Highly effective and fast removal of bisphenol A from environmental samples by an eco-friendly surface molecularly imprinted polymer based on MIL-100(Fe)

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1. Materials and reagents

Iron powder, 1,3,5-benzenetricarboxylic acid, 2-hydroxyethyl methacrylate, N,N′-methylenebis(acrylamide), bisphenol B and sulfathiazole were purchased from J&K Scientific Ltd (Beijing, China). 1-Allyl-3-vinylimidazolium bromide was brought from Cheng Jie Chemical Co. Ltd (Shanghai, China). Bisphenol A, 2-hydroxynaphthalene and 2,4-dinitrophenol were acquired from Guangfu Fine Chemical Research Institute (Tianjin, China). 2,2'-Azobis(2-methylpropionitrile) was provided by Beijing Chemical Reagents Co., Ltd

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(Beijing, China). Methanol, anhydrous ethanol, hydrofluoric acid, nitric acid and acetic acid were obtained from De'en Chemical Reagents Co., Ltd (Tianjin, China). HPLC grade acetonitrile and pure water were separately supplied from Tedia Co. Ltd (Fairfield, USA) and Wahaha Co. Ltd (Henan, China).

2. Instruments

The morphology and size were measured by a Supra 40 field scanning electron microscopy (SEM) (Carl Zeiss, Germany). X-ray diffraction patterns (XRD) were obtained from a D-8 Discovery diffractometer (Bruker, Germany). Fourier transform infrared spectroscopy (FT-IR) measurements were performed on a Model Perkin-Elmer 983 spectrometer (Perkin Elmer, USA). X-ray photoelectron spectra (XPS) were carried out on an ESCALAB 250Xi spectrometer (Thermo Fisher, USA). The specific surface area parameters were achieved by a Model ASAP 2020 automatic surface area and porosity analyzer (Micromeritics, USA). The thermal stability was determined by a STA449C thermogravimetric analyzer (Netzsch, Germany). Absorption measurements were obtained from a Model T6 UV-vis spectrophotometer (Pgeneral, China). HPLC evaluation was measured with an Alliance 2489 high-performance liquid chromatography system (Waters, USA).

3. HPLC analysis

The concentration of the BPA before and after adsorption by the MIL-100(Fe)@MIP was detected by HPLC with an ultraviolet detector at 278 nm (Alliance 2695-2489). The

chromatography system was equipped with a C_{18} column (4.6 mm×150 mm, 5 μm) and the mobile phase was a 70:30 (V/V) mixture of acetonitrile and water containing 0.1% acetic acid (V/V). A volume of 20 μL was injected into the HPLC system with a flow rate of 1.0 mL min^{-1} at 30 °C for analysis.

4. Characterization

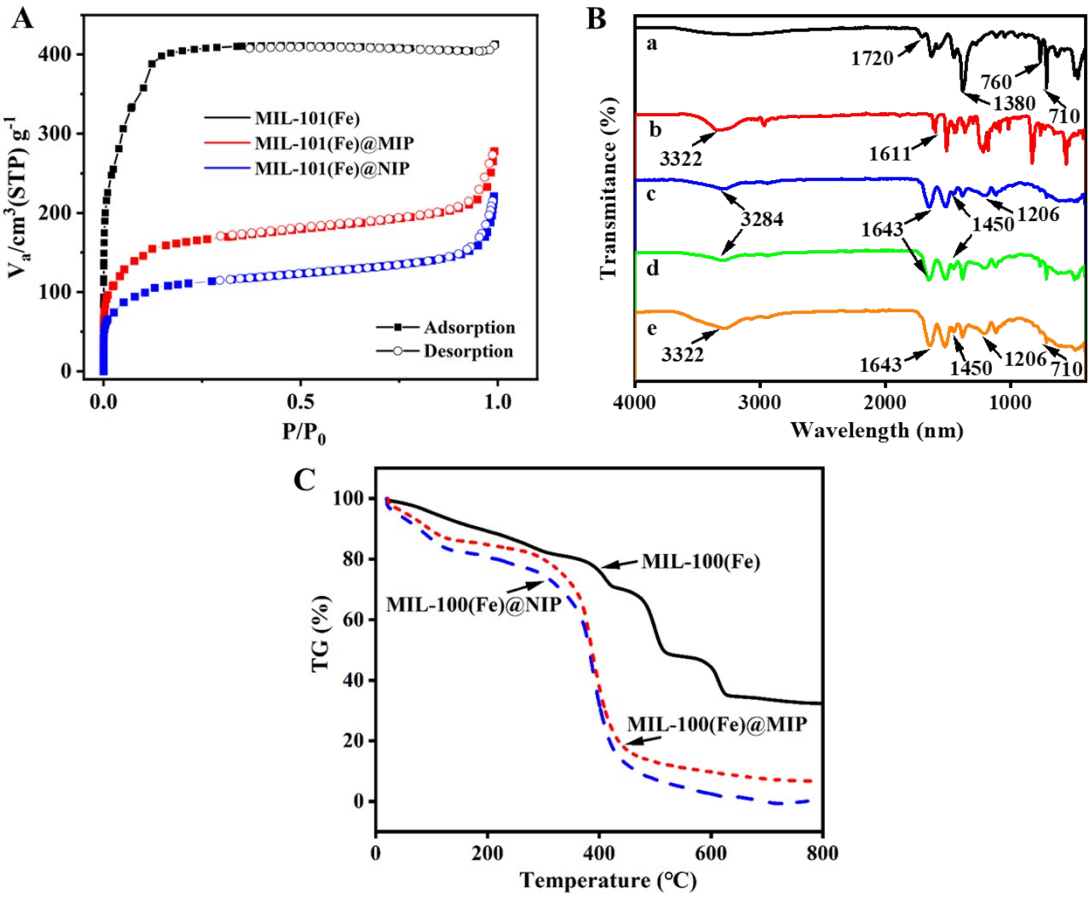

Fig. S1 (A) Nitrogen adsorption–desorption isotherms of MIL-100(Fe), MIL-100(Fe)@MIP, and MIL-100(Fe)@NIP. (B) Fourier-transform infrared spectra of MIL-100(Fe) (a), BPA (b), MIL-100(Fe)@MIP (c), MIL-100(Fe)@NIP (d), and MIL-100(Fe)@MIP after adsorption of BPA (e). (C) TGA of MIL-100(Fe), MIL-100(Fe)@MIP, and MIL-100(Fe)@NIP. BPA: bisphenol A.

5. The adsorption kinetic properties of MIL-100(Fe)@MIP and MIL-100(Fe)@NIP

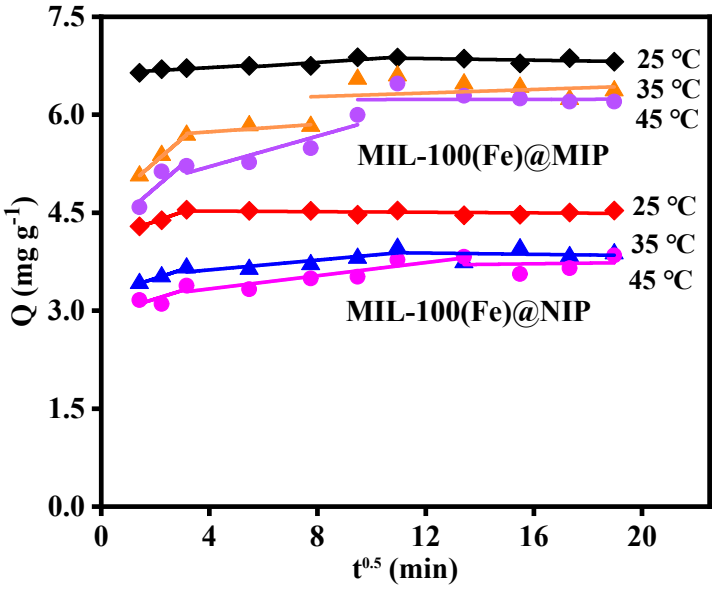

Fig. S2 Intra-particle diffusion model fitting curves of the MIL-100(Fe)@MIP and MIL-100(Fe)@NIP toward BPA at 25 ℃, 35 ℃ and 45 ℃, respectively.

6. Selectivity

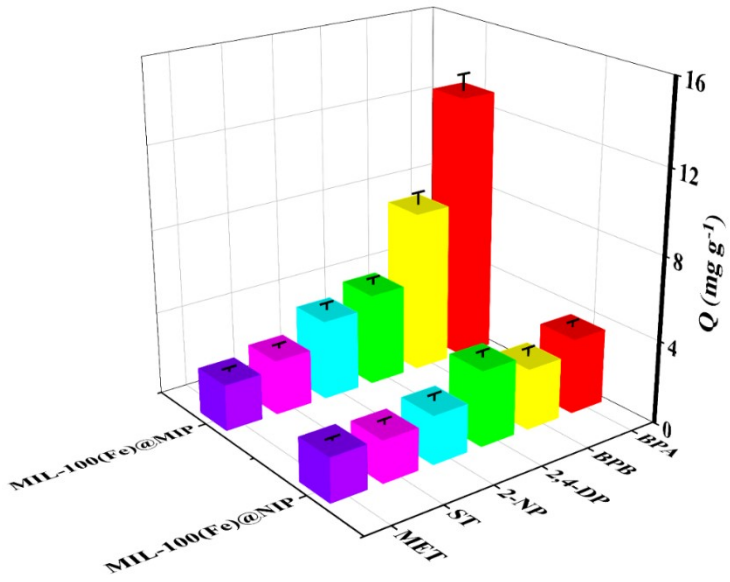

Fig. S3 Selectivity of MIL-100(Fe)@MIP and MIL-100(Fe)@NIP towards BPA and interferents

7. Synthesis process of MIL-100(Fe)@MIP

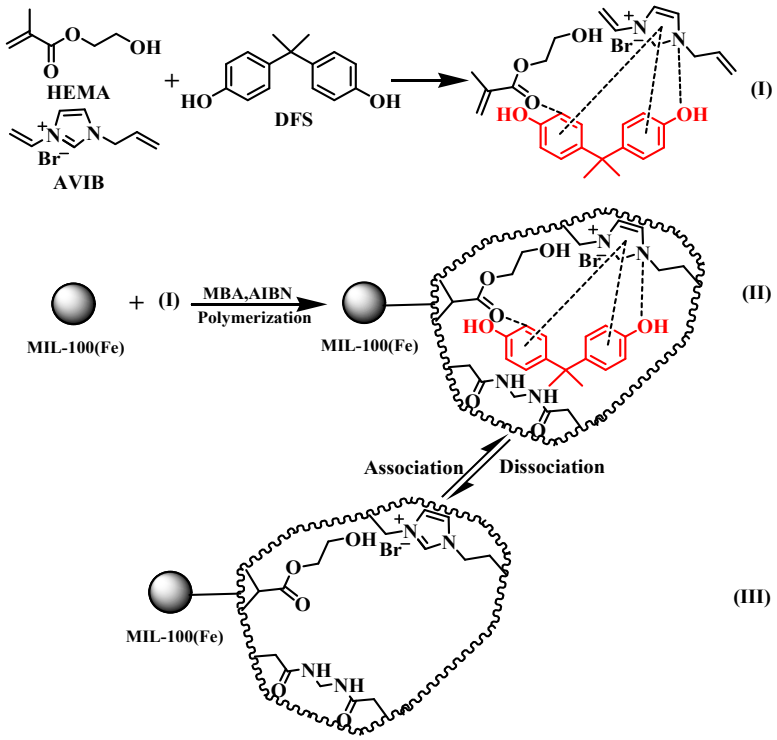

Fig. S4 Schematic diagram of synthesis process of MIL-100(Fe)@MIP

8. Solid phase extraction and optimization of SPE

A solid phase extraction (SPE) column was firstly prepared by packing 65 mg of the MIL-100(Fe)@MIP into an empty 3 mL polypropylene column (Waters, USA), and the SPE column was firstly activated by chromatographic methanol and pure water. Afterwards, 0.1 mg L^{-1} of BPA aqueous solution was passed through the cartridge under the certain condition followed by washed with designed different eluents. The concentration of BPA in eluant was determined using HPLC.

To obtain excellent extraction performance, some important parameters such as sample flow rate, sample volume, eluent type were further optimized. To estimate the influence of the

flow rate on extraction efficiency, the flow rate was varied from to 0.4 mL min^{-1} to 1.2 mL min^{-1}. As shown in Fig. S4A, when the flow rate was lower than 0.7 mL min^{-1}, the recoveries of BPA were kept at 100%, and those decreased as the flow rate continued to increase. Thus, 0.6 mL min^{-1} was used as the best flow rate for loading the sample onto the SPE column. The effect of sample volume was investigated in the range of 0-14 mL, and the results were displayed in Fig. S4B. When the sample volume was lower than 11 mL, the recoveries of BPA were kept at 100%, and then decreased as sample volume further increased. Elution of BPA was a key step in the SPE procedure. The complete elution of BPA was depended on the appropriate elution solvent. Six kinds of mixed solutions were selected as eluents which contained acetonitrile, methanol, methanol/water (70/30, V/V), methanol/water (80/20, V/V), methanol/water/acid (80/19/1, V/V/V) and methanol/water/acid (80/18/2, V/V/V), and the recoveries were demonstrated in Fig. S4C. When methanol/water/glacial acetic acid (80/18/2, V/V/V) was served as eluent, the recovery reached to 100%. However, the recoveries of BPA were all less than 100% while the other five mixed solutions were used as eluent. Therefore, methanol/water/glacial acetic acid (80/18/2, V/V/V) was finally selected as the eluent.

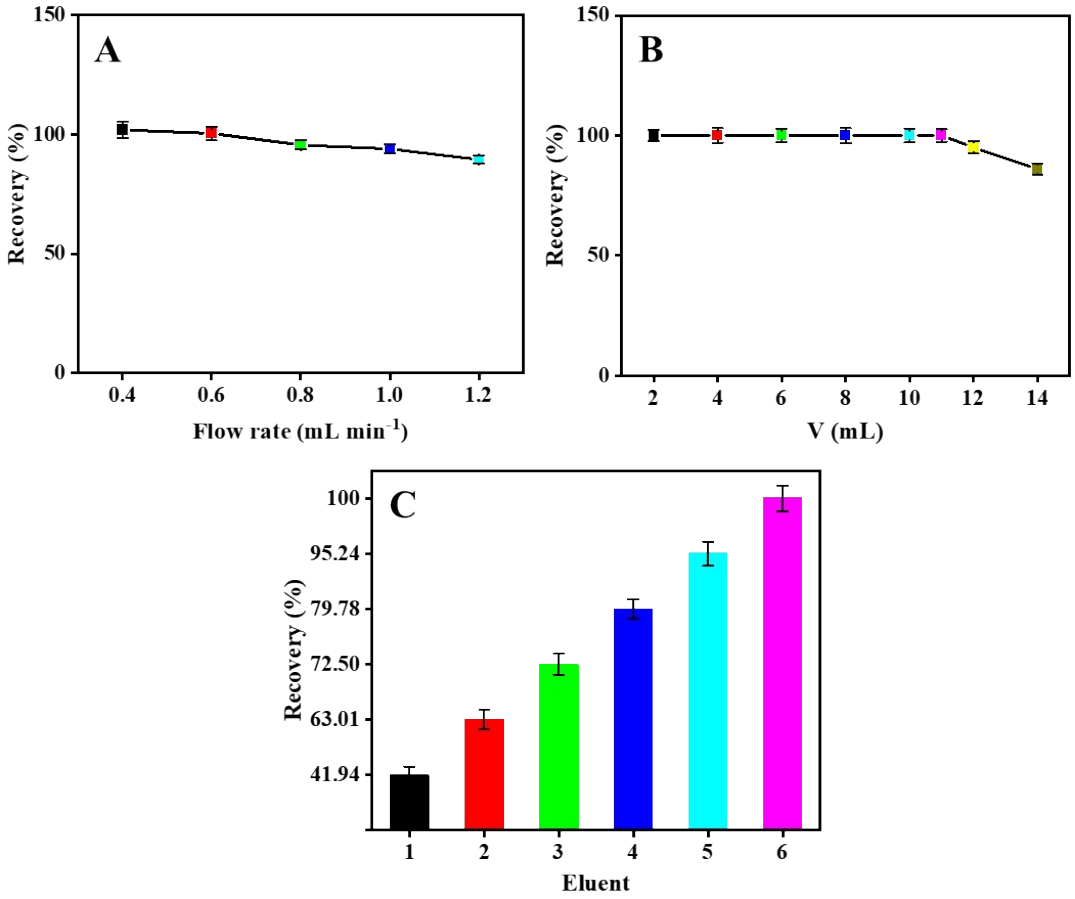

Fig. S5 (A) Optimization of flow rate (B) Optimization of sample volume (C) Optimization of eluent: 1 stands for acetonitrile; 2 stands for acetonitrile methanol; 3 stands for methanol:water =70:30, V/V; 4 stands for methanol:water =80:20, V/V; 5 stands for methanol:water:acid =80:19:1, V/V/V; 6 stands for methanol: water: acid =80:18:2, V/V/V

9. Establishment of analytical method

The linearity range, correlation coefficient, limits of detection, and repeatability were investigated under optimum experimental conditions. A good linearity with the correlation coefficient of 0.9994 was found in the BPA concentration range of 0.001–0.4 mg L^{-1} with the

linear equation y=31684x+173.29. The limit of detection was are 0.5 μg L^{-1}, which was calculated based on signal-to-noise ratio equal to 3. Additionally, the BPA concentration of 0.1 mg L^{-1} was selected to investigate precision analysis. The RSDs of intra-day and inter-day precision were 1.45% and 2.53%, respectively (n=3).

10. Chromatograms of real samples analysis

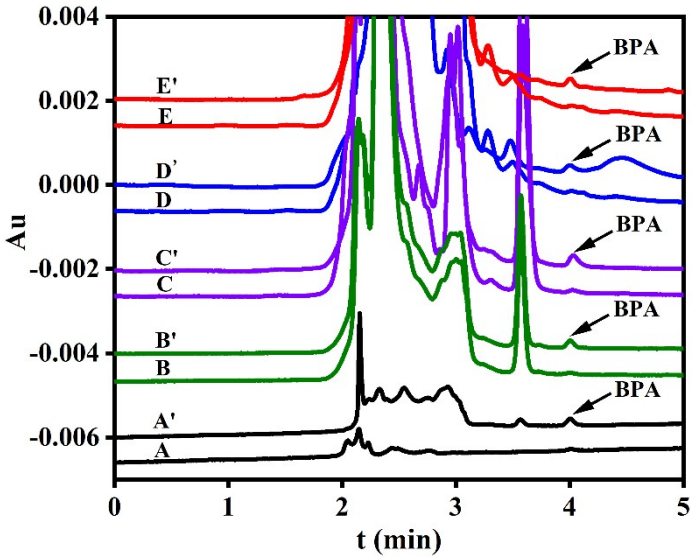

Fig. S6 Chromatograms of real samples without and with spiked 20 μg L^{-1} of BPA after MIL-100(Fe)@MIP-SPE extraction. Plots A, B, C, D, and E show the elution of the original treatment sewage from disposable lunch box, canned yellow peach, orange juice, soybean milk and teabag samples without extraction. Plots A′, B′, C′ D′, and E′ represent the spiked 20 μg L^{-1} of BPA elution from the same sources. BPA: bisphenol A

11. Regeneration

The regeneration of adsorbents is one of the most important criteria for the purpose of cost

and efficiency. In order to investigate the regeneration of MIL-100(Fe)@MIP, the adsorption-desorption procedure was repeated. Briefly, 0.1 mg L^{-1} of BPA was passed through the MIL-100(Fe)@MIP-SPE column under the optimized condition followed by washing with the mixed solution of methanol/water/acetic acid (80/18/2, V/V/V). The concentration of BPA in eluent was measured using HPLC at 278 nm, and the result was shown in Fig. S6. It can be clearly seen that approximately 90.10% of BPA can be obtained by this MIL-100(Fe)@MIP-SPE cartridge after 20 cycles, indicating that MIL-100(Fe)@MIP exhibit excellent regeneration and good stability.

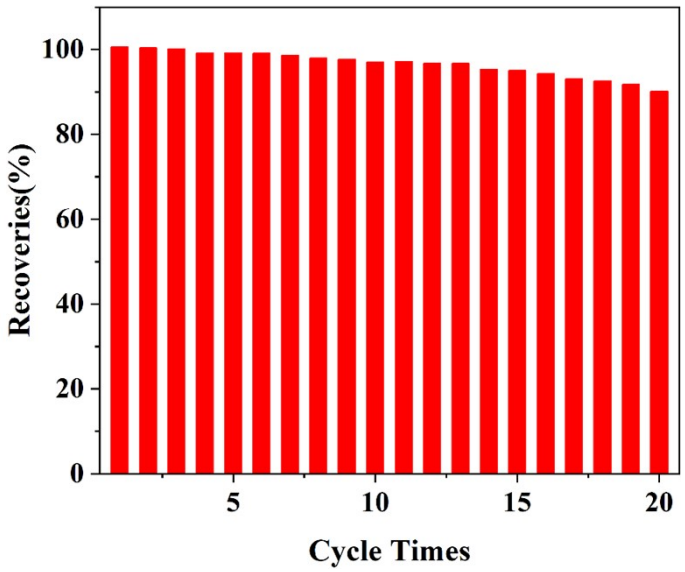

Fig. S7 The regeneration performance of MIL-100(Fe)@MIP-SPE after 20 cycles

Table S1 Partial BET parameters of MIL-100(Fe), MIL-100(Fe)@MIP, and MIL-100(Fe)@NIP

Material	Specific surface area ($m^2\ g^{-1}$)	Total pore volume ($cm^3\ g^{-1}$)	Mean pore diameter (nm)
MIL-100(Fe)	2049.00	0.8930	1.74
MIL-100(Fe)@MIP	589.74	0.4229	2.87
MIL-100(Fe)@NIP	394.83	0.3403	3.45

Table S2 Parameters of adsorption kinetic models for the MIL-100(Fe)@MIP and MIL-100(Fe)@NIP at various temperatures.

T (ºC)		Intra-particle diffusion								
		K_{d1} (mg g^{-1} $min^{-0.5}$)	I_1	R_1^2	K_{d2} (mg g^{-1} $min^{-0.5}$)	I_2	R_2^2	K_{d3} (mg g^{-1} $min^{-0.5}$)	I_3	R_3^2
25	MIL-100(Fe)@MIP	0.0231	6.6296	0.8081	0.0277	6.5794	0.6551	-0.0060	6.9356	0.0151
	MIL-100(Fe)@NIP	0.1453	4.0773	0.9699	-0.0023	4.5340	0.0135	-	-	-
35	MIL-100(Fe)@MIP	0.3582	4.5620	0.9974	0.0293	5.6212	0.4012	0.0136	6.1703	0.0467
	MIL-100(Fe)@NIP	0.1356	3.2229	0.9940	0.0376	3.4741	0.7035	-0.0048	3.9406	0.0271
45	MIL-100(Fe)@MIP	0.3564	4.1689	0.6464	0.1169	4.7381	0.7249	0.0005	6.2273	0.0002
	MIL-100(Fe)@NIP	0.1285	2.9241	0.1668	0.0503	3.1326	0.8034	0.0557	3.6382	0.0076

Table S3

Thermodynamic parameters of BPA adsorbed by the MIL-100(Fe)@MIP and MIL-100(Fe)@NIP

	T(K)	K_L (L mol^{-1})	ΔG^0(kJ mol^{-1})	ΔH^0(kJ mol^{-1})	ΔS^0(kJ $mol^{-1}K^{-1}$)
MIL-100(Fe)@MIP	298.15	49013.86	-26.7709	-3.7349	0.0772
	308.15	45566.68	-27.4820		
	318.15	44607.87	-28.3175		
MIL-100(Fe)@NIP	298.15	19724.26	-24.5145	-0.6489	0.0800
	308.15	19450.31	-25.3009		
	318.15	19404.65	-26.1158		