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A core-shell 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

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Abstract

A magnetic covalent organic framework (Fe$_3$O$_4$@COF) with core–shell structure was fabricated at room temperature and used as an adsorbent for magnetic solid-phase extraction of polar endocrine-disrupting phenols (4-n-nonylphenol, 4-n-octylphenol, bisphenol A and bisphenol AF). The sorbent was characterized by transmission electron microscopy, FTIR, powder X-ray diffraction and other techniques. The main parameters governing the extraction efficiency were optimized. The phenols were quantified by HPLC with fluorometric detection. The method has attractive features such as low limits of detection (0.08–0.21 ng.mL^{-1}), wide linear ranges (0.5–1000 ng.mL^{-1}), and good repeatability (intra-day: 0.39%–4.99%; inter-day: 1.57%–5.21%). Satisfactory results were obtained when the developed method was applied to determine the four target pollutants in real world drink samples with spiked recoveries over the range of 81.3~118.0%. This indicates that the method is a powerful tool for the enrichment and determination of endocrine-disrupting phenols in drink samples.

Keywords Core–shell structured magnetic microspheres · Fe$_3$O$_4$@COFs · Bisphenols · 4-n-nonylphenol · 4-n-octylphenol · Absorption · Pretreatment · Determination · Optimization · Drink samples

Introduction

Endocrine-disrupting chemicals (EDCs) are exogenous substances that can interfere with the maintenance of organisms' balance, reproduction, development, and the synthesis, release, transmission, binding, excretion, action, or removal of

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hormones [1, 2]. EDCs can be divided into polychlorinated biphenyls, phthalates, phenols, heavy metals, organotins, and other substances based on their structural characteristics [1]. Among them, endocrine-disrupting phenols mainly include 4-n-nonylphenol (NP), 4-n-octylphenol (OP), and bisphenols (BPs), which are widely used as surfactants and plasticizers in the production and synthesis of food packaging materials [3]. These phenols are also widespread in food and the environment [4]. Environmental endocrine disruptors are associated with abnormalities in the reproductive, immune, and nervous systems of humans and animals as well as increased incidence of certain tumors [3].

Several different techniques, such as fluorescent molecular sensing [5], biometrics-chemical analysis methods [6], gas chromatography-mass spectrometrometry (GC–MS) [7], liquid chromatography (LC) [8], and liquid chromatography-mass spectrometrometry (LC/MS–MS) [9], can be used to determine endocrine-disrupting phenols in various samples, but modern chromatographic techniques are commonly used because of their low limits of detection, rapidity, high sensitivity, and convenience. The direct determination of endocrine-disrupting phenols by chromatographic techniques is usually difficult because the concentrations of endocrine-

disrupting phenols is becoming lower and lower in different kinds of samples and the sample matrices are very complex. As a consequence, quick, easy, and efficient sample pretreatment techniques are in urgent need for chromatographic analysis [10].

Several sample pretreatment techniques, such as solid-phase extraction (SPE) [7, 9, 11], liquid–liquid extraction [12], soxhlet extraction [13, 14], and solid-phase micro-extraction [15], have been utilized to enrich endocrine-disrupting phenols prior to chromatographic analysis. By introducing magnetic or magnetizable sorbents into the sample solution, magnetic solid-phase extraction (MSPE) has been discovered as a novel sample pretreatment technique for the enrichment and determination of trace pollutants [16]. In MSPE, target analytes are absorbed by magnetic solid sorbents dispersing completely in the sample solution, and magnetic solid sorbents can be rapidly separated from suspensions by using an external magnetic field easily and quickly [17]. MSPE is a prospective method for sample preparations considering its convenience, rapidity, saving expenditure, labor, and spending less time [18]. Studies have focused on exploring and synthesizing novel MSPE adsorbents because of the importance of magnetic adsorbents in the improvement of the extraction efficiency of MSPE for various targets [19]. Various magnetic materials were used to extract trace endocrine-disrupting phenols from foods and other samples, such as magnetic three-dimensional graphene composite [20], Fe_3O_4@ MIPs [21, 22],, Fe_3O_4@SiO_2@[OMIM] [23], iron-ferric oxide/graphene oxide composite ($Fe@Fe_2O_3$/GO) [24] and so on.

Covalent organic frameworks (COFs) are polyporous crystal-structured polymers with building blocks which was linked with covalent bond, and they have been extensively investigated since they were first reported in the year of 2005 [25]. COFs are widely applied as catalysts, gas storage containers, optoelectronics carriers, pretreatment materials for chromatographic separation, chemical sensing sensors and so on because of their good properties, such as tunable pore size, high-porosity, low crystalline density, and super structural stability compared with those of MOFs and other new materials [26–30]. This kind of easily synthesized magnetic covalent organic frameworks which have core–shell structure have been used to achieve the selective enrichment and elimination of peptides from complex biologic samples and they may show great capacity for MSPE adsorbent applications to enrich endocrine-disrupting phenols in food samples [31].

In this work, magnetic covalent organic frameworks which have core–shell structure (Fe_3O_4@COFs) were synthesized for the selective extraction of four kinds of endocrine-disrupting phenols (4-n-nonylphenol (NP), 4-n-octylphenol (OP), bisphenol A (BPA) and bisphenol AF (BPAF)). And

then, we characterized the Fe_3O_4@COFs microspheres which have a core–shell structure. The feasibility of employing these magnetic covalent organic framework microspheres to be a kind of novel MSPE adsorbent was explored. Four kinds of endocrine-disrupting phenols were chosen as aiming analytes, and HPLC equipped with fluorescence detector was utilized for detection precisely. Groups of single-factor experiments were designated to evaluate the effects of the experimental parameters. The possible mechanism of the Fe_3O_4@COFs microspheres to extract endocrine-disrupting phenols was also discussed. In short, we established an effective MSPE method which can be utilized for the enrichment and sensitive detection of endocrine-disrupting phenols in plastic-packaged drink samples.
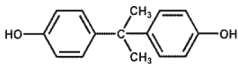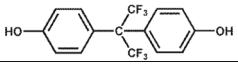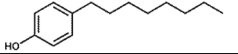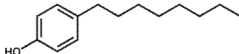
Experimental

Chemicals and reagents

The chemicals and reagents used in this work were as follows: 4-n-Octylphenol (OP) and 4-n-nonylphenol (NP) (Supelco, Bellefonte, PA, USA, www.sigmaaldrich.com); BPA and BPAF (Aladdin Industrial Corporation, Shanghai, China, www.aladdin-e.com) (Table 1); ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), sodium citrate dehydrate ($Na_3Cit \cdot 2H_2O$), dimethyl sulfoxide (DMSO), tetrahydrofuran, ethylene glycol, acetic acid, HPLC-grade water, ethanol, and molecular sieve type 4A (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China, www.sinoreagent.com); 1,3,5-tris(4-aminophenyl)benzene (TAPB) and terephthaldicarboxaldehyde (TPA) (Shanghai Macklin Biochemical Technology Co., Ltd., Shanghai, China, www.macklin.cn); methanol, acetone, and acetonitrile (Tedia Company, Ohio, USA, www.tedia.com); and dichloromethane and n-hexane (Concord Technology, Tianjin, China, tjconcord.labscn.com.cn). Reagents and chemicals at least analytical grade were used in this work. Stock solution containing BPA, BPAF, OP, and NP at 1 mg·mL^{-1} was prepared by dissolving the four kinds of endocrine-disrupting phenols in a 25 mL volumetric flask. The stock solution was diluted gradually using methanol to obtain a series of standard solutions with different concentration, and all of the solutions were placed in the dark at 4 °C prior to use.

Synthesis of Fe_3O_4 and Fe_3O_4@COFs

Fe_3O_4 and Fe_3O_4@COFs were synthesized refer to the method in reference [31] with slight modifications. The specific details about synthesis are given in the Electronic Supporting Material.

Table 1 Chemical structure, physical–chemical properties of the different analytes

Analytes	Abbr.	Chemical structure	Molecular weight	Bolting point(℃)	Log Kow [10]	pKa [10]
bisphenol A	BPA		228.29	220	3.6	10.3
bisphenol AF	BPAF		336.23	350-400	4.0	8.70
octyl phenol	OP		206.32	278.9	5.3	10.4
nonyl phenol	NP		220.35	293-297	6.0	10.3

Instruments

A Shimadzu LC-20A HPLC (Shimadzu Scientific, Japan) furnished with an RF-20A fluorescence detector (FLD) (Shimadzu Scientific, Japan) was used for the analysis. Chromatographic separation was conducted on an Agilent Zorbax Eclipse XDB-C8 column (150 mm × 4.6 mm, 5 μm) under the column oven temperature of 35 °C. 1 mL·min^{-1} was set as the experimental flow rate. 20 μL was set as the injection volume, and the HPLC-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, 40% B; (2) 24 min, 80% B; (3) 28 min, 80%B; (4) 28.2 min, 45% B, and (5) 30 min, 45% B. The following parameters were the settings of FLD: 220 nm excitation and 315 nm emission.

The images of Fe_3O_4 and Fe_3O_4@COFs microspheres were got using a JEOL model JEM-2010 (HR) transmission electron microscope (TEM; Tokyo, Japan). The Cu-Kα radiation ($\gamma = 1.5478$ Å) mode of the D/max-Rb diffractometer (Rigaku, Japan) was used to achieve X-ray diffraction (XRD) measurements and the angular measurement was ranged from 10° to 80°. Small angle XRD measurements were got using Ultima IV mode of the D/max-Rb diffractometer (Rigaku, Japan). SQUID-VSM (Quantum Design, San Diego, CA, USA) was used to measure the magnetic properties of these two kinds of synthesized microspheres at 25 °C. Nicolet 710 IR infrared spectrometer (Thermo Scientific, Waltham, MA, USA) was used to obtain the data of the Fourier transform infrared (FT-IR) spectra. N_2 (99.995%) on Fe_3O_4 and Fe_3O_4@COFs was subjected to gas adsorption–desorption measurements on a Micromeritics ASAP 2020 surface area and pore size analyzer (Norcross, GA, USA).

MSPE process

For the MSPE of the four kinds of phenols, 25 mL of the sample solution was added in a glass bottle, and 40 mg of Fe_3O_4@COFs microspheres was added to the solution. The mixture solution was shaken at 300 times min^{-1} in a water bath chader for 30 min at room temperature. The sorbents were separated from the aqueous phase with the assist of the external magnet located outside the glass vial, and the supernatant was discarded entirely. Subsequently, 3 mL addition of methanol was put into the isolated MSPE sorbents, and the analytes were eluted by sonicating for 3 min and vortexing for 3 min. Then, this operation was repeated again to ensure the process of desorption is complete. The eluted solution was mixed and dried under N_2 at 35 °C. Finally, the residue was redissolved using 250 μL of methanol. The redissolved samples were injected to LC, and the recoveries were considered to assess the enrichment efficiency of the four kinds of endocrine-disrupting phenols. The used Fe_3O_4@COFs microspheres were ultrasonically washed using methanol thrice prior to their next use.

Sample collection

In this work, four kinds of different plastic-packaged tea drinks from four different manufacturers were used as the real samples. These four kinds of tea drinks were as follows: ice black tea from Uni-President China Holdings Ltd. (Taiwan, China), jasmine tea from Master Kong Holdings Ltd. (Tianjin, China), greengage green tea from Dali Foods Group (Quanzhou, Fujian, China), chapai peach oolong tea from Nongfu Spring Co., Ltd. (Hangzhou, Zhejiang, China). These four kinds of tea drinks were purchased from a local supermarket (Jinan, China), and then they were centrifuged for 10 min under the condition of 4 °C and at the speed of 10,000 rpm (9×g) to get rid of the precipitate. Besides, to ensure the clarity of the supernatants and prevent the blocking of the injector, they were filtered through micropore membranes which were 0.22 μm. The processed tea drink samples were reserved in clean glass bottles colored brown under the temperature of 4 °C for the following MSPE experiments.

Before the MSPE process, 5 mL of processed tea drink samples was diluted to 25 mL with ultrapure water, and then the pH of the diluted samples was adjusted using 1 mol·L^{-1} NaOH or 1 mol·L^{-1} HCl.

Results and discussion

Choice of materials

Numerous materials, such as Fe_3O_4@MIPs [21, 22], and Fe_3O_4@SiO_2@[OMIM] [24], Fe_3O_4@COF(TpBD) [32] can be used as MSPE adsorbents. Fe_3O_4@COFs is a kind of novel easily synthesized magnetic COFs. It can be synthesized at room temperature in 15 min, which is much shorter than the synthesis time of the material synthesized in the analogous article (more than 12 h) (the time does not include the time of Fe_3O_4 preparation) [32]. The new material possesses optimal properties, such as high surface area (178.87 m^2·g^{-1}), numerous specific adsorption sites, large pore volume (0.43 cm^3·g^{-1}), and numerous surface functional groups (C=N, –COOH, –NH$_2$, and so on) [31]. These functional groups may form π interactions, hydrogen bonds and other acting forces with target sites on the molecules, which make them appropriate as candidate adsorbents of MSPE to enrich target pollutants from various samples.

Characterization of Fe_3O_4@COFs

The high-magnification morphologies of the prepared Fe_3O_4 and Fe_3O_4@COFs microspheres were observed under a TEM (Fig. 1a and b). Both of the images show that the bare Fe_3O_4 core was nearly spherical and its average diameter was 150–250 nm. A typical core–shell structure made up of a Fe_3O_4 core and a COF shell was formed and the thickness of the COF shell was 25 nm approximately.

FT-IR was performed to determine the specific functional groups on the Fe_3O_4@COFs microspheres and the successful synthesis of them (Fig. 1c). A typical absorption band at 585 cm^{-1} was assigned to the Fe–O–Fe vibration, and the absorption bands at 3421, 1640, and 1388 cm^{-1} indicated the existence of carboxyl groups. In comparison with the bare Fe_3O_4 core and the TAPB and TPA monomers, the prepared Fe_3O_4@COFs exhibited new characteristic peaks at 1450–1600 and 1610 cm^{-1}, which were ascribed to the benzene skeleton and C=N vibrations of the COF material, respectively. The FT-IR data were consistent with previous findings [31], which suggested the successful formation of the COF shell through the process of condensation polymerization.

XRD (Fig. 1d) was performed to confirm the crystalline structure and phase purity of Fe_3O_4 with and without the COF shell. The positions of all of the diffraction peaks at 2.7°, 19.5°, 31°, 35.5°, 43.5°, 57.5°, and 62.5° for Fe_3O_4

and Fe_3O_4@COFs confirmed that the products had great crystal structure and the XRD pattern of the synthesized Fe_3O_4@COFs was consistent with previous observations, implying the successful synthesis of the material [31]. The XRD of Fe_3O_4 was compared with Fe_3O_4@COFs, and the XRD of the Fe_3O_4@COFs suggested broad diffraction peaks at approximately 2.7 ° and 19.5 °, which might be ascribed to the lower crystallinity after the coating of the COF shell.

The chemical stability of Fe_3O_4@COFs microspheres in organic solvents and aqueous solutions with different pH values remarkably affects the process of adsorption and elution as well as confirms if a novel material is a suitable MSPE sorbent. Therefore, their chemical stability is important. In Fig. 1e, there are no distinct changes in the FT-IR spectra were discovered in aqueous solutions with 1 mol·L^{-1} NaOH and 1 mol·L^{-1} HCl, as well as organic solvents, indicating that Fe_3O_4@COF microspheres were stable under different experimental conditions apparently because of the strong C=N covalent bond in polyimine-linkage skeletons. Therefore, Fe_3O_4@COFs microspheres can work as a suitable MSPE adsorbent.

The magnetization curves of Fe_3O_4 and Fe_3O_4@COFs microspheres are shown in Fig. 1f. Hysteresis, coercivity, or remanence was not found in the magnetization process of the two kinds of synthesized microspheres. The two microspheres exhibited a super paramagnetic characters, and the Fe_3O_4@COFs possessed a saturated magnetization value of 62.5 emu·g^{-1}, although this value slightly decreased compared with that of the bare Fe_3O_4 (81.5 emu·g^{-1}). Fe_3O_4@COFs was sensitive to an external magnetic field owing to such high saturation magnetization. In the inset of Fig. 1f, Fe_3O_4@COFs achieved excellent dispersion in water, thereby forming a brown suspension that was uniform overnight without precipitation. However, with the help of an external magnet, Fe_3O_4@COFs was well collected (~1 min) from their uniform dispersion solution. Then, the dispersion became transparent.

As are shown in Fig. 1g and h, the Brunauer–Emmett–Teller surface area of Fe_3O_4@COFs calculated from the N$_2$ sorption isotherm was 166.5 m^2·g^{-1}, and the volume of its pore was 0.26 cm^3·g^{-1}. And the values for bare Fe_3O_4 were 10.7 m^2·g^{-1} and 0.11 cm^3·g^{-1}, respectively, which were much lower than those of Fe_3O_4@COFs. By this

Fig. 1 **a** TEM images of Fe_3O_4 microspheres at 25,000× magnification; **b** ▶ TEM images of Fe_3O_4@COFs microspheres at 25,000× magnification; **c** FT-IR spectra of TAPB, TPA, Fe_3O_4, and Fe_3O_4@COFs; **d** XRD patterns of Fe_3O_4 and Fe_3O_4@COFs microspheres in air; **e** FT-IR spectra of the Fe_3O_4@COFs microspheres in air, in MA, in 1 mol L^{-1} HCl for 24 h, in 1 mol L^{-1} NaOH for 24 h, and in water for 24 h; **f** magnetization curves of Fe_3O_4 and Fe_3O_4@COFs microspheres; (G1 and 2) N$_2$ adsorption–desorption isotherm and pore size distribution of Fe_3O_4@COFs microspheres
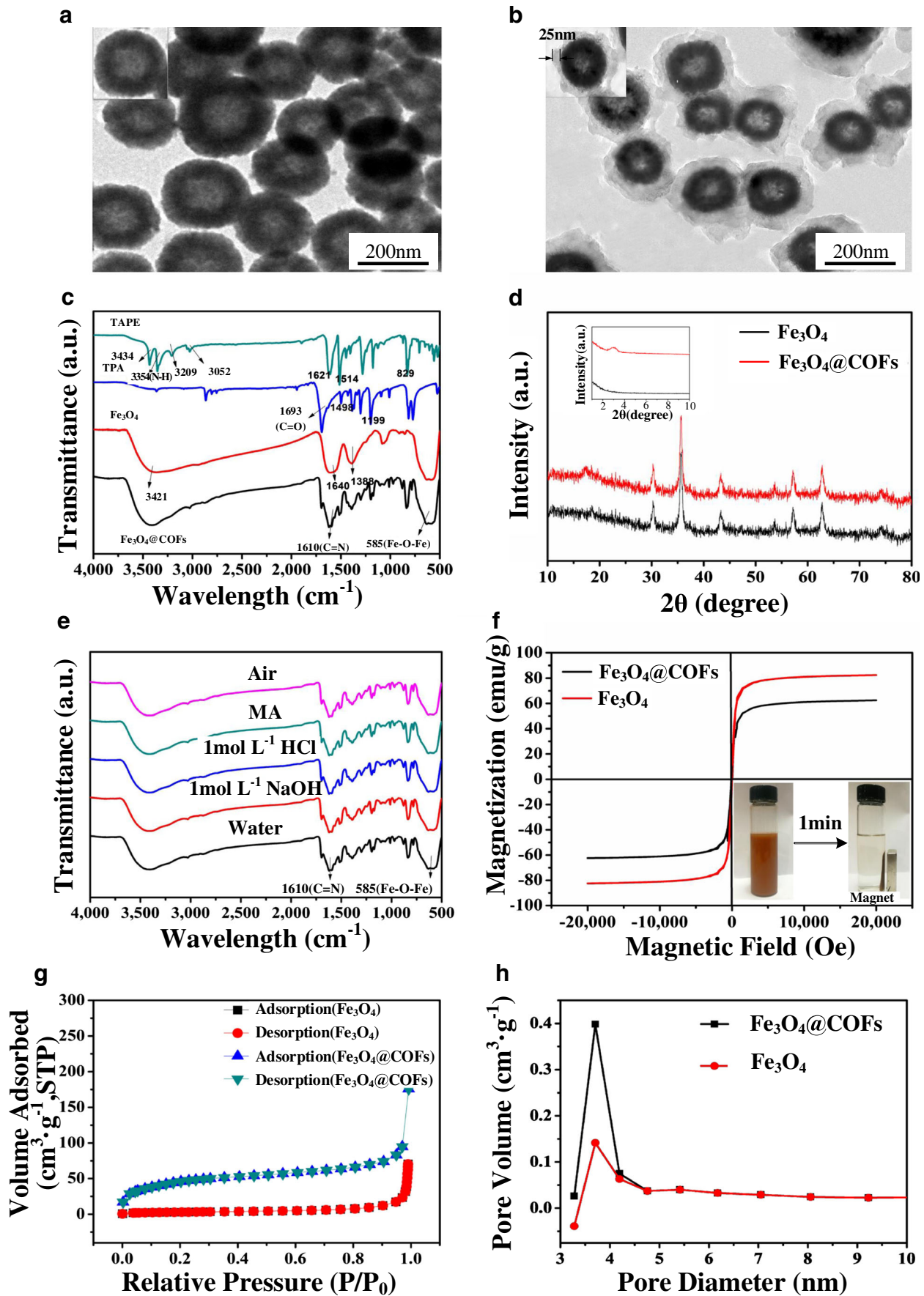
Table 2 Different analysts and recoveries using Fe_3O_4@COFs as MSPE adsorbent

Analytes	Recoveries (%)	RSD (%)
Phenols[a] (7)	40.4–63.6	0.4–4.3
PAHs[b] (16)	6.8–33.1	1.5–3.3
PCBs[c] (7)	12.8–42.5	1.1–5.7
2,4-D[d]	27.4	2.1
PFASs[e] (6)	19.8–42.3	1.5–3.4
Gatifloxacin	11.6	3.1
Sulfonamides[f] (6)	22.3–29.4	0.3–2.7
Endocrine-disrupting phenols [g] (4)	70.8–86.2	2.8–4.2

[a] Phenols (include P, 4-NP, 2-NP, 2-CP, PCMC, 2,4-DCP, 2,4,6-TCP)

[b] Polycyclic aromatic hydrocarbons (include Nap, AcPy, AcP, Flu, Phe, Ant, Flt, Pyr, BaA, Chr, BbFL, BbFL, Bap, Inp, DBA, Bghip)

[c] Polychlorinated biphenyls (include PCB-28, PCB-52, PCB-101, PCB-123, PCB-137, PCB-153, PCB-180)

[d] 2,4-dichlorophenoxyacetic acid

[e] Perfluoroalkyl Substances (include PFHpA, PFOA, PFNA, PFDA, PFHxS, PFOS)

[f] Sulfonamides (include sulfadiazine, sulfathiazole, sulfapyridine, sulfamerazine, sulfamethazine and sulfamethoxazole)

[g] Endocrine-disrupting phenols (include BPA, BPAF, OP and NP)

token, Fe_3O_4@COFs were more suitable as magnetic solid-phase sorbents than bare Fe_3O_4 because of their large pore volume (0.26 $cm^3 \cdot g^{-1}$) and large surface area (166.5 $m^2 \cdot g^{-1}$).

Optimization of method

The following parameters were optimized: (a) eluent; (b) amount of sorbent; (c) sample pH value; (d) extraction time; (e) ionic strength; (f) volume of eluent. Respective data and Figures are given in the Electronic Supporting Material. The following experimental conditions were able to achieve the best results: (a) volume of MA, 6 mL (3 mL × 2); (b) pH of the sample, 6; (c) amount of Fe_3O_4@COFs, 40 mg; (d) NaCl, 0%; (e) extraction time, 30 min.

Possible extraction mechanisms of Fe_3O_4@COFs for endocrine-disrupting phenols

The physicochemical properties of the four kinds of endocrine-disrupting phenols obtained with the optimal conditions are shown in Table 1. The MSPE performance was excellent because of the following reasons: Firstly, the hydrogen bonding between the hydroxyl groups of the endocrine-disrupting phenols and the amino groups as well as the C=N group on the surface of the Fe_3O_4@COFs microspheres might improve the extraction efficiency. Besides, the hydrophilicity and polarity of the particles improved because of the existence of the amino groups on Fe_3O_4@COFs, resulting in their suitability for the extraction of these four kinds of endocrine-disrupting phenols. Secondly, the large logKow values of the endocrine-disrupting phenols indicated that they have a large tendency to escape from the water phase to the surface of the Fe_3O_4@COF microspheres. And the large pKa values of the endocrine-disrupting phenols further contributed to this tendency. Thirdly, π interaction may exist among the benzene rings of the endocrine-disrupting phenols and the benzene rings of the COF shell coating on the Fe_3O_4@COFs microspheres and then as a result, the adsorption phenomena possibly occurred. Fourthly, as a kind of magnetic COF material, Fe_3O_4@COFs has an indicative mesoporous feature owing to the typical type IV characteristics which was presented [31]. The Brunauer–Emmett–Teller (BET) surface areas of Fe_3O_4@COFs calculated from the N_2 sorption isotherm were 166.5 $m^2 \cdot g^{-1}$, and the volume of its pore was 0.26 $cm^3 \cdot g^{-1}$. Fe_3O_4@COFs was considered as an adsorbent with good performance as a result of their large external surface area and mesoporous structure. In summary, the hydrophobicity and ionization of the endocrine-disrupting phenols were essential for the remarkable adsorption performance of Fe_3O_4@COFs for the analytes. In addition to hydrogen bonding, the π stacking interaction between endocrine-disrupting phenols and Fe_3O_4@COF microspheres as well as the mesoporous structure of Fe_3O_4@COFs also played important roles.

Table 3 Analytical data of the MSPE method

Compounds	Linear range (ng mL^{-1})	R	LODs (ng mL^{-1})	LOQs (ng mL^{-1})	Repeatability (%, $n = 5$)	
					Intra day	Inter day
BPA	0.5–1000	0.999	0.08	0.39	1.73	1.57
BPAF	1.0–1000	0.999	0.21	0.85	4.99	5.21
OP	1.0–1000	0.995	0.17	0.54	0.39	2.48
NP	0.5–1000	0.999	0.12	0.45	3.85	1.66

Table 4 Method comparisons for the analysis of the four kinds of endocrine-disrupting phenols

Sample	Material	Analytical Methods	Linear range (ng mL^{-1})	LODs (ng mL^{-1})	EFs[i]	References
Canned Orange/ milk	Fe$_3$O$_4$@MIP [a]	MSPE-HPLC-FLD	0.5–100	0.1–0.3	150	[21]
Seawater	WC-TMMIPs[b]	MSPE-HPLC-UV	22.8–3310	4.5	1	[22]
Water	magG@PDA@Zr-MOF[c]	MSPE-HPLC-UV[f]	50-20,000	0.1-1	10	[33]
Human urine	MIPMS[d]	SPE-HPLC-DAD	20–2000	1.2–2.0	1	[34]
Honey	BPA MIP[e]	MISPE–LC–IT–MS[g]	–	0.1–3.8[h]	100	[35]
Milk	C18	SPE-LC-ESI-MS	−700	0.7	10/3	[36]
Tea drinks	Fe$_3$O$_4$@COFs	MSPE-HPLC–FLD	0.5–1000	0.08–0.21	100	this work

[a] Molecularly imprinted polymer (MIP) coated Fe$_3$O$_4$ nanoparticles

[b] water-compatible temperature and magnetic dual-responsive MIPs

[c] the prepared zirconium-based magnetic MOFs

[d] molecularly imprinted polymer microsphere particles

[e] BPA molecularly imprinted polymer

[f] a diode array UV-visible detector

[g] electrospray ionisation-ion trap mass spectrometry

[h] The unit is ng g^{-1}

[i] Enhancement factors

Method evaluation

The analytical data under the optimal conditions are summarized in Table 2 and Table 3. As is demonstrated in Table 2, the recoveries for endocrine-disrupting phenols were much higher than other pollutants under the optimal experimental conditions respectively, so that Fe$_3$O$_4$@COFs absorbs endocrine-disrupting phenols selectively and can get satisfying results. And as shown in Table 3, within the concentration range of 0.05–1000 ng·mL^{-1}, the optimized MSPE displayed excellent linearity ($R \geq 0.995$). The limits of detection (LODs) which was based on signal-to-noise (S/N) ratios of 3 was within the scope of 0.08 ng·mL^{-1} to 0.21 ng·mL^{-1}. The limits of quantification (LOQs) calculated by the S/N ratios of 10 was in the

Table 5 Analytical results for the determination of the four endocrine-disrupting phenols in real samples

Samples	Added (ng mL^{-1})	BPA	BPAF	OP	NP
Ice black tea	0.0	N.D [a]	N.D	N.D	N.D
	5.0	114.4 ± 0.6 [b]	99.3 ± 3.1	87.3 ± 0.4	106.3 ± 3.1
	50.0	81.3 ± 0.7	100.3 ± 0.8	103.3 ± 0.3	102.2 ± 0.1
	100.0	82.6 ± 1.3	94.8 ± 4.8	103.2 ± 1.2	94.9 ± 5.2
Jasmine tea	0.0	N.D	N.D	N.D	N.D
	5.0	105.6 ± 8.3	102.1 ± 7.8	104.3 ± 2.2	111.4 ± 7.8
	50.0	84.1 ± 1.3	96.3 ± 0.7	99.9 ± 2.7	104.5 ± 1.1
	100.0	92.4 ± 6.0	96.2 ± 5.0	116.2 ± 2.2	98.7 ± 2.7
Green tea	0.0	N.D	N.D	N.D	N.D
	5.0	103.4 ± 0.6	104.6 ± 1.1	113.4 ± 3.7	106.0 ± 3.1
	50.0	96.1 ± 1.9	92.5 ± 0.7	101.4 ± 1.8	101.5 ± 1.7
	100.0	82.1 ± 0.6	118.0 ± 0.4	83.4 ± 0.3	90.4 ± 0.6
Peach oolong tea	0.0	N.D	N.D	N.D	N.D
	5.0	100.5 ± 2.8	102.8 ± 4.6	112.4 ± 0.4	99.4 ± 1.4
	50.0	99.2 ± 2.5	95.9 ± 1.6	100.9 ± 4.1	98.6 ± 0.2
	100.0	82.4 ± 3.0	98.8 ± 0.5	84.5 ± 4.0	81.3 ± 5.2

[a] Not detected

[b] Mean value of the recoveries±standard deviation ($n = 3$)

range of 0.39 ng·mL^{-1} to 0.85 ng·mL^{-1}. The relative standard deviations (RSDs) of interday ($n = 5$) and intraday (n = 5) assays were in the range of 1.57%–5.21% and 0.39%–4.99% respectively for the four kinds of endocrine-disrupting phenols. In Table 4, the LODs of the method were much lower than those of else methods, and the linear range of this method was wider than others [21, 22, 33–36] for endocrine-disrupting phenols. The Fe$_3$O$_4$@COFs microspheres can be used more than 20 times repeatedly without loss of enrichment efficiency. These experimental data showed that Fe$_3$O$_4$@COFs were novel extraction adsorbents, which were adaptable for the extraction of endocrine-disrupting phenols in MSPE.

Analysis of real drink samples

Four different kinds of plastic-packaged tea drinks were analyzed under optimized conditions to verify the practicability of the recommended method. Recoveries of the real samples were obtained via adding the standard solutions of endocrine-disrupting phenols at concentrations of 5, 50, and 100 ng·mL^{-1}. In Table 5, no endocrine-disrupting phenols were detected in the four plastic-packaged tea drinks, and the recoveries were between 81.3% and 118.0% with RSDs (0.1%–8.3%). These results revealed that different drink matrices hardly influenced this novel MSPE. Therefore, the method with convenience and competitive sensitivity was precise for the enrichment and determination of the target endocrine-disrupting phenols in real plastic-packaging drink samples. The typical chromatograms of real tea drink samples are displayed in Fig. 2. Conclusion can be drawn on the basis of these results that novel MSPE method can be used to determine four kinds of endocrine-disrupting phenols in real drink samples.
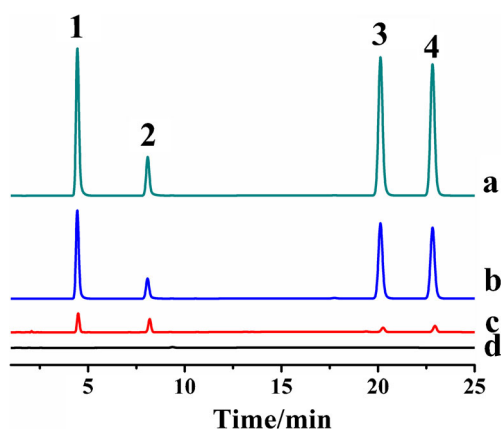

Fig. 2 Typical chromatograms of the four kinds of endocrine-disrupting phenols in green tea drinks (**a**) spiked with 100 ng mL^{-1}, **b** 50 ng mL^{-1}, and **c** 5 ng mL^{-1} and **d** in blank green tea drinks. (1) BPA; (2) BPAF; (3) OP; and (4) NP

Conclusion

The purpose of this paper was to investigate the possibility of magnetic covalent organic framework to enrich endocrine-disrupting phenols with high enrichment factor in environmental water systems. This paper had described a novel, rapid, convenient and sensitive determination method of endocrine-disrupting phenols. This method earned good linear range, reproducibility and low detection limit at several ng mL^{-1} level for OP, NP, BPA and BPAF. These facts demonstrated that magnetic COFs were of great potential to be applied as adsorbent for MSPE of endocrine-disrupting phenols in plastic-packaged food, drinks and environmental waters. It is expected that magnetic COFs may be a kind of efficient MSPE adsorbents for monitoring many other pollutants in food due to its merits exhibited in this work.

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