Article

Determination of Bisphenol A by High-Performance Liquid Chromatography Based on Graphene Magnetic Dispersion Solid Phase Extraction

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Abstract

Bisphenol A (BPA), as one of the environmental endocrine disruptors, is extensively existing and threatening to human health. To evaluate the environmental exposure level and protect human from the hazard of BPA, a precise and sensitive method is established. In this work, Graphene@ Fe_3O_4 (G@Fe_3O_4) is prepared by chemical coprecipitation method as magnetic dispersion solid phase extraction (MDSPE) material. The rapid and specific detection method of BPA is carried out by high-performance liquid chromatography (HPLC). Properties of G@Fe_3O_4 are identified by the fourier infrared spectrum and scanning electron microscopy. Conditions of solid phase extraction are optimized. Under the optimal extraction conditions, G@Fe_3O_4 has perfect enrichment effect on BPA. There is a good linear relationship in the range of 5.0∼1000.0 µg/L with the correlation coefficient of 0.9997. The detection limit is 0.1 µg/L. This method is applied to water samples successfully, and recoveries of BPA are between 88.19% and 99.56% (RSDs < 3.00%). G@Fe_3O_4 was synthesized, which was used to extract BPA in water samples before HPLC analysis, and has shown perfect extraction ability toward BPA, which indicates that the determination method of BPA by HPLC based on graphene MDSPE is faster and more precise.

Introduction

Environmental endocrine disruptors (EDCs), due to their potential health hazards to humans and animals, have drawn public attention (1–2). The 2,2-(4,4-dihydroxy diphenyl) propane, also known as bisphenol A (BPA), is one of these EDCs, which was extensively used in the manufacture of drinking bottles, construction materials and food cans inner coatings (3). The occurrences of BPA in the environment have been reported by a large number of studies (4–5), which indicated the concentration of BPA in the ranges of 0.1–0.3 µg/L in river waters, 0.01–3.6 µg/L in wastewater, 2–208 ng/m³

in air and 0.2–199 ng/g in dust. BPA has caused environmental contamination, which can affect the hormonal system of human and wildlife at low concentrations. In addition, the estrogenic activity of BPA oxidative metabolites has been determined in several studies (6).

In recent years, problems caused by BPA contaminations have greatly accelerated the development of BPA analysis technologies, such as high-performance liquid chromatography (HPLC), liquid chromatography–mass spectrometry, gas chromatography–mass spectrometry and electrochemical sensor (7–9). Among these methods, HPLC has advantages of reliability, excellent sensitivity
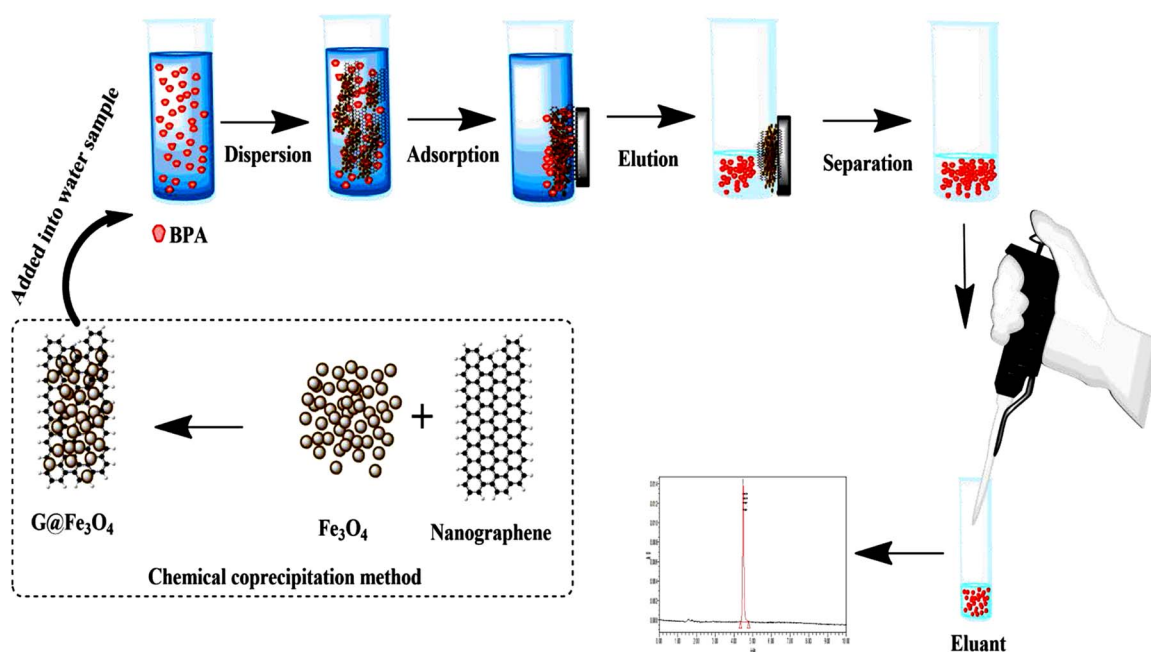
Figure 1. Graph abstract 297 × 209 mm (300 × 300 DPI).

and simple manipulation. According to the complexity of the sample composition and the essential properties of the matrixes and the targets, it can be combined with different sample pre-treatment techniques to meet different analytical needs (10–12).

Graphene (G), as a 2D honeycomb lattice, has shown tremendous potential applications in many fields because of its unique planar structure (13). Graphene-based materials were used as adsorbents for removing antibiotics from pharmaceutical wastewater (14) and sensors for the detection of biomolecules (15). Besides, graphene is an extraordinarily wonderful adsorbent or extraction material due to its large specific area and π–π electrostatic stacking property (16). However, it is cumbersome to operate. Graphene was normally dispersed into the sample solution and then needed to separate by centrifugation (17). Magnetic dispersion solid phase extraction (MDSPE) has been widely applied in DNA separation (18), enzyme immobilization (19), protein separation (20) and enrichment of organic compounds (21) and metal ions (22). In recent years, MDSPE has attracted tremendous research interests owing to its exceptional properties, such as huge surface area, easy modification, excellent mechanical and thermal stability and strong magnetic responsiveness (23). In addition, surface-functionalized magnetic nanoparticles are easy to modify and use for analysis (24). Some studies have evaluated the ability of different functional magnetic materials to adsorb BPA, such as the hydrophilic carbon-functionalized magnetic microspheres (FeO@C@CHI) prepared by Geng *et al.* (25) and zirconium-based magnetic organometallic frame composite (magG@PDA@Zr-MOF) prepared by Wang and Deng (26). These two functional magnetic materials were both used as adsorbents for extraction of BPA from water samples, and a good recovery was obtained.

In this study, G@Fe$_3$O$_4$ was prepared by chemical coprecipitation method. Compared with others, the method established in this paper was simpler, more accurate, faster and cheaper. The prepared G@Fe$_3$O$_4$ is more dispersible. The feasibility of rapid separation and enrichment of BPA in water samples using G@Fe$_3$O$_4$ magnetic
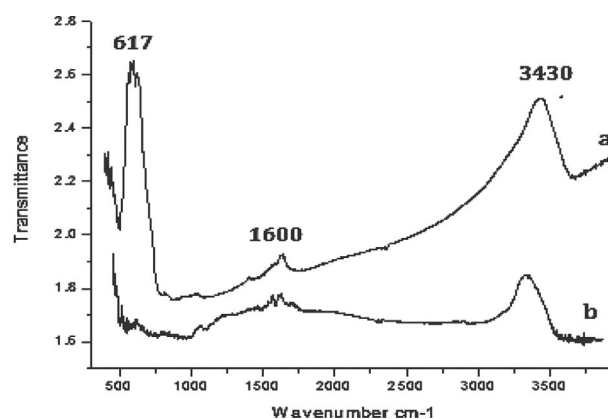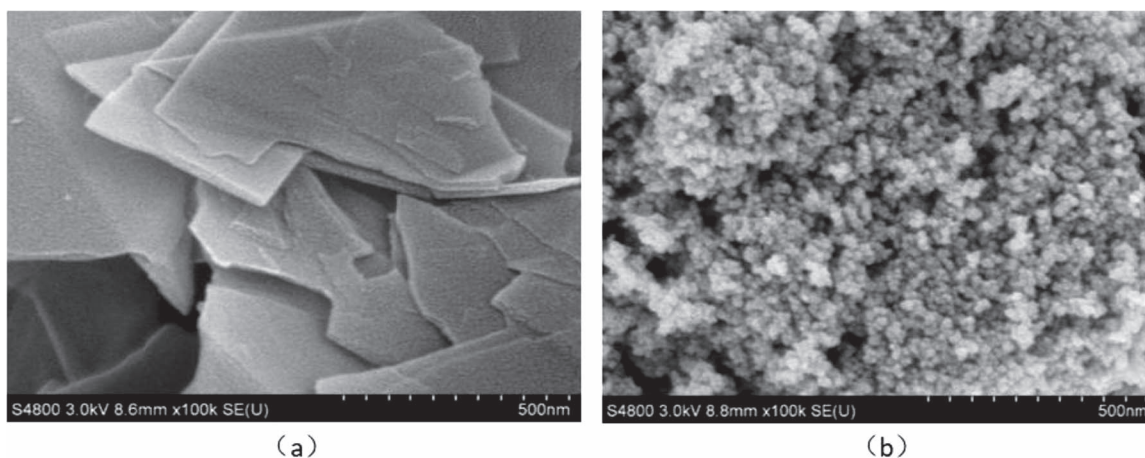

Figure 2. The FTIR spectra of magnetic graphene (a) and graphene (b) 297 × 209 mm (300 × 300 DPI).

particles was investigated. The results show that G@Fe$_3$O$_4$ has good magnetic dispersion property and excellent adsorption ability.

Experimental

Instrumentation and Reagents

The quantitative analysis was performed on an HPLC (Waters Alliance 2695, Milford, MA, USA) system with PAD detector (Waters 2998, USA). BPA was purchased from Sigma (USA). Nanographene powder was purchased from Strem Chemicals (USA). Methanol, acetonitrile and ethanol were HPLC grade and purchased from Concord Reagent (Tianjin, China). Hydrochloric acid, ammonia, ferrous sulfate heptahydrate, hydroxide and ferric chloride were analytical grade and purchased from Sailboat Chemical Reagent (Tianjin, China). Ultrapure water was obtained from a Millipore water purification system with an electric resistance

Figure 3. The SEM spectra of graphene (a) and magnetic graphene (b) (10000×) 297 × 209 mm (300 × 300 DPI).
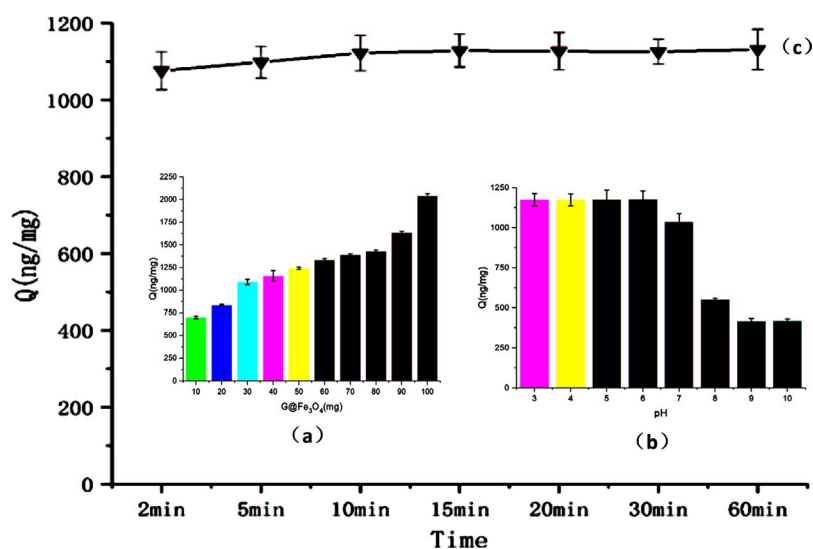
Figure 4. Optimization results of the adsorption conditions 297 × 209 mm (300 × 300 DPI).

>18.2 MΩ • cm (Millipore, Eschborn, Germany). A stock solution of BPA (1000 μg/L) was prepared in methanol and properly diluted to produce working standards with ultrapure water. The stock standard solution was stored at 20°C, and other reagents were stored at 4°C.

Methods

Preparation of G@Fe$_3$O$_4$

The preparation of G@Fe$_3$O$_4$ is as follows: 0.24 g nanographene powder, 4.17 g ferrous sulfate heptahydrate and 5.41 g ferric chloride were dispersed into 200.0 mL mixture of water and ethanol (v/v = 1:1) at a molar ratio of 4:3:4. A total of 0.8 mL hydrochloric acid was added into the mixture, ultrasound for 5 min and stirred for 10 min at room temperature. The reaction temperature was gradually increased and maintained at 80°C. Then about 80 mL ammonia was quickly added into the mixture to adjust pH > 10 and stirred for 40 min. The product was washed with ultrapure water and ethanol

repeatedly five times to remove impurities free of magnetic properties and dried under vacuum at 60°C.

HPLC conditions

The conditions of HPLC are as follows: separations were carried out on a Capcell Pak C18 column (1 μm particle size, 150 × 4.6 mm). A mixture of water and acetonitrile (35:65, v/v) at a flow rate of 1.0 mL/min was used as a mobile phase on isocratic elution mode. A total of 20 μL injection volume was used and the detection wavelength was set at 227 nm. The determination was performed at ambient temperature (~25°C).

Sample analysis

A total of 100.0 mL water sample was adjusted to pH 6 with HCl (1.0 mol/L). A total of 30.0 mg G@Fe$_3$O$_4$ was added into the sample and stirred for 15 min then removed supernatant by a magnetic separator. The analytics was eluted by 2.0 mL acetonitrile
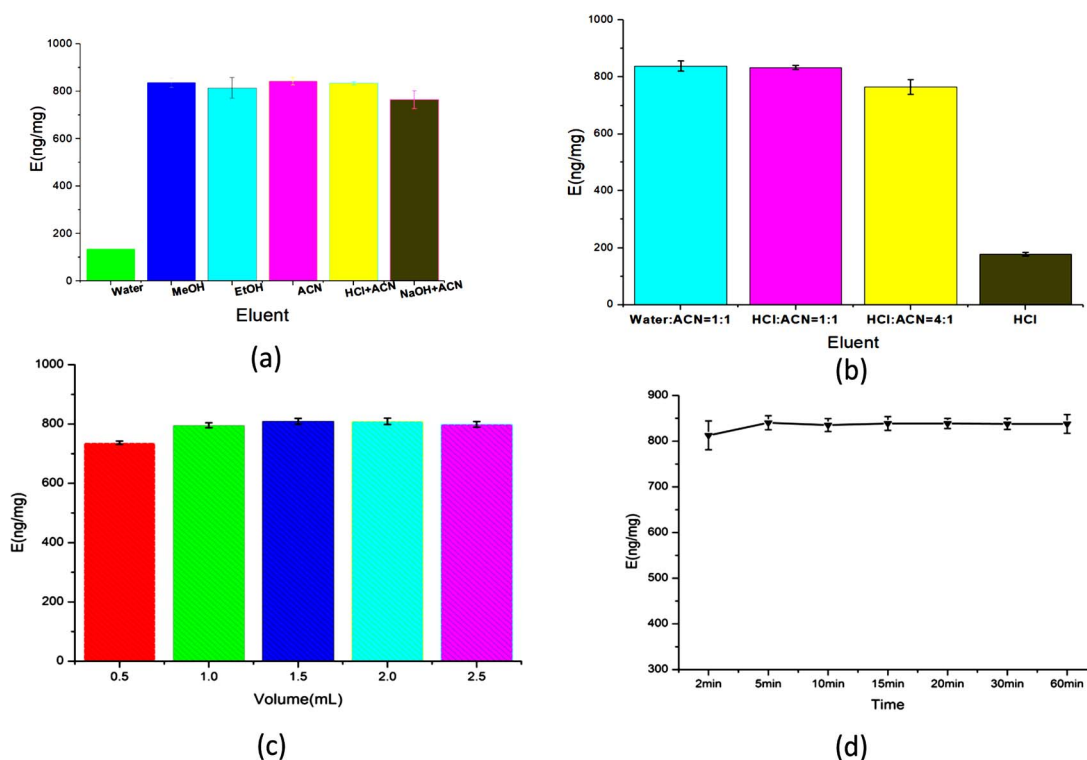
Figure 5. Optimization of the desorption conditions 297 × 209 mm (300 × 300 DPI).
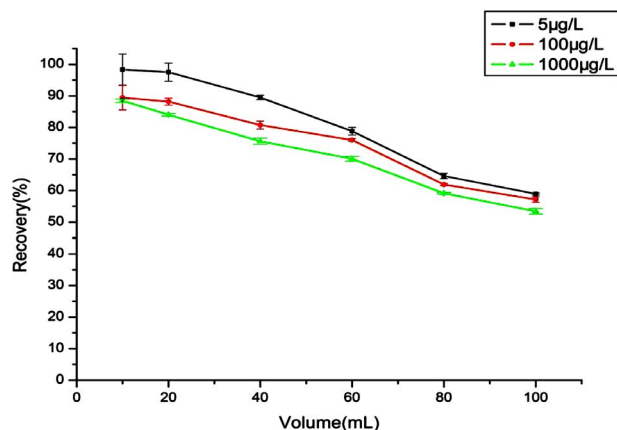

Figure 6. Optimization of adsorption volume 297 × 209 mm (300 × 300 DPI).

Table I. The Comparison of Two Methods

| Concentration (µg/L)	SPE recovery (%)	MSPE recovery (%)
50	92.62 ± 0.80	92.83 ± 0.68
100	91.55 ± 0.81	90.34 ± 2.49
1000	91.21 ± 0.84	90.41 ± 0.55

vibration of the Fe–O bond. The spectrum of graphene has no such absorption peak, indicating that Fe_3O_4 nanoparticles were fixed on the thin layer of graphene (Figure 2).

A scanning electron microscope (SEM) was used to characterize the surface morphologies of Graphene and $G@Fe_3O_4$. The graphene (Figure 3A) image had a clear lamellar shape with a smooth surface, while in the image of $G@Fe_3O_4$ (Figure 3B), the graphene sheet surface was coated with numbers of particles, indicating the surface of the graphene surface was occupied by Fe_3O_4 nanoparticles. These results suggested that $G@Fe_3O_4$ was successfully prepared.

for 5 min. After magnetic separation, the eluent was filtered through a membrane for HPLC analysis. The graph abstract (Figure 1) shows the analysis procedure.

Results

Characterization of $G@Fe_3O_4$

The interaction between graphene and Fe_3O_4 was investigated by Fourier Transform Infrared spectrometer (FTIR). Graphene and $G@Fe_3O_4$ both had absorption peaks at 1600 cm^{-1} and 3430 cm^{-1}. The medium-intensity absorption peak at 3430 cm^{-1} was caused by O–H bond stretching vibration, and the weak absorption peak at 1600 cm^{-1} was caused by C=C stretching vibration. $G@Fe_3O_4$ had a strong absorption peak at 617 cm^{-1}, which was a stretching

Optimization of the adsorption conditions

The amount of $G@Fe_3O_4$ was investigated in the range of 10.0∼100.0 mg (Figure 4C). The results showed that as the amount increased, the adsorption amount (Q) gradually increased. The adsorption increment tended to be moderate, and the adsorption capacity of the material became to be relatively saturated. Therefore, 30.0 mg was selected for the further experiments.

The pH of the solution was investigated (Figure 4B). The pH of the solution was adjusted to 3, 4, 5, 6, 7, 8, 9 and 10, respectively, with hydrochloric acid (1.0 mol/L) and sodium hydroxide solution
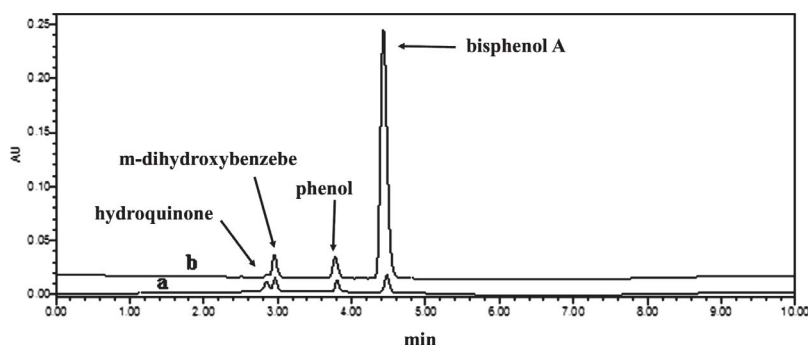
Figure 7. Typical HPLC spectrum of four standard solution (100 μg/L) without (a) and with (b) MDPSE procedure 297 × 209 mm (300 × 300 DPI).
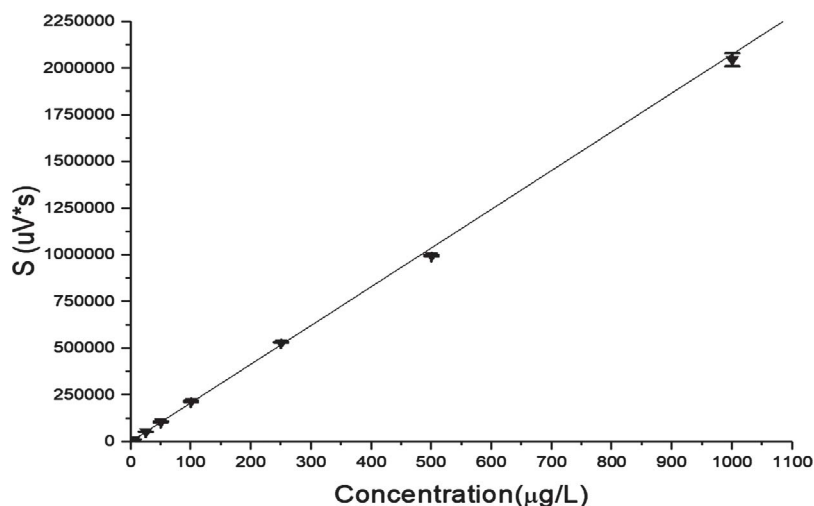
Figure 8. Working curve of BPA detection method based on magnetic graphene material 297 × 209 mm (300 × 300 DPI).

Table II. Analytical Results of Real Samples and Recovery ($n = 3$)

| Sample | Found (μg/L) | Spiked samples | | Recovery (%) | RSD (%, $n = 3$) |
		Added (μg/L)	Found (μg/L)		
		5	4.50	90.00	3.00
Tap water	n.d.[a]	50	45.77	91.53	1.38
		500	465.71	93.14	0.71
		5	4.98	99.56	0.83
Hai River	n.d.	50	47.33	94.65	1.25
		500	457.52	91.50	0.86
		5	4.41	88.19	1.67
Weijin River	n.d.	50	49.10	98.21	0.71
		500	456.82	91.36	0.93

[a]not detected

(1.0 mol/L). The adsorption amount did not change significantly in the range of pH 3~6. The adsorption amount decreased slightly at pH 7. The adsorption amount decreased significantly when the solution was alkaline. Therefore, pH 6 was selected for the following experiments.

The adsorption time was optimized by changing the shaking time from 2 to 60 min (Figure 4C). After the shaking was completed, G@Fe$_3$O$_4$ was separated from the solution by a magnet. The supernatant was filtered through a filter for detection. The results showed that the adsorption equilibrium could be reached in 10 min. To ensure the complete adsorption, 15 min was selected as the extraction time.

Optimization of the desorption conditions

The kind of the eluent was investigated. Ultrapure water, methanol, ethanol, acetonitrile, the mixture of hydrochloric acid and acetonitrile (v/v = 1:1) and the mixture of sodium hydroxide and acetonitrile (v/v = 1:1) were studied as the eluents. The results showed that acetonitrile, methanol and the mixture of sodium hydroxide and acetonitrile (v/v = 1:1) had similar elution effects (Figure 5A). Besides, the proportion of hydrochloric acid in the eluent was optimized (Figure 5B). It was found that as the proportion of hydrochloric acid increased, the elution amount (E) decreased. Acetonitrile was selected as the eluent, which was consistent with the mobile phase.

The amount of eluent in the range of 0.5–2.5 mL (Figure 5C) and the desorption time in the range of 2–60 min were also investigated (Figure 5D). The results indicated that the satisfactory elution amounts were obtained with 2.0 mL acetonitrile and shaking for 5 min.

Optimization of the sample volume

The effects of the sample solutions in the range of 10.0–100.0 mL were investigated (Figure 6). Different concentrations of BPA (5 μg/L, 100 μg/L and 1000 μg/L) were selected for experiments. As the extraction volume increased, the recoveries of BPA at the same concentration reduced. A total of 100.0 mL was chosen, which could meet the detection requirements.

Comparison with standard method

To evaluate the applicability of the proposed method, Sep-Pak Vac C18 solid phase extraction (SPE) column was used under optimized conditions. As shown in Table I, the recovery of these two methods is similar.

The selectivity of $G@Fe_3O_4$

The selectivity of the method was evaluated. The structural analogues, such as phenol, hydroquinone and *m*-dihydroxybenzene were selected as interferents. Tap water was selected as the matrix. The adsorption capacity of $G@Fe_3O_4$ was observed when the analytes and interferents at the same concentration (10, 100 and 1000 μg/L) were added into the matrix. As shown in Figure 7, under the given analysis conditions, a small amount of phenol, hydroquinone and *m*-dihydroxybenzene could be detected. Compared with these three interferents, $G@Fe_3O_4$ had a higher adsorption capacity to BPA.

Quantitative analysis

Under the optimized conditions, a good linearity of the proposed method was obtained in the range of 5.0–1000.0 μg/L, $y = 2032.9x + 5677.6$, with correlation coefficient r^2 values of 0.9997 (shown in Figure 8).

Real sample analysis

The established method was applied to the actual water samples from tap water, Hai River and Weijin River to evaluate its feasibility. Under the optimized conditions, the actual samples were extracted with $G@Fe_3O_4$ and followed by HPLC analysis. The results showed that none of the samples detects BPA. It is possible that the residual concentration of BPA in water samples was below the detection limit. To estimate the accuracy of the proposed method, three types of spiked water samples were prepared. The samples that did not detect the analytes were selected as blank samples. As listed in Table II, the recoveries were in the range of 88.19–99.56% for the water sample with the relative standard deviations ranging between 0.71% and 3.00%.

Discussion

Graphene was applied in SPE material other than oxidized graphene so that the process of preparation could be safer and eco-friendly. Oxidized graphene might be a higher specific surface area than graphene, but we abandoned it due to the risk of exploding by using potassium permanganate in the process of preparation. To make up for the deficiency of lower specific surface area, we optimized conditions of SPE. Fe_3O_4 nanoparticles distributed on the surface of graphene by chemical coprecipitation method; the graphene could provide a reducibility condition for the stability of Fe^{2+} in the crystal structure to ensure the stability of magnetism.

A study by Homem and Santos (27) indicated that $\pi-\pi$ interaction was considered as a main driving force to explain the mechanism by which graphene absorbs aromatic substances. Therefore, $\pi-\pi$ interaction probably dominates the adsorption of BPA on $G@Fe_3O_4$. The electrostatic attraction probably was another important factor affecting the adsorption of BPA on $G@Fe_3O_4$. The ionization of a compound in solution is associated with the pH of the solution and the dissociation constant (pKa) of the compound. The pKa of BPA was 9.59 (28). When the pH of the solution was in the range of 3–6, BPA was positively charged. Due to electrostatic attraction, higher adsorption efficiency was obtained. The pH of the solution was gradually higher; the adsorption efficiency was weakened due to the electrostatic repulsion between graphene and BPA (29).

Contrasting with traditional C18 SPE methods, this MDSPE method has the same veracity; the adsorption efficiency was improved and verified by HPLC.

Conclusion

In this work, $G@Fe_3O_4$ was synthesized, which was used to extract BPA in water samples before HPLC analysis. Easier and safer preparation, eco-friendliness, efficiency and steadiness are the typical advantages of $G@Fe_3O_4$ SPE material. With this MDSPE method, the detection efficiency of HPLC could be prominently improved. $G@Fe_3O_4$ has shown higher extraction ability toward BPA, which indicates that $G@Fe_3O_4$ can be a new adsorbent for SPE to extract BPA.

Funding

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