



Magnetic mesoporous polymelamine-formaldehyde resin as an adsorbent for endocrine disrupting chemicals

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Abstract

A magnetic mesoporous poly(melamine-formaldehyde) composite (Fe₃O₄-mPMF) was prepared via grafting poly(melamine-formaldehyde) onto the surface of amino-functionalized magnetite (Fe₃O₄) nanoparticles. The material was characterized by scanning electron micrography, transmission electron microscopy, X-ray diffraction, Fourier transform-infrared spectroscopy, nitrogen adsorption-desorption isotherms, and thermogravimetric analysis. It has a large surface area, a typical mesoporous structure, and a high thermal stability. It was employed as a magnetic sorbent for the solid phase extraction of the following endocrine disrupting chemicals (EDCs): Bisphenol A, 4-tert-butylphenol, 4-tert-octylphenol and nonylphenol. The EDCs were then quantified by HPLC. Under the optimized conditions, the response to the EDCs is linear in the range of 0.5–100 ng·mL⁻¹, and the limits of detection are 0.02–0.1 ng·mL⁻¹. The high adsorption capability of the Fe₃O₄-mPMF is mainly attributed to multiple interactions including π -stacking, hydrogen bonding, and hydrophobic interactions. The method was applied to the extraction of EDCs from spiked river water and bottled juice samples. The results demonstrated that the Fe₃O₄-mPMF is an efficient adsorbent for the extraction of organic compounds with large conjugated π -system, plenty of hydrogen-bonding sites, and strong hydrophobicity.

Keywords High-performance liquid chromatography · Magnetic solid phase extraction · Adsorption mechanism · Fourier transform infrared spectra · Powder X-ray diffraction · Transmission electron microscopy · X-ray photoelectron spectroscopy · Magnetic adsorbent · River water · Bottled juice

Introduction

Endocrine disrupting chemicals (EDCs) are exogenous chemical compounds that interfere with the hormone actions

responsible for the maintenance of homeostasis and the regulation of developmental processes [1, 2]. EDCs, as a class of organic pollutants, have raised serious public concerns because they can cause various hormone-related cancers by altering the normal hormone functions and physiological status in humans and wildlife [3, 4]. Previous studies have shown detectable levels of EDCs in food and water samples [5, 6]. Therefore, to ensure human health, it is necessary to develop simple, fast and sensitive analytical methods for the determination of EDCs in environmental and food samples.

Since EDCs usually exist at trace concentration levels in real samples, it is difficult to determine them directly by instrumental analysis. Thus sample preparation before instrumental analysis is often a necessary and crucial step in a whole analytical process [7]. The purpose of sample preparation is not only to reduce or eliminate the interfering components from the sample, but also to preconcentrate and enrich the target analytes, so as to realize trace analysis [8]. Up to now, many sample preparation methods including solid phase

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extraction (SPE) [9], liquid-phase micro-extraction (LPME) [10] and solid phase microextraction (SPME) [11] have been used for the analysis of EDCs. Magnetic solid phase extraction (MSPE) [12], as a relatively new sample preparation technique, has been used for the extraction and preconcentration of some environmental contaminants from different samples due to its advantages of simplicity, high efficiency, ease of operation and low solvent consumption [13, 14].

In MSPE, the magnetic adsorbent plays a key role because it determines the extraction efficiency for the analytes. Therefore, the development of new MSPE adsorbents with high adsorption capacity has become the focus of research attention. Porous materials have received much attention in the past decades due to their unique physicochemical properties. The developments of novel nano-porous materials and amorphous microporous/porous organic polymers (POPs) [15] have paid a lot of attention from both the academic and the industrial communities due to their potential applications in energy storage, separation and catalysis [16, 17]. POPs are a new class of highly crosslinked amorphous polymers constructed by covalent connection of rigid organic molecular building blocks and they have intrigued a growing research interest due to their porous network, good porosity, high thermal and hydrothermal stability, size adjustable pore structure and high surface area. As a new kind of POPs, mesoporous polymelamine-formaldehyde (mPMF) has been synthesized through the polycondensation of melamine with paraformaldehyde [18]. The mPMF was rich in amination ($-\text{NH}-\text{CH}_2-\text{NH}-$) and triazine groups, and possessed high surface area, well defined pore structure and high physicochemical stability. It has showed good performances in CO_2 capture [19], the adsorption of dye [18] and ethylene glycol [20], and the removal of toxic metal ions [21]. However, since mPMF has a light density, it is difficult to precipitate it from the sample solution by centrifugation, which brings inconvenience and obstacle in its applications [22]. To overcome this problem, the incorporation of magnetic property into the mPMF to construct a nanocomposite with both enhanced functionality and magnetic separability would be a good choice. Magnetic Fe_3O_4 nanoparticles are widely used due to their remarkable superparamagnetism and stability [23]. Also, the surface of Fe_3O_4 nanoparticles can be grafted with a wide variety of functional groups such as $-\text{NH}_2$, and then the amino functionalized Fe_3O_4 nanoparticles can be modified further [24].

In this work, Fe_3O_4 nanoparticles were first functionalized with amino groups and then, paraformaldehyde, as the monomer of the mPMF, was grafted onto the surface of the $\text{NH}_2\text{-Fe}_3\text{O}_4$ via Schiff base reaction, in which the aldehyde group of the paraformaldehyde reacted with the amino group on the surface of the Fe_3O_4 . After that,

melamine was introduced for subsequent growth of the mPMF. Finally, a magnetism modified mPMF composite ($\text{Fe}_3\text{O}_4\text{-mPMF}$) was synthesized. Because the large number of triazine and amination groups in the $\text{Fe}_3\text{O}_4\text{-mPMF}$ can supply hydrogen-bonding sites and large π electron conjugated system, the $\text{Fe}_3\text{O}_4\text{-mPMF}$ should be a promising adsorbent for the extraction of the compounds having aromatic rings and hydrogen-bonding sites by hydrogen-bonding and π -stacking interactions. The adsorption performance of the $\text{Fe}_3\text{O}_4\text{-mPMF}$ was explored by using it as the magnetic adsorbent for the MSPE of the four commonly used EDCs (bisphenol A (BPA), 4-tert-butylphenol (4-*t*-BP), 4-tert-octylphenol (4-*t*-OP) and nonylphenol (NP)). In the end, a new analytical method with the $\text{Fe}_3\text{O}_4\text{-mPMF}$ based MSPE coupled with high-performance liquid chromatographic detection was developed and successfully used for the determination of the EDCs in river water and bottled juice samples.

Experimental

Reagents and materials

The HPLC-grade methanol and acetonitrile were provided by Huaxin Chemical Reagent Company (Baoding, China, <http://huaxinsjyq.cn.busytrade.com>), and melamine and paraformaldehyde by Shanghai Maclin Biochemical Co. Ltd. (Shanghai, China). Hydrochloric acid (HCl), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, sodium hydroxide (NaOH), sodium chloride (NaCl), sodium acetate anhydrous and all other reagents were purchased from Beijing Chemical Reagents Company (Beijing, China). Double-distilled water was made from Yarong SZ-93A automatic double-distilled system (Shanghai, China, <http://ssyarong.1688.com>). The standards of the EDCs (BPA, 4-*t*-BP, 4-*t*-OP, NP) and the polycyclic aromatic hydrocarbons (PAHs) (fluoranthene, phenanthrene, anthracene, fluoranthene and pyrene) were bought from Agricultural Environmental Protection Institution of Tianjin (Tianjin, China). The standards of the phthalate esters (PAEs) (diallyl phthalate (DAP), diisobutyl phthalate (DIBP) and dibutyl phthalate (DBP)), the carbamates (propoxur, isoprocarb and fenobucarb), the benzoylurea insecticides (BUs) (teflubenzuron, flufenoxuron, triflumuron), the phenylurea herbicides (PUHs) (monolinuron, isoproturon, monuron), and the estrogens (progesterone, oestrone, diethylstilbestrol) were all purchased from Aladdin-Reagent (Shanghai, China, <http://www.aladdin-e.com/>). The commercial multi-walled carbon nanotubes (MWCNT), ODS C18 and graphitized carbon black (GCB) sorbents were purchased from Boaxin Chemical Reagents Company (Baoding, China).

The individual standard stock solutions at $1 \text{ mg}\cdot\text{mL}^{-1}$ for each of the EDCs were prepared in methanol. The mixed standard stock solution at $40 \text{ }\mu\text{g}\cdot\text{mL}^{-1}$ each of the EDCs was prepared in methanol by diluting the individual standard stock solution in a 10 mL volumetric flask. The six mixture stock solutions for the six different groups of the compounds were individually prepared in methanol at the concentration of $40.0 \text{ }\mu\text{g}\cdot\text{mL}^{-1}$ for BUs and $20.0 \text{ }\mu\text{g}\cdot\text{mL}^{-1}$ for PAHs, PAEs, PUHs, carbamates and estrogens, respectively. Lower concentrations of the mixture standard solutions were prepared by diluting an appropriate amount of the mixture stock solution with methanol to the required concentration in a 10 mL volumetric flask. All the standard solutions were stored at $4 \text{ }^\circ\text{C}$ and protected from light.

Synthesis of Fe_3O_4 -mPMF

The amino-functionalized Fe_3O_4 nanoparticles ($\text{NH}_2\text{-Fe}_3\text{O}_4$) with the size about 25 nm was synthesized by a one-pot hydrothermal procedure according to the previous report [25]. The synthetic process is given in the Electronic Supporting Material (ESM). The prepared $\text{NH}_2\text{-Fe}_3\text{O}_4$ (250 mg) and paraformaldehyde (0.486 g) were added to 15 mL dimethyl sulfoxide (DMSO) in a round-bottom flask and subjected to ultrasonic treatment for 15 min to form a homogenous solution. Then the mixture was heated to $120 \text{ }^\circ\text{C}$ in an oil bath for 1 h under mechanical stirring. After that, melamine (1.134 g, 8.99 mmol) was added into the above mixture, and then the mixture was heated at $170 \text{ }^\circ\text{C}$ for 12 h. After the reaction, in order to remove the unreacted reactants and other impurities, the product was washed with DMSO, tetrahydrofuran, acetone and dichloromethane each for three times, respectively. Finally, the resulting solid was dried under vacuum to obtain the desired Fe_3O_4 -mPMF. The mPMF was prepared according to the above same procedures except in the absence of $\text{NH}_2\text{-Fe}_3\text{O}_4$. The procedures for the preparation of the Fe_3O_4 -mPMF are shown in the ESM Fig. S1.

The morphology of the Fe_3O_4 -mPMF was observed by transmission electron microscopy (TEM) on a JEOL model JEM-2011 (HR) (Tokyo, Japan, <https://www.fei.com/products/tem/tecna/>) and scanning electron microscopy (SEM) with an S-4800 instrument (Hitachi, Japan, <http://www.hitachi.com>). The X-ray diffraction (XRD) graphs were recorded with a Bruker D8 ADVANCE (Bruker, Germany, <http://www.chem17.com/brands/detail/16046.html>). The Brunauer-Emmett-Teller (BET) surface areas were determined by the nitrogen adsorption-desorption isotherms at liquid nitrogen temperature (77 K) using a Micromeritics V-sorb-2800 instrument (Jinaipu, China, <http://jinaipu.m.china-p.com>). The Fourier transform-infrared spectra (FT-IR) were determined on a WQF-510 IR spectrometer (Bruker, Germany, <https://www.bruker.com/cn.html>). The thermal stability of the Fe_3O_4 -mPMF composite was analyzed by

thermal gravimetric (TG) analysis with a TG 209F1 instrument (Henvin HCT-2, Beijing, China, <http://www.instrument.com.cn/netshow/SH101731/>).

Samples preparation and MSPE procedures

The river water samples were collected from Baoding (Hebei, China), and the bottled juice samples were bought from local supermarket at Baoding (Hebei, China). Both the river water and the bottled juice samples were filtered through a $0.45 \text{ }\mu\text{m}$ membrane before the following MSPE extraction.

The MSPE extraction procedures are depicted in the ESM Fig. S2. In a typical MSPE process, 12 mg of the Fe_3O_4 -mPMF was added into a 150 mL conical flask containing 50.0 mL of sample solution at room temperature, and the mixture was shaken on a slow-moving platform shaker for 10 min to extract the target analytes. After the extraction, the Fe_3O_4 -mPMF was collected with a magnet and the supernatant was discarded. Then, the adsorbent and residual supernatant was totally transferred to a 10 mL centrifuge tube. The adsorbent was aggregated again by using a magnet and the residual supernatant was completely removed by a pipette. After the adsorbent was washed with 1 mL water, the adsorbed EDCs were desorbed from the adsorbent with 0.2 mL of alkaline acetonitrile ($1 \text{ mol}\cdot\text{L}^{-1}$ NaOH: acetonitrile = 1:99, v/v). Then, about $2 \text{ }\mu\text{L}$ of $1 \text{ mol}\cdot\text{L}^{-1}$ HCl solution was added into the eluent to neutralize its pH (the final pH value of the eluent was about 6). Finally, the resulting eluent was filtered through a $0.45 \text{ }\mu\text{m}$ membrane and $20.0 \text{ }\mu\text{L}$ of it was injected into the HPLC system for analysis. After the Fe_3O_4 -mPMF was washed with 1.0 mL of 1% alkaline acetonitrile by vortexing for 1 min for three times and then with 2 mL water, it was reused for the next extraction.

HPLC conditions

High performance liquid chromatography (HPLC) system was an Agilent Technologies 1260 Infinity LC/G1314F system equipped with two pumps, online-degasser and 1260 VWD detector (Agilent, USA, <http://www.instrument.com.cn/netshow/SH100320/>). A Promosil C18 column (4.6 i.d. \times 150 mm, $5.0 \text{ }\mu\text{m}$) from Dalian Johnsson Separation Science Technology Corporation (Dalian, China, <http://www.johnsson.cn/>) was used for separations. The mobile phase was acetonitrile-water with the following gradient elution: 0–9 min, acetonitrile from 48% to 78%; 9–17 min, acetonitrile at 78%; 17–22 min, acetonitrile from 78% to 48%. The flow rate of the mobile phase was 1 mL min^{-1} . The UV monitoring wavelength was chosen at 225 nm. The injection volume of the sample was $20.0 \text{ }\mu\text{L}$.

Results and discussion

Choice of materials

Selecting an appropriate and efficient adsorbent material is essential for the preconcentration of the analytes in trace analysis. To evaluate the adsorption capability of the Fe_3O_4 -mPMF, a comparison study with the commonly used and commercially available adsorbents, i.e., ODS C18, GCB and MWCNTs, was performed. Because the ODS C18, GCB and MWCNTs have no magnetism, the SPE method was used in the study. The same amount (12 mg) of the different adsorbents was weighed and packed into 3 mL SPE cartridges, respectively. Then, the water solution (50 mL) containing 80.0 ng mL^{-1} each of the analytes was loaded, and then washed and eluted under the optimized experimental conditions. The results shown in the Electronic Supplementary Material (ESM) Fig. S3 indicate that the Fe_3O_4 -mPMF exhibits a better adsorption power than the other adsorbents. The good adsorption capability of the Fe_3O_4 -mPMF for the analytes probably resulted from the stronger π -stacking, hydrogen bonding and hydrophobic interactions with the EDCs. Thus, the Fe_3O_4 -mPMF was chosen as the adsorbent for the EDCs for further studies.

Characterization of the Fe_3O_4 -mPMF

The morphology and structure of the Fe_3O_4 -mPMF were investigated by both TEM and SEM, and the relevant images are shown in Fig. 1. The TEM image in Fig. 1a shows that the NH_2 - Fe_3O_4 nanoparticles were cubic crystals, which has a similar morphology with the NH_2 - Fe_3O_4 nanoparticles reported in the literature as shown in the ESM Fig. S4 [26]. Meanwhile, the TEM image in Fig. 1b illustrates that the mPMF is amorphous with a foam-like interconnected structure. Both the TEM (Fig. 1c) and SEM (Fig. 1d) images of the Fe_3O_4 -mPMF reveal that the mPMF was successfully grafted to the surface of the NH_2 - Fe_3O_4 nanoparticles. The foam-like structure with interconnected mesoporous network in the prepared Fe_3O_4 -mPMF can be clearly seen from the SEM image in Fig. 1d.

The crystal structure of the NH_2 - Fe_3O_4 , mPMF and Fe_3O_4 -mPMF were measured by XRD and the results are shown in Fig. 2a. For the NH_2 - Fe_3O_4 , six diffraction peaks that appear at 30.1° , 35.4° , 43.1° , 53.4° , 57.0° and 62.7° are matched well with the crystal indexes of (141), (352), (108), (45), (80) and (141) of the crystalline Fe_3O_4 (JCPDS file 19-0629) [27], respectively. For the mPMF, only two broad diffraction peaks located at the 2θ of 24° and 40° are found, suggesting its amorphous nature. For the Fe_3O_4 -mPMF, in addition to the

Fig. 1 The TEM images of amino-functionalized Fe_3O_4 nano-particles (NH_2 - Fe_3O_4) (a), mesoporous polymelamine-formaldehyde (mPMF) (b) and Fe_3O_4 -mPMF (c). The SEM image of Fe_3O_4 -mPMF (d)

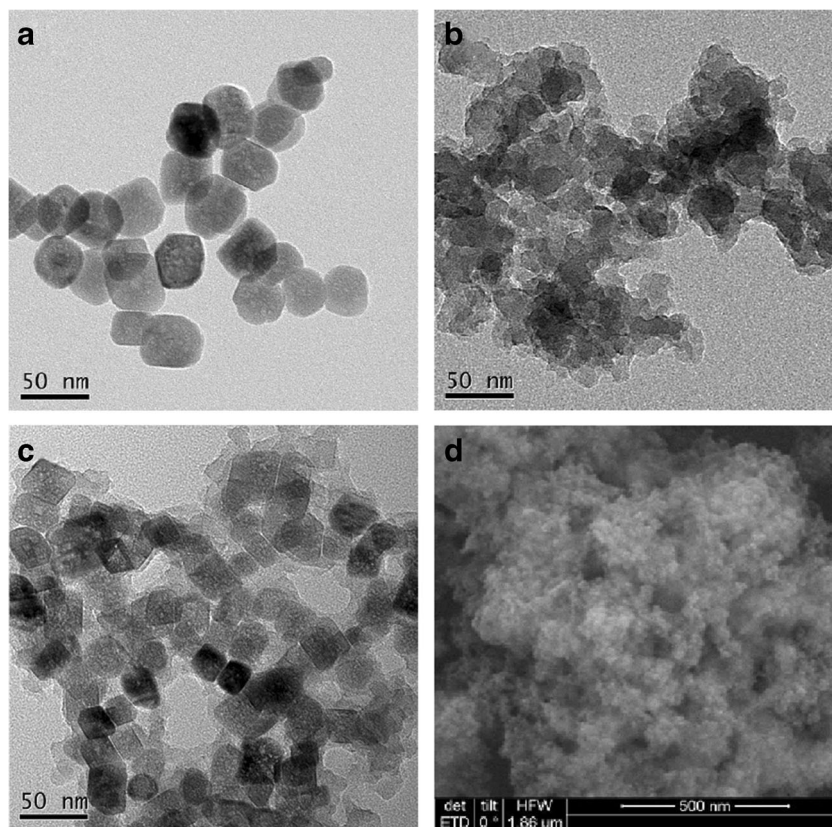
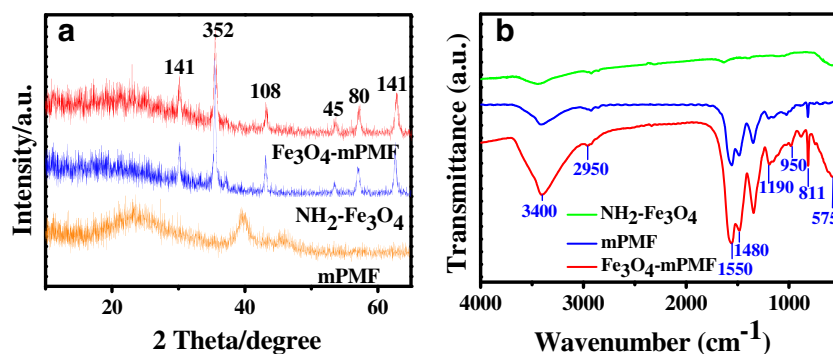


Fig. 2 **a** The XRD graphs of $\text{NH}_2\text{-Fe}_3\text{O}_4$, mPMF and $\text{Fe}_3\text{O}_4\text{-mPMF}$; **b** the FT-IR spectra of $\text{NH}_2\text{-Fe}_3\text{O}_4$, mPMF and $\text{Fe}_3\text{O}_4\text{-mPMF}$



six characteristic diffraction peaks from $\text{NH}_2\text{-Fe}_3\text{O}_4$, the broad diffraction peak at 2θ of 24° from the mPMF was also observed, suggesting the successful synthesis of the $\text{Fe}_3\text{O}_4\text{-mPMF}$.

The $\text{Fe}_3\text{O}_4\text{-mPMF}$ possesses a large number of triazine and amination ($-\text{NH}-\text{CH}_2-\text{NH}-$) functional groups. To elucidate its functional groups, the FT-IR spectra of the $\text{NH}_2\text{-Fe}_3\text{O}_4$, mPMF and $\text{Fe}_3\text{O}_4\text{-mPMF}$ composite were recorded and are shown in Fig. 2b. The spectrum of the $\text{Fe}_3\text{O}_4\text{-mPMF}$ shows eight absorption bands at 3400, 2950, 1550, 1480, 1190, 950, 811 and 575 cm^{-1} , respectively. The peak at 3400 cm^{-1} can be assigned to $-\text{NH}_2$ stretching vibration. The peak at 2950 cm^{-1} can be ascribed to $-\text{NH}-$ stretching vibration. The peaks at 1550 and 811 cm^{-1} are attributed to triazine stretching vibration; the weak peaks at 1480 and 1190 cm^{-1} are attributed to $-\text{CH}_2-$ stretching vibration; the weak peak at 950 cm^{-1} belongs to the $-\text{OH}$ out-of-plane bending vibration; the peak at 575 cm^{-1} is attributed to $\text{Fe}-\text{O}$ stretching vibration [28, 29]. The spectrum confirms that the $\text{Fe}_3\text{O}_4\text{-mPMF}$ was rich in amination ($-\text{NH}-\text{CH}_2-\text{NH}-$) and triazine groups.

To examine the surface areas and the porosity of the $\text{Fe}_3\text{O}_4\text{-mPMF}$, nitrogen adsorption experiments were performed at 77 K. Fig. S5a in the ESM describes the N_2 adsorption isotherms of the $\text{Fe}_3\text{O}_4\text{-mPMF}$. The gradual increase of the adsorbed volume at medium relative pressures with an evident hysteresis loop confirms that the $\text{Fe}_3\text{O}_4\text{-mPMF}$ contained abundant mesopores, which can also be proven from the Barrett-Joyner-Halenda (BJH)

adsorption average pore width of 11.15 nm. Moreover, there is a rapid increase of the adsorbed volume at low relative pressures, proving the presence of some micropores in the $\text{Fe}_3\text{O}_4\text{-mPMF}$. According to the N_2 adsorption data, the Brunauer-Emmett-Teller (BET) specific surface area and total pore volume of the $\text{Fe}_3\text{O}_4\text{-mPMF}$ were $509.87\text{ m}^2\cdot\text{g}^{-1}$ and $1.08\text{ cm}^3\cdot\text{g}^{-1}$, respectively.

The thermogravimetric analysis was carried out to evaluate the thermal stability of the $\text{Fe}_3\text{O}_4\text{-mPMF}$ (Fig. S5b). The slight weight loss at the temperature lower than 100°C was observed, which was attributed to the volatilization of entrapped solvent molecules in the pores of the $\text{Fe}_3\text{O}_4\text{-mPMF}$. The thermal decomposition temperature of the $\text{Fe}_3\text{O}_4\text{-mPMF}$ was approximately at 325°C .

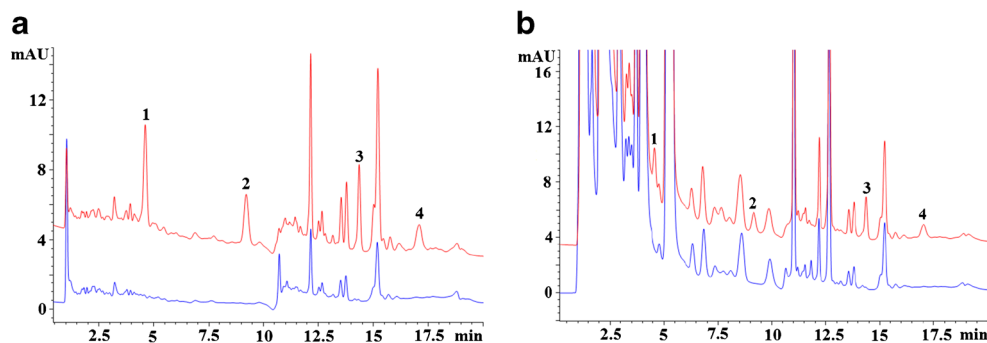
Optimization of the MSPE procedures

For the optimization experiments, 50 mL double-distilled water spiked with $80.0\text{ ng}\cdot\text{mL}^{-1}$ each of the four EDCs was used to study the extraction performance of the MSPE under different experimental conditions. The main influencing experimental parameters including the effect of the amount of the $\text{Fe}_3\text{O}_4\text{-mPMF}$ (a), extraction time (b), sample solution pH (c), eluent type (d), desorption solvent volume (e) on the extraction recovery and the effect of the desorption solvent volume on the peak areas of the analytes (f) were optimized. All the experiments were performed in triplicate. The respective data and Figures are given in the ESM Fig. S6. The following

Table 1 The linear range (LR), correlation coefficients (r), limits of detection (LODs), limits of quantitation (LOQs) and relative standard deviations (RSDs) for river water and bottled juice samples

Samples	EDCs	LR ($\text{ng}\cdot\text{mL}^{-1}$)	r	RSD (%) ($n=5$)	LOD ($\text{ng}\cdot\text{mL}^{-1}$)	LOQ ($\text{ng}\cdot\text{mL}^{-1}$)
River water	BPA	0.5–100.0	0.9995	5.4	0.02	0.06
	4-t-BP	0.5–100.0	0.9995	6.1	0.02	0.06
	4-t-OP	0.5–100.0	0.9997	4.3	0.05	0.15
	NP	0.5–100.0	0.9995	6.4	0.1	0.3
Bottled juice	BPA	0.5–100.0	0.9927	3.2	0.05	0.15
	4-t-BP	0.5–100.0	0.9988	4.2	0.03	0.09
	4-t-OP	0.5–100.0	0.9939	5.9	0.05	0.15
	NP	0.5–100.0	0.9929	5.2	0.08	0.24

Fig. 3 Chromatograms of river water sample (a) and bottled juice sample (b) (bottom) and the river water and bottled juice samples spiked with the EDCs at each concentration of $5.0 \text{ ng}\cdot\text{mL}^{-1}$ (top). Peak identification: (1) bisphenol A (BPA), (2) 4-tert-butylphenol (4-t-BP), (3) 4-tert-octylphenol (4-t-OP) and (4) nonylphenol (NP). Detection wavelength: 225 nm



experimental conditions were found to give the best results: (a) the amount of the $\text{Fe}_3\text{O}_4\text{-mPMF}$: 12 mg, (b) extraction time: 10 min, (c) no adjustment of the pH of the samples, (d) eluent type: alkaline acetonitrile, (e) desorption solvent volume: 0.2 mL.

Quantitative analysis

Under the above optimized conditions, the quantitative parameters including linear range, limits of detection (LODs), limits of quantification (LOQs), correlation coefficients (r) and the repeatability of the method was investigated to evaluate the method performance (Table 1). 50 mL EDCs-free river water samples and bottled juice samples spiked with the EDCs standard at nine concentration levels of 0.5, 1.0, 2.0, 5.0, 10.0, 20.0, 50.0, 80.0 and $100.0 \text{ ng}\cdot\text{mL}^{-1}$ were prepared for the construction of the calibration curves. A good linearity was observed in the concentration range of $0.5\text{--}100 \text{ ng}\cdot\text{mL}^{-1}$ with the correlation coefficients (r) larger than 0.9927. The LODs and LOQs for the analytes, which were determined on the basis of a signal-to-noise ratio of 3 and 9, respectively, were $0.02\text{--}0.1$ and $0.06\text{--}0.3 \text{ ng}\cdot\text{mL}^{-1}$, respectively, depending on both the analytes and the samples. The

repeatability study was carried out by performing five parallel experiments at the spiked concentration of $20.0 \text{ ng}\cdot\text{mL}^{-1}$ for each of the four EDCs in the sample. The resulting repeatabilities expressed as the RSDs were 3.2%–6.4%, indicating a good repeatability of the method.

To test the practical applicability of the established method, it was used for the determination of the EDCs in river water and bottled juice samples. As a result (see the ESM Table S1), NP was found at $0.27 \text{ ng}\cdot\text{mL}^{-1}$ in the river water and 4-t-OP at $0.32 \text{ ng}\cdot\text{mL}^{-1}$ in juice samples. To test the accuracy of the method, the recoveries of the four EDCs for the method were investigated by spiking the standard EDCs into the samples at the concentrations of 5.0 and $15.0 \text{ ng}\cdot\text{mL}^{-1}$, respectively, and then analyzing the samples by the current method. For each concentration level, five measurements were carried out under the same conditions. The recoveries of the four EDCs were found in the range from 85.4% to 109% with the RSDs between 3.7% and 6.9%. Figure 3 shows the typical chromatograms of the river water and bottled juice samples before and after being spiked at $5.0 \text{ ng}\cdot\text{mL}^{-1}$. These results showed that the $\text{Fe}_3\text{O}_4\text{-mPMF}$ can be successfully used to extract the four EDCs from real river water and bottled juice samples.

Table 2 Comparison of the current method with other relevant reported methods

Method	Material	Linear ranges ($\text{ng}\cdot\text{mL}^{-1}$)	LODs ($\text{ng}\cdot\text{mL}^{-1}$)	Ref.
MSPE-HPLC	MMFR ^a	1.0–5000	0.2	[30]
SPME-HPLC	TADC/MMF ^b	0.1–200	0.011–0.21	[31]
SPE-HPLC	MOF-5-C ^c	0.15–100	0.04	[32]
MSPE-HPLC	Fe@Fe ₂ O ₃ /GO ^d	0.5–100	0.08–0.10	[33]
MSPE-HPLC	3D-G-Iron oxide ^e	0.05–20	0.01–0.025	[34]
MSPE-HPLC	Fe ₃ O ₄ -mPMF	0.5–100	0.02–0.1	This work

^a Magnetic melamine-formaldehyde resin

^b 1-Trimethyl-(4-vinylbenzyl) aminium chloride and dual cross-linkers (divinylbenzene and ethylenedimethacrylate)/monolithic fiber

^c Metal-organic frameworks-derived carbon materials

^d Iron-ferric oxide/graphene oxide composite

^e 3D-Graphene magnetic nanoparticles

Adsorption mechanism of the Fe₃O₄-mPMF

To understand the possible adsorption mechanism of the Fe₃O₄-mPMF towards the analytes, a number of experiments were conducted to examine the extraction performance of the Fe₃O₄-mPMF for different types of organic compounds including some PAHs, PAEs, BUs, PUHs, carbamates, EDCs and estrogens. The H bond acceptors and H bond donors are indicators for hydrogen bonding preferences. The octanol/water partition coefficient, $\log K_{ow}$, is an indicator for hydrophobicity. A high extraction recovery value indicates a high adsorption affinity of the adsorbent to the analytes.

As shown in the ESM Table S2, the extraction recoveries of the Fe₃O₄-mPMF for the PAHs, PAEs and BUs are in the range of 86.3–99.1%, which are higher than those for the PUHs (59.4–74.3%), carbamates (70.8–82.9%) and EDCs (79.5%–83%). Since the PAHs, PAEs and BUs possess larger conjugated systems than those of the PUHs, carbamates and EDCs, the results suggest that π -stacking interactions between the Fe₃O₄-mPMF and the analytes play a key role in the extraction process. It can be seen from their molecular structures that although the conjugated systems in both the PAEs and BUs are weaker than that in PAHs, however, the extraction recoveries for the PAEs and BUs (86.3–99.1%) are similar to that for the PAHs (91.3–97.8%). A further comparison shows that the $\log K_{ow}$ values of the PAEs, BUs and the PAHs are similar to each other, but there are more H-bond sites in both the PAEs and BUs (from 4 to 7) than that in the PAHs (0), indicating that the hydrogen bonds between the Fe₃O₄-mPMF and the analytes also play an important role for the extraction. Moreover, although the estrogens possess less H-bond sites (2–4) than that of the PUHs and carbamates (4–5), the extraction recoveries for the estrogens (89.5–92.6%) with larger $\log K_{ow}$ values (3.67–6.78) are higher than that for the PUHs and the carbamates (59.4–82.9%) with smaller $\log K_{ow}$ values (1.90–2.86), indicating that hydrophobic interactions also play a role in the adsorption process.

Based on the above results, the adsorption mechanism of the Fe₃O₄-mPMF toward the analytes can be mainly attributed to the π -stacking, hydrogen bond and hydrophobic interactions. Therefore, the Fe₃O₄-mPMF should be more favorable for the extraction of the organic compounds with large π -electron conjugated system, more hydrogen bond sites and strong hydrophobicity.

Comparison with other reported methods

For the evaluation of the current method, a comparison of it with other reported methods [29–33] for the extraction of EDCs was made from the viewpoint of the extraction method, adsorbent material used, LR and LODs (Table 2). The

comparison results illustrate that the current method has a comparable or even better LODs than the other reported methods, which can meet the needs for the determination of the EDCs in real samples.

Conclusion

A magnetic polymelamine-formaldehyde mesoporous composite Fe₃O₄-mPMF was prepared and applied for the extraction of trace levels of EDCs in the river water and bottled juice samples. The Fe₃O₄-mPMF possessed high surface area, good porous structure, and sufficient magnetism. The low cost, efficient adsorption and easy phase separation make the Fe₃O₄-mPMF an attractive adsorbent for the extraction of the organic compounds with large conjugated system, more hydrogen bond sites and strong hydrophobicity. However, the applications of the Fe₃O₄-mPMF for the extraction of more organic compounds in different samples still needs to be further explored.

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