RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

RSC Advances

ARTICLE

Hydrothermal synthesis of functionalized magnetic MIL-101 for magnetic enrichment of estrogens in environmental water samples

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Yan-Feng Huang,*[a,b] Min Liu,[a] Yan-Qi Wang,[a] Ying Li,*[a] Ji-Mei Zhang[a] and Shu-Hui Huo[c]

A simple hydrofluoric acid-free one-pot method was developed for the preparation of three functionalized magnetic MIL-101 composites (Fe_3O_4-NH_2@MIL-101, Fe_3O_4-COOH@MIL-101 and Fe_3O_4/C@MIL-101). As magnetic solid-phase extraction materials, they exhibited the remarkable preconcentration ability for estrone (E1), 17β-estradiol (E2), estriol (E3) and bisphenol-A (BPA). However, because the incorporated magnetic particles were decorated with different surface functional groups, the three magnetic MIL-101 composites exhibited certain differences in extraction efficiency of the four target estrogens. Herein, Fe_3O_4-NH_2@MIL-101 composite as adsorbents were applied for magnetic solid-exrraction coupled with high performance liquid chromatography (HPLC) to determine the estrogens content in aqueous samples. The dominant parameters affecting enrichment efficiency including extraction time, sample pH, extraction temperature and desorption condition were investigated. Under the optimized conditions, the developed method showed good linearity within the range of 0.2–100 μg L^{-1}, low detection limits (0.06–0.22 μg L^{-1}) and high repeatability (RSD, 5.9–8.3%). The recoveries were between 80.6 and 99.6% with the spiked level of 10 μg L^{-1}. The proposed m ethod was successfully applied to determine the estrogens content in real water samples.

1. Introduction

Metal-organic frameworks (MOFs), also called coordination polymers, are a class of ultraporous crystalline materials with infinite tunability resulting from the limitless choice of metals and organic bridging ligands.[1,2] The diverse structures and unique properties, such as permanent nanoscale porosity, high surface area and uniform structured cavities make MOFs attractive for analytical applications.[3,4]

To date, there are very few MOFs that remain stable after the adsorption of large amounts of water.[5] Chromium terephthalate (MIL-101) which is known for exceptional hydrothermal stability and large sorption uptakes, represents candidate for water phase applications as useful contaminants sorbents.[6] It has been used widely for the adsorption or enrichment of various environmental contaminants, such as phenoxyacids,[7] phenols,[8] phathalate esters[9] and organochlorine.[10] Recently, Hian Kee Lee group explored the application of TritonX-114 modified MIL-101 in dispersive solid-phase extraction for endocrine disrupting chemicals.[11] However, when MIL-101 is used for sorptive applications, efficient separation and enrichment of trace chemical species is essential in the whole process. Magnetic separation technique is strong candidates due to its speed, compatibility, no need of centrifugation or filtration.

Recently, great progress has been made in the use of magnetic nano- and microparticles for the preparation of framework composites with magnetic properties.[12-17] Herein, we report a simple hydrofluoric acid-free one-pot method based on functionalized Fe_3O_4 particles for the preparation of magnetic MIL-101 composites. The magnetic particles were decorated with suitable surface functional groups (amine, carboxylic acid) or carbon coating that can not only improve the affinity between the magnetic particles and MIL-101 to promote a controlled crystal growth, but also impart new functionalities to magnetic MIL-101 composites and regulate their adsorption properties.

The as-prepared functionalized magnetic MIL-101 composites (Fe_3O_4-NH_2@MIL-101, Fe_3O_4-COOH@MIL-101 and Fe_3O_4/C@MIL-101) were applied to magnetic separation and enrichment of estrogens from water samples. They all had the remarkable preconcentration ability for estrone (E1), 17β-estradiol (E2), estriol (E3) and bisphenol-A (BPA). However, due to the fact that the incorporated magnetic particles were decorated with different surface functional groups, the three magnetic MIL-101 composites exhibited certain differences in extraction efficiency of the four target estrogens.

Estrogens are a group of natural and synthetic steroid hormones. They have received much attention due to their wide occurrence and high risk to humans and wildlife, and their association with many types of hormone-dependent cancers. Although the environmental concentrations of estrogens are very low, their adverse effect on the reproduction of wildlife and humans is significant.[18] Their

[a] State Key Laboratory of Hollow Fiber Membrane Material and Membrane Process, and College of Environmental and Chemical Engineering Sciences, Tianjin Polytechnic University, 399 West Binshui Road, Tianjin 300387, China. E-mail: huangyanfeng@tjpu.edu.cn, ly@tjpu.edu.cn; Tel: +86-22-83955167; fax: +86-22-83955167
[b] State Key Laboratory of Medicinal Chemical Biology (Nankai University), Nankai University, 94 Weijin Road, Tianjin 300071, China.
[c] Key Laboratory of Eco-Environment-Related Polymer Materials of Education, College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070, China.

monitoring has become therefore important in various environmental matrixes.[19] Herein, we developed an effective method based on Fe_3O_4-NH_2@MIL-101 as sorbent of magnetic solid-extraction to determine estrogens in environmental water samples.

2. Experimental

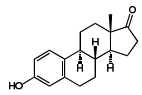
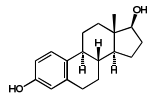
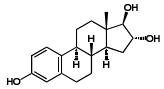
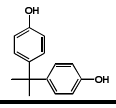
2.1 Materials and chemicals

Estrone (E1, >98.0%), 17β-estradiol (E2, >97.0%), estriol (E3, >98.0%) and bisphenol-A (BPA, >98.0%) were purchased from Alfa Aesar. The physical–chemical properties of the four estrogens are shown in Table 1.[20] Chromium (III) nitrate nonahydrate ($Cr(NO_3)_3{\cdot}9H_2O$), terephthalic acid (BDC), ferric chloride ($FeCl_3{\cdot}6H_2O$), glycol, diethylene glycol, anhydrous sodium acetate, trisodium citrate (Na_3Cit), 1,6-hexanediamine (HDA) and glucose were obtained from Guangfu Fine Chemical Research Institute (Tianjin, China). Acetonitrile and methanol were from Thermo Fisher Scientific Inc. (Waltham, MA, USA). Ultrapure water (18.2 MΩ cm) was obtained from a Milli-Q water purification system (Millipore, Milford, MA, USA). Stock solutions of estrone, 17β-estradiol, estriol and bisphenol-A of 1000 mg L^{-1} were prepared using methanol as solvent and stored at 4 °C in the refrigerator.

2.2 Apparatus

Samples were analyzed with a CoMetro 6000 HPLC system (USA) that included two HPLC pumps, a UV-detector and an injection valve with a 20 μL injection loop. Analytical separations were performed using a reversed-phase C18 (150 mm×4.6 mm, Agilent Technologies) and maintained at room temperature. The mobile phase was composed of methanol, acetonitrile and 50 mmol L^{-1} NaH_2PO_4 (v/v/v, 30:30:40), and pH was adjusted to 3.0 by dilute H_3PO_4 to obtain the optimum chromatographic separation conditions of estrogens. The mobile phase flow-rate through the column was 1.0 mL min^{-1} under isocratic conditions. UV wavelength was set at 230 nm for the quantification of estrogens.

Table 1. Physical–chemical properties of the estrogens

Estrogens	Structure	Molecular weight	pK_a	log K_{ow}
Estrone (E1)		270	10.34	3.68
17β-Estradiol (E2)		272	10.46	4.13
Estriol (E3)		288	10.38	2.94
Bisphenol-A (BPA)		228	9.73	3.43

K_{ow}: octanol–water partitioning coefficients

The scanning electron microscopy (SEM) micrographs were recorded on a Hitachi S4800 SEM (Japan). X-ray diffractometry (XRD) was measured using a Miniflex 600 diffractometer (Rigaku, Japan) with $Cu_{K\alpha}$ radiation source (λ=1.5418 Å). Magnetic measurements were performed using a LDJ 9600-1 vibrating sample magnetometer (LDJ Electronics Inc., USA) at room temperature. Variable-temperature magnetic susceptibilities were measured with a Quantum Design MPMS-7 SQUID magnetometer. The magnetic field used to perform magnetic measurements is 100 Oe. Infrared absorption spectra were conducted on a Nicolet iS50 Fourier transform infrared (FT-IR) spectrometer (Thermo Scientific, USA). Surface electronic states were analyzed by X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PHI 5000C, Al KR).

2.3 Synthesis of functionalized Fe_3O_4 particles

2.3.1 Synthesis of carboxylic-functionalized Fe_3O_4 particles

Carboxylic-functionalized Fe_3O_4 particles (Fe_3O_4-COOH) were prepared according to Deng *et al*.[21] Typically, $FeCl_3$ (0.65 g, 4.0 mmol) and trisodium citrate (0.20 g, 0.68 mmol) were first dissolved in ethylene glycol (20 mL), afterward, NaAc (1.2 g) was added with stirring. The mixture was stirred vigorously for 30 min and then sealed in a Teflon-lined stainless-steel autoclave (50 mL capacity). The autoclave was heated at 200°C and maintained for 10 h, and then allowed to cool to room temperature. The black products were washed with ethanol and distilled water for several times.

2.3.2 Synthesis of amine-functionalized Fe_3O_4 particles

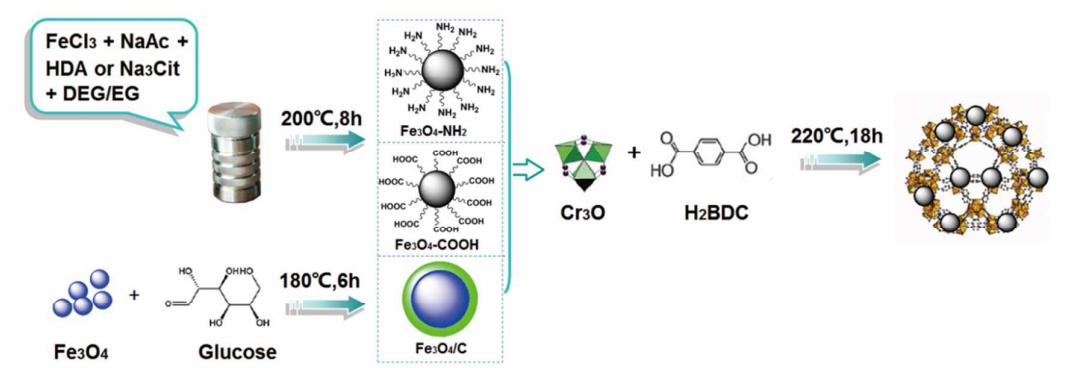
Amine-functionalized Fe_3O_4 particles (Fe_3O_4-NH_2) were prepared according to Li *et al*.[22] A solution of 1, 6-hexanediamine (5 mL), anhydrous sodium acetate (2.0 g) and $FeCl_3.6H_2O$ (1.0 g) as a ferric source in glycol (30 mL) was stirred vigorously at 50°C to give a transparent solution. This solution was then transferred into a Teflon-lined autoclave and reacted at 190°C for 6 h. The magnetite particles were then rinsed with water and ethanol to effectively remove the solvent and unbound 1,6-hexanediamine, and then dried at 50°C.

2.3.3 Synthesis of carbon coating Fe_3O_4 particles

Carbon coating Fe_3O_4 particles (Fe_3O_4/C) were prepared according to the previously reported method.[23] Firstly Fe_3O_4 particles were hydrothermally synthesized. Typically, $FeCl_3$ (0.325 g) and anhydrous sodium acetate (1.5 g) were dissolved in the mixture of glycol and diethylene glycol (V/V, 3/17, total volume is 20 mL). The mixture was stirred vigorously for 30 min and then sealed in a Teflon-lined autoclave. The autoclave was heated at 200°C and maintained for 12 h, and then allowed to cool to room temperature. The black products were washed with ethanol and distilled water for several times, and then dried at 50°C. Secondly, Fe_3O_4 microparticles (200 mg) was treated with 0.1 M HNO_3 by ultrasonication for 10 min, then washed with distilled water for several times until neutral. Finally, 20 mL 0.5 M glucose aqueous solution was added and mixed uniformly, then sealed in a Teflon-lined autoclave. The autoclave was heated at 180°C and maintained for 6 h. The black products were washed with ethanol and distilled water for several times, and Fe_3O_4/C particles were obtained.

2.4 Synthesis of functionalized magnetic MIL-101 composites

$Cr(NO_3)_3{\cdot}9H_2O$ (2.5 mmol) and BDC (2.5 mmol) were dissolved in 10 mL distilled water, magnetic stirring for 30 min. The aqueous suspension (5 mL) containing the above-mentioned functionalized



Scheme 1. Synthesis procedure of functionalized magnetic MIL-101 composites.

magnetic Fe_3O_4 particles (100 mg) was obtained under ultrasonication for 10 min, and then was added with stirring. The mixture were stirred
uniformly then sealed in a Teflon-lined autoclave (20 mL). The autoclave was heated at 218°C and maintained for 18 h. The products were separated from the reaction media by an external magnetic field. The composites washed with distilled water at 100°C, ethanol at 60°C for 3h, respectively, and then dried at 120°C overnight in a vacuum oven.

The synthesis procedure of MIL-101 was same as that of functionalized magnetic MIL-101 composites except without adding 100 mg functionalized magnetic particles.[24]

2.5 Procedure of magnetic separation and enrichment

Functionalized magnetic MIL-101 composites (5 mg) were dispersed in 30 mL of standard solution or sample solution under ultrasonication. The suspension was placed in a 50 mL centrifuge tube and stirred on a rotary shaker at 250 rpm for a certain period for the extraction. Then, the estrogens loaded functionalized magnetic MIL-101 composites were separated by applying a magnet to the outer wall of the centrifuge tube, and the supernatant was discarded. The analytes were desorbed from the composites with 0.5 mL of eluent under ultrasonication. The eluate was collected with magnetic separation and filtered through a 0.45 μm nylon membrane, followed by HPLC analysis.

3. Results and discussion

3.1 Fabrication and characterization of three functionalized magnetic MIL-101 composites

The synthesis procedure of three functionalized magnetic MIL-101 composites is illustrated in scheme 1. We fabricated these magnetic composites by a simple hydrofluoric acid-free one-pot method. The presynthesized Fe_3O_4-NH_2, Fe_3O_4-COOH and Fe_3O_4/C magnetic particles were respectively added into the MIL-101 precursors solution containing $Cr(NO_3)_3 \cdot 9H_2O$, terephthalic acid and distilled water, and then the mixture were maintained at 218°C for 18 h to produce the corresponding functionalized magnetic composites, denoted as Fe_3O_4-NH_2@MIL-101, Fe_3O_4-COOH@MIL-101 and Fe_3O_4/C@MIL-101, respectively.

The structures of three functionalized magnetic MIL-101 composites were investigated using powder X-ray diffraction (PXRD), shown in Fig.1. XRD patterns of these magnetic MIL-101 composites obviously consisted of diffraction peaks from both MIL-101 and the magnetic particles, indicating the coexistence of MIL-101 and the magnetic particles in the composites. Just because of the incorporation of the magnetic particles to MIL-101 crystals, magnetic MIL-101 composites not only possessed outstanding sorption properties originating from the microporous MIL-101, but also exhibited magnetic properties derived from the magnetic Fe_3O_4 particles.

The saturation magnetization values of Fe_3O_4-NH_2, Fe_3O_4-COOH and Fe_3O_4/C magnetic particles were found to be 65.5, 50.5 and 29.6 emu g^{-1}, which decreased to 18.4, 10.5 and 10.7 emu g^{-1} for Fe_3O_4-NH_2@MIL-101, Fe_3O_4-COOH@MIL-101 and Fe_3O_4/C@MIL-101 composites, respectively (Fig .2), indicating that the mass fraction of magnetic particles in the composites is about 28, 21 and 36 (wt%). In fact, the saturation magnetization of these magnetic MIL-101 could

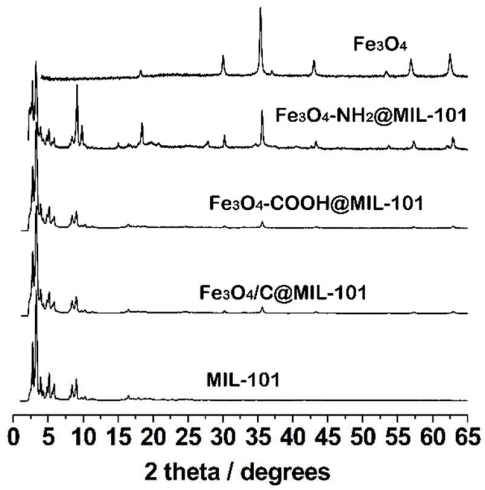


Fig. 1. XRD pattern of the as-synthesized MIL-101 and the three magnetic functionalized MIL-101 composites: Fe_3O_4 particles, Fe_3O_4-NH_2@MIL-101, Fe_3O_4-COOH@MIL-101 and Fe_3O_4/C@MIL-101 composites.

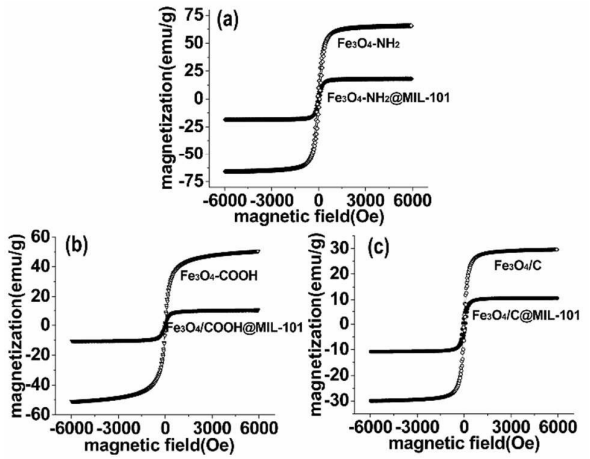


Fig. 2. The magnetization curves of functionalized magnetic particles and the corresponding magnetic MIL-101 composites.

be regulate by altering the addition content of Fe_3O_4 particles during their preparation. The content of magnetic Fe_3O_4 particles was optimized to ensure sufficient magnetization of MIL-101.

The magnetic saturation values of these magnetic MIL-101 composites were enough to retrieve the composites readily from sample matrix by applying a magnetic field. Their room-temperature magnetic curves exhibited low remnant magnetization or coercivity, which is desirable for the magnetic extraction. Moreover, in the temperature dependent magnetization curves (Fig S1), the magnetic behavior of Fe_3O_4-NH_2@MIL-101 composites exhibited differences compared with those for the other composites. Antiferromagnetic interaction between chromium ions mediated by hydrogen-bonding could influence the magnetic behavior of Fe_3O_4-NH_2@MIL-101 composites.[26]

Although the synthetic procedure of MIL-101 particles was a hydrofluoric acid-free alternative preparation, MIL-101 particles appeared to be monodisperse in size and possessed well-defined octahedral shape (Fig. 3a and b). The SEM images (Fig. 3c, d, e, f, g and h) also showed the morphological structures and size of the three magnetic particles and the corresponding functionalized magnetic MIL-101 composites. The magnetic particles were narrowly distributed and non-uniformly deposited on the surface of MIL-101 particles, no significant formation of aggregates was observed.

The FT-IR spectra illustrated in Fig. 4 revealed the chemical structure of these materials. The FT-IR spectra of magnetic MIL-101 composites exhibit the typical bands of MIL-101 as well as some of the vibrational modes of these functionalized magnetic particles.

The strong bands, at 1625, 1506, 1400 cm^{-1}, can be assigned to the C═C and O─C═O vibrations of the benzene dicarboxylate organic skeleton.[25] The bands at 1017 and 748 cm^{-1} can be assigned to the vibrations of benzene rings.[27] All above these characteristic peaks of MIL-101 were observed in the FT-IR spectrum of the magnetic MIL-101 composites.

For Fe_3O_4-NH_2@MIL-101 composites, the peak at 1639 and 778 cm^{-1} was observed and assigned to N─H stretch.[22,28] For Fe_3O_4-COOH@MIL-101 and Fe_3O_4/C@MIL-101 composites, The band at 1396 cm^{-1} was associated with carboxylate group on the surface of Fe_3O_4-COOH and Fe_3O_4/C particles, which overlapped with the C─O

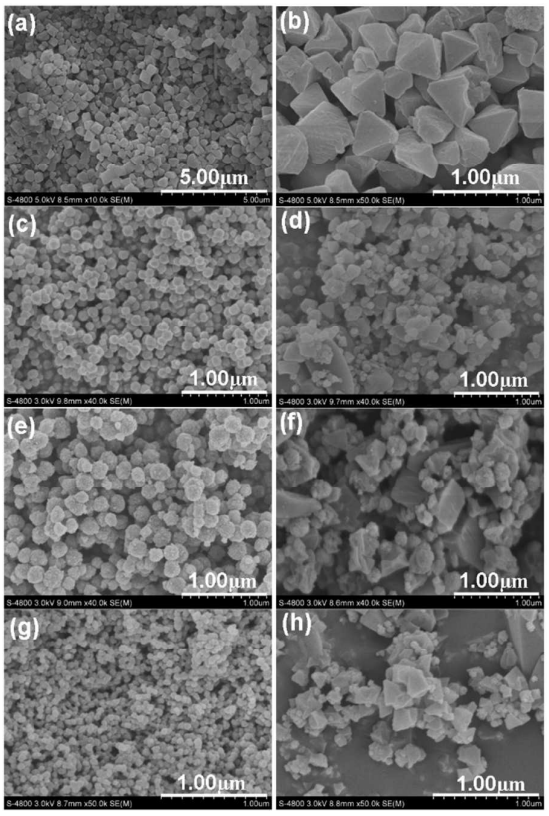


Fig. 3. SEM images of MIL-101、magnetic particles and magnetic MIL-101 composites: the crystal MIL-101 at 10000-fold (a) and at 50000-fold (b), Fe_3O_4-NH_2 (c), Fe_3O_4-NH_2@MIL-101(d), Fe_3O_4-COOH(e), Fe_3O_4-COOH@MIL-101(f), Fe_3O_4/C (g) and Fe_3O_4/C@MIL-101(h).

bond at 1400 cm^{-1} in terephthalic acid of MIL-101 framework. The stretching bands around 1630 cm^{-1} of COO^- on the surface of Fe_3O_4--COOH and Fe_3O_4/C particles shifted to lower wave numbers, as the coordination to the unsaturated chromium sites of MIL-101 reduced the electron density.[29] The results from FT-IR revealed that the functionalized magnetic particles were incorporated to MIL-101 crystals and imparted them new functional groups.

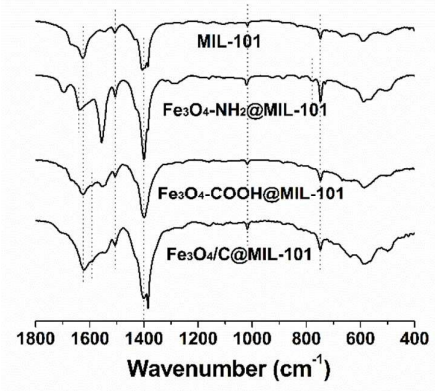


Fig. 4. FT-IR spectra of MIL-101, Fe_3O_4-NH_2@MIL-101, Fe_3O_4-COOH@MIL-101 and Fe_3O_4/C@MIL-101

The surface chemical states of Fe_3O_4-NH_2@MIL-101, Fe_3O_4-COOH@MIL-101 and Fe_3O_4/C@MIL-101 were analyzed by X-rayphotoelectron spectroscopy (XPS) measurements. The XPS spectrum (Fig. S2-5) demonstrated that Cr, C, O, and Fe atoms all existed in these magnetic MIL-101 composites, while only the peaks of Cr, C, and O appeared in pure MIL-101. And Fe_3O_4-NH_2, Fe_3O_4-COOH and Fe_3O_4/C magnetic were successfully immobilized on the surface of the MIL-101. We speculate that the functional groups on magnetic particles could act as reactive centers to bind to the unsaturated chromium sites of MIL-101 to promote the formation of functionalized magnetic MIL-101 composites.

The textural properties of the MIL-101 and the functionalized magnetic MIL-101 composites were confirmed by nitrogen-sorption measurements (Fig S6-8) and summarized in Table S1. Although the BET surface areas and pore volume of the composites significantly decreased due to the incorporation of Fe_3O_4 particles, the remaining high surface area were good enough for enrichment purposes. Furthermore, the incorporation of Fe_3O_4 particles did not alter the pore size distribution of MIL-101 matrix.

3.2 Adsorption characteristics of the functionalized magnetic MIL-101 composites

The incorporation of functionalized magnetic particles not only provided magnetic properties to the inherent MIL-101 properties, but also imparted new functional groups to magnetic MIL-101 composites and regulated their adsorption properties. The as-prepared MIL-101

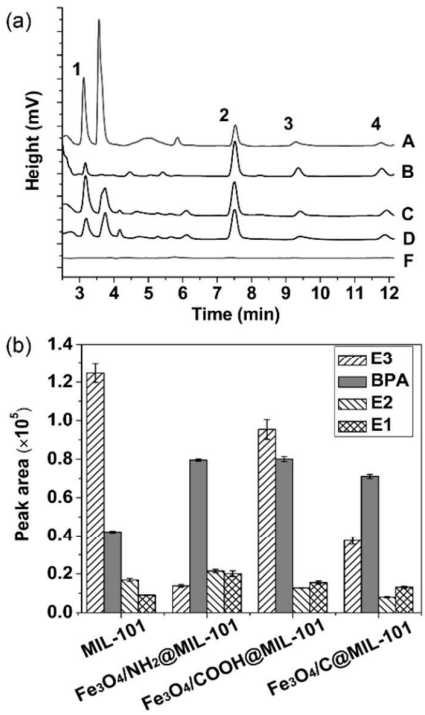


Fig. 5. (a) HPLC chromatograms of 50 μg L^{-1} estrogens obtained by the developed method with different adsorbents (A: MIL-101, B: Fe_3O_4-NH_2@MIL-101, C: Fe_3O_4-COOH@MIL-101, D: Fe_3O_4/C@MIL-101) and direct injection without enrichment (F). Peak identities: (1) E3; (2) BPA; (3) E2 and (4) E1. (b) Comparison of extraction efficiency for estrogens by different materials.

and functionalized magnetic MIL-101 composites were as pollutant-sequestering materials to apply to magnetic separation and enrichment of estrogens from water samples. Their extraction efficiencies were estimated by comparing the peak areas obtained from analysis of estrogens at concentration of 50 μg L^{-1} (shown in Fig. 5a and b).

In contrast to the chromatogram of direct injection without enrichment (Fig. 5a curve F), the obvious target peaks are observed (Fig. 5a curve A, B, C and D), indicating that the remarkable preconcentration ability of MIL-101 and three MIL-101 composites to estrogens. High BET surface area and pore volume of these materials are beneficial for high adsorption. The hydroxyl group of estrogens is also a charge donor, and MIL-101 could be acceptor, the coordination interaction is also expected to exist between MIL-101 framework and the estrogens. At the same time, π-π stacking interaction between the benzene rings in the estrogens and MIL-101 framework also make important contributions to the extraction. Furthermore, large octanol–water partitioning coefficients of the estrogens allow their hydrophobic interaction with the hydrophobic MIL-101 framework.[19,30] All these interactions are responsible for the excellent extraction performance of MIL-101 and MIL-101 composites as solid-phase extraction sorbent.

In figure 5a, the dominant peak at retention time between 3.5 and 4 min arose from the residual terephthalic acid within the pores of MIL-101, but there was no interference to the measurement.

As the incorporated magnetic particles were decorated with amine, carboxylic groups or carbon coating, respectively, the three magnetic MIL-101 composites exhibited the differences of adsorbing estrogens. Improved extraction efficiency for E1 and BPA was achieved by three magnetic MIL-101 composites, while extraction efficiency for E3 decreased significantly compared to MIL-101 crystals. It can be seen that Fe_3O_4-NH_2@MIL-101 exhibited better extraction efficiency than MIL-101 crystals for E1, E2 and BPA except E3. Therefore, Fe_3O_4-NH_2@MIL-101 was chosen for the determination of target estrogens in this work.

3.3 Optimization of the solid-phase extraction conditions

3.3.1 Effect of extraction time

The sample suspension was incubated on a rotary shaker at 250 rpm for different time periods varied from 2 to 30 min. Extraction time profiles for four estrogens are shown in Fig. 6a. The extraction equilibrium was almost reached after 10 min of extraction, indicating that the kinetics for the adsorption of estrogens by Fe_3O_4-NH_2@MIL-101 composites was very fast. Finally, 10 min was chosen as the extraction time.

3.3.2 Effect of solution pH

Estrogens are ionizable compounds due to their hydroxyl group, the pH of the sample solution determines the ionization degree of Estrogens, and thus it is an important factor influencing the extraction efficiency. The effect of pH value on estrogens extraction efficiency was evaluated in the range of 3 to 11.5 (Fig. 6b). The results showed that the effect of the pH was not obvious in the range of 2–9. However, when the pH increase to above 10, a distinct decrease of extraction efficiency was found. Better extraction efficiency was observed at pH < pKa. Under such condition, the target estrogens mainly existed as molecular form, which would facilitate their adsorption onto the composites. Herein, pH 7.0 was

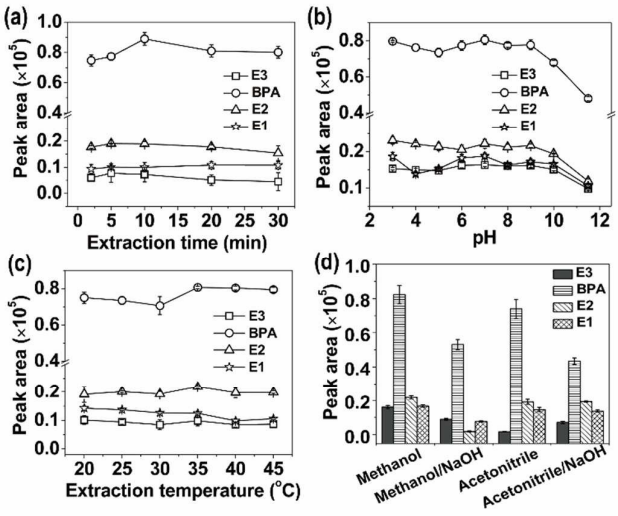


Fig. 6. Factors affecting the extraction efficiency for 50 μg L^{-1} estrogens: effect of the extraction time (a), effect of pH (b), effect of temperature (c) and effect of eluent (d).

selected for extraction of four target estrogens by Fe_3O_4-NH_2@MIL-101compsite.

3.3.3 Effect of temperature

The effect of temperature on the extraction efficiency of estrogens was investigated at 20, 25, 30, 35, 40 and 45°C, respectively (shown in Fig. 6c). Increasing the extraction temperature could accelerate the masstransfer rates of analytes and reach a faster equilibrium. At the same time, an increase of temperature also could lead to a declining partition coefficient and cause desorption of the analytes from the sorbent.[19] In this work, 35°C was chosen as the optimum extraction temperature.

3.3.4 Choice of solvent for desorption

Due to the estrogens' relatively polar properties, weakly polar desorption solvents methanol and acetonitrile were considered. And considering four target estrogens contain phenolic hydroxyl groups presenting weak acidic, and the basic desorption solvent maybe favorable for estrogens desorption. Methanol, acetonitrile, 10 mmol L^{-1} NaOH methanol solution and 10 mmol L^{-1} NaOH acetonitrile solution were tested for the desorption of estrogens from Fe_3O_4-NH_2@MIL-101 composite. The extraction efficiency was shown in Fig. 6d, methanol gained the better desorption performance than the other options of elute.

Herein, the influence of desorption time varying in 1−9 min on desorption efficiency was investigated by using 500 μL of methanol as the desorption solvent under ultrasonic irradiation. It was found that only 7 min enabled quantitative stripping of the adsorbed estrogens from Fe_3O_4-NH_2@MIL-101 composite.

Based on the above optimization, the extraction conditions were as follows: 5 mg Fe_3O_4-NH_2@MIL-101 composite as sorbent, extraction for 10 min at 35°C, sample solutions pH at 7, and ultrasonication desorption time of 7 min using methanol. All the subsequent experiments were carried out under the optimized conditions.

Table 2. Performance of the proposed method

Analytes	Linear range (μg L^{-1})	Correlation coefficient	Limit of detection (μg L^{-1})	RSD (n=5, %)
E1	0.2–100	0.9956	0.22	8.3
E2	0.2–100	0.9946	0.1	6.1
E3	0.2–100	0.9941	0.22	5.9
BPA	0.2–100	0.9955	0.06	7.8

Table 3. Analytical results for determination of estrogens in real water samples

Analytes	River water		Lake water	
	Concentration (μg L^{-1})	Recovery [a] (%, n= 3)	Concentration (μg $^{-1}$)	Recovery [a] (%, n=3)
E1	1.815	80.6 ± 3.49	1.251	86.7 ± 3.86
E2	ND [b]	99.6 ± 1.53	ND [b]	84.3 ± 1.69
E3	ND	82.0 ± 6.60	4.958	87.9 ± 4.39
BPA	0.926	93.9 ± 1.74	0.958	84.9 ± 0.90

[a] For spiked 10 μg L^{-1}; [b] not detected.

3.4 Method evaluation

Under the optimized conditions described above, the analytical characteristic data of Fe_3O_4-NH_2@MIL-101 composite for magnetic solid extraction couple with HPLC for the determination of the four target estrogens is summarized in Table 2. Good linearity was obtained within the concentration range of 0.2–100 μg L^{-1} for E1, E2, E3 and BPA, and the correlation coefficients were all above 0.994. The detection limits (S/N = 3) for the estrogens were in the range of0.06–0.22 μg L^{-1}. The precision (relative standard deviations, RSDs) for five parallel extractions of spiked samples at concentration of mixture of estrogens (50 μg L^{-1} for each) was in the range of 5.9–8.3%.

3.5 Sample analysis

We further verified the applicability of the proposed method by analyzing lake and rive water samples collected from Xiqing District of Tianjin. The recoveries of three replicate extraction obtained by spiking with 10 μg L^{-1} standard solution of four target estrogens in water samples were from 80.6% to 99.6%, and relative standard deviation (RSD) were in the range of 0.90−6.60% (Table 3). These results indicated that Fe_3O_4-NH_2@MIL-101 composite can be used as efficient magnetic solid extraction adsorbents for determining typical environmental estrogens in real water samples.

4. Conclusion

We developed a simple hydrofluoric acid-free one-pot method for the preparation of three functionalized magnetic MIL-101 composites (Fe_3O_4-NH_2@MIL-101, Fe_3O_4-COOH@MIL-101 and Fe_3O_4/C@MIL-101 composite) which exhibited the differences of adsorbing estrogens as magnetic solid-phase extraction materials. Taking Fe_3O_4-NH_2@MIL-101 composite as an example, the dominant parameters affecting enrichment efficiency including extraction time, sample pH, extraction temperature and desorption condition were investigated. Fe_3O_4-NH_2@MIL-101 composite as magnetic solid-extraction adsorbent could meet the demand of determination in the environmental level analytics, and the proposed

method achieved wide linear range, low limits of detection and satisfactory measurement precision in a fast and convenient way.

Acknowledgments

This work was supported by National Natural Science Foundation of China (Grants 21475095, 21305112, 21106101 and), the Tianjin Natural Science Foundation (12JCZDJC29500, 13JCQNJC06300)

References

1 G. Xu, T. Yamada, K. Otsubo, S. Sakaida, H. Kitagawa, Facile "modular assembly" for fast construction of a highly oriented crystalline MOF nanofilm, *J. Am. Chem. Soc.*, 2012, **134,** 16524−16527.

2 Z.-J. Lin, J. Lü, M. Hong, R. Cao, Metal–organic frameworks based on flexible ligands (FL-MOFs): structures and applications, *Chem. Soc. Rev.*, 2014, **43**, 5867−5895.

3 Z.-Y. Gu, C.-X. Yang, N. Chang, X.-P. Yan, Metal-organic frameworks for analytical chemistry: from sample collection to chromatographic separation, *Acc. Chem. Res*., 2012, **45**, 734−745.

4 B. V. de Voorde, B. Bueken, J. Denayer, D. De Vos, Adsorptive separation on metal–organic frameworks in the liquid phase, *Chem. Soc. Rev.,* 2014, **43**, 5766−5788.

5 H. Jasuja, Y. Huang, K. S. Walton, Adjusting the stability of metal−organic frameworks under humid conditions by ligand functionalization, *Langmuir*, 2012, **28**, 16874−16880.

6 Y.-K. Seo, J. W. Yoon, J. S. Lee, Y. K. Hwang, C.-H. Jun, J.-S. Chang, S. Wuttke, P. Bazin, A. Vimont, M. Daturi, S. Bourrelly, P. L. Llewellyn, P. Horcajada, C. Serre, G. Férey, Energy-efficient dehumidification over hierachically porous metal–organic frameworks as advanced water adsorbents, *Adv. Mater.*, 2012, **24**, 806−810.

7 Y. S. Seo, N. A. Khan, S. H. Jhung, Adsorptive removal of methylchlorophenoxypropionic acid from water with a metal-organic framework, *Chem. Eng. J.*, 2015, **270**, 22−27.

8 B. Liu, F. Yang, Y. Zou, Y. Peng, Adsorption of phenol and p-nitrophenol from aqueous solutions on metal−organic frameworks: effect of hydrogen bonding, *J. Chem. Eng. Data*, 2014, **59**, 1476−1482.

9 T. Wang, J. Wang, C. Zhang, Z. Yang, X. Dai, M. Cheng, X. Hou, Metal–organic framework MIL-101(Cr) as a sorbent of porous membrane-protected micro-solid-phase extraction for the analysis of six phthalate esters from drinking water: a combination of experimental and computational study, *Analyst,* 2015, **140**, 5308−5316.

10 Z. Huang, H. K. Lee, Micro-solid-phase extraction of organochlorine pesticides using porous metal-organic framework MIL-101 as sorbent, *J. Chromatogr. A*, 2015, **1401**, 9−16.

11 Z. Huang, H. K. Lee, Performance of metal-organic framework MIL-101 after surfactant modification in the extraction of endocrine disrupting chemicals from environmental water samples, *Talanta*, 2015, **143**, 366−373.

12 G. Lu, S. Li, Z. Guo, O. K. Farha, B. G. Hauser, X. Qi, Y. Wang, X. Wang, S. Han, X. Liu, J. S. DuChene, H. Zhang, Q. Zhang, X. Chen, J. Ma, S. C. Joachim Loo, W. D. Wei, Y. Yang, J. T. Hupp, F. Huo, Imparting functionality to a metal-organic frameworkmaterial by controlled nanoparticle encapsulation, *Nat Chem.*, 2012, **4**, 310−316.

13 M. E. Silvestre, M. Franzreb, P. G. Weidler, O. Shekhah, C. Wöll, Magnetic cores with porous coatings: growth of metal-organic frameworks on particles using liquid phase epitaxy, *Adv. Funct. Mater*., 2013, **23**, 1210−1213.

14 F. Ke, L.-G. Qiu, Y.-P. Yuan, X. Jiang, J.-F. Zhu, Fe_3O_4@MOF core–shell magnetic microspheres with a designable metal–organic framework shell, *J. Mater. Chem.*, 2012, **22**, 9497−9500.

15 S.-H. Huo, X.-P. Yan, Facile magnetization of metal–organic framework MIL-101 for magnetic solid-phase extraction of polycyclic aromatic hydrocarbons in environmental water samples, *Analyst*, 2012, **137**, 3445−3451.

16 Y. Hu, Z. Huang, J. Liao, G. Li, Chemical bonding approach for fabrication of hybrid magnetic metal−organic framework-5: high efficient adsorbents for magnetic enrichment of trace analytes, *Anal. Chem.*, 2013, **85**, 6885−6893.

17 C. Zhang, L. Ai, J. Jiang, Solvothermal synthesis of MIL–53(Fe) hybrid magnetic composites for photoelectrochemical water oxidation and organic pollutant photodegradation under visible light, *J. Mater. Chem. A*, 2015, **3**, 3074–3081.

18 V. Pacáková, L. Loukotková, Z. Bosáková, K. Štulík, Analysis for estrogens as environmental pollutants – A review, *J. Sep. Sci.*, 2009, **32**, 867–882.

19 Y. Wang, S. Jin, Q. Wang, G. Lu, J. Jiang, D. Zhu, Zeolitic I midazolate framework-8 as sorbent of micro-solid-phase extraction to determine estrogens in environmental water samples, *J. Chromatogr. A*, 2013, **1291**, 27−32.

20 B. Chen, Y. Huang, M. He, B. Hu, Hollow fiber liquid-liquid-liquid microextraction combined with high performance liquid chromatography-ultraviolet detection for the determination of various environmental estrogens in environmental and biological samples, *J. Chromatogr. A,* 2013, **1305**, 17−26.

21 J. Liu, Z. Sun, Y. Deng, Y. Zou, C. Li, X. Guo, L. Xiong, Y. Gao, F. Li, D. Zhao, Highly water-dispersible biocompatible magnetite articles with low cytotoxicity stabilized by citrate groups, *Angew. Chem. Int. Ed.*, 2009, **48**, 5875−5879.

22 L. Wang, J. Bao, L. Wang, F. Zhang, Y. Li, One-pot synthesis and bioapplication of amine-functionalized magnetite nanoparticles and hollow nanospheres, *Chem. Eur. J.*, 2006, **12**, 6341−6347.

23 D. Qi, H. Zhang, J. Tang, C. Deng, X. Zhang, Facile Synthesis of mercaptophenylboronic acid-functionalized core-shell structure Fe_3O_4@C@Au magnetic microspheres for selective enrichment of glycopeptides and glycoproteins, *J. Phys. Chem. C*, 2010, **114**, 9221−9226.

24 L. Bromberg, Y. Diao, H. Wu, S. A. Speakman, T. A. Hatton, Chromium(III) terephthalate metal organic framework (MIL-101): HF-free synthesis, structure, polyoxometalate composites, and catalytic properties, *Chem. Mater*., 2012, **24**, 1664−1675.

25 S. Wang, L. Bromberg, H. Schreuder-Gibson, T. A. Hatton, Organophophorous ester degradation by chromium(III) terephthalate metal−organic framework (MIL-101) chelated to N,N‑dimethylaminopyridine and related aminopyridines, *ACS Appl. Mater. Interfaces,* 2013, **5**, 1269−1278.

26. J.-Z. Zhang, W.-R. Cao, J.-X. Pan, Q.-W. Chen, A novel two-dimensional square grid cobalt complex: Synthesis, structure, luminescent and magnetic properties, *Inorg. Chem.Commun.* 2007, **10**, 1360–1364.

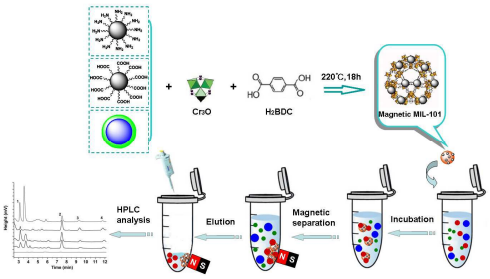
27 Z. Hasan, E.-J. Choi, S. H. Jhung, Ad*sorption of naproxen and clofibric aci*d over a metal–organic framework MIL-101 functionalized with acidic and basic groups, *Chem. Eng. J,* 2013, **219**, 537−544.

28 K. M. Choi, K. Na, G. A. Somorjai, O. M. Yaghi, Chemical environment control and enhanced catalytic performance of platinum nanoparticles embedded in nanocrystalline metal−organic frameworks, *J. Am. Chem. Soc.*, 2015, **137**, 7810−7816.

29 J.-P. Wei, B. Qiao, W.-J. Song, T. Chen, F. li, B.-Z. Li, J. Wang, Y. Han, Y.-F. Huang, Z.-J. Zhou, Synthesis of magnetic framework composites for the discrimination of *Escherichia coli* at the strain level, *Anal. Chim. Acta*, 2015, **868**, 36–44.

30 N. A. Khan, Z. Hasan, S. H. Jhung, Adsorptive removal of hazardous materials using metal-organic frameworks (MOFs): A review, *J. Hazard. Mater.*, 2013, **244–245**, 444−456.

Graphic Abstract



Three functionalized magnetic MIL-101 composites were synthesized by a simple one-pot method and exhibited certain differences in extraction efficiency of target estrogens.