Supplementary Material

Development of a chromium-based metal-organic framework MIL-88B(Cr) modified by deep eutectic solvents for efficient simultaneous removal of bisphenol A and bisphenol S

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1. Materials and instruments

Bisphenol A, bisphenol S, methacrylatoethyl trimethyl ammonium chloride (DMC), acrylamide, caffeic acid, 2,2'-azobis(2-methylpropionitrile) (AIBN), and humic acid were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Chromium nitrate nonahydrate and sodium hydroxide were obtained from Tianjin Tianli Chemical Reagent Co., Ltd. Terephthalic acid was supplied by Beijing J&K Scientific Ltd. Sodium chloride and N,N-dimethylformamide (DMF) were procured from Tianjin Dern Chemical Reagent Co., Ltd.

The morphologies of samples were observed with a scanning electron microscopy (SEM, JSM-5610LV, JEOL, Japan). Fourier transform infrared spectroscopy (FT-IR, Thermo Nicolet Co., USA) at 4000-400 cm^{-1} and X-ray powder diffraction (XRD, Brukeraxs Co., Germany) was used to determine the structure of samples. Nitrogen adsorption/desorption isotherms were measured at 77.3 K by a physisorption analyzer (ASAP 2020, Micromeritics, USA). The thermal stability of the polymers was evaluated by a STA449C thermal analyzer (TGA, Netzsch, Germany). The elements and structures of samples by X-ray photoelectron spectroscopy (XPS, ESCALAB250Xi, Thermo Scientific, USA).

2. HPLC analysis

All samples in this work were analyzed using a high-performance liquid chromatography (HPLC) system equipped with a diode array detector (DAD) (Agilent 1260 Infinity, USA). Separation of BPA and BPS was performed on a reverse-phase C18 column (250 mm × 4.6 mm, 5 μm) with a mobile phase consisting of acetonitrile and water (60:40, v/v) at a flow rate of 1 $mL \cdot min^{-1}$. The column temperature was maintained at 30°C, detection wavelength was set at 277 nm, and the injection volume was 20 μL.

3. Optimization of preparation conditions

Table S1 Effect of DES dosage on the adsorption capacity of polymers for BPS.

DES dosage (mL)	$Q_{DES@MIL-88B(Cr)}$ (mg g^{-1})
0.2	78.82
0.4	80.77
0.6	83.48
0.8	85.15
1.0	82.29

Table S2 Effect of MIL-88B(Cr) and H_2O dosage on the adsorption capacity of polymers for BPS.

MIL-88B(Cr) dosage (g)	H_2O dosage (mL)	$Q_{DES@MIL-88B(Cr)}$ (mg g^{-1})
0.10	30	72.81
0.15	30	74.97
0.20	30	85.96
0.25	30	81.23
0.20	20	80.11
0.20	40	79.48
0.20	50	76.07

4. Characterization

Table S3 Specific surface area and pore structure parameters of MIL-88B(Cr) and DES@MIL-88B(Cr)

Material	Specific surface area (m^2 g^{-1})	Total pore volume (cm^3 g^{-1})	Average pore size (nm)
MIL-88B(Cr)	19.312	0.025	5.275

DES@MIL-88B(Cr)	16.541	0.061	14.794

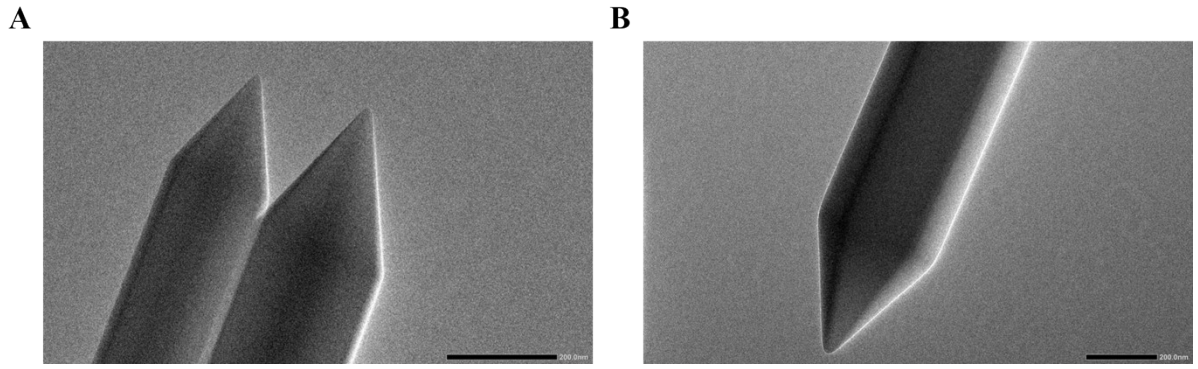

Fig. S1 TEM images of MIL-88B(Cr) (A), and DES@MIL-88B(Cr) (B).

5 Effect of initial pH on adsorption capacity

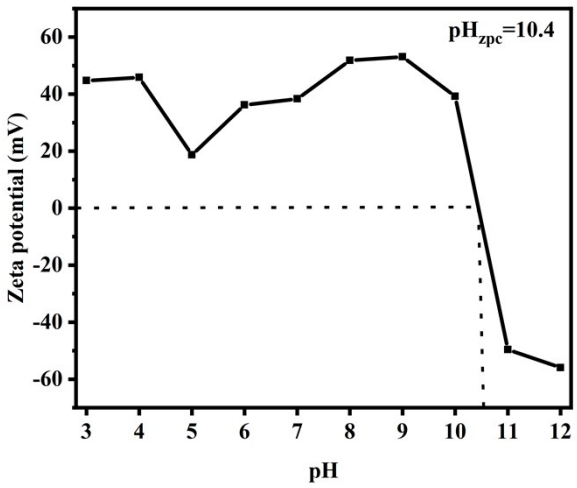

Fig. S2 Zeta potential of DES@MIL-88B(Cr) at different pH

6. Adsorption thermodynamics

Table S4 Specific surface area and pore structure parameters of MIL-88B(Cr) and DES@MIL-88B(Cr)

		T (K)	ΔG^0 (kJ mol^{-1})	ΔH^0 (kJ mol^{-1})	ΔS^0 (kJ mol^{-1} K^{-1})
BPA	MIL-88B(Cr)	298.15	-17.98	-6.9760	0.0368
		308.15	-18.23		
		318.15	-18.72		
	DES@MIL-88B(Cr)	298.15	-17.02	-7.1506	0.0332
		308.15	-17.46		
		318.15	-17.68		
BPS	MIL-88B(Cr)	298.15	-19.61	-11.7305	0.0264
		308.15	-19.81		
		318.15	-20.14		
	DES@MIL-88B(Cr)	298.15	-18.72	-6.8210	0.0397
		308.15	-18.98		
		318.15	-19.52		

7. Analysis of real samples and reusability

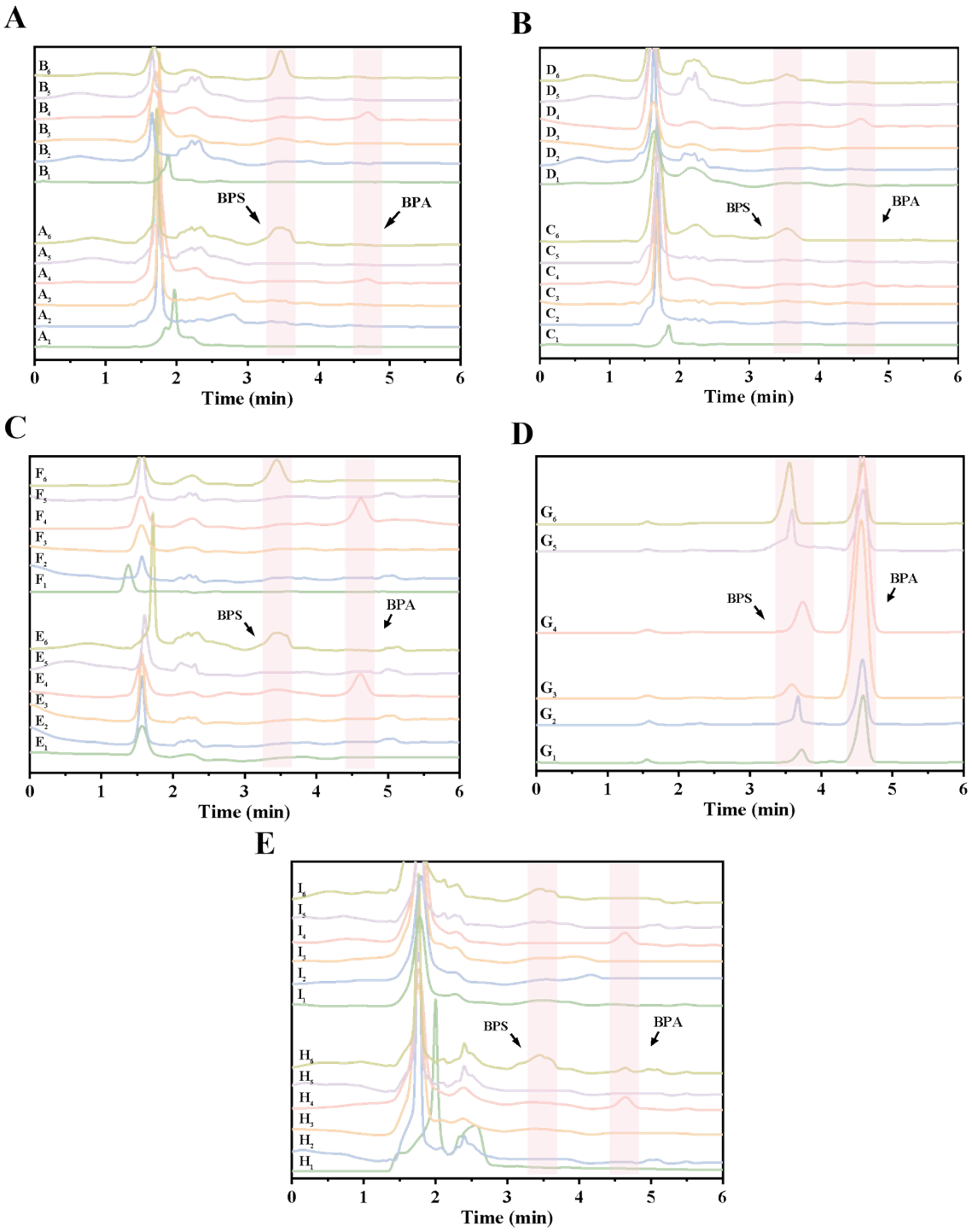

Fig S3 Chromatograms of blank samples and spiked samples before and after DES@MIL-88B(Cr) extraction. A_1, B_1, C_1, D_1, E_1, F_1, G_1, H_1 and I_1 respectively represent the chromatograms of lake water 1, lake water 2, river water 1, river water 2, the influent of a certain sewage treatment plant, the effluent of a certain sewage treatment plant, takeout label, plastic plate and plastic spoon before extraction; A_2, B_2, C_2, D_2, E_2, F_2,

G_2, H_2 and I_2 respectively represent the chromatograms of lake water 1, lake water 2, river water 1, river water 2, the influent of a certain sewage treatment plant, the effluent of a certain sewage treatment plant, takeout label, plastic plate and plastic spoon after DES@MIL-88B(Cr) extraction; A_3, B_3, C_3, D_3, E_3, F_3, G_3, H_3 and I_3 respectively represent the chromatograms of lake water 1, lake water 2, river water 1, river water 2, the influent of a certain sewage treatment plant, the effluent of a certain sewage treatment plant, takeout label, plastic plate and plastic spoon with spiked BPA before DES@MIL-88B(Cr) extraction; A_4, B_4, C_4, D_4, E_4, F_4, G_4, H_4 and I_4 respectively represent the chromatograms of lake water 1, lake water 2, river water 1, river water 2, the influent of a certain sewage treatment plant, the effluent of a certain sewage treatment plant, takeout label, plastic plate and plastic spoon with added BPA after DES@MIL-88B(Cr) extraction; A_5, B_5, C_5, D_5, E_5, F_5, G_5, H_5 and I_5 respectively represent the chromatograms of lake water 1, lake water 2, river water 1, river water 2, the influent of a certain sewage treatment plant, the effluent of a certain sewage treatment plant, takeout label, plastic plate and plastic spoon with spiked BPS before DES@MIL-88B(Cr) extraction; A_6, B_6, C_6, D_6, E_6, F6, G_6, H_6 and I_6 respectively represent the chromatograms of lake water 1, lake water 2, river water 1, river water 2, the influent of a certain sewage treatment plant, the effluent of a certain sewage treatment plant, takeout label, plastic plate and plastic spoon with spiked BPS after DES@MIL-88B(Cr) extraction.

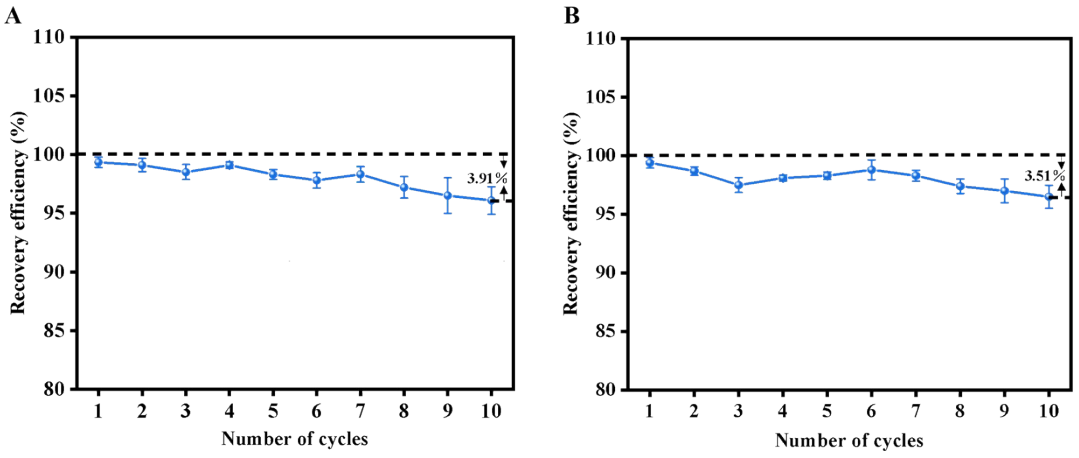

Fig. S4 (A) The regeneration and recycling performance of DES@MIL-88B(Cr) material for

adsorbing and desorbing BPA, (B) The regeneration and recycling performance of DES@MIL-88B(Cr) material for adsorbing and desorbing BPS.