine, and the as-made nanocomposites were successfully applied as an effective adsorbent for the preconcentration of the four bisphenols in environmental water samples prior to high-performance liquid chromatography. The polydopamine coated magnetic Fe_3O_4 composites have several advantages such as large surface area, fast separation ability, super-hydrophilicity, higher peak intensities for aromatic analytes. Various parameters, including eluting solvent and volume, the amounts of absorbents, extraction time and elution time were optimized. Validation experiments showed that the optimized method had good linearity ($r^2 > 0.9990$), satisfactory precision (RSD < 6.2 %) and high recovery (92 – 105 %). The limits of detection were 0.030 – 0.043 μg/L and the limits of quantification ranged from 0.10 to 0.14 μg/L. The results indicated that the proposed method had advantages of convenience, good sensitivity, and high efficiency. The method has been applied successfully to analyze bisphenols in real water sample.

Keywords: polydopamine coated magnetic Fe_3O_4; bisphenols; magnetic solid phase extraction; environmental water; high performance liquid chromatography

1 Introduction

Bisphenols (BPs) are a group of chemicals with two hydroxyphenyl functionalities and include several analogues such as bisphenol A (BPA), bisphenol F (BPF), bisphenol B (BPB), bisphenol E (BPE) and bisphenol AP (BPAP) [1]. Bisphenol A is the most popular representative of this group widely used in the manufacture of polycarbonate plastics and epoxy resins, the latter used in the production of food contact surface lacquers for cans. bisphenol F (BPF) and bisphenol B (BPB) may be developed as substitution in the manufacture of epoxy resin and polycarbonates [2,3] bisphenol AP (BPAP) is widely appeared in the fine chemical and medicine industry, especially used as an indispensable plasticizer and flame retardant [4]. Bisphenols (BPs) are considered endocrine disruptor chemicals (EDCs). They show estrogenic activity and have been suspected as potential carcinogenic and mutagenic compounds, producing adverse effects in animals, aquatic life and humans [5]. The determination of BPs present in environmental samples is becoming an urgent task due to their toxic or carcinogenic characteristics. Gas chromatography (GC) and liquid chromatography (HPLC) are the most widely used techniques for trace analysis of BPs. Due to the complexity of environmental matrixes and the low concentration level of BPs existing in the environmental samples, extraction and preconcentration of BPs are essential before chromatographic separation. Many pre-treatment methods were developed for the analysis of BPs over the past decades, such as solid-phase extraction(SPE) [1,6,7], matrix solid phase dispersion (MSPD) [8], Stir bar sorptive extraction (SBSE) [5,9], Ultrasound-assisted emulsification microextraction [10] and dispersive liquid–liquid microextraction (DLLME) [11]. Recently, a new mode of SPE termed as magnetic solid-phase extraction (MSPE) has been developed. It has several advantages in comparison with traditional SPE. The separation process can be performed directly in crude samples containing suspended solid materials without the need of additional centrifugation or filtration, which makes the separation easier and faster. Therefore, MSPE has found wide applications in sample pretreatment [12–22] and preconcentration of bisphenols [23-27]. In MSPE, the adsorbent material is a key factor. The current research in MSPE is oriented on the development of novel adsorbents with high adsorption capacity, good selectivity, and good dispersibility in aqueous matrix.

Dopamine was a neurotransmitter. At room temperature, it could be self-polymerized in weak alkaline condition, and be coated on a wide range of organic or inorganic materials surface such as metal oxides [28, 29], polymers [30], carbon nanotubes [31] and graphene [18, 32]. The use of PDA as affinity material for organic pollutants has several significant advantages, including good biocompatibility, excellent dispersibility in water, great environmental stability [33]. Moreover, it has π electrons that could help absorb aromatic ccompounds via π–π interaction [18].

In this study, we successfully synthesized polydopamine coated magnetic Fe_3O_4 nanocomposites (Fe_3O_4@PDA) microspheres, and applied it as the magnetic adsorbent to extract and analyze BPs in water by HPLC.

2 Experimental

2.1 Reagents and materials

Bisphenol A (BPA), bis (4-hydroxyphenyl) methane (BPF), Bisphenol B (BPB), 4, 4'- (alpha-methylbenzylidene) bisphenol (BPAP) and were acquired from J&K Chemical Corporation (Beijing, China). Dopamine hydrochloride was purchased from Sigma–Aldrich (St. Louis, MO, USA). Methanol and acetonitrile (HPLC grade) were purchased from Merck (Darmstadt, Germany). All of other chemicals were of analytical grade, and were purchased from Shanghai Chemical Reagent Co. (Shanghai, China). Bisphenols stock standards were prepared in methanol, with concentration levels of 100 mg/L for each compound, and were stored in a freezer at –4 °C.

Working standard solutions were prepared by dilution of an appropriate amount of the above stock solution in methanol. The water used was MilliQ grade (Millipore, Bedford, MA, USA).

2.2 HPLC analysis

Chromatographic measurements were carried out using a LC-2010A H HPLC system (Shimadzu, Kyoto, Japan), consisting of a quaternary pump and a diode array UV-visible detector. The chromatographic separation was performed on Diamonsil C18 (2) column (250 mm × 4.6 mm i.d., 5 μm; Dikma Technologies Inc., China) at 30 ℃. The detection wavelength was 225 nm and the injection volume was 20 μL. The flow rate was set as 1.0 mL/min, and the mobile phase was a mixture of water and acetonitrile (55:45, v/v).

2.3 Synthesis and characterization of Fe_3O_4@PDA

The magnetic Fe_3O_4 microspheres were synthesized through solvothermal reaction in our previous work [34]. In detail, 1.35 g of Iron (III) chloride ($FeCl_3\cdot 6H_2O$) was first dissolved in 75 ml Ethylene glycol under magnetic stirring at room temperature. Afterward, 3.6 g of anhydrous sodium acetate was added. The obtained solution was stirred for 0.5 h and then transferred to a sealed vessel and heated at 200 ^oC for 16 h, and then cooled overnight at room temperature subsequently. The product was obtained by separating with magnet and repeated washing with water，and then dried in vacuum at 50 ^oC to gain the black powder.

The magnetic Fe_3O_4@PDA was prepared through the self-polymerization of dopamine. First of all, 300 mL ethanol and 150 mL Tris buffer (10 mM, pH=8.5) was added in a 1000 mL three neck round bottom flask. Then 150 mg magnetic Fe_3O_4 was added into the flask and was adequately blended under ultrasonication. Afterwards, 600 mg of dopamine hydrochloride was dissolved in 225 mL of deionized water and was added into the flask. After that, the mixture solution was stirred at room temperature for 8 h. The synthesized magnetic Fe_3O_4@PDA was isolated by magnetic separation, and washed with deionized water and ethanol several times. Eventually, the Fe_3O_4@PDA composites were dried in vacuum at 50 ^{o}C.

Transmission electron microscopy (TEM) images were taken on a JEOL 2011 microscope (Japan) operating at 200 kV. Scanning electronic microscope (SEM) images were recorded on a Philips XL30 electron microscope (Netherlands) operating at 20 kV. Fourier transform infrared spectra (FT-IR) were collected on Nicolet Fourier spectrophotometer using KBr pellets (USA). Powder X-ray diffraction (XRD) patterns of the samples were taken using a Rikagu MiniFlex X-ray apparatus equipped with Cu K_α radiation (λ=0.15418 nm).

2.4 MSPE procedure

MSPE procedure for the extraction of BPs was as follows: Firstly, 40 mL of water sample containing BPs with a concentration of 50 μg/L was added in a 50 mL vial with PTFE-silicone septum. Then 30 mg of Fe_3O_4@PDA composites were added in the vial to extract the analytes, and the mixture was vortexed for 15 min. Next, a magnet bar was placed beside the vial to hold the Fe_3O_4@PDA composits which had already extracted the analytes. Subsequently the water was removed from the vial with the sorbent remained in the vial. 0.8 mL acetonitrile introduced to the vial and then the mixture was ultrasonicated for 15 min to desorb the analytes. Finally, 20.0

μL of the obtained solution was injected into HPLC system for detection.

2.5 Validation of the method

The linearity was investigated by replicating three analyses of the interesting concentration range (0.5-2000 μg/L). The method precision was studied by six replicate analyses of BPs in water by MSPE under the optimum conditions. The relative standard deviation (RSD) was calculated on the basis of the obtained peak areas. Recovery was also investigated by adding 40 μL of standard stock solution (50 μg/mL) to 40 mL water samples containing known amounts of BPs. Triplicate measurements were performed by MSPE–HPLC. The limits of detection (LOD) were calculated by analyzing standard solutions of a low concentration on the basis of signal to noise ratio (S/N=3). And the limits of quantification (LOQ) were evaluated on the basis of S/N=10.

3. Result and discussion

3.1 Characterization of the Fe_3O_4@PDA composites

The TEM image of Fe_3O_4 nanoparticles was shown in Fig. 1a. The TEM and SEM image of Fe_3O_4@PDA composites was shown in Fig. 1b and Fig. 1c. As can be seen from Fig. 1(a, b and c), it was observed that the diameter of Fe_3O_4 was about 200 nm and the polydopamine layer was successfully coated on the Fe_3O_4 and the coating layer was about 60 nm. The FT-IR spectra of Fe_3O_4@PDA were showed in Fig. 2.

The peak 582 cm^{-1} was attributed to the Fe-O-Fe stretching vibration of Fe_3O_4. The adsorption peaks at 1290, 1523 and 1298 cm^{-1} resulted from the aromatic ring in the PDA polymer [35]. The wide angle X-ray diffraction patterns of Fe_3O_4@PDA composites were showed in Fig. 3. The typical diffraction peaks around 18.4°, 30.4°, 35.7°, 43.4°, 53.6°, 57.3° and 62.8° were related to Fe_3O_4 microspheres [36, 37].

3.2 Optimization of extraction conditions

In order to obtain the maximal extraction efficiency, several important parameters, such as type and volume of elution solvent, amounts of the Fe_3O_4@PDA, adsorption time and elution time, were studied and optimized. Analytes in aqueous matrix were extracted, concentrated and injected into the HPLC for analysis.

3.2.1 Type and volume of elution solvent selection

The selection of the eluting solvent is quite important for the extraction of analytes by the Fe_3O_4@PDA compositesIn this study, we selected methanol, ethanol acetonitrile as eluting solvent, and then compared their eluting efficiencies. The results were shown in Fig. 4. As seen from Fig. 4, acetonitrile had the highest desorption ability, while ethanol had a relative low eluting efficiency. The results could be explained that acetonitrile had a similar polarity to the targets and possessed the hydrophobicity which could facilitate interaction with bisphenols [26]. So, acetonitrile was selected as the optimized eluting solvent in the following work. The volume of elution solvent is also an important factor to obtain reliable and reproducible analytical results. In this work, to investigate the influence to the extraction efficiency, 0.4, 0.6, 0.8 and 1.0 mL acetonitrile were selected. Fig. 5 shows that the maximum extraction efficiency of these analytes was obtained when the elution volume reached to 0.8mL.

3.2.2 Amounts of the Fe_3O_4 @PDA composites selection

The adsorbent amount had a significant effect on extraction efficiency. In this work, the different amounts of the Fe_3O_4@PDA composites (10, 20, 30, 40, 50 mg) were used for the extraction the analytes. According to the results shown in Fig. 6, more analytes could be extracted as the amount of the Fe_3O_4@PDA composites increases. When the amount reached to 30 mg, the curves turned out to be flat, and there was no distinct increase to extraction efficiency. So, we selected 30 mg the Fe_3O_4@PDA composites as the optimized amount.

3.2.3 Effect of extraction time and elution time

Extraction time is also an important parameter which can affect the efficiency. In this work, different extraction time (5, 10, 15 , 20 and 30 min) was studied. As is shown in Fig. 7, the extraction efficiency increased with the increased extraction time from 5 to 15 min and then remained almost constant after 15 min. Therefore, the extraction time of 15 min was selected as the optimal extraction time. At extraction time 15 min, different eluting time (5, 10, 15 and 25 min) was also investigated. The results were shown in Fig. 8. The results showed that 15 min was enough to receive the maximum extraction efficiency of all the analytes. So, the elution time of 15 min was selected.

3.3 Reusability of the magnetic adsorbent

The reusability of the Fe_3O_4@PDA composites was investigated in this study. After each use of the magnetic adsorbent, it was washed with acetonitrile twice (each time washed 1 hour with 5 mL acetonitrile) and dried at 50 ºC in vacuum for 24 h. Subsequently, 30 mg regenesis magnetic adsorbent was added in a 50 mL vial with 40 mL distilled water. Next, we tested according to Section 2.4 procedure and no BPs were detected in acetonitrile. So no carry-over of the analytes was detected on the adsorbent. Then the adsorbent was reused for the next MSPE for the BPs. The results showed that the magnetic adsorbent can be reused at least 8 times without a significant loss of the sorption capacity.

3.4 Validations of the method

Under the optimal experimental conditions, the linearity, precision, limit of detection, the limit of quantification, and recovery of the proposed method were studied. The linear ranges and correlation coefficients (r^2) obtained for each BPs were given in Table 1. As seen from Table 1, the corresponding values (r) were more

0.9990 and the method had good linearity. Precision of the method varied from 3.9-6.2 %. The LOD values were calculated on basis of S/N ratio of 3 and the values of the analytes were from 0.03-0.043 μg/L. On basis of S/N ratio of 10, the LOQ values of analytes were 0.1-0.14 μg/L. These results showed that our method had good linear range, low detection limits and high reproducibility. So the proposed method was reliable.

3.5 Quantitative analysis of BPs in water sample

The proposed method was applied for the extraction of BPs from a tap water sample and a pond water sample. In this study, the spiked water samples containing 50 μg/L BPs were investigated. The water samples were filtered through a 0.45 mm membrane filter prior to analysis. The chromatogram of the BPs spiked tap water was showed in Fig. 9. The BPs concentrations were calculated by the external standard method and the results were summarized in Table 2. To investigate the effect of sample matrices on extraction efficiency, the samples were spiked with each target compound at the concentrations of 50 μg/L. The relative recovery (RR) was obtained as the following equation: RR = $(C_{\text{founded}} - C_{\text{real}}) / C_{\text{added}} \times 100\%$, where C_{founded}, C_{real}, and C_{added} are the concentrations of analyte after addition of known amount of standard in the real sample, the concentration of analyte in real sample and the concentration of known amount of standard which was spiked to the real sample respectively. The relative recoveries of the seven BPs ranged from 92 % to 105 %. The results showed that the method enabled the precise and sensitive determination of standards and can be applied to detect BPs in real samples.

To further demonstrate the advantages of the proposed method, the proposed method was compared with previous methods (Table 3). It could be seen that the developed method had comparable LOD values and precisions. The extraction time of the proposed method is shorter than most of the previous methods. This shows that the proposed method is very rapid. These results further demonstrated that the proposed method is rapid, sensitive, and repeatable tool for the analysis of BPs in water samples.

4 Conclusions

In this work, Fe_3O_4@PDA composites were synthesized via a simple solvothermal reaction and self-polymerization of dopamine. The Fe_3O_4@PDA composites used as the adsorbents for BPs analysis have several advantages including high adsorption capacity, super-hydrophilicity, strong magnetic responsivity, and abundant π-electron system. Under optimized conditions, a rapid and sensitive method for the determination of BPs was established by MSPE coupling with HPLC. Finally, the proposed method was successfully applied for the analysis of BPs from environmental water.

Acknowledgements

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Figure captions:

Fig.1. The TEM image of Fe_3O_4 nanoparticles the TEM and SEM image of Fe_3O_4@PDA composites.

Fig. 2. FT-IR spectra of Fe_3O_4@PDA microspheres.

Fig. 3. XRD patterns of Fe_3O_4@PDA microspheres.

Fig.4. The optimization of eluting solvent.

Fig. 5. The effect of volume of eluting solvent.

Fig. 6. The effect of amount of Fe_3O_4@PDA microspheres.

Fig.7. The effect of different extraction time.

Fig.8. The effect of different elution time.

Fig. 9. The HPLC chromatograms of the spiked-tap water by the proposed method.

Table 1 The validation data of MSPE-HPLC procedure

Compounds	calibration curve	R^2	Linear range μg/L	RSD (%) (n=5)	LOD μg/L	LOQ μg/L
BPF	Y=1244.6X+31088	0.999	0.5− 2000	3.9	0.030	0.10
BPA	Y=1582.4X+42165	0.998	0.5− 2000	6.2	0.032	0.10
BPB	Y=964.41X+26835	0.997	0.5− 2000	4.7	0.043	0.13
BPAP	Y=1268.3X+32890	0.998	0.5− 2000	4.5	0.041	0.14

Table 2 Analytical results for the four BPs in water samples (n=3)

Compound	Concentrations (µg/L)		Relative recovery %	
	River water	Tap water	River water	Tap water
BPF	ND	ND	103	103
BPA	ND	ND	92	95
BPB	ND	ND	105	104
BPAP	ND	ND	96	97

ND: means no detection

Table 3 Comparison of the proposed method with other methods for determination of bisphenols in various samples

Extraction method	Sample	Extraction time(min)	Adsorbent	LR μ g/L	LODs μ g/L	RSDs %	Recovery %	Ref.
MSPE	water	30	$Fe_3O_4@SiO_2$-NH-G	0.05-2.5	0.01	2.1-5.8	93.5-104.3	23
MSPE	water	20	Fe_3O_4/GQDs	0.1-300	0.012	3.6-5.2	96.3-104.9	24
MSPE	seawater	180	WC-TMMIPs	22.8-3310	4.5	2.12-4.33	86.3-103.5	25
MSPE	water	10	magG@PDA@ZrMOF	50-20000	0.1-1	0.62-4.89	64.8-92.8	26
MSPE	plastic tableware	10	$Fe_3O_4@SiO_2$	0.5-20000	0.09	1.2	99.6-100.4	27
SPE	urine	30	MIP	20-2000	1.2-2.2	0.78-8.3	81.3-106.7	6
MSPE		10		0.5-2000	0.03-0.041	3.9-6.2	92-105	The work

Fe3O4@SiO2-NH-G: Graphene grafted magnetic ferroferric oxide microspheres

Fe3O4/GQDs: Fe3O4/graphene quantum dots

WC-TMMIPs: water-compatible temperature and magnetic dual-responsive molecularly imprinted polymers

magG@PDA@ZrMOF: Magnetic graphene@polydopamine@Zr- metal-organic frameworks

MIP: molecularly imprinted polymer

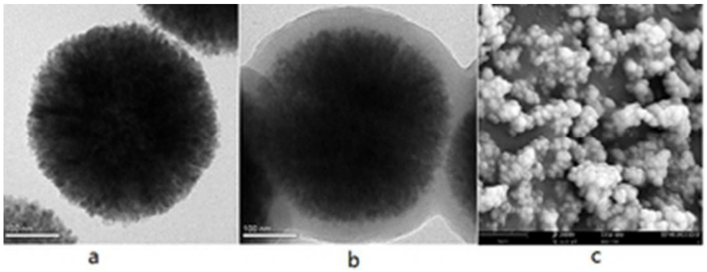

Fig.1. The TEM image of Fe3O4 nanoparticles the TEM and SEM image of Fe3O4@PDA composites.
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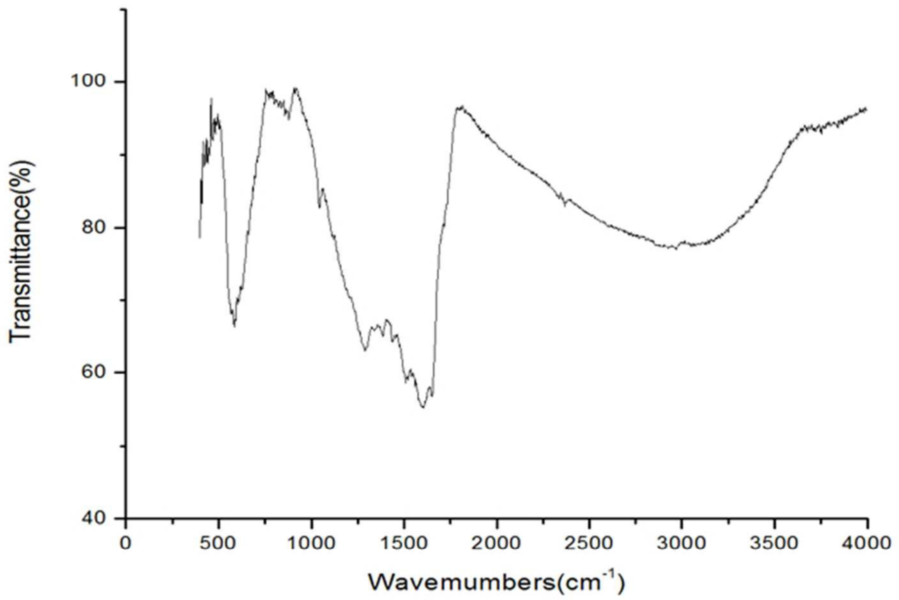

Fig. 2. FT-IR spectra of Fe_3O_4 @PDA microspheres.
60x39mm (300 x 300 DPI)

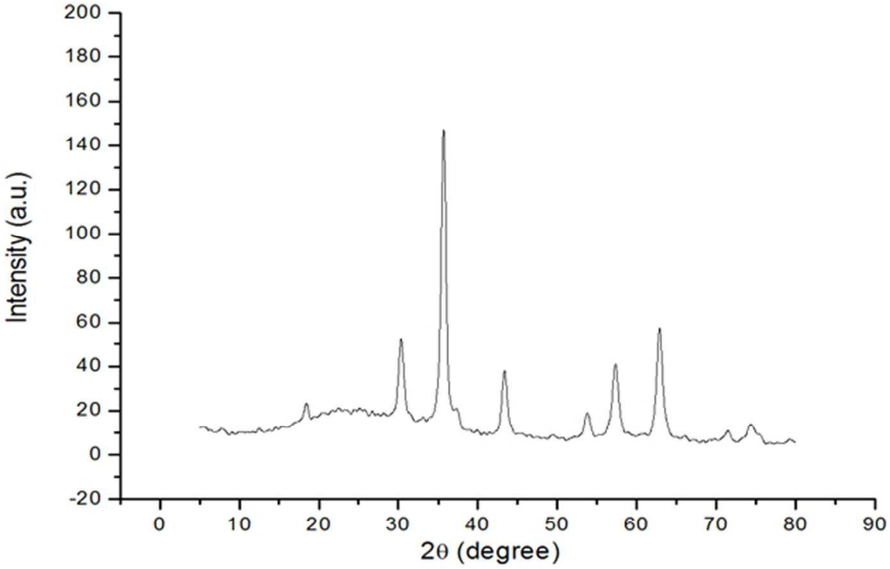

Fig. 3. XRD patterns of Fe3O4 @PDA microspheres.
60x39mm (300 x 300 DPI)

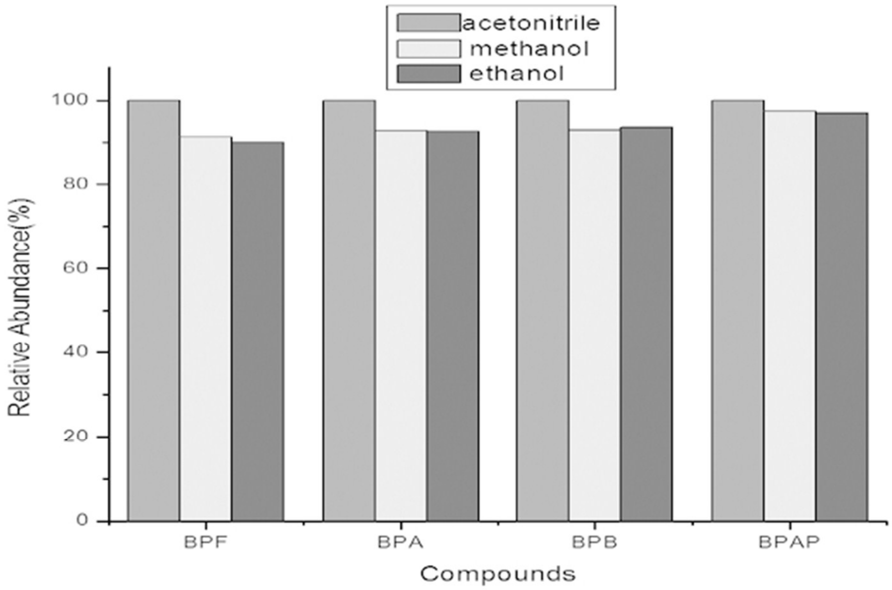

Fig.4. The optimization of eluting solvent.
60x39mm (300 x 300 DPI)

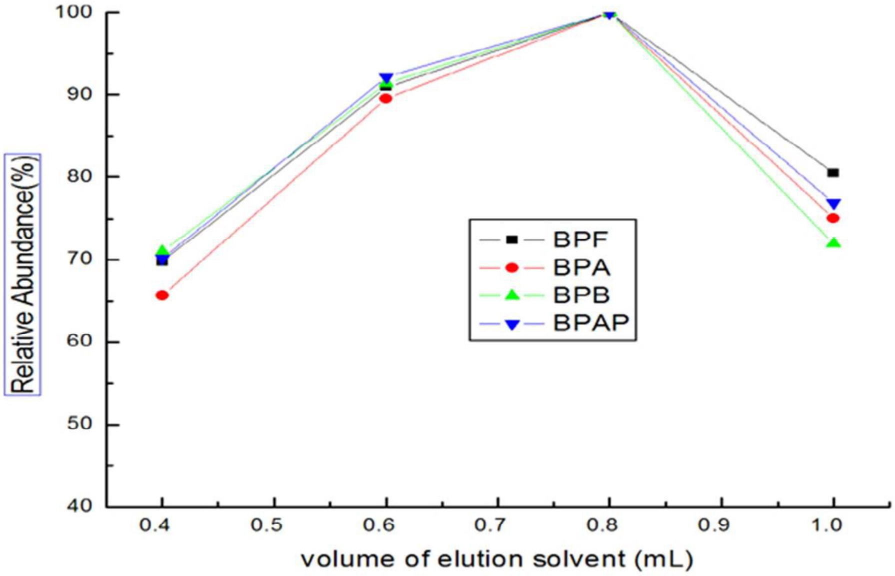

Fig. 5. The effect of volume of eluting solvent.
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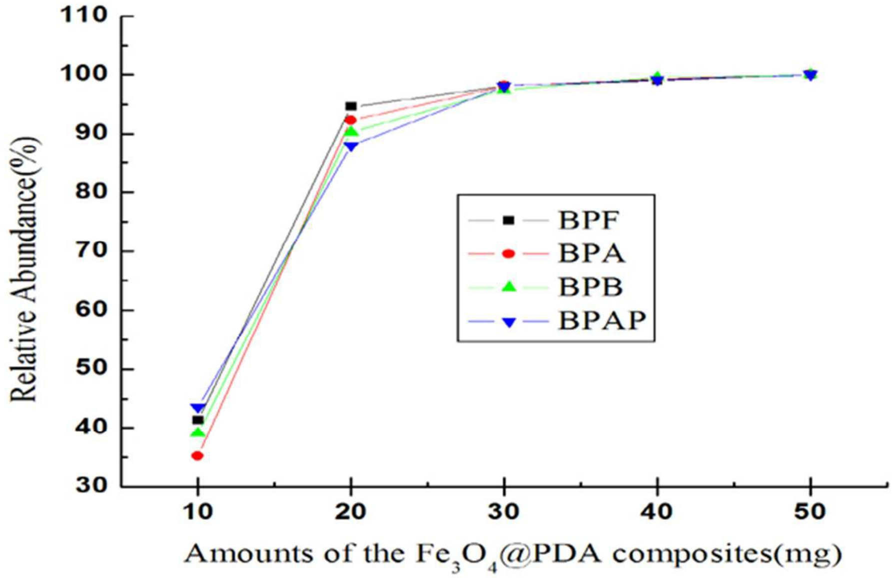

Fig. 6. The effect of amount of Fe3O4 @PDA microspheres.
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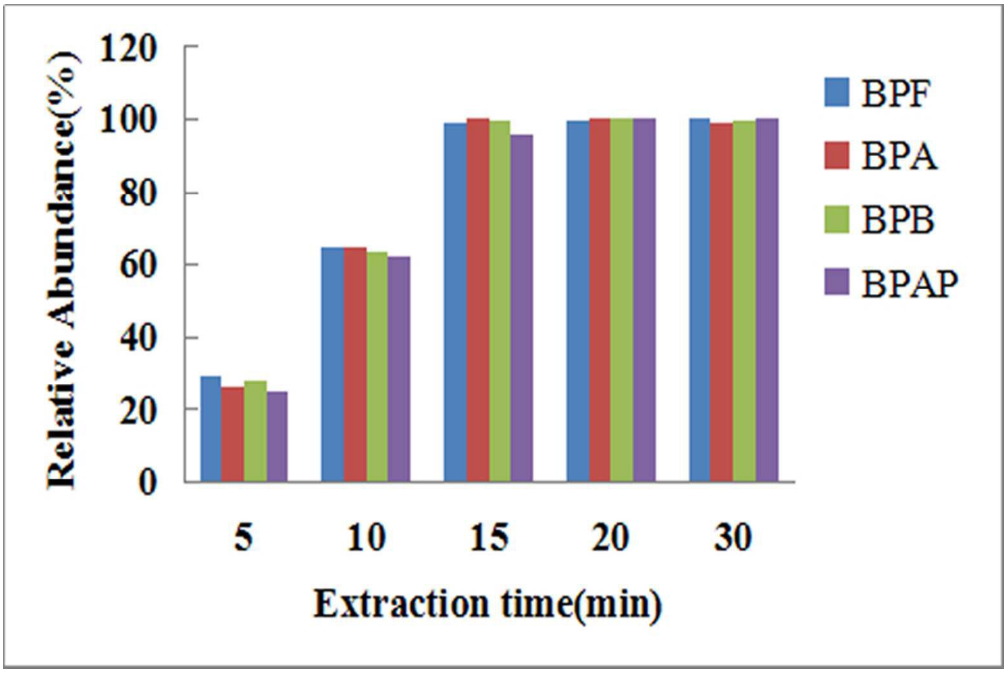


Fig.7. The effect of different extraction time.
60x39mm (300 x 300 DPI)

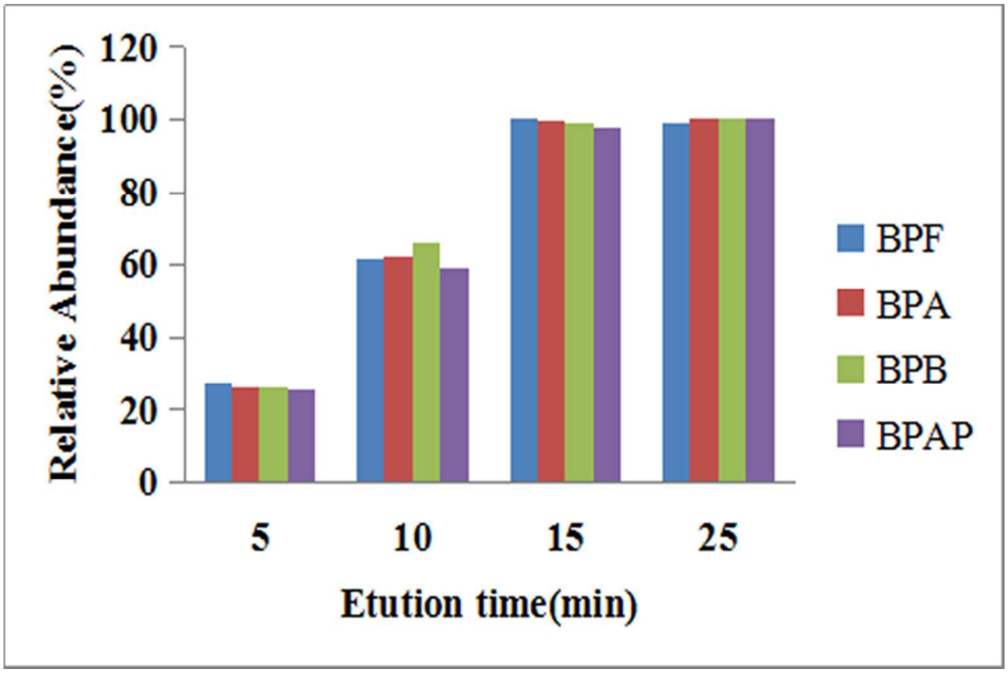


Fig.8. The effect of different elution time.
60x39mm (300 x 300 DPI)

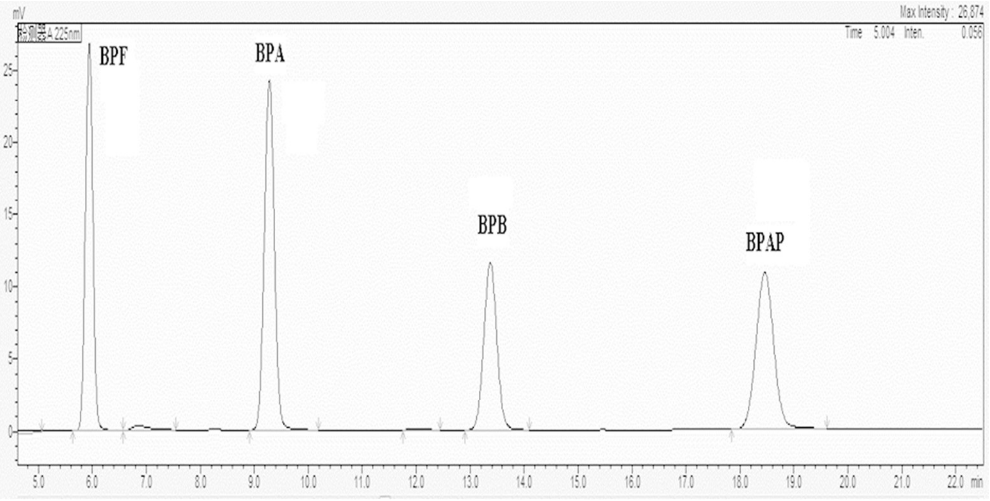
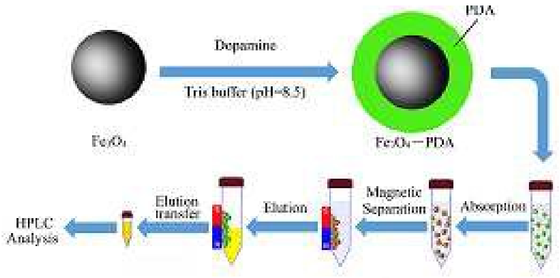


Fig. 9. The HPLC chromatograms of the spiked-tap water by the proposed method.
80x39mm (300 x 300 DPI)

A colour image for the Table of Contents



The Fe_3O_4@polydopamine composites were synthesized and applied it as the magnetic adsorbent to extract and analyze bisphenols in water by HPLC.