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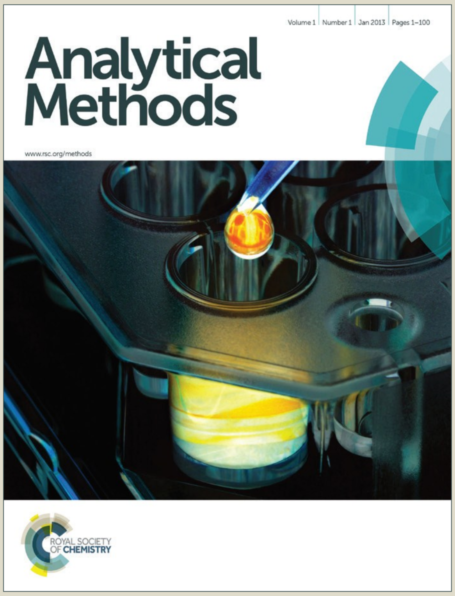

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Metal-organic framework-derived nanoporous carbon/iron composite for enrichment of endocrine disrupting compounds from fruit juices and milk samples

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Abstract: In this work, a nanoporous carbon/iron composite material designated as MIL-53-C was fabricated by one-step carbonization of Fe-based metal-organic framework material MIL-53. The obtained MIL-53-C showed a high Brunauer Emmett Teller surface area (249.33 m^2 g^{-1}), large pore volume (0.57 cm^3 g^{-1}) and an excellent magnetic property (127.95 emu g^{-1}). It was used as magnetic solid-phase extraction adsorbent for the enrichment of some endocrine disrupting compounds from fruit juice and milk samples followed by high performance liquid chromatographic analysis. Under the optimum conditions, a good linearity for all analytes over the studied concentration range were achieved with correlation coefficient higher than 0.9995. The limits of detection, based on $S/N = 3$, were 0.05-0.10 ng mL^{-1} for fruit juice and 0.10-0.20 ng mL^{-1} for milk sample, respectively. The recoveries of spiked samples ranged from 92.2% to 108.3%. The results indicated that the MIL-53-C exhibited an excellent adsorption capability for trace levels of EDCs, and it may also be a promising adsorbent for extraction and enrichment of other organic pollutants.

Keywords: Metal-organic framework-derived nanoporous carbon/iron composite; Magnetic solid-phase extraction; High performance liquid chromatography; Endocrine disrupting compounds; Fruit juice; Milk

1. Introduction

During the last decade, a class of emerging pollutants termed as endocrine disrupting compounds (EDCs), which can interfere with the endocrine system of living organisms, has received much research attention[1, 2]. Some EDCs, such as bisphenol A (BPA), 4-*tert*-butylphenol (4-*t*-BP), 4-*tert*-octylphenol (4-*t*-OP) and 4-nonylphenol (4-NP), have a broad range of applications in industry (liners lacquers, adhesives, plastics, drink packages and food cans) and agricultural purposes[3, 4]. Especially, the use of EDCs in diverse plastic materials and products led to its presence in food and drink[4]. Many studies have reported that EDCs can mimic or block the actions of natural hormones in living organisms, and impair their normal functioning, such as growth, metabolism and reproduction even at trace level[5]. Therefore, it is necessary to develop highly sensitive analytical method for monitoring of trace level of EDCs in different matrix samples.

To achieve a high level of sensitivity, a sample preparation step for the efficient extraction of the target analytes from sample matrix is frequently required prior to chromatographic analysis. Up to now, several sample preparation techniques including liquid-liquid extraction[6], solid-phase extraction (SPE)[7, 8] and solid-phase micro-extraction (SPME)[4, 9] have been developed to isolate and enrich EDCs from different samples. In recent years, a new mode of SPE called magnetic solid-phase extraction (MSPE), based on the use of magnetic or magnetically modified adsorbents, has drawn considerable attention because the phase separation can be performed easily by using an external magnet[10, 11]. In MSPE, the adsorbent material plays a key role because it determines the extraction efficiency. Therefore, the exploration of new adsorbents with high adsorption capacity and good reusability received considerable attention.

Owing to their high surface area, narrow pore-size distribution, good chemical resistance, and affinity to organic contaminations, nanoporous carbon materials have been used as adsorbents for gas adsorption/storage and adsorption of environment pollutants[12-15]. Recent research focuses on the template-based synthesis of nanoporous carbons for a better control on their physical and chemical properties in addition to the desired morphology[16]. Traditional inorganic porous materials, such as mesoporous silica[17] and zeolites[18], have been successfully used as templates for preparing nanoporous carbons. As a novel class of porous materials, metal-organic frameworks (MOFs) which are formed by the self-assembly of metallic centers and organic linkers, have found many applications in respect of gas storage[19], separation[20], catalysis[21] and adsorption material[22, 23]. Due to their high stability, low framework density and tunable yet high porosity by changing the connectivity of the inorganic moiety and the nature of organic linkers, MOFs have been considered as novel templates to prepare nanoporous carbons[24]. So far, several MOFs, such as MOF-5[25, 26], Al-porous coordination polymers (Al-PCP)[27, 28] and zeolitic imidazolate framework-8 (ZIF-8)[29, 30] have been successfully used as templates to prepare nanoporous carbon materials. The obtained MOF-derived nanoporous carbon materials present high specific surface area, large pore volume, high thermal stability and excellent electrochemical performance, which make them attractive for a wide range of applications in gas storage[25], catalysis[31] and supercapacitors[30]. However, their application as adsorbent in sample preparation such as SPE[26, 30], SPME[29] and MSPE[11] is emerging. For instance, we have prepared Fe_3O_4-MOF-5-C through a co-precipitation method as MSPE absorbent[11], but this method was too cumbersome, and the introduction of Fe_3O_4 particles was easy to destroy the structure of MOF-based porous carbon and reduce their surface area and pore size.

Fe-based materials institute lavoisier-53 (Fe-MIL-53), which is formed by Fe metallic centers and terephthalic acid organic linkers, with high surface area, large pore size and good thermal stability has been used as adsorbents for adsorption of environment pollutants[23]. In addition, the high carbon content of organic ligands in Fe-MIL-53 can eliminate the need of an additional carbon source, it can produce nanoporous carbon by one-step direct carbonization. The obtained MIL-53-C maintained the parent porosity, showed a high Brunauer Emmett Teller surface area (249.33 m^2 g^{-1}), large pore volume (0.57 cm^3 g^{-1}), and excellent magnetic property (127.95 emu g^{-1}) due to the presence of Fe nanoparticles. Besides, due to the presence of graphitic sp^2-hybridized carbons, the MIL-53-C material can form a strong π-stacking interaction with the benzene ring, so it is a good adsorbent for the adsorption of aromatic compounds, such as phenols. To evaluate its adsorption performance, the MIL-53-C was used as magnetic solid phase extraction adsorbent for the extraction of four phenols EDCs from fruit juices and milk samples followed by high performance liquid chromatographic-ultraviolet detector (HPLC-UV) analysis. The effects of various experimental parameters, such as the type and volume of the desorption solvent, the amount of adsorbent, extraction time, pH and salt effect were studied.

2. Experimental

2.1. Chemicals and materials

Standards of the EDCs, i.e., BPA, 4-*t*-BP, 4-*t*-OP and 4-NP, were purchased from Aladdin-reagent (Shanghai, China). The chemical structures of the four EDCs evaluated here were shown in Fig. 1. Chromatography-grade acetonitrile and methanol was purchased from Huaxin Chemical Reagent Company (Baoding, China). Ferric trichloride hexahydrate ($FeCl_3 \cdot 6H_2O$), terephthalic acid, trichloroacetic acid, acetone, hydrochloric acid (HCl) and sodium hydroxide (NaOH) were purchased from Beijing Chemical Reagents Company (Beijing, China). N,N-dimethylformamide (DMF), sodium chloride (NaCl) and all other reagents were purchased from Boaixin Chemical Reagents Company (Baoding, China). The water used throughout the work was double-distilled on a SZ-93 automatic double-distiller purchased from Shanghai Yarong Biochemistry Instrumental Factory (Shanghai, China). The fruit juices and milk samples were bought from the local market (Baoding, China).

A mixture stock solution containing BPA, 4-*t*-BP, 4-*t*-OP and 4-NP each at 20.0 μg mL^{-1} was prepared in methanol. A series of standard solutions were prepared by mixing an appropriate amount of the stock solution with methanol in a 10-mL volumetric flask. All the standard solutions were stored at 4 ^{o}C and protected from light.

2.2. Apparatus

The HPLC system was LC-20AT (Shimadzu, Japan), which was equipped with two LC-20AT pumps, a SPD-20A UV/vis detector and a LC-solution software. Chromatographic separations were performed on a Promosil C18 column (150 mm × 4.6 mm I.D., 5.0 μm) from Bonna-Agela technologies (Tianjin, China). Acetonitrile-water was used as the mobile phase. The system was run in the following gradient elution: 0-9 min, 48% acetonitrile, 9-10 min, acetonitrile from 48% to 70%, 10-40 min, acetonitrile held for 70%; 40-40.1 min, acetonitrile from 70% to 48%, held for 5 min, stopped at 45 min. The flow rate of the mobile phase was 1 mL min^{-1}. The UV monitoring wavelength was chosen at 225 nm. The sample injection volume was 20 μL.

The size and morphology of the MIL-53-C were observed by scanning electron microscopy (SEM) with a S-4800 instrument (Hitachi, Japan) and transmission electron microscopy (TEM) using a JEOL model JEM-2011(HR) (Tokyo, Japan). The X-ray diffraction (XRD) patterns of the samples were recorded with a Bruker D8 ADVANCE (Germany). The magnetic property was analyzed using a MPMS-XL-7 vibrating sample magnetometer (Quantum Design, America) at room temperature. Nitrogen adsorption and desorption isotherms were measured at liquid nitrogen temperature (77 K) using a V-Sorb 2800P (Jinaipu, China). Prior to the measurement, the samples were degassed at 120 ^{o}C for 4 h.

2.3. Sample pretreatment

Fruit juices sample was filtered through a 0.45-μm membrane and stored at 4 ^{o}C for the following experiments. For milk samples, 50 mL of the milk was put in a centrifuge tube and 0.4 mL trichloroacetic acid was added. The solution was vortexed for 1 min and then centrifuged for 5 min at 4000 rpm to isolate proteins. Then, the supernatant was collected. After that, 3.0 mL acetone was added to the sediment and vortexed for 1 min. The solution was centrifuged and the supernatant solution was collected. The same procedures for the acetone extraction were performed another time. All the supernatants were combined together, filtered through a 0.45-μm membrane and stored at 4 ^{o}C for the following experiments.

2.4. Synthesis of MIL-53-C

The MIL-53-C material was prepared via a two-step route (Fig. 2) involving the fabrication of MIL-53 (Fe) and the subsequent calcination treatment. In the first step, the MIL-53 (Fe) was fabricated according to a previously reported procedure[32]. Typically, terephthalic acid (0.166 g, 1 mmol) and $FeCl_3 \cdot 6H_2O$ (0.275 g, 1 mmol) were dissolved in 5 mL DMF. The mixture was treated ultrasonically for about 15 min until the solid completely dissolved and then loaded into a teflonliner steel autoclave, which was then sealed and placed in an oven at 150 ^{o}C for 2 h. After cooling down to room temperature, a yellow precipitate was obtained. It was separated by centrifugation, then washed with DMF and water, and finally dried at 100 ^{o}C. In the second step, the MIL-53 were loaded in a quartz boat and then transferred to a tube furnace and heat-treated at 700 ^{o}C for 6 h under nitrogen to pyrolyze the organic species. After the above calcination treatment, the yellow precursor was finally converted into the black powder, and this resulting black powder carbon material was denoted as MIL-53-C.

2.5. MSPE procedures

For the MSPE, 12 mg of MIL-53-C was placed in a 150 mL conical flask containing 50 mL of sample solution. The mixture was shaken on a slow-moving platform shaker for 20 min for extraction. Then, the MIL-53-C adsorbent was separated from the aqueous phase by placing a strong magnet at the bottom of the conical flask. The supernatant was discarded and then the residual mixture was totally transferred to a 10-mL centrifuge tube. Subsequently, the MIL-53-C was aggregated again by positioning a magnet to the outside of the tube wall so that the residual solution could be completely removed by a pipette. At last, 0.2 mL alkaline acetone (1% 1 mol L^{-1} NaOH) was added to the centrifuge tube and was vortexed for 60 s to elute the analytes from the MIL-53-C. After positioning a magnet to the outside of the centrifuge tube to gather the MIL-53-C, the desorption solution was collected using a micropipette. The same desorption procedures were performed for another two times. The eluent was combined together and 6.0 μL of 1 mol L^{-1} HCl aqueous solution was added into the solution to neutralize its pH. Finally 20.0 μL of the resultant desorption solution was injected into the HPLC system for analysis.

3. Results and discussion

3.1. Characterization of the MIL-53-C

SEM and TEM were taken to characterize the morphology of the MIL-53-C. The SEM image (Fig. 3A) shows the high porosity structure of the MIL-53-C. From the TEM image (Figure 3B), we can see that the iron particles were deposited in the carbon matrix. In addition, the prepared MIL-53-C was characterized by XRD. The XRD (Fig. 4A) pattern for the MIL-53-C sample displays a broad peak at $2\theta = 23^{\circ}$, this signal belongs to a typical (002) interlayer peak of graphite-type carbon, indicating that the carbon material has a typical graphite structure. The diffraction peaks locating at 2θ of 45° and 65° correspond to the metal iron (JCPDS card no. 52-0513), further confirming the presence of the iron in the MIL-53-C.

To evaluate the magnetic behavior of the MIL-53-C, the magnetic measurement was carried out at 300 K. Fig. 4B shows the field-dependent magnetization curves of the MIL-53-C. In the magnetization curves, there is no hysteresis, remanence and coercivity, indicating that the MIL-53-C was superparamagnetic. The saturation magnetization value of the MIL-53-C was 127.95 emu g^{-1}, showing that the materials had a sufficient magnetism which is desirable for their applications in magnetic separation.

Nitrogen sorption experiments were performed to examine the surface areas and the porosity of the MIL-53-C (Fig. 4C). The MIL-53-C exhibits a type IV isotherm. It steeply increases at low relative pressure, indicating that the dominating microporous structure. The durative small slope increase of the adsorption capacity at medium relative pressure and the slight hysteresis of the desorption curve reveal the presence of mesoporosity. The Brunauer Emmett Teller (BET) surface area, total pore volume and total adsorption average pore width of the MIL-53-C are 249.33 m^2 g^{-1}, 0.57 cm^3 g^{-1} and 9.05 nm, respectively.

3.2. Optimization of the extraction conditions

To obtain the optimum extraction conditions, several experimental parameters including the amount of adsorbents, extraction time, sample pH, salinity and desorption conditions were investigated and optimized. All the optimization was performed in triplicate and using 50 mL double-distilled water spiked with the concentration of each of the EDCs at 40 ng mL^{-1} except the amount of adsorbents with the concentration of each of the EDCs at 100 ng mL^{-1}.

3.2.1. Effect of the amount of the MIL-53-C To choose the optimum amount of the MIL-53-C adsorbent, the amount of the MIL-53-C was investigated from 5 to 15 mg in 50 mL aqueous solution containing each analyte at 100 ng mL^{-1}. The result (Fig. 5A) showed that the extraction recoveries for these EDCs were first increased rapidly when the amount of MIL-53-C was increased from 5 to 10 mg, and then enhanced slightly as the amount of MIL-53-C was changed from 10 to 12 mg, and finally remained almost constant when the amount of MIL-53-C was higher than 12 mg. Therefore, 12 mg MIL-53-C was chosen for the following experiments.

3.2.2. Effect of desorption conditions For the desorption process, two parameters need to be optimized including the type and the volume of desorption solvent. To elute EDCs from the MIL-53-C, methanol, acetonitrile, acetone, alkaline methanol (1% 1 mol L^{-1} NaOH), alkaline acetonitrile (1% 1 mol L^{-1} NaOH) and alkaline acetone (1% 1 mol L^{-1} NaOH) were studied as the desorption solvent. The results showed that the desorption capabilitiy of alkaline acetone was stronger than other solvents. So, alkaline acetone was chosen as the desorption solvent. The volume of desorption solvent was also studied (Fig. 5B). It was found that the EDCs could be desorbed effectively when the adsorbent was desorbed with 0.2 mL alkaline acetone for thrice. Thus, 0.6 mL alkaline acetone (0.2 mL × 3) was selected as the desorption solvent.

3.2.3. Effect of the extraction time MSPE is an equilibrium-based process, to reach the adsorption equilibrium, a certain extraction time is required. To investigate the optimum extraction time, different extraction time ranging from 5 to 30 min was studied. As can be observed in Fig. 5C, the extraction recoveries of the analytes increased with increased extraction time from 5 to 20 min and then remained constant after 20 min. Therefore the extraction time was selected at 20 min in all the subsequent experiments.

3.2.4. Effect of the sample solution pH It can be seen from the structures that the target analytes have abundant polar phenolic hydroxyl groups. Therefore, the pH of the sample solution will affect the existing forms of the compounds. To investigate the optimum sample solution pH, different sample solution pH ranging from 4 to 10 was studied. As can be seen from Fig. 5D, the extraction efficiencies had no significant changes in the range of pH 4-7, but slightly decreased when the sample solution pH was increased from 7 to 10. The reason for this could be that when the pH values increased, EDCs became ionic forms because of the dissociation of phenolic hydroxyl groups, which cause the increase of their solubility in aqueous solution. The pH of the fruit juices and milk samples were below 7, so there was no need to adjust the sample solution pH in the subsequent experiments.

3.2.5. Effect of salinity To investigate the effect of salinity on the extraction efficiency, a series of experiments was performed by adding different amounts of NaCl (0, 2, 4, 6, 8, and 10% (w/v)) into the sample solution. The results showed that the addition of NaCl had no significant effect on the extraction efficiency in the concentration range investigated. Based on the result, all the subsequent experiments were performed without the addition of NaCl.

3.2.6. Reusability of the adsorbent The reusability of the MIL-53-C was investigated. After extraction, the used adsorbent was washed with 1 mL alkaline acetone twice and 1 mL double-distilled water, respectively. After such washing, no analytes carry-over was detected. It was found that the MIL-53-C adsorbent could be used at least 12 times for the MSPE program without significant loss of its adsorption ability (Fig. 5E).

3.3. Method evaluation

A series of experiments with regard to the linearity, limits of detection (LOD), and repeatability were performed to evaluate the developed method under the optimized conditions. For fruit juice and milk sample, the experiments for the establishment of the calibration curves for the analytes were performed in the concentration range of 0.1-100.0 ng mL^{-1} at seven different levels (0.1, 0.5, 1.0, 5.0, 10.0, 50.0, 100.0 ng mL^{-1}). The results are summarized in Table 1. As a result, good linearity for all analytes over the studied concentration range were achieved with correlation coefficient (r) higher than 0.9995. The LODs, based on $S/N = 3$, were 0.05-0.10 ng mL^{-1} for fruit juice and 0.10-0.20 ng mL^{-1} for milk sample, respectively. The repeatability of the method was evaluated by calculating the RSD values, which was acquired by conducting five parallel experiments at the concentration of the EDCs of 10.0 ng mL^{-1}. The resultant relative standard deviation (RSD) values varied from 5.1% to 6.5%, indicating that the repeatability of the current method was acceptable.

3.4. Real sample analysis

To assess the utility of the developed method, it was used for applied to the analysis of EDCs in fruit juice and milk samples. As a result, 4.47 ng mL^{-1} 4-*t*-OP in fruit juice sample, and 2.07 ng mL^{-1} 4-*t*-OP in milk sample were detected. To test the accuracy of the method, the fruit juice and milk sample were spiked with the target analytes at 10.0 and 40.0 ng mL^{-1}, and then analyzed by the current method. As listed in Table 2, the recoveries of the four EDCs were in the range from 92.2% to 108.3% with the RSD less than 7.1%. To validate the stability of the method, significance test was made by conducting five parallel experiments, the results of determination were below $t_{0.05, 4}$=2.78, so there is no significant difference between them at 5% level. Fig. 6 shows a typical chromatogram of the milk sample before and after being spiked at 10.0 ng mL^{-1} each of the four EDCs.

$$t = \frac{|\bar{x} - \mu|}{s}\sqrt{n}$$

$\overline{x}$ is the sample mean, μ is the true value, s is the sample standard deviation of the sample, n is the sample size.

3.5. Comparison with other extraction methods

The performance of the developed MSPE-HPLC-UV method was compared with other reported sample preparation methods for the determination of EDCs from the viewpoint of linearity, LOD and RSD. The comparison results (Table 3) show that the current method exhibits comparable linearity, good precision and adequately low detection limits except for the MSPE-HPLC-fluorescence (MSPE-HPLC-FLD)[33] method, and this is because the sensitivity of FLD is higher than that of UV. Moreover, the MSPE-HPLC-UV method is simple and easy to operate since the use of magnetic adsorbent can make the phase separation process easier and faster without the need of additional centrifugation or filtration procedures and also can avoid the time-consuming column passing operations encountered in SPE. Therefore, the current method is indeed a simple and effective method.

4. Conclusion

In this work, a MIL-53-C was prepared by direct carbonization of Fe-based MOF (MIL-53). The obtained MIL-53-C showed high surface area and excellent magnetic property. It was used as MSPE adsorbent for the enrichment of some EDCs from fruit juice and milk samples. The results indicated that the MIL-53-C exhibited an excellent adsorption capability for trace levels of EDCs, and it could be a promising magnetic solid phase extraction adsorbent for preconcentration of other organic compounds.

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Table Captions

Table 1 Analytical performance data for the EDCs by the MSPE method.

Table 2 The precision and recoveries of EDCs of the method for fruit juice and milk samples.

Table 3 Comparison of the MSPE-HPLC-UV method with other reported method for the extraction and determination of the EDCs.

Figure Captions

Fig. 1 Chemical structures of the the four EDCs.

Fig. 2 Procedures for the preparation of MIL-53-C.

Fig. 3 The typical SEM (A) and TEM (B) images of the MIL-53-C.

Fig. 4 The XRD spectrum (A) of MIL-53 and MIL-53-C, the magnetic hysteresis of the MIL-53-C (B) and the N_2 sorption isotherms of the MIL-53-C (C).

Fig. 5 Effect of extraction conditions on the extraction efficiencies. (A) Effect of the amount of the MIL-53-C; (B) Effect of the volume of desorption solvent; (C) Effect of extraction time; (D) Effect of the sample solution pH; (E) The reusability of the MIL-53-C.

Fig. 6 The chromatography of EDCs standard sample (A) at each concentration of 10.0 μg mL^{-1}, the typical chromatograms of (b) milk sample and (a) milk sample spiked with the EDCs at each concentration of 10.0 ng mL^{-1} (B). Peak identification: 1. BPA, 2. 4-*t*-BP, 3. 4-*t*-OP, 4. 4-NP. Detection wavelength: 225 nm.

Table 1 Analytical performance data for the EDCs by the MSPE method.

Samples	EDCs	Linearity (ng mL^{-1})	*r*	LODs (ng mL^{-1})	RSDs (%) (*n* = 5)
Fruit juice	BPA	0.5-100.0	0.9997	0.05	5.8
	4-*t*-BP	1.0-100.0	0.9996	0.10	6.2
	4-*t*-OP	1.0-100.0	0.9998	0.10	5.1
	4-NP	1.0-100.0	0.9997	0.10	6.2
Milk	BPA	1.0-100.0	0.9996	0.10	6.1
	4-*t*-BP	2.0-100.0	0.9995	0.20	6.5
	4-*t*-OP	2.0-100.0	0.9997	0.20	5.7
	4-NP	2.0-100.0	0.9997	0.20	6.2

Table 2 The precision and recoveries of EDCs of the method for fruit juice and milk samples.

EDCs	Spiked (ng mL^{-1})	Fruit juice sample (n = 5)				Milk sample (n = 5)			
		Found (ng mL^{-1})	R[a] (%)	RSDs (%)	t	Found (ng mL^{-1})	R[a] (%)	RSDs (%)	t
	0	nd[b]				nd[b]			
BPA	10.0	10.06	100.6	5.6	0.23	9.68	96.8	6.4	1.15
	40.0	38.25	95.6	6.3	1.62	38.32	95.8	7.1	1.38
	0	nd[b]				nd[b]			
4-*t*-BP	10.0	9.56	95.6	6.7	1.54	9. 94	99.4	5.5	0.25
	40.0	41.68	104.2	6.2	1.45	43.31	108.3	6.3	2.71
	0	4.47				2.07			
4-*t*-OP	10.0	14.69	102.2	6.1	0.55	12.30	102.3	5.7	0.73
	40.0	41.79	93.3	6.3	2.28	39.04	92.4	6.3	2.75
	0	nd[b]				nd[b]			
4-NP	10.0	9.62	96.2	6.2	1.42	9.86	98.6	6.2	0.51
	40.0	37.64	94.1	6.7	2.09	36.88	92.2	6.9	2.74

[a] R: recovery.

[b] nd: not detected.

Table 3 Comparison of the MSPE-HPLC-UV method with other reported method for the extraction and determination of the EDCs.

Methods	Adsorbent materials	Sample	Linearity (ng mL^{-1})	LOD (ng mL^{-1})	RSD (%)	Ref.
SPE-HPLC-FLD	C18	wine	-	0.1	9.9-14.9	7
SPE-UPLC-MS/MS[a]	oasis HLB cartridge	urine	1-500	0.10-0.15	7.08-9.11	8
SPME-HPLC-DAD[b]	multi-walled carbon nanotubes	water	2-500	0.1-0.3	1.26-4.84	4
MSPE-HPLC-FLD	Fe_3O_4@ Molecularly imprinted polymer	canned orange	0.5-100	0.1	6.4-10.5	34
		milk	1-100	0.3	8.9-12.6	
MSPE-HPLC-FLD	Magnetic three-dimensional graphene nanoparticles	honey peach juice	0.05-20	0.010-0.025	6.3-7.3	33
MSPE-HPLC-UV	MIL-53-C	fruit juice	0.5-100	0.05-0.10	5.1-6.2	This method
		milk	1.0-100	0.10-0.20	5.7-6.5	

[a] UPLC-MS/MS: ultra performance liquid chromatography-mass spectrometry/mass spectrometry;

[b] DAD: diode array detection;

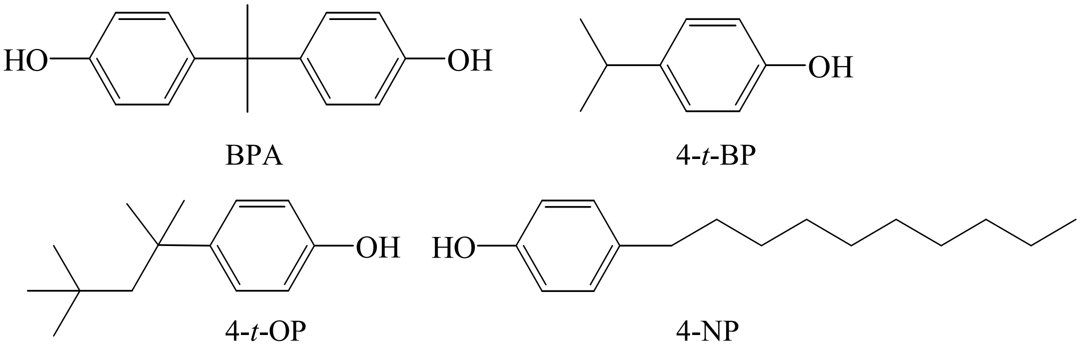

Fig. 1 Chemical structures of the the four EDCs.

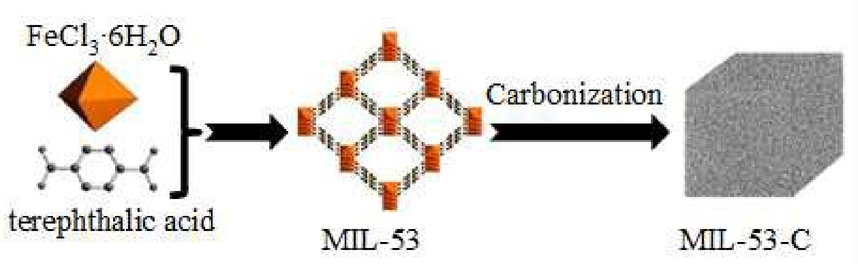

Fig. 2 Procedures for the preparation of MIL-53-C.

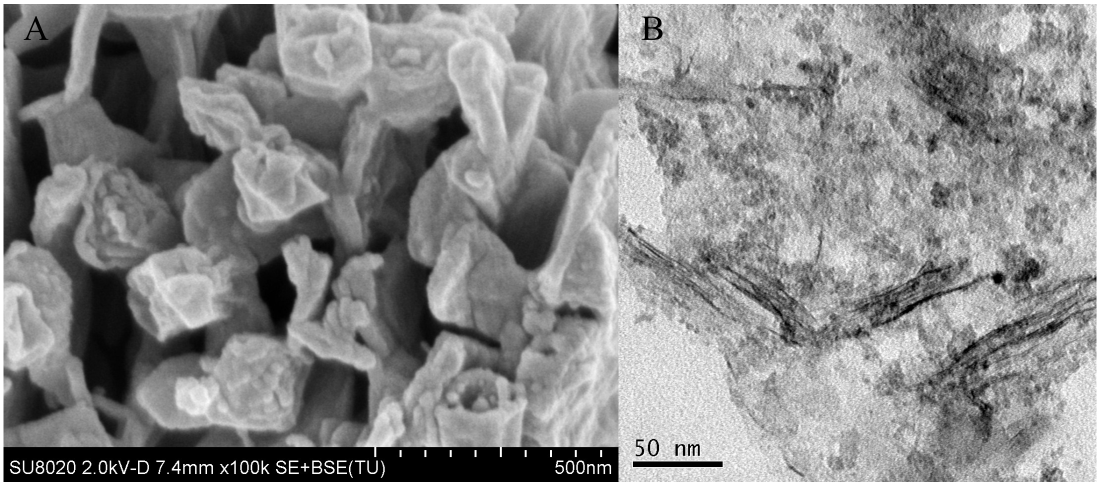

Fig. 3 The typical SEM (A) and TEM (B) images of the MIL-53-C.

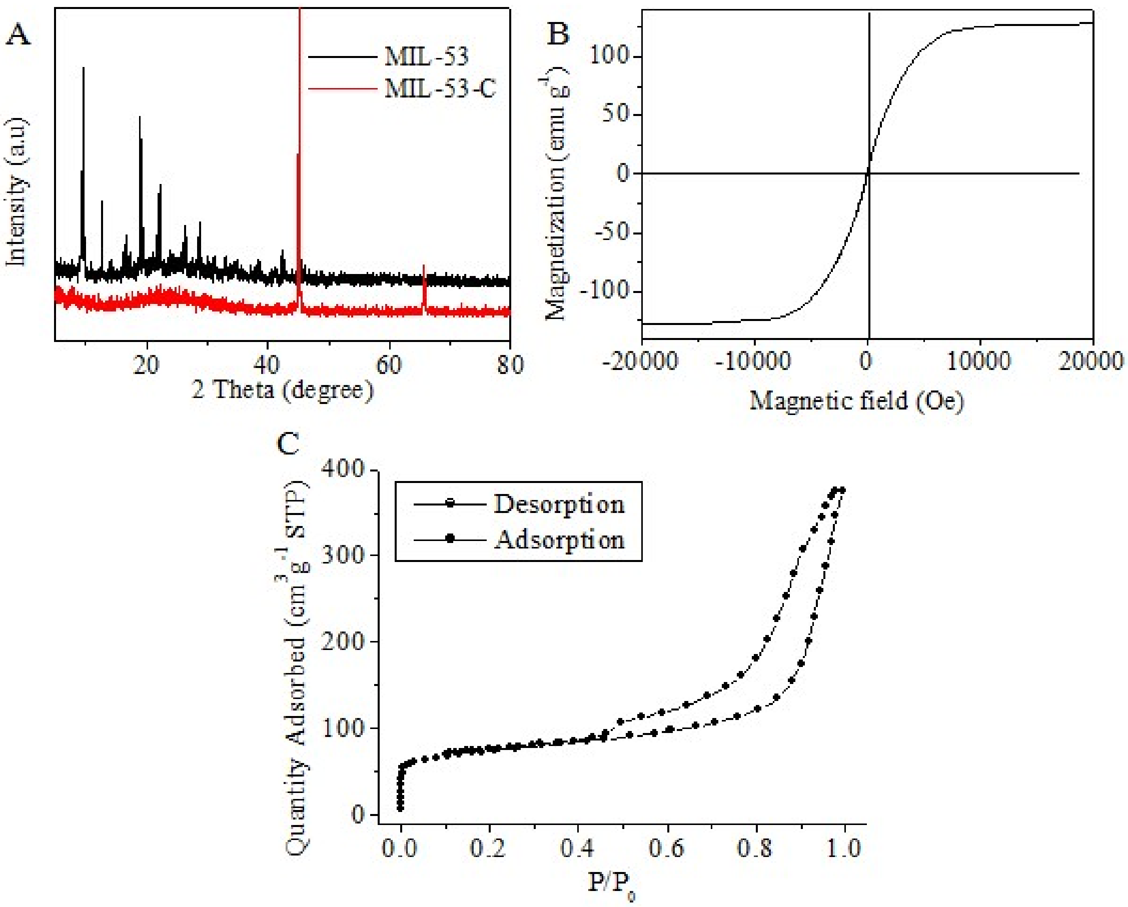

Fig. 4 The XRD spectrum (A) of MIL-53 and MIL-53-C, the magnetic hysteresis of the MIL-53-C (B) and the N_2 sorption isotherms of the MIL-53-C (C).

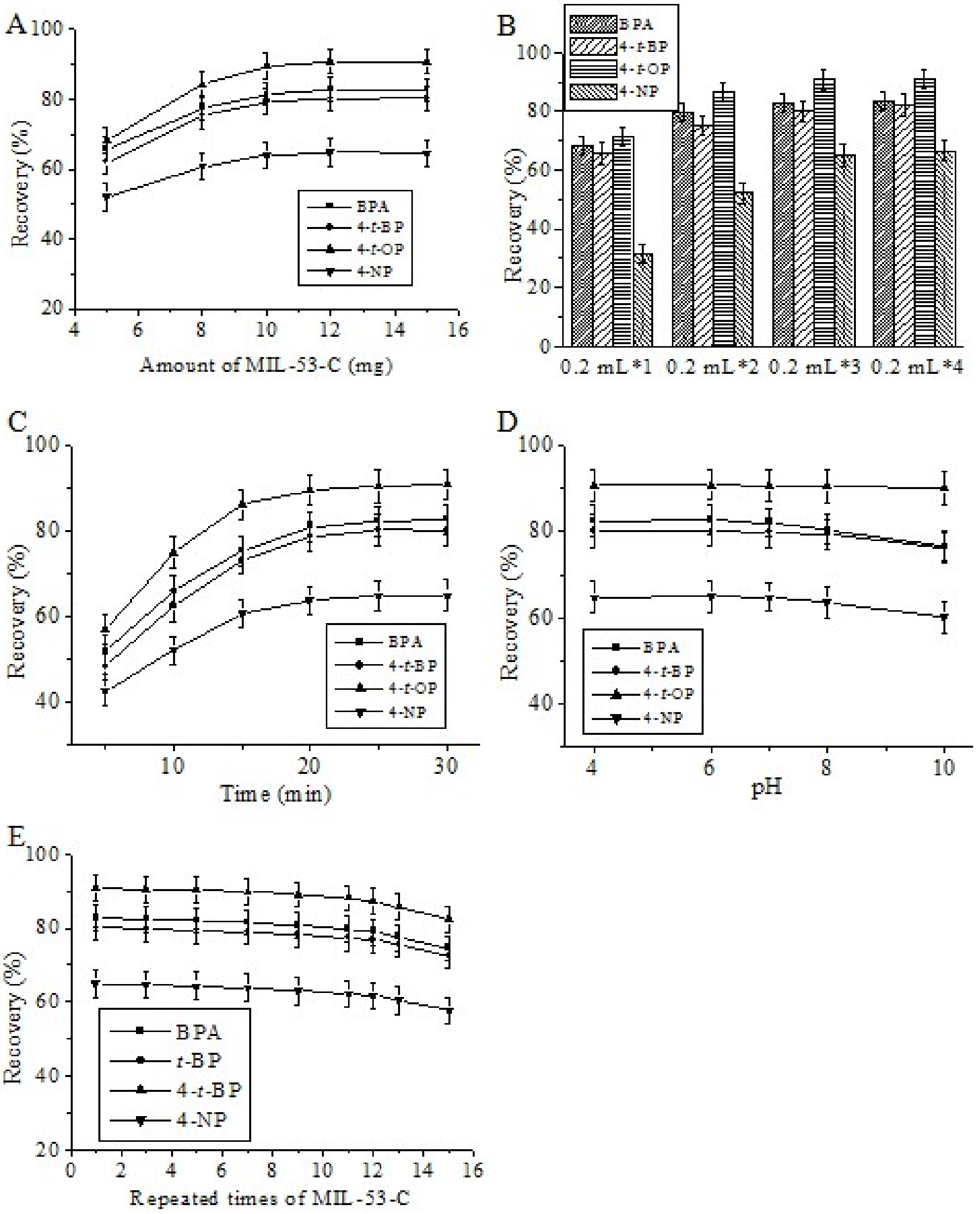

Fig. 5 Effect of extraction conditions on the extraction efficiencies. (A) Effect of the amount of the MIL-53-C; (B) Effect of the volume of desorption solvent; (C) Effect of extraction time; (D) Effect of the sample solution pH; (E) The reusability of the MIL-53-C.

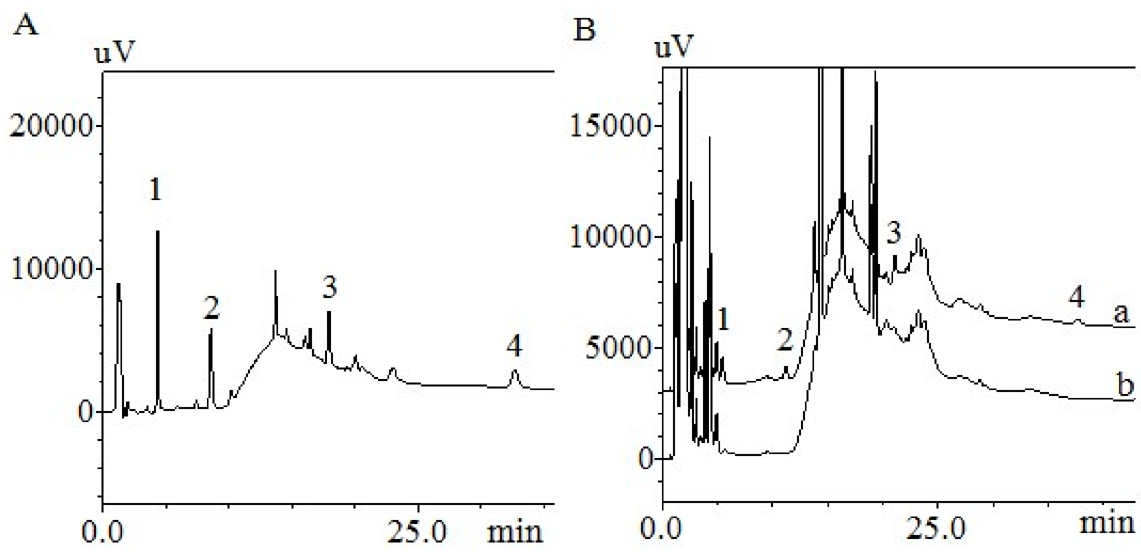

Fig. 6 The chromatography of EDCs standard sample (A) at each concentration of 10.0 μg mL^{-1}, the typical chromatograms of (b) milk sample and (a) milk sample spiked with the EDCs at each concentration of 10.0 ng mL^{-1} (B). Peak identification: 1. BPA, 2. 4-*t*-BP, 3. 4-*t*-OP, 4. 4-NP. Detection wavelength: 225 nm.

Metal-organic framework-derived nanoporous carbon/iron composite for enrichment of endocrine disrupting compounds from fruit juices and milk samples

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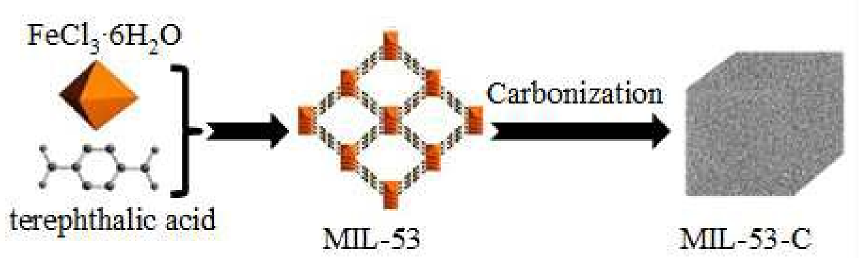
A nanoporous carbon/iron composite (MIL-53-C) was prepared by direct carbonization of Fe-based metal-organic framework (MIL-53) and used as magnetic solid-phase extraction adsorbent for the enrichment of some endocrine disrupting compounds from fruit juice and milk samples followed by high performance liquid chromatographic analysis.



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