Development of a hydrophilic magnetic amino-functionalized metal-organic framework for the highly efficient enrichment of trace bisphenols in river water samples

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ABSTRACT

Bisphenols, a typical pollutant with endocrine acting the scientific attention for their ascertained toxicity and wide uses. The magnetic Zr-MOFs (Fe_3O_4@PDA@UiO-66-NH_2), functionalized with amino groups and proved by a series of material characterization techniques, were successfully prepared as adsorbents for magnetic solid-phase extraction (MSPE) of five bisphenols (including bisphenol A, bisphenol B, bisphenol S, bisphenol AP and bisphenol AF) from water samples. Liquid chromatography coupled with tandem mass spectrometry was used for sample analysis and quantification. Good linearity was obtained for each analyte with correlation coefficients larger than 0.990. The low limits of detection (LOD) and qualification (LOQ) were 0.013–0.290 μg/L (S/N = 3) and 0.088–1.800 μg/L (S/N = 10), respectively. The repeatability standard deviations in spiked lake water samples were 0.57–1.67%. In addition, the amount of the materials (40 mg), the adsorption time (30 min), pH value (7), elution time (30 min) and elution solvent (methanol) were determined as the optimal parameters in bisphenol extraction. Satisfactory results were obtained when the developed MSPE method was applied to determine the five bisphenols in real lake water samples, and the maximum extraction efficiency was up to 78.2%. The developed MSPE method using the Fe_3O_4@PDA@UiO-66-NH_2 as adsorbent provides time saving, high selectivity and sensitivity for the analysis of trace bisphenols, suggesting that the Fe_3O_4@PDA@UiO-66-NH_2 had a broad application prospect in water analysis.

1. Introduction

The rapid development of industry and agriculture has led to an increase in the use of chemical compounds, some of which may escape to the environment in various ways and result in adverse effects on both environment and human health [1]. Endocrine disrupting chemicals (EDCs), a kind of chemical compounds commonly found in various environmental media, such as drinking water sources [2], have potential effects on mimicking or inducing estrogen-like responses in organisms at low concentrations. More specifically, EDCs could directly affect human endocrine system, thereby indirectly interfering with immune system, reproductive system, brain and nervous system by direct ingestion or by bioaccumulation along the food chain [3]. Among of EDCs, bisphenols are typical and increasingly gathering the attention

of the scientific community [4]. For having the functions of improving the heat resistance, moisture resistance and optical properties, bisphenols can be used as stabilizers, promoters and modifiers in the synthesis of epoxy resin, polycarbonate, phenolic resin, polyurethane and other macromolecular materials [5]. More specifically, bisphenols are widely used in industrial, institutional application and household as plastics, pesticides, textiles, flame retardant, packaging materials and so on [1,5–11].

Bisphenol A (BPA) is one of the main monomers used worldwide in plastic manufacture, and more than two million tons of BPA a year are used for the synthesis of polycarbonates, epoxy resins and PVC [3]. In addition, due to its estrogenic properties, BPA can alter animals' normal hormonal systems, causing some adverse health effects including morphological changes, reduction of fertility and sex differentiation

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[12]. Because of the wide application and certified toxicity of BPA, the industry has gradually started to use bisphenol B (BPB), bisphenol S (BPS), bisphenol AP (BPAP) and bisphenol AF (BPAF) with similar structure as potential substitutes [13,14], however, these substitutes also share the similar dilemma of acute toxicity, genotoxicity, and estrogenic activity [15].

Recently, many studies have revealed that the accumulation of bisphenols exits widely in atmosphere, surface water, sediment, soil, indoor dust, food and even human serum and urine [3,9,10,15–18]. However, in these environmental media, it is difficult to achieve high sensitivity and selectivity in direct analysis of the bisphenols for the abundance being usually low and the environmental matrix being complex. Thereby, the environmental samples usually require separation and enrichment prior to analysis by liquid chromatography (LC) and gas chromatography (GC) combined with mass spectrometric (MS) detection, which are common techniques for determining EDCs in various samples [19–21]. There are various enrichment methods of bisphenols, and among of those methods, traditional techniques, such as liquid-liquid extraction (LLE) [22] and solid-phase extraction (SPE) [23,24], are time consuming and often involve the extensive use of organic solvents that are harmful to the environment and human health. To address these issues, organic less solvent methods such as solid phase microextraction (SPME) and MSPE have been developed [4,11] and the synthesis of adsorbents has been paid more and more attention to improve the efficiency of enrichment and selectivity.

In the past decades, metal-organic frameworks (MOFs), a new fascinating kind of porous material prepared by metal-containing nodes and organic linkers [25], have gained a lot of potential applications such as tools of separation and enrichment due to their comparatively high surface area, various functional sites and modifiability [26,27]. MOFs have been widely employed in various fields including adsorption, enrichment, separation and catalysis [28–30]. Over the several years, the MOFs have been successfully used to remove different types of hazardous chemicals with different processes [31,32]. Zr-MOF, one of promising MOFs, contains metal clusters of zirconium as the center and terephthalic acid or its modified derivatives as organic ligands, which makes the Zr-MOF have the homogeneity and relatively stable characteristics of crystal structure [33]. However, most mesoporous MOFs are hydrophobic and could not disperse well in water matrix [34].

In this study, we prepared a hydrophilic Zr-MOF containing –NH$_2$ groups as hydrophilic functional moieties by using amino-functionalized terephthalic acid (i.e., 2-amino-terephthalicacid), and magnetic Fe$_3$O$_4$ microspheres are added to simplify the extraction procedure and facilitate collecting the material from water samples and reuse of materials via the external magnetic field. In the meanwhile, dopamine, which can be easily coated on the inorganic or surface such as metal oxides, polymers and graphene [35] and shows excellent dispersion and good environmental stability in water matrix [36], is considered to combine MOFs with Fe$_3$O$_4$ to improve the adsorbent's stability and hydrophilicity. Then, a hydrophilic magnetic amino-functionalized MOF (Fe$_3$O$_4$@PDA@UiO-66-NH$_2$) were synthesized and used as sorbents for MSPE of bisphenols to improve the enrichment performance of bisphenols and shorten the separation time. To achieve simultaneous determination, five bisphenols (Fig. 1) that could have synergistic interference in analysis were examined with MSPE, a promising future for hydrophilic MOFs' excellent performance in bisphenols enrichment could be anticipated.

2. Experimental

2.1. Reagents and materials

2, 2-bis (4-hydroxyphenyl) propane (BPA; 99%), 4, 4′-sulfonyldiphenol and (BPS; 98%) were purchased from Sigma Aldrich Chemical Company (Shanghai, China). 2, 2-Bis (4-hydroxyphenyl) butane (BPB;

99%) and 4,4′- (alpha-methyl benzylidene) bisphenol (BPAP; 99%) were acquired from J&K Chemical Corporation (Beijing, China). 4, 4′-(hexafluoroisopropylidene) diphenol (BPAF; 98%) and dopamine hydrochloride were purchased from Alfa Aesar (Tianjin, China). Zirconium (IV) chloride (ZrCl$_4$, 99.5%), 2-aminoterephthalic acid (H$_2$BDC-NH$_2$), N, N′ Dimethylformamide (DMF) was purchased from Aladdin Industry Co. Ltd. (Shanghai, China). Iron (III) chloride hexahydrate (FeCl$_3$·6H$_2$O), sodium acetate (CH$_3$COONa), ethanol, ethylene glycol, acetonitrile (ACN), tris(hydroxymethyl) aminomethane (Tris) were purchased from Merck.

All other chemicals were of the top grade commercially available. Deionized water was purified using Milli-Q system (Millipore, Bedford, MA). Stock solutions containing bisphenols at 10 mg mL^{-1} were prepared by dissolving the five kinds of bisphenols with methanol in a 25 mL volumetric flask. All solutions were kept in dark at 4 °C before use.

2.2. Synthesis of Fe$_3$O$_4$@PDA@UiO-66-NH$_2$

As shown in Fig. 2, the whole synthetic scheme of Fe$_3$O$_4$@PDA@ UiO-66-NH$_2$ consists of three steps.

Firstly, the Fe$_3$O$_4$ microparticles were synthesized following the solvothermal reaction [37]. FeCl$_3$·6H$_2$O (1.35 g) and CH$_3$COONa (3.60 g) were dispersed in 75 mL of ethylene glycol and stirred for 40 min until a homogeneous solution was obtained. The solution was then transferred into a Teflon-lined stainless-steel autoclave (100 mL capacity) and kept at 200 °C for 16 h. The solution was naturally cooled to room temperature after the reaction. The obtained black magnetic sphere Fe$_3$O$_4$ was collected by magnetic separation and washed with deionized water and ethanol at least three times, and finally dried under vacuum at 50 °C.

Secondly, Fe$_3$O$_4$@PDA was obtained by the polymerization of dopamine on the magnetic sphere surface in basic solution. Briefly, 1.20 g Fe$_3$O$_4$ was added into 750 mL Tris buffer, which contained 0.18 g Tris and 0.60 g dopamine hydrochloride in deionized water. The solution was kept mechanical stirring at room temperature for 5 h. The obtained Fe$_3$O$_4$@PDA was collected by magnetic separation and then washed with deionized water and ethanol at least three times, and finally dried under vacuum at 50 °C.

Finally, Fe$_3$O$_4$@PDA@UiO-66-NH$_2$ was prepared by a simple one-pot reaction. 0.50 g Fe$_3$O$_4$@PDA and 0.80 g ZrCl$_4$ (9 mM) were dispersed in 375 mL of DMF and stirred at room temperature for 1 h. Then 0.12 g (9 mM) 2-aminoterephthalic acid (H$_2$BDC-NH$_2$) was added to the solution until the system temperature went up to 120 °C and stirred for 45 min. The obtained Fe$_3$O$_4$@PDA@ UiO-66-NH$_2$ was collected by magnetic separation and washed with DMF and ethanol at least three times. Then, the material was dried in a vacuum oven at 50 °C prior to characterization and application.

2.3. Instruments

The instruments used for the material characterization were as follows: 1) Philips XL30 electron microscope (Netherlands) at 20 kV which offered scanning electron microscopy (SEM) images and energy dispersive X-ray (EDX) results to observe the morphology and the structure; 2) JEOL 2011 microscope (Japan) at 200 kV which offered transmission electron microscopy (TEM) images to take an internal look at the structure; 3) Nicolet Fourier spectrophotometer (U.S.A.) which achieved fourier-transform infrared (FTIR) spectroscopic analysis to analyze the functional groups of the materials; 4) Bruker D4 X-ray diffractometer at 40 kV, 40 mA which allowed powder X-ray diffraction patterns (XRD) being operated to identify the phase purity and crystallinity of the materials; 5) Micromeritics Tristar 3000 analyzer (U.S.A.) at 77 K which identified the nitrogen sorption isotherms to determine surface area, pore volume, and pore size distribution.

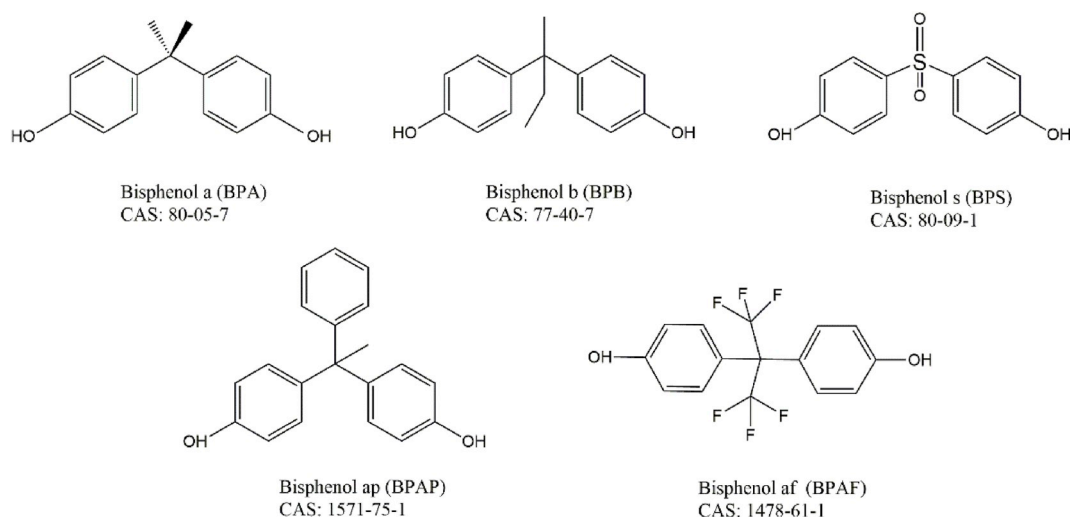The LC-MS measurements were carried out with an Agilent 1260 LC

Fig. 1. Names, acronyms, structures, and Chemical Abstracts Service (CAS) numbers of test chemicals.
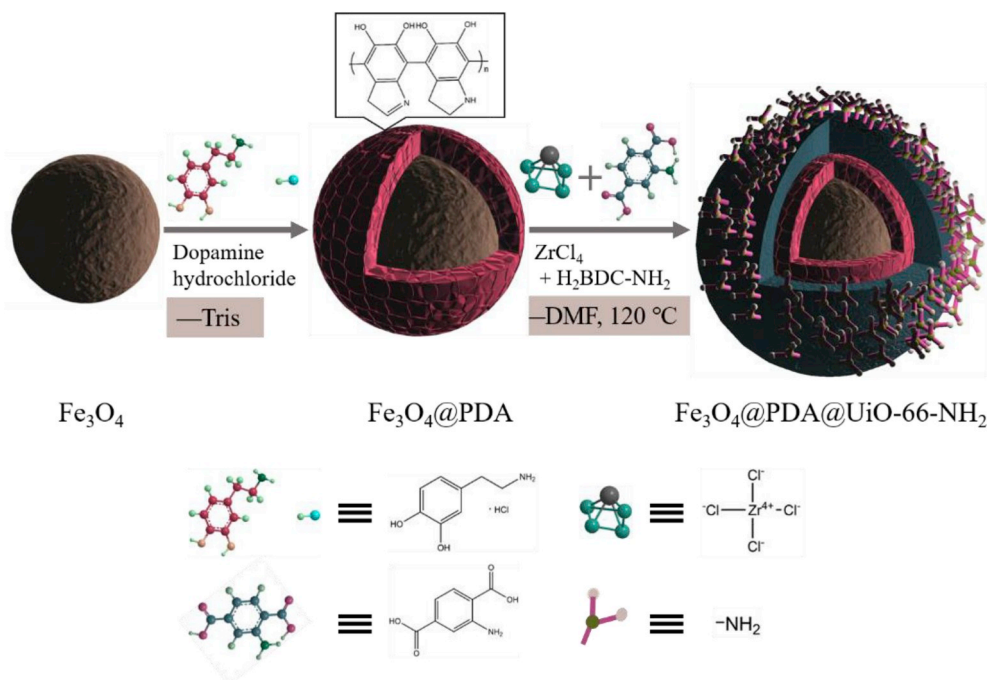
Bisphenol a (BPA)
CAS: 80-05-7

Bisphenol b (BPB)
CAS: 77-40-7

Bisphenol s (BPS)
CAS: 80-09-1

Bisphenol ap (BPAP)
CAS: 1571-75-1

Bisphenol af (BPAF)
CAS: 1478-61-1

Fig. 2. Scheme of the synthesis process of Fe$_3$O$_4$@PDA@UiO-66-NH$_2$

system (Agilent, USA) coupled to an Agilent 6120 single quadrupole mass spectrometer (Agilent, USA). Chromatographic separation was conducted on an Agilent CORTECS® C18 column (100 mm × 2.1 mm, 2.7 μm) with 0.3 mL min^{-1} as the experimental flow rate, and the column oven temperature was set at 40 °C. 10 μL was set as the injection volume, and the LC-grade water (A) and acetonitrile (B) were used as the mobile phases of this LC detection method. The following was the gradient elution of this method: (1) 0 min, 90% A; (2) 0.5 min, 90% A; (3) 1.0 min, 10% A; (4) 3.5 min, 10% A; (5) 4 min, 90% A. The mass spectra were acquired at negative mode using Agilent Jet Stream electrospray ionization, and quantifications of all analytes were performed in multiple reaction monitoring (MRM) mode. The other operating parameters were as follows: 1) nebulizer gas pressure, 35 psi; 2) drying gas flow, 9 L/min; 3) drying gas temperature, 350 °C. The LC-MS instrument was controlled by OpenLAB CDS (Agilent) software, and data acquisition and processing were carried out.

2.4. Optimization of magnetic solid-phase extraction parameters

The good adsorption ability of the synthesized materials may be due to the unique structure of Fe$_3$O$_4$@PDA@UiO-66-NH$_2$ which was suitable for the adsorption and elution of bisphenols. Except that the large specific surface area and mesoporous structure of synthesized materials can adsorb bisphenols, possible extraction mechanisms of the good MSPE performance may be may be related to the following mechanisms (Fig. 3). Firstly, the hydrogen bonds are formed between the amino groups on the surface of the Fe$_3$O$_4$@PDA@UiO-66-NH$_2$ and the hydroxyl groups of the bisphenols to improve the extraction efficiency [4]. Secondly, the π–π interaction between aromatic rings of Zr-MOFs and bisphenols may cause the adsorption [33,38]. Thirdly, the bisphenols have a high logKow value, indicating that they are likely to escape from the water phase to the surface of Fe$_3$O$_4$@PDA@UiO-66-NH$_2$.

When materials are prepared for practical use, optimization of the method parameters is always needed. The working solutions with a
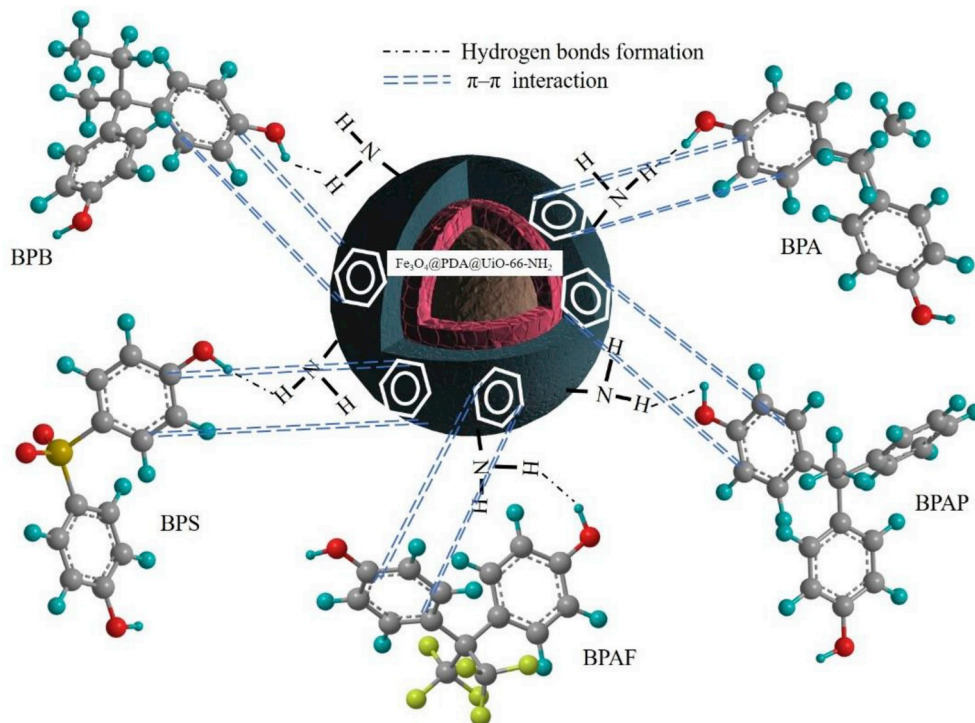
Fig. 3. Possible mechanisms for the adsorption of five bisphenols on Fe_3O_4@PDA@UiO-66-NH_2.

specific concentration were prepared by diluting the stock solution with deionized water. 10 mL of deionized water containing 50 μg/L of five bisphenols standard solution was placed in a vial with PTFE-silicone septum. The effect of the amount of Fe_3O_4@PDA@UiO-66-NH_2 on the extraction was investigated, ranging from 10 mg to 50 mg. The material was dispersed into the prepared solution, and after incubation for different adsorption times (10, 20, 30 and 40 min) the supernatant was then discarded with an external magnetic field to separate the material from the water sample. The material was then eluted with 1 mL of different elution solvents (including Methanol, Acetonitrile, Acetone and Isopropanol) with continuous vibration for different times (10, 20, 30 and 40 min), and the supernatant was obtained by a magnet bar for further quantitative detection by LC-MS. The effect of pH on enrichment was also considered in the optimization experiment.

2.5. Analytical validations

To investigate the performance of the developed MSPE method for bisphenols, a series of water samples containing various concentrations of bisphenols (0.5–100 μg/L) were prepared for calibration. The limits of detection (LOD) and the limits of quantification (LOQ) were calculated by analyzing water samples spiked with bisphenols of a low concentration on the basis of signal-to-noise ratio of 3 and 10 (S/N = 3 and S/N = 10), respectively.

In addition, the repeatability standard deviations (RSD) were used to estimate the precision of the developed MSPE method by measuring bisphenols in water samples at the concentration of 50 μg/L in 5 replicates under the optimized conditions. The recoveries of the bisphenols were calculated as magnetic solid-phase extracting standard-spiked samples divided by the standard concentrations.

2.6. Magnetic solid-phase extraction of the real water samples

To evaluate the extraction performance of the synthetic materials in real water examples based on interference effects of complex compounds. The real water samples, taken from the Riyue lake at Fudan University (Shanghai, China), were spiked with different bisphenols to achieve a final concentration of 50 μg/L, and then used to investigate the extraction efficiency under the optimal extraction conditions.

3. Results and discussion

3.1. Characteristics of Fe_3O_4@PDA@UiO-66-NH_2

The morphologies of Fe_3O_4, Fe_3O_4@PDA and Fe_3O_4@PDA@UiO-66-NH_2 were investigated by TEM and SEM. As shown in Fig. 4a–4c, when the magnetic microsphere was sequentially coated with PDA and UIO-66-NH_2 layer, the particle size increased gradually. The TEM images (Fig. 4d–f) showed that the magnetic microspheres (size of about 100 nm) were coated with a thin PDA layer (thickness of about 20 nm). After MOF modification, the crystalline morphology of outer layer of magnetic microsphere (thickness of about 45 nm) was coarser than that of the smooth PDA layer, suggesting that this special structure may improve the adsorption capacity of Fe_3O_4@PDA@UiO-66-NH_2 on bisphenols. EDX analysis was carried out to quantitatively and qualitatively determine the elemental compositions of the adsorbent. As shown in Fig. 5, the synthetic material consisted of oxygen (35.59%, weight concentration), carbon (23.55%, weight concentration), nitrogen (8.89%, weight concentration), iron (18.53%, weight concentration) and zirconium (13.43%, weight concentration). The presence of zirconium in the Fe_3O_4@PDA@UiO-66-NH_2 proved that the third step in material synthesis process was carried out successfully.

FTIR spectroscopic analysis was carried out to investigate the functional groups present on the material samples by identifying the appearance of the characteristic peaks. The FT-IR spectra of Fe_3O_4, Fe_3O_4@PDA and Fe_3O_4@PDA@UiO-66-NH_2 were shown in Fig. 6. For all samples, the broad absorption bands detected at 566 cm^{-1} may be due to the Fe–O–Fe stretching vibrations. The stretching N–H groups at about 3400 cm^{-1}, and the presence of distinct peak at about 3000-2750 cm^{-1} could be attributed to the aliphatic C–H groups [39]. The two distinct peaks at 1379 cm^{-1} and 1565 cm^{-1} can be attributed to the symmetric and asymmetric stretching of carboxyl functional groups, respectively [40,41]. The adsorption band observed at 1617 cm^{-1} was due to the C = C vibration of the SP2 hybridized carbon skeleton [42],
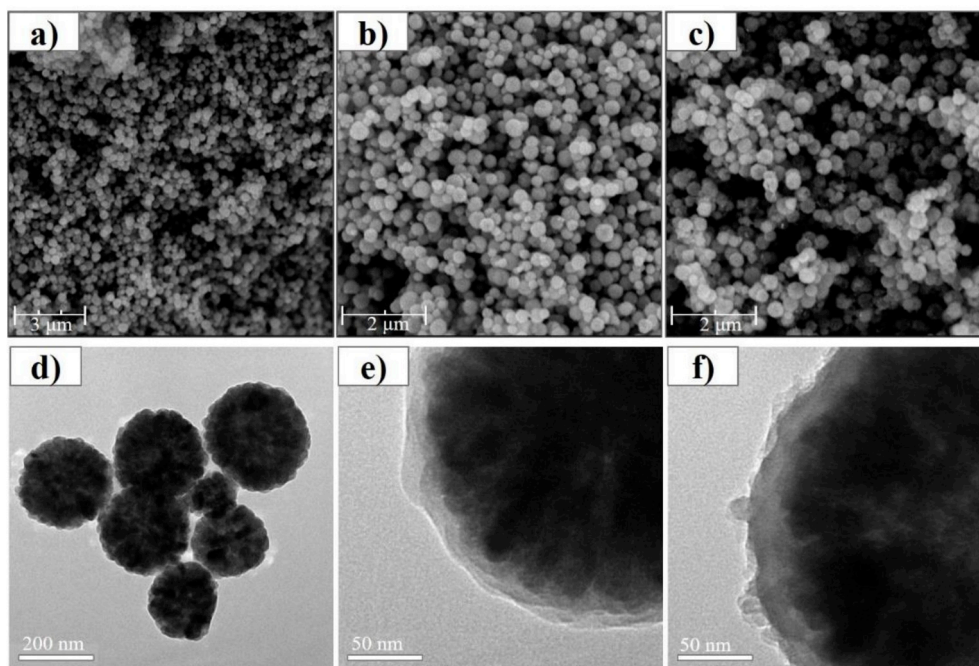
Fig. 4. SEM images of Fe_3O_4 (a), $Fe_3O_4@PDA$ (b), and $Fe_3O_4@PDA@UiO-66-NH_2$ (c), and TEM images of Fe_3O_4 (d), $Fe_3O_4@PDA$ (e), and $Fe_3O_4@PDA@UiO-66-NH_2$ (f).

and the peak appearing around 1253 cm^{-1} could be due to C–N stretching vibration from polydopamine and 2-aminoterephthalic acid [26]. The other significant adsorption bands observed at about 768 cm^{-1} and 1433 cm^{-1} could be attributed to the stretching vibration of the C = O groups [43].

The XRD patterns of the synthesized materials were presented in Fig. 7. It was found that the typical diffraction peaks at $2\theta = 5.2°$, $7.0°$, $12.3°$, $16.7°$, $18.2°$ and $22.3°$ were from the UiO-66-NH$_2$ MOFs, while diffraction peaks around $30.3°$, $35.4°$, $43.1°$, $53.5°$, $57.2°$ and $62.6°$ were related to Fe_3O_4 microspheres [44,45]. The synthesized UiO-66-NH$_2$ was consistent with simulative XRD pattern of UiO-66-NH$_2$, and the recorded pattern showing crystalline nature of the material was in good agreement with the earlier reports [27,46,47]. The appearance of sharp peaks in the XRD patterns of the samples were the evidences of good crystallinity in the prepared MOFs, indicating that the material was successfully synthesized as expected without changing the internal

structure of the magnetic microsphere.

As shown in Fig. 4f, the MOF layer may have a subtle pore structure. To further investigate the internal architectures of $Fe_3O_4@PDA@UiO$-66-NH$_2$ and characterize the pore size distribution, an N$_2$ adsorption-desorption measurement was performed. The nitrogen adsorption-desorption curves and pore size distribution curve were shown in Fig. 8. At relatively low pressure, the adsorption quantity rised rapidly, and the inflection point of the convex isotherm curve was usually close to the monolayer adsorption. As the relative pressure continued to increase, the multi-layer adsorption gradually formed, and finally the vapor pressure reached saturation. The isotherm showed the II type curve, which was frequently described for the existing active interaction on the surface of adsorbent [48]. The pore distribution of the material was relatively uniform with an average pore diameter of 5.61 nm. What's more, when MOF is coated on Fe_3O_4 sphere, the rough surface of the magnetic microsphere would limit the extension of the MOF [49], while
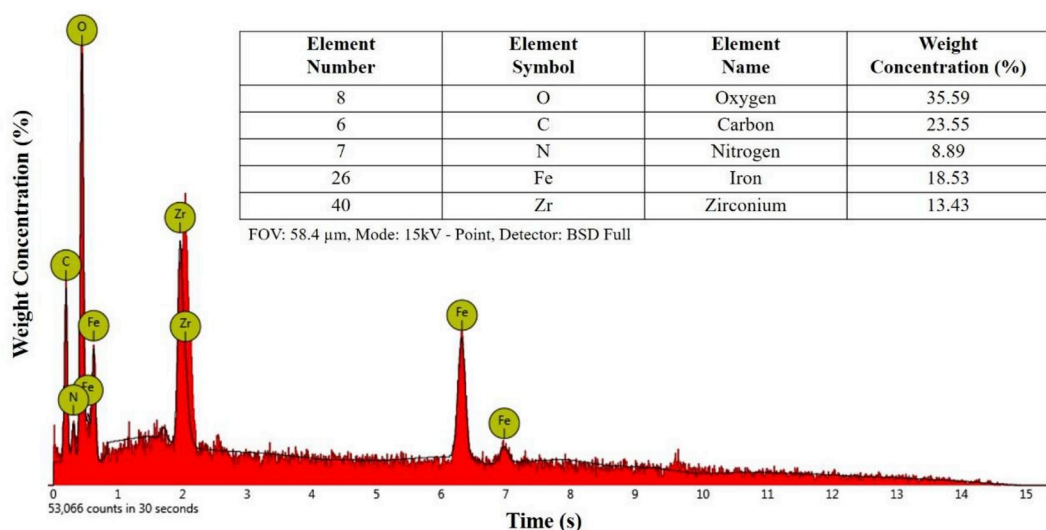

Element Number	Element Symbol	Element Name	Weight Concentration (%)
8	O	Oxygen	35.59
6	C	Carbon	23.55
7	N	Nitrogen	8.89
26	Fe	Iron	18.53
40	Zr	Zirconium	13.43

FOV: 58.4 μm, Mode: 15kV - Point, Detector: BSD Full

Fig. 5. Energy dispersive X-ray spectroscopy analysis of $Fe_3O_4@PDA@UiO-66-NH_2$
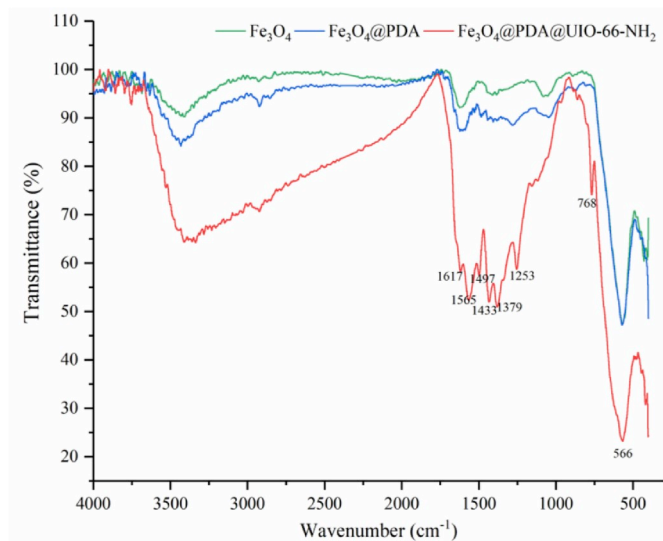
Fig. 6. FT-IR spectra of Fe_3O_4, Fe_3O_4@PDA and Fe_3O_4@PDA@UiO-66-NH$_2$
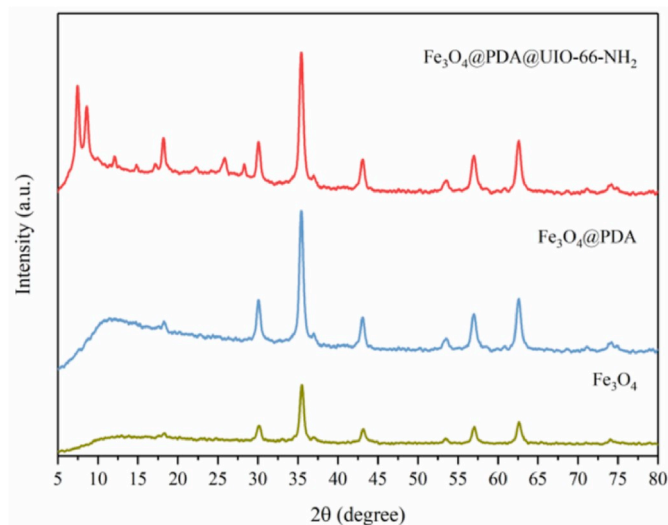
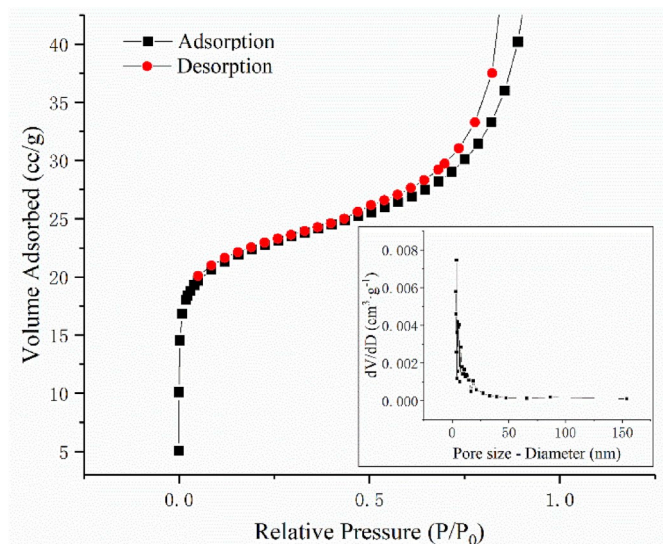**Fig. 7.** XRD patterns of Fe_3O_4, Fe_3O_4@PDA and Fe_3O_4@PDA@UiO-66-NH$_2$

Fig. 8. Nitrogen adsorption–desorption isotherms and pore size distribution of Fe_3O_4@PDA@UiO-66-NH$_2$

the Brunauer–Emmett–Teller (BET) surface area of the synthetic material was still calculated to be 83.53 $\pm$ 0.17 m^2/g and the volume of its pore was 0.12 cm^3/g, indicating that the prepared material can provide more binding sites for enrichment of small molecules.

3.2. Optimization of conditions for MSPE of bisphenols

The optimization results for five parameters (including the amount of material, adsorption time, pH, elution time, and elution solvent) that may have a significant effect on the MSPE performance of bisphenols were shown in Fig. 9a. When the amount of Fe_3O_4@PDA@UiO-66-NH$_2$ was increased from 10 mg to 40 mg, the extraction efficiency of bisphenols gradually increased. However, as the amount of the materials continued to increase from 40 mg to 50 mg, the rate of increase in extraction efficiency remained constant, indicating that the bisphenols were sufficiently adsorbed on the materials when the amount of Fe_3O_4@PDA@UiO-66-NH$_2$ was 40 mg. Therefore, 40 mg of Fe_3O_4@ PDA@UiO-66-NH$_2$ was further used for MSPE.

To determine the effect of extraction time on the adsorption of bisphenols, the extraction time ranging from 10 min to 40 min was tested. As shown in Fig. 9b, as time went on, the extraction efficiency also increased rapidly and remained stable at 30 min, indicating that the optimal extraction time was 30 min. The pH is one of the conditions for ensuring adsorption efficiency, because it may have a considerable effect on the presence of the bisphenols existing form and the charge situations on adsorbent's surface [50]. Therefore, the extraction efficiency in acidic, neutral and alkaline adsorptive environments was studied (Fig. 9c). The result showed that the adsorption efficiency was very poor in an alkaline environment, while there was high extraction efficiency in acidic or alkaline environment with no significant difference, suggesting that the pH = 7 was the optimal condition. The type of eluent is also a key factor in extraction efficiency, and four elution solvents (including methanol, acetone, isopropanol and acetonitrile) were selected for optimization studies in this study. As shown in Fig. 9e, compared with the other 3 eluents, methanol showed the better extraction efficiency for bisphenols. On the basis of selecting methanol as elution solvent, the effect of elution time on extraction efficiency was also investigated. As shown in Fig. 9d, the extraction efficiency kept stability generally after 30 min of elution, so 30 min was chosen as the elution time.

3.3. Analytical validation

The quantitative analytical parameters of the MSPE method under the optimal conditions were summarized in Table 1. Good linearity was obtained for each analyte with correlation coefficients larger than 0.990. The low limits of detection and qualification were 0.013–0.290 μg/L (S/N = 3) and 0.088–1.800 μg/L (S/N = 10), respectively. The mean RSDs value ranged from 0.58% to 1.68%. As shown in Table 2, the LODs/LOQs of the method were lower than most of those of else methods [4,51,52], indicating that a lower concentration of bisphenols can be detected. It is worth mentioning that the LODs/LOQs of the five target bisphenols were in the range of 0.013–0.290 μg/L, which were lower than those of the reported data of the latest proposed technologies such as SBSE, DLLME and MSPE [4,51,52]. Compared with other methods analyzing the real water sample, the MSPE method in this study showed the lower LODs/LOQs than that of the SPME-HPLC-DAD method developed by Wang [17] (0.10–0.30 μg/L) and the SBSE-HPLC-DAD method developed by Xu [52] (1.0 μg/L), but a bit higher than that of the DMIP- SPE-HPLC-DAD method (2.1–3.6 ng/L) [15]. Furthermore, as shown in Table 2, most conventional technologies (e.g. Liquid-liquid extraction and solid-phase extraction) were time-consuming and often use large amounts of harmful organic solvents. In this study, the time of the whole pretreatment process for LC-MS analysis was reduced from 3 to 5 h with conventional enrichment methods to 1 h with the MSPE of Fe_3O_4@
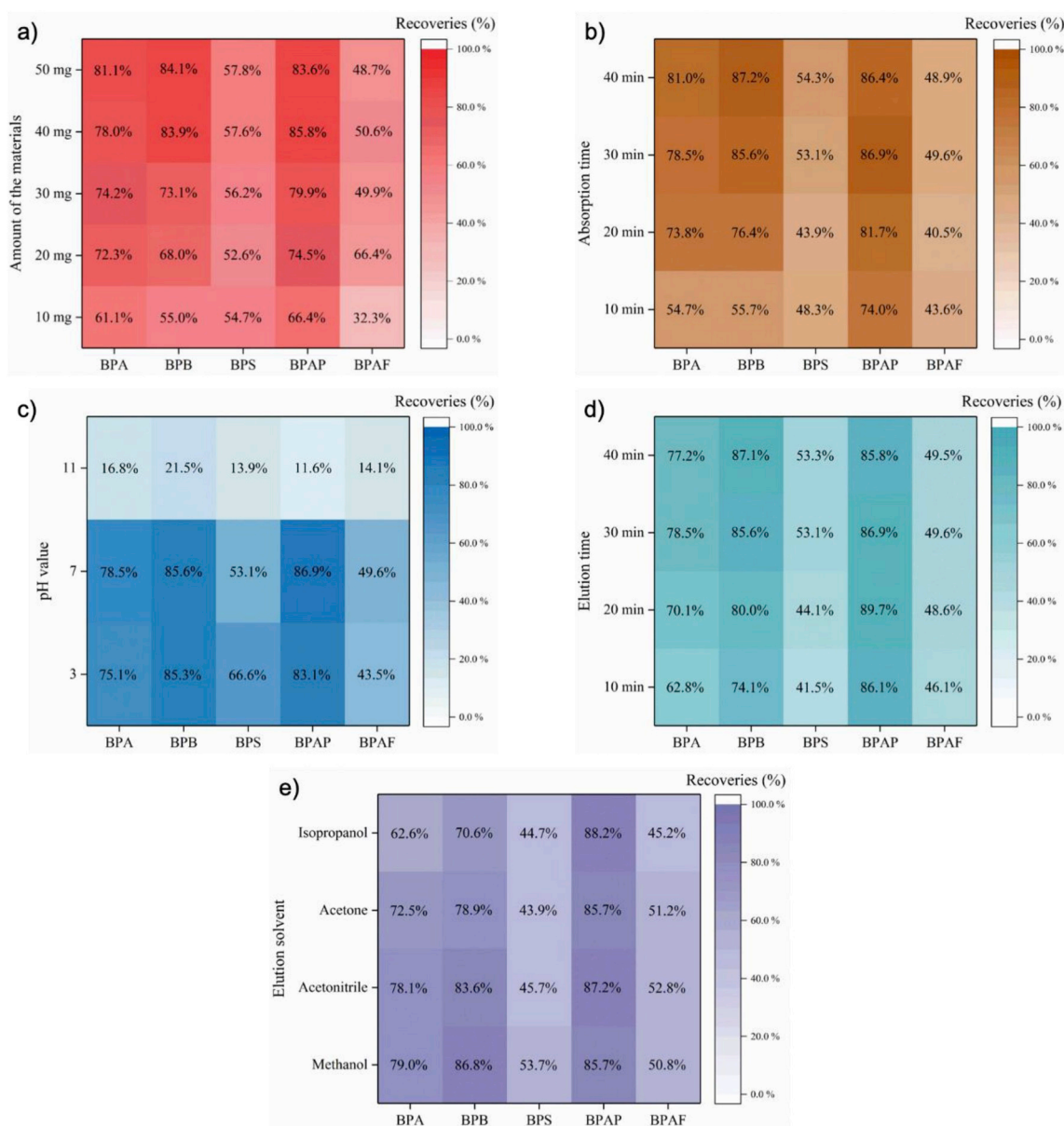
Fig. 9. Effect of five parameters on the MSPE efficiency for bisphenols of Fe₃O₄@PDA@UiO-66-NH₂: a) amount of the materials, b) adsorption time, c) pH, d) elution time and e) elution solvent.

PDA@UiO-66-NH₂, which can be attributed to the fast-magnetic separation extraction and the adsorbent's properties. Moreover, the amount of organic solvent used for eluting was greatly reduced, only 1 mL for each sample was used to elute the bisphenols.

3.4. Real samples analysis

According to the optimal conditions of MSPE, the analysis of real samples was carried out. First, a 10 mL lake samples containing 50 μg/L

of five bisphenols standard solution was placed in a vial with PTFE-silicone septum. Then, 40 mg of Fe₃O₄@PDA@UiO-66-NH₂ was added into the prepared solution, and after enrichment for 30 min, the supernatant was discarded with an external magnetic field separating the material from the water sample. Finally, the bisphenols on material were eluted with 1 mL of methanol with continuous vibration for 30 min, and the supernatant was obtained with a magnet bar for further quantitative detection by LC–MS.

The LC-MS chromatograms of lake water samples, spiked with five

Table 1
Validation of Fe₃O₄@PDA@UiO-66-NH₂ based on LC-MS method.

Bisphenols	Linear range (μg/L)	Regression equation	R^2	LOD (μg/L)	LOQ (μg/L)	RSD (%)
BPA	0.5–100	Y = 50058.83x + 4481.42	0.9993	0.036	0.128	1.26
BPB	0.5–100	Y = 80088.58x + 9342.62	0.9996	0.030	0.112	1.68
BPS	0.5–100	Y = 60610.18x + 6993.89	0.9996	0.120	0.590	0.58
BPAP	0.5–100	Y = 100595.46x + 18851.64	0.9982	0.097	0.088	1.29
BPAF	0.5–100	Y = 208268.58x + 85989.814	0.9921	0.290	1.800	1.56

Table 2

Comparison of Fe_3O_4@PDA@UiO-66-NH_2 with previous reported alternatives for the determination of bisphenols.

Method	Matrix	Adsorbent	Analyte number	LOD	References
SPE-HPLC-DAD	Tap and river water	DMIP	5	2.1–3.6 ng/L	[15]
SPE-LC-MS/MS	Soft drinks	C18 silica	5	5–50 ng/L	[53]
SPE-HPLC-DAD	Human urine	MISMS[a]	8	1.2–2.2 µg/L	[11]
SPE-HPLC-DAD	Sediment, milk and urine	THPE-DMIP[b]	8	0.6–1.1 µg/L	[10]
SBSE [c]-HPLC-DAD	Water, plastic	Dual-template MIP	2	1.0 µg/L	[52]
DLLME[d] -GC-MS/MS	Urine	Trichloroethane	2	0.1–0.2 µg/L	[51]
MSPE-HPLC–FLD	Tea drinks	Fe_3O_4@COFs	2	0.08–0.21 µg/L	[4]
SPME–HPLC–DAD	River water	MWCNTs[e]	4	0.10–0.30 µg/L	[17]
MSPE-LC-MS	Lake water	Fe_3O_4@PDA@UiO-66-NH_2	5	0.013–0.290 µg/L	This study

[a] MISMS: Molecularly imprinted sponge mesoporous silica.
[b] THPE-DMIP: 1,1,1-tris (4-hydroxyphenyl) ethane - Dummy molecularly imprinted polymers.
[c] SBSE: Stir bar sorptive extraction.
[d] DLLME: Dispersive liquid–liquid microextraction.
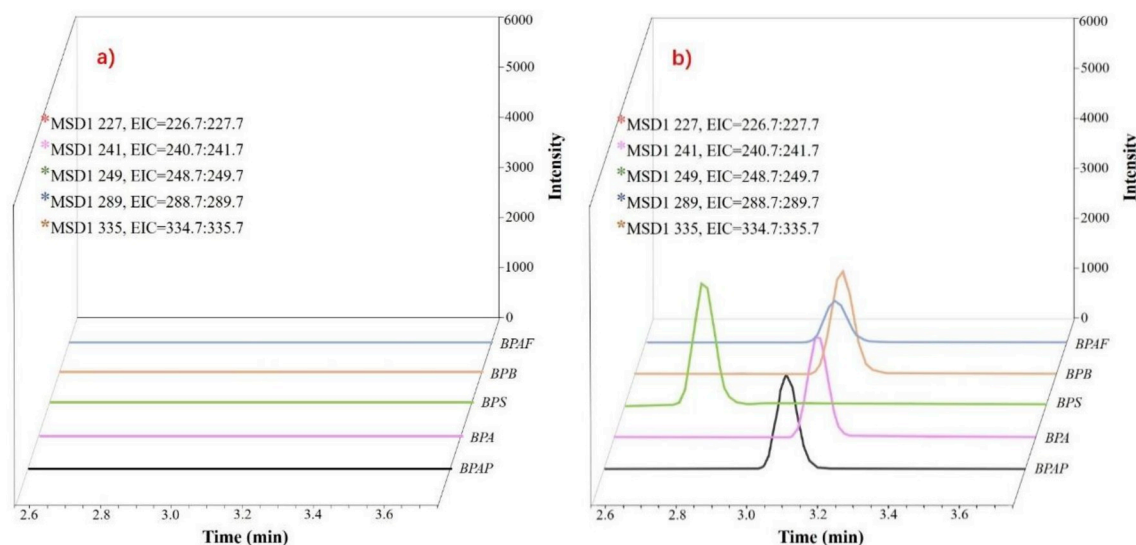[e] MWCNTs: Multi-wall carbon nanotubes.

Fig. 10. The ion chromatograms of spiked lake sample of five bisphenols at 50 µg/L by direct injection into the LC-MS instrument without enrichment (a) and spiked lake sample of five bisphenols at 50 µg/L with Fe_3O_4@PDA@UiO-66-NH_2 enrichment before analysis by LC-MS (b).

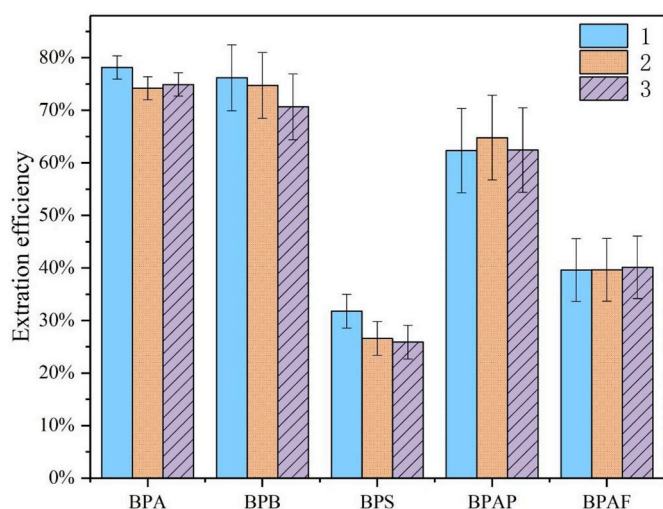**Fig. 11.** Reusability in three cycles of the Fe_3O_4@PDA@UiO-66-NH_2 as SPME adsorbents for extraction of five bisphenols in lake water samples.

bisphenols at the concentration of 50 µg/L, were injected into the LC-MS instrument with or without Fe_3O_4@PDA@UiO-66-NH_2 enrichment before LC-MS analysis. It can be observed that the peak signal of

bisphenols cannot be detected by direct injection into the LC-MS instrument without enrichment (Fig. 10a), which may be related to the poor analysis sensitivity of LC-MS for such low concentration or the complexity of the lake water component. However, when the enrichment of Fe_3O_4@PDA@UiO-66-NH_2 was used prior to LC-MS analysis, the five bisphenols' signals of spiked water sample can be detected and identified by the retention time and the molecular weight of each bisphenol (Fig. 10b). At the same time, satisfactory bisphenol extraction efficiencies of BPA, BPB and BPAP with MSPE enrichment were obtained (Fig. 11), and there was also no denying that the materials had high selectivity for all bisphenols, indicating that the synthetic materials could be used for environmental analysis.

3.5. The reusability of Fe_3O_4@PDA@UiO-66-NH_2

To evaluate the reusability and stability of Fe_3O_4@PDA@UiO-66-NH_2, three batches of bisphenols' enrichment experiment were carried out under the similar conditions. As shown in Fig. 10, it was obvious that the adsorption efficiency of bisphenols was steadily with increase of the cycle number, which indicated that the Fe_3O_4@PDA@UiO-66-NH_2 had high stability and good reusability, which could be used at least three cycles.

4. Conclusion

In summary, a novel Zr-MOFs functionalized with amino groups and magnetic Fe_3O_4 microspheres were prepared and applied to MSPE of the analysis for bisphenols. Compared with the conventional MOF, the amino-functionalized MOFs not only preserved the unique advantages of large specific surface area, mesoporous structure and abundant inorganic sites, but also improved the hydrophilicity to facilitate the enrichment of pollutants in water and offered the possibility of forming hydrogen bonds between the amino groups on the surface of the Fe_3O_4@PDA@UiO-66-NH_2 and the hydroxyl groups of bisphenols to improve the extraction efficiency. The MSPE method earned good linear range, low detection limit and intermediate precision for BPA, BPB, BPS, BPAP, and BPAF, indicating that the Fe_3O_4@PDA@UiO-66-NH_2 can used as suitable sorbents for bisphenols in water. The proposed MSPE method provides a good choice and sensitivity for the analysis of trace bisphenols, which indicates that the magnetic Fe_3O_4@PDA@UiO-66-NH_2 could have a wide potential application in water analysis including analysis of bisphenols and the removal of bisphenols by adsorption.

Declaration of competing interests

We declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

References

[1] G. Russo, A. Capuozzo, F. Barbato, C. Irace, R. Santamaria, L. Grumetto, Cytotoxicity of seven bisphenol analogues compared to bisphenol A and relationships with membrane affinity data, Chemosphere 201 (2018) 432–440.

[2] H.M. Kuch, K. Ballschmiter, Determination of endocrine-disrupting phenolic compounds and estrogens in surface and drinking water by HRGC−(NCI)−MS in the picogram per liter range, Environ. Sci. Technol. 35 (15) (2001) 3201–3206.

[3] N. Salgueiro-Gonzalez, S. Castiglioni, E. Zuccato, I. Turnes-Carou, P. Lopez-Mahia, S. Muniategui-Lorenzo, Recent advances in analytical methods for the determination of 4-alkylphenols and bisphenol A in solid environmental matrices: a critical review, Anal. Chim. Acta 1024 (2018) 39–51.

[4] Z.H. Deng, X. Wang, X.L. Wang, C.L. Gao, L. Dong, M.L. Wang, R.S. Zhao, A coreshell structured magnetic covalent organic framework (type Fe3O4@COF) as a sorbent for solid-phase extraction of endocrine-disrupting phenols prior to their quantitation by HPLC, Microchim. Acta. 186 (2) (2019).

[5] N. Caballero-Casero, L. Lunar, S. Rubio, Analytical methods for the determination of mixtures of bisphenols and derivatives in human and environmental exposure sources and biological fluids. A review, Anal. Chim. Acta 908 (2016) 22–53.

[6] A. Moral, M.D. Sicilia, S. Rubio, D. Perez-Bendito, Determination of bisphenols in sewage based on supramolecular solid-phase extraction/liquid chromatography/fluorimetry, J. Chromatogr. A 1100 (1) (2005) 8–14.

[7] C.H. Lin, S.L. Chang, T.P. Wei, High-T-g transparent poly(ether sulfone)s based on phosphinated bisphenols, Macromol. Chem. Phys. 212 (5) (2011) 455–464.

[8] H.C. Chang, H.T. Lin, C.H. Lin, Benzoxazine-based phosphinated bisphenols and their application in preparing flame-retardant, low dielectric cyanate ester thermosets, Polym Chem-Uk 3 (4) (2012) 970–978.

[9] C.Y. Liao, K. Kannan, A survey of alkylphenols, bisphenols, and triclosan in personal care products from China and the United States, Arch. Environ. Contam. Toxicol. 67 (1) (2014) 50–59.

[10] X.L. Sun, J.C. Wang, Y. Li, J. Jin, J.J. Yang, F. Li, S.M. Shah, J.P. Chen, Highly classselective solid-phase extraction of bisphenols in milk, sediment and human urine samples using well-designed dummy molecularly imprinted polymers, J. Chromatogr. A 1360 (2014) 9–16.

[11] J.J. Yang, Y. Li, J.C. Wang, X.L. Sun, R. Cao, H. Sun, C.N. Huang, J.P. Chen, Molecularly imprinted polymer microspheres prepared by Pickering emulsion polymerization for selective solid-phase extraction of eight bisphenols from human urine samples, Anal. Chim. Acta 872 (2015) 35–45.

[12] C.E. Gattullo, H. Bahrs, C.E.W. Steinberg, E. Loffredo, Removal of bisphenol A by the freshwater green alga Monoraphidium braunii and the role of natural organic matter, Sci. Total Environ. 416 (2012) 501–506.

[13] Y.X. Feng, J. Yin, Z.H. Jiao, J.C. Shi, M. Li, B. Shao, Bisphenol AF may cause testosterone reduction by directly affecting testis function in adult male rats, Toxicol. Lett. 211 (2) (2012) 201–209.

[14] S. Eladak, T. Grisin, D. Moison, M.J. Guerquin, T. N'Tumba-Byn, S. Pozzi-Gaudin, A. Benachi, G. Livera, V. Rouiller-Fabre, R. Habert, A new chapter in the bisphenol A story: bisphenol S and bisphenol F are not safe alternatives to this compound, Fertil. Steril 103 (1) (2015) 11–21.

[15] X.L. Sun, J.C. Wang, Y. Li, J. Jin, B.Q. Zhang, S.M. Shah, X.L. Wang, J.P. Chen, Highly selective dummy molecularly imprinted polymer as a solid-phase extraction sorbent for five bisphenols in tap and river water, J. Chromatogr. A 1343 (2014) 33–41.

[16] C.Y. Liao, F. Liu, H. Alomirah, V.D. Loi, M.A. Mohd, H.B. Moon, H. Nakata, K. Kannan, Bisphenol S in urine from the United States and seven asian countries: occurrence and human exposures, Environ. Sci. Technol. 46 (12) (2012) 6860–6866.

[17] L.L. Wang, Z.Z. Zhang, X. Xu, D.F. Zhang, F. Wang, L. Zhang, Simultaneous determination of four trace level endocrine disrupting compounds in environmental samples by solid-phase microextraction coupled with HPLC, Talanta 142 (2015) 97–103.

[18] C.Y. Liao, F. Liu, H.B. Moon, N. Yamashita, S.H. Yun, K. Kannan, Bisphenol analogues in sediments from industrialized areas in the United States, Japan, and korea: spatial and temporal distributions, Environ. Sci. Technol. 46 (21) (2012) 11558–11565.

[19] G. Mascolo, V. Locaputo, G. Mininni, New perspective on the determination of flame retardants in sewage sludge by using ultrahigh pressure liquid chromatography-tandem mass spectrometry with different ion sources, J. Chromatogr. A 1217 (27) (2010) 4601–4611.

[20] M. Polo, M. Llompart, C. Garcia-Jares, G. Gomez-Noya, M.H. Bollain, R. Cela, Development of a solid-phase microextraction method for the analysis of phenolic flame retardants in water samples, J. Chromatogr. A 1124 (1–2) (2006) 11–21.

[21] N.H. Tran, J.Y. Hu, S.L. Ong, Simultaneous determination of PPCPs, EDCs, and artificial sweeteners in environmental water samples using a single-step SPE coupled with HPLC-MS/MS and isotope dilution, Talanta 113 (2013) 82–92.

[22] D. Podlipna, M. Cichna-Markl, Determination of bisphenol A in canned fish by solgel immunoaffinity chromatography, HPLC and fluorescence detection, Eur. Food Res. Technol. 224 (5) (2007) 629–634.

[23] J.H. Kang, F. Kondo, Determination of bisphenol A in canned pet foods, Res. Vet. Sci. 73 (2) (2002) 177–182.

[24] W. Wang, K.O. Abualnaja, A.G. Asimakopoulos, A. Covaci, B. Gevao, B. Johnson-Restrepo, T.A. Kumosani, G. Malarvannan, T.B. Minh, H.B. Moon, H. Nakata, R.K. Sinha, K. Kannan, A comparative assessment of human exposure to tetrabromobisphenol A and eight bisphenols including bisphenol A via indoor dust ingestion in twelve countries, Environ. Int. 83 (2015) 183–191.

[25] H.C. Zhou, S. Kitagawa, Metal-organic frameworks (MOFs), Chem. Soc. Rev. 43 (16) (2014) 5415–5418.

[26] I. Ahmed, S.H. Jhung, Effective adsorptive removal of indole from model fuel using a metal-organic framework functionalized with amino groups, J. Hazard Mater. 283 (2015) 544–550.

[27] Y.Q. Xie, C.H. Deng, Designed synthesis of a "One for Two" hydrophilic magnetic amino-functionalized metal-organic framework for highly efficient enrichment of glycopeptides and phosphopeptides, Sci. Rep. 7 (2017).

[28] J.R. Li, R.J. Kuppler, H.C. Zhou, Selective gas adsorption and separation in metalorganic frameworks, Chem. Soc. Rev. 38 (5) (2009) 1477–1504.

[29] H. Furukawa, K.E. Cordova, M. O'Keeffe, O.M. Yaghi, The chemistry and applications of metal-organic frameworks, Science 341 (6149) (2013) 974–+.

[30] J.W. Liu, L.F. Chen, H. Cui, J.Y. Zhang, L. Zhang, C.Y. Su, Applications of metalorganic frameworks in heterogeneous supramolecular catalysis, Chem. Soc. Rev. 43 (16) (2014) 6011–6061.

[31] N.A. Khan, S.H. Jhung, Remarkable adsorption capacity of CuCl2-loaded porous vanadium benzenedicarboxylate for benzothiophene, Angew. Chem. Int. Ed. 51 (5) (2012) 1198–1201.

[32] L. Joseph, B.M. Jun, M. Jang, C.M. Park, J.C. Munoz-Senmache, A.J. Hernandez-Maldonado, A. Heyden, M. Yu, Y. Yoon, Removal of contaminants of emerging concern by metal-organic framework nanoadsorbents: a review, Chem. Eng. J. 369 (2019) 928–946.

[33] Y.Q. Xie, C.H. Deng, Y. Li, Designed synthesis of ultra-hydrophilic sulfo-functionalized metal-organic frameworks with a magnetic core for highly efficient enrichment of the N-linked glycopeptides, J. Chromatogr. A 1508 (2017) 1–6.

[34] X.Y. Wang, C.H. Deng, Preparation of magnetic graphene @polydopamine @Zr-MOF material for the extraction and analysis of bisphenols in water samples, Talanta 144 (2015) 1329–1335.

[35] Y.H. Yan, Z.F. Zheng, C.H. Deng, Y. Li, X.M. Zhang, P.Y. Yang, Hydrophilic polydopamine-coated graphene for metal ion immobilization as a novel immobilized metal ion affinity chromatography platform for phosphoproteome analysis, Anal. Chem. 85 (18) (2013) 8483–8487.

[36] M. Zhao, C.J. Dai, Nonlinear dynamic in an ecological system with impulsive effect and optimal foraging, Abstr. Appl. Anal. 2014 (2014) 169609.

[37] R.S. Juang, C.J. Su, M.C. Wu, H.C. Lu, S.F. Wang, A.C. Sun, Fabrication of magnetic Fe3O4 nanoparticles with unidirectional extension pattern by a facile and ecofriendly microwave-assisted solvothermal method, J. Nanosci. Nanotechnol. 19 (12) (2019) 7645–7653.

[38] Y.Q. Xie, C.H. Deng, Highly efficient enrichment of phosphopeptides by a magnetic lanthanide metal-organic framework, Talanta 159 (2016) 1–6.

[39] M. Mahdiani, A. Sobhani, F. Ansari, M. Salavati-Niasari, Lead hexaferrite nanostructures: green amino acid sol-gel auto-combustion synthesis, characterization and considering magnetic property, J. Mater. Sci. Mater. Electron. 28 (23) (2017) 17627–17634.

[40] S.N. Tambat, P.K. Sane, S. Suresh, O.N. Varadan, A.B. Pandit, S.M. Sontakke, Hydrothermal synthesis of NH2-UiO-66 and its application for adsorptive removal of dye, Adv. Powder Technol. 29 (11) (2018) 2626–2632.

[41] J.Y. Hou, Y. Luan, J. Tang, A.M. Wensley, M. Yang, Y.F. Lu, Synthesis of UiO-66-NH2 derived heterogeneous copper (II) catalyst and study of its application in the selective aerobic oxidation of alcohols, J. Mol. Catal. A Chem. 407 (2015) 53–59.

[42] J.J. Wang, W.J. Xu, J.W. Ren, X.H. Liu, G.Z. Lu, Y.Q. Wang, Efficient catalytic conversion of fructose into hydroxymethylfurfural by a novel carbon-based solid acid, Green Chem. 13 (10) (2011) 2678–2681.

[43] A. Ebrahimian Pirbazari, E. Saberikhah, M. Badrouh, M.S. Emami, Alkali treated Foumanat tea waste as an efficient adsorbent for methylene blue adsorption from aqueous solution, Water Resources and Industry 6 (2014) 64–80.

[44] M. Zhao, C.H. Deng, Designed synthesis of fluorous-functionalized magnetic mesoporous microspheres for specific enrichment of phosphopeptides with fluorous derivatization, Proteomics 16 (7) (2016) 1051–1058.

[45] J.B. Jiang, X.N. Sun, Y. Li, C.H. Deng, G.L. Duan, Facile synthesis of Fe3O4@PDA core-shell microspheres functionalized with various metal ions: a systematic comparison of commonly-used metal ions for IMAC enrichment, Talanta 178 (2018) 600–607.

[46] W.J. Zhang, H.L. Huang, C.L. Zhong, D.H. Liu, Cooperative effect of temperature and linker functionality on CO2 capture from industrial gas mixtures in metal-organic frameworks: a combined experimental and molecular simulation study, Phys. Chem. Chem. Phys. 14 (7) (2012) 2317–2325.

[47] J.H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga,

K.P. Lillerud, A new zirconium inorganic building brick forming metal organic frameworks with exceptional stability, J. Am. Chem. Soc. 130 (42) (2008) 13850–13851.

[48] P.P. Zolotarev, V.V. Ugrozov, I.A. Yabko, Theoretical-analysis of kinetic curves for biporous sorbents in the case of linear sorption isotherms based on sorption in transport pores .1. Case of sorption from an unbounded volume, Zh. Fiz. Khim. 58 (7) (1984) 1658–1661.

[49] Q.J. Liu, C.H. Deng, N.R. Sun, Hydrophilic tripeptide-functionalized magnetic metal-organic frameworks for the highly efficient enrichment of N-linked glyco-peptides, Nanoscale 10 (25) (2018) 12149–12155.

[50] J. Li, X.X. Wang, G.X. Zhao, C.L. Chen, Z.F. Chai, A. Alsaedi, T. Hayat, X.K. Wang, Metal-organic framework-based materials: superior adsorbents for the capture of toxic and radioactive metal ions, Chem. Soc. Rev. 47 (7) (2018) 2322–2356.

[51] F. Vela-Soria, O. Ballesteros, A. Zafra-Gomez, L. Ballesteros, A. Navalon, A multi-class method for the analysis of endocrine disrupting chemicals in human urine samples. Sample treatment by dispersive liquid-liquid microextraction, Talanta 129 (2014) 209–218.

[52] Z.G. Xu, Z.L. Yang, Z.M. Liu, Development of dual-templates molecularly imprinted stir bar sorptive extraction and its application for the analysis of environmental estrogens in water and plastic samples, J. Chromatogr. A 1358 (2014) 52–59.

[53] H. Gallart-Ayala, E. Moyano, M.T. Galceran, Analysis of bisphenols in soft drinks by on-line solid phase extraction fast liquid chromatography tandem mass spectrometry, Anal. Chim. Acta 683 (2) (2011) 227–233.