Supplementary Material

Synthesis, structural characteristics, and adsorption properties of benzimidazole-functionalized hyper-cross-linked resin

Jixia Li[a,‡], Yang Tan[a,‡], Wenkai Chen[b], Gui Chen[a,c]*, Lizhi Chen[a], Jiahui He[a], Sitong Wang[a], Haizhou Zhang[a,c] and Ye Yuan[a,c]*

[a] *College of Chemistry and Materials, Huaihua University, Huaihua 418000, P. R. China*

[b] *China Coal Research Institute Corporation Ltd., Beijing 100013, P. R. China*

[c] *Hunan Engineering Laboratory for Preparation Technology of Polyvinyl Alcohol (PVA) Fiber Materia, Huaihua University, Huaihua 418000, P. R. China*

*** Corresponding author**

Tel.: +86-745-2851014.

E-mail address: cg@hhtc.edu.cn (G. Chen); yuanye@hhtc.edu.cn (Y. Yuan)

‡ Jixia Li and Yang Tan contributed equally to this work.

1. Experimental section

1.1. Reagents and instrument

Macroporous chloromethylated polystyrene (CMPs, with a cross-linking degree of 6.0% and a chlorine content of 17.3% w/w) was purchased from Tianjin Nankai Hecheng Co., Ltd, China. Benzimidazole (BZI, AR, 99.5%), Anhydrous ferric chloride (AR, 99.5%), 1,2-dichloroethane (DCE, AR, 99.5%), anhydrous ethanol (AR, 99.5%) were obtained from Aladdin Reagent Co. Ltd. China. Salicylic acid (SA, AR, 99.5%) was acquired from Tianjin Photovoltaic Surprise Chemical Research Institute, China. All other reagents were of commercial grade and used without further treatment.

1.2. Adsorbent characterizations

FT-IR spectra of the resin were recorded using a Nicolet 6700 Fourier Transform Infrared Spectrophotometer (Thermo Scientific Co., USA) via the potassium bromide (KBr) disk method in the wavenumber range of 400-4000 cm^{-1}. The textural properties of the samples were analyzed by N_2 physisorption at 77 K using a Micromeritics ASAP 2020 surface area analyzer. The polymer morphology was studied with Sigma HD Scanning Electron Microscopy (SEM). HRTEM images were captured with a JEM-2100. XPS measurements were carried out using an

ESCALAB 250Xi analyzer. The SA concentration was measured using a Shimadzu UV2600 UV-Vis absorption spectrometer.

1.3. Thermodynamic parameters

These parameters such as ΔH, ΔS, and ΔG were calculated in accordance with Eqs (S1) and (S2) were derived by quantifying the adsorption of SA on BZI-HCMPs at various temperatures. According to Freundlich model, the parameters were obtained as follows:

$$lg(q_e / C_e) = \Delta S / (2.303R) - \Delta H / (2.303RT) \quad \text{(S1)}$$

$$\Delta G = \Delta H - T\Delta S \quad \text{(S2)}$$

Where q_e represents the equilibrium capacity (mg/g), C_e signifies the equilibrium concentration (mg/L), R represents the general gas constant (8.314 J/(mol·K)), and T denotes temperature (K).

Fig. S1 SEM images of (A) CMPs, (B) HCMPs and (C) BZI-HCMPs.

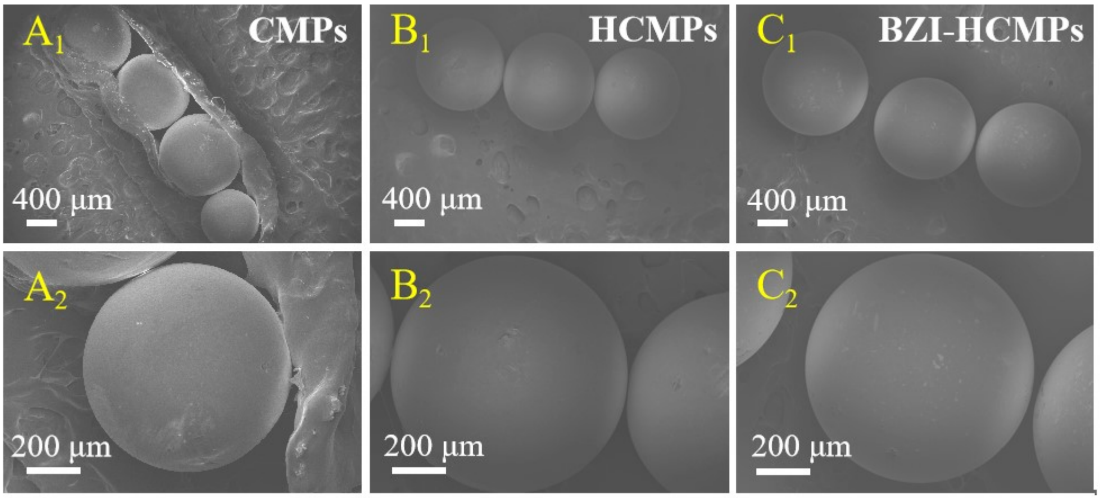


Fig. S2 XRD patterns of CMPs, HCMPs, and BZI-HCMPs.

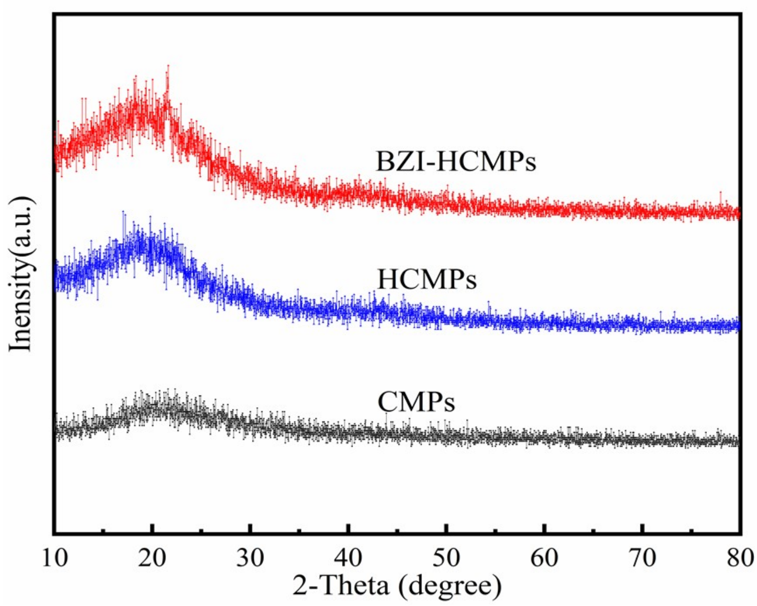
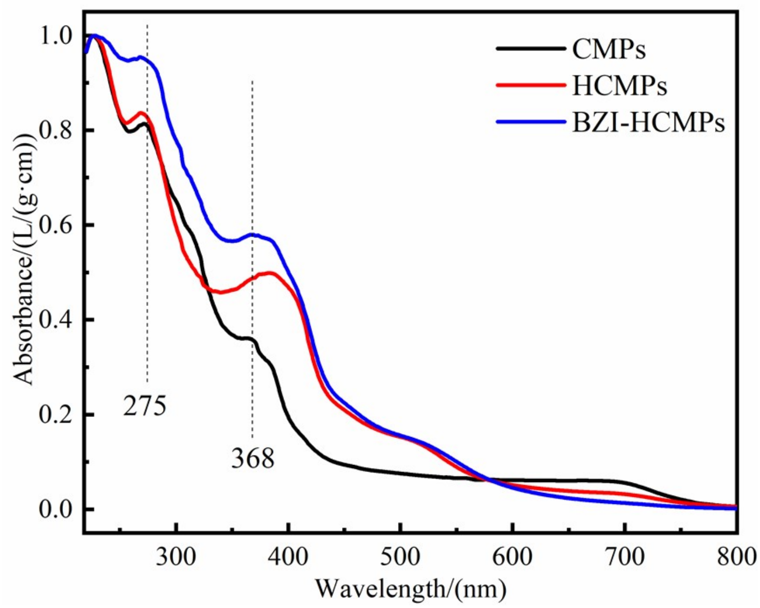


Fig. S3 UV-vis DRS of CMPs, HCMPs, and BZI-HCMPs.



Scheme S1 Potential interaction between BZI-HCMPs and SA.

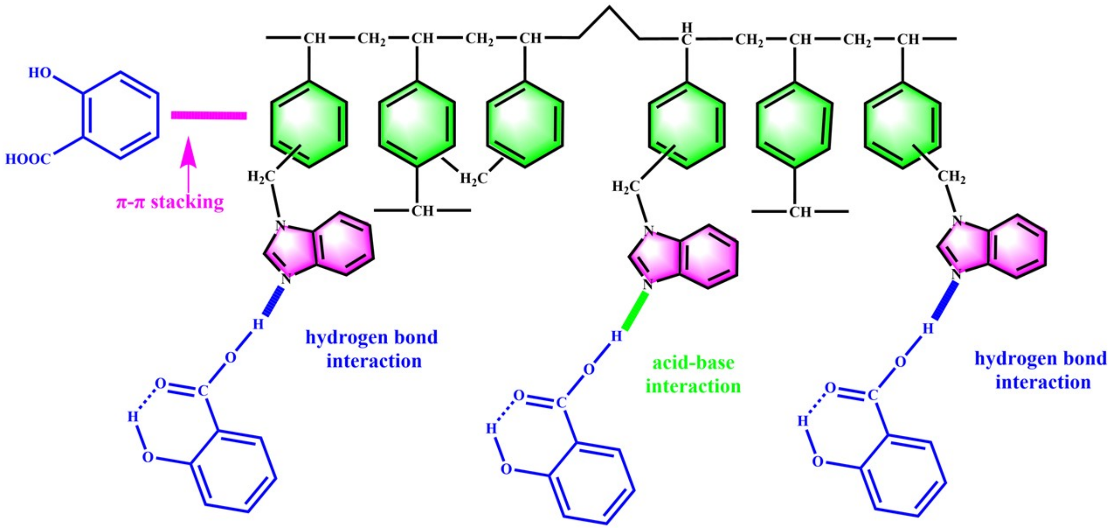


Table S1 Correlated parameters of the equilibrium data for the adsorption of SA on BZI-HCMPs at 293, 303, and 313 K according to the Langmuir and Freundlich models.

	Langmuir model			Freundlich model		
	K_L/(L/mg)	q_m/(mg/g)	R^2	K_F/((mg/g)(L/mg)$^{1/n}$)	n	R^2
BZI-HCMPs (293K)	0.01443	243.1817	0.9797	11.0641	1.88	0.9966
BZI-HCMPs (303K)	0.01423	275.0057	0.9897	12.2036	1.86	0.9887
BZI-HCMPs (313K)	0.02142	295.1372	0.9437	13.1782	1.82	0.9639

Fig. S4 Vant-Hoff plotting of log (q_e/C_e) versus 1/T (BZI-HCMPs).

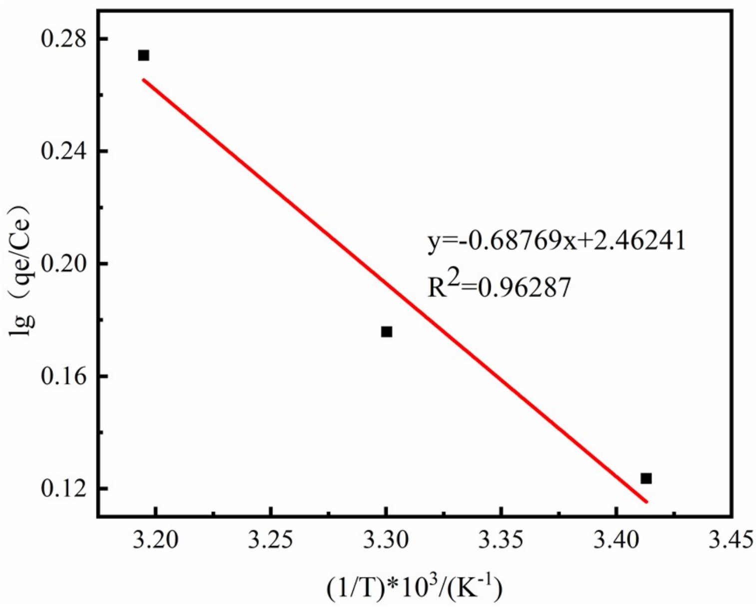


Table S2 Adsorption thermodynamic parameters of BZI-HCMPs.

Temp. (K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/(mol·K))
293	-0.647	13.167	47.148
303	-1.119	13.167	47.148
313	-1.590	13.167	47.148

Table S3 Relevant parameters of kinetic data for the adsorption of SA on the BZI-HCMPs at 293, 303, and 313K.

	Pseudo-first-order			Pseudo-second-order		
	q_e/(mg/g)	k_1/(min^{-1})	R^2	q_e/(mg/g)	k_2/(g/(mg•min))	R^2
BZI-HCMPs (293 K)	180.3308	0.03182	0.9730	177.8354	0.003797	0.9329
BZI-HCMPs (303 K)	188.1661	0.03175	0.9826	186.7358	0.005174	0.9204
BZI-HCMPs (313 K)	198.6579	0.03237	0.9724	196.3758	0.005322	0.9025

Fig. S5 The removal efficiency of SA as a function of the concentration of the polymers.

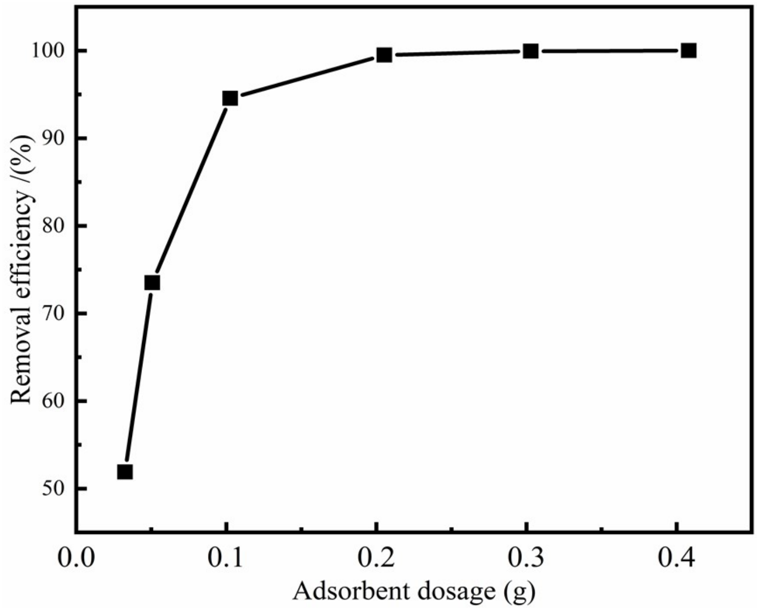


Fig. S6 Effect of the concentration of the polymer on the adsorption.

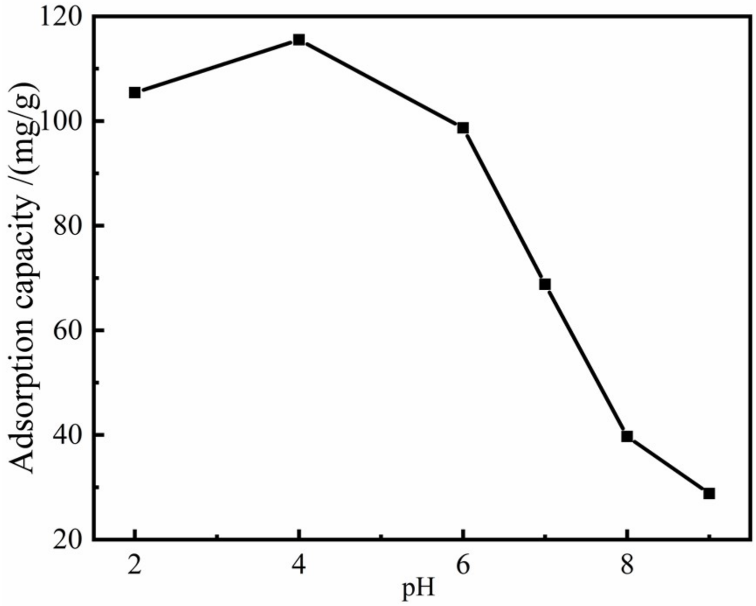


Fig. S7 The recycling times of SA adsorption on BZI-HCMPs.

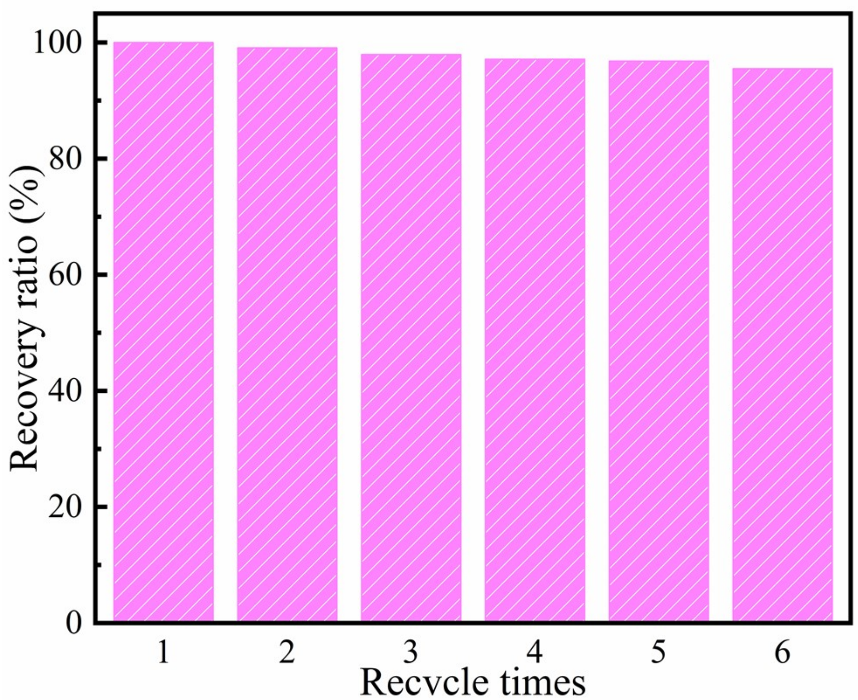


Fig. S8 (A) Adsorption of SA in tap water; (B) Effect of Na_2SO_4 concentration on SA adsorption.

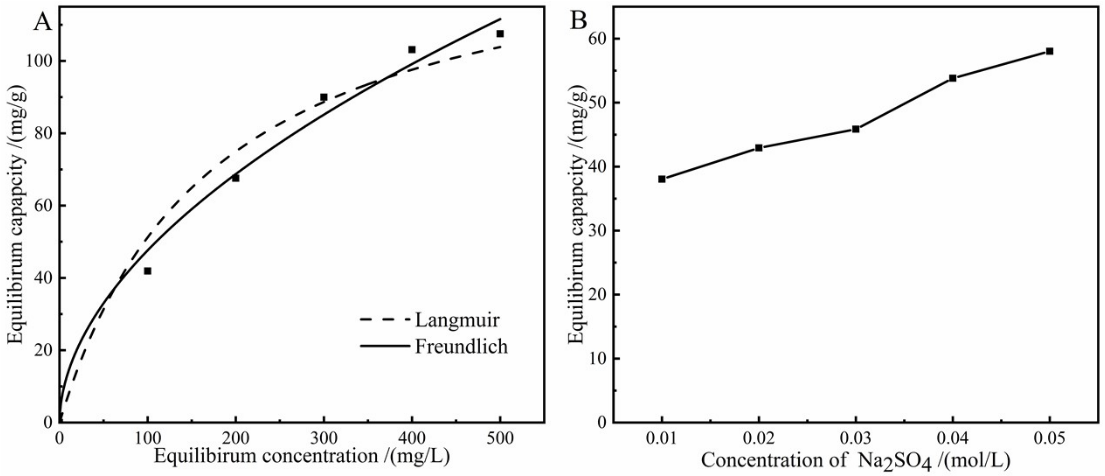


Table S4 Fitting parameters of adsorption model after replacing deionized water with tap water on BZI-HCMPs.

	Langmuir model			Freundlich model		
	K_L/(L/mg)	q_e/(mg/g)	R^2	K_F/((mg/g)(L/mg)$^{1/n}$)	n	R^2
BZI-HCMPs (298 K)	0.0058	139.7405	0.9782	4.1706	1.89	0.9896

Table S5 Environmentally-friendly and cost-effective simple analysis of synthesized BZI-HCMPs.

Cost of raw materials				Synthesis Energy consumption analysis		
Raw	Dosage	Unit price (RMB/kg)	Cost (RMB)	Process	Time(h)& Tem.(°C)	Energy consumption calculation (RMB)
CMPs	20.0 g	250	5.0	Friedel-Crafts alkylation reaction	0.25, 80	0.5 kW×0.25 h×1.2 RMB/(kW·h)=0.15
DCE	200 mL	8.0	2.0			
$FeCl_3$	4.0 g	20.0	0.1	nucleophilic substitution	12.0, 85	0.5 kW×12.0 h×1.2 RMB/(kW·h)=7.2
NaOH	8.0 g	6.0	0.05			
C_2H_5OH	1000 mL	10.0	8.0	Soxhlet extractor washing	48.0, 60	1.0 kW×48.0 h×1.2 RMB/(kW·h)=57.6
CH_3OH	200 mL	12.0	1.9	Stoving	12.0, 60	1.0 kW×12.0 h×1.2 RMB/(kW·h)=14.4
Hot H_2O	2000 mL	0.01	0.01	Equipment /Labor	-	0.5
Total	-	-	17.06	Total	-	79.85