Supporting information

Preparation of Hyper-cross-linked Hydroxylated Polystyrene for Adsorptive Removal of Methylene Blue

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1 Adsorption isotherms, kinetics and thermodynamics

1.1 Adsorption isotherms

The adsorption data were fitted by the Langmuir (Eq.(S1)), Freundlich (Eq.(S2)), and Redlich-Peterson isotherm equations (Eq.(S3)), repectively.

$$q_e = K_L c_e q_m/(1 + K_L c_e) \quad \text{(S1)}$$

$$q_e = K_F c_e^{1/n} \quad \text{(S2)}$$

$$q_e = q_{mon} b_{RP} c_e/(1 + b_{RP} c_e^{\alpha}) \quad \text{(S3)}$$

where q_e and q_m (mg/g) is the equilibrium capacity and maximum monolayer adsorption capacity, K_L (L/mg) is the Langmuir binding constant, K_F [(mg/g)·(L/mg)$^{1/n}$] and n are the Freundlich constants, q_{mon} and b_{RP} are the Redlich-Peterson constants, α is the empirical constant. The Redlich-Peterson isotherm equation combines the characteristics of the Langmuir and Frenundlich isotherm equation, suiting with uniform and non-uniform adsorption on binding sites.

1.2 Adsorption kinetics

The kinetics data were fitted using pseudo-first-order rate equation (Eq.(S4)), pseudo-second-order rate equation (Eq.(S5)), and the intra-particle diffusion model (Eq.(S6)), respectively.

$$q_t = q_e(1 - e^{k_1 t}) \quad \text{(S4)}$$

$$q_t = q_e^2 k_2 t/(1 + q_e k_2 t) \quad \text{(S5)}$$

$$q_t = k_{ip} t^{1/2} + C \quad \text{(S6)}$$

where q_t (mg/g) is the adsorption capacity at the given time t (min), k_1 (min^{-1}) and k_2 (g/(mg·min)) are rate constant, respectively, and k_{ip} ([(mg/g)/(min)$^{1/2}$]) is the diffusion rate constant, C is related to thickness and boundary layer of resin.

1.3 Adsorption thermodynamics

Adsorption thermodynamic function parameters, including Gibbs free energy change (ΔG, kJ/mol), enthalpy change (ΔH, kJ/mol), and entropy change (ΔS, J/(mol·K)) were obtained by Eq. (S7), (S8) and (S9).

$$\Delta G = -RT\ln K_c \quad \text{(S7)}$$

$$\Delta G = \Delta H - T\Delta S \quad \text{(S8)}$$

$$\ln K_c = -\Delta H/RT + \Delta S/R \quad \text{(S9)}$$

where T (K) is the temperature of adsorption system, K_c (L/mol) is the thermodynamic equilibrium constant, $K_c = K_L \cdot M$ (M is molar mass of methylene blue 319.85 g/mol).

Table section

Table S1 The preparation of $PS\text{-}NO_2$

Code	*Temperature* (°C)	*Time* (h)	$V_{\text{nitric acid}}$ (mL)	$V_{\text{acetic anhydride}}$ (mL)	*Moisture content* (%)
$PS\text{-}NO_2$-1	5	1	20	66	44.1
$PS\text{-}NO_2$-2	5	2	20	66	46.3
$PS\text{-}NO_2$-3	25	10	60	200	50.6
$PS\text{-}NO_2$-4	40	10	60	200	51.8

Table S2 The preparation of PS-NH_2

Code	*Time* (h)	m_{SnCl2} (g)	$V_{ethanol}$ (mL)	V_{HCl} (mL)	Q_{NH2} (mmol/g)[a]	*Moisture content* (%)	X_{Cl} (%)[b]
PS-NH_2-1	24	120	130	130	1.5	47.4	-
PS-NH_2-2	24	160	170	170	2.5	50.2	-
PS-NH_2-3	24	200	210	210	4.4	53.3	0.11
PS-NH_2-4	24	240	250	250	6.3	58.9	0.12

[a] Quantity of amino groups determined by weak base exchange capacity analysis,

[b] by Volhard method.

Table S3 The preparation of PS-OH

Code	*Time* (h)	V_{NaNO_2} (mL)	$V_{H_2SO_4}$ (mL)	Q_{OH} (mmol/g)[a]	*Moisture content* (%)
PS-OH-1	2	33	33	1.2	46.4
PS-OH-2	2	55	55	2.3	49.9
PS-OH-3	2	96	96	3.9	52.7
PS-OH-4	2	138	138	5.4	57.4

[a] Quantity of hydroxyl groups determined by weak acid exchange capacity analysis

Table S4 The preparation of HCPS-OH

Code	*Time* (h)	*Catalyst*	X_{Cl} (%)[a]	Q_{OH} (mmol/g)[b]	*Moisture content* (%)
HCPS-OH-1	36	$FeCl_3$	0.38	1.4	52.6
HCPS-OH-2	36	$FeCl_3$	0.35	2.2	53.9
HCPS-OH-3	36	$FeCl_3$	0.32	3.7	54.2
HCPS-OH-4	36	$FeCl_3$	0.27	5.0	57.8

[a] by Volhard method, [b] Quantity of hydroxyl groups determined by weak acid exchange capacity analysis

Table S5 The adsorption of thermodynamic parameters evaluated for MB on resins

Code	$K_c/10^3$ (L/mol)			ΔH (kJ/mol)	ΔS (J/(mol·K))	ΔG (kJ/mol)		
	298 K	308 K	318 K			298 K	308 K	318 K
HCPS-OH-1	5.49	5.94	7.64	12.92	114.70	-21.33	-22.25	-23.64
HCPS-OH-2	37.67	50.48	67.07	22.45	162.95	-26.11	-27.73	-29.37
HCPS-OH-3	43.08	52.92	70.41	19.26	153.23	-26.44	-27.85	-29.51
HCPS-OH-4	78.61	102.03	152.64	26.16	181.28	-27.92	-29.53	-31.55

Table S6 Adsorption isotherm model parameters for the adsorption of AN and PNA into HCPS-OH

Code		Langmuir model			Freundlich model		
		q_m (mg/g)	K_L /10^{-3} (L/mg)	R^2	K_F [(mg/g)·(L/mg)$^{1/n}$]	1/n	R^2
HCPS-OH-1	AN	110.7	12.38	0.991	5.88	0.497	0.993
	PNA	222.8	15.58	0.980	14.42	0.477	0.998
HCPS-OH-2	AN	144.6	12.77	0.989	6.13	0.556	0.997
	PNA	231.4	24.95	0.977	20.75	0.446	0.994
HCPS-OH-3	AN	62.0	23.90	0.883	8.29	0.343	0.995
	PNA	212.0	13.44	0.986	12.83	0.476	0.995
HCPS-OH-4	AN	71.6	8.75	0.994	3.70	0.467	0.981
	PNA	217.3	11.30	0.978	11.60	0.486	0.996

Figure section

Fig. S1 The FT-IR spectrum of the PS-NO_2, PS-NH_2 and PS-OH resins

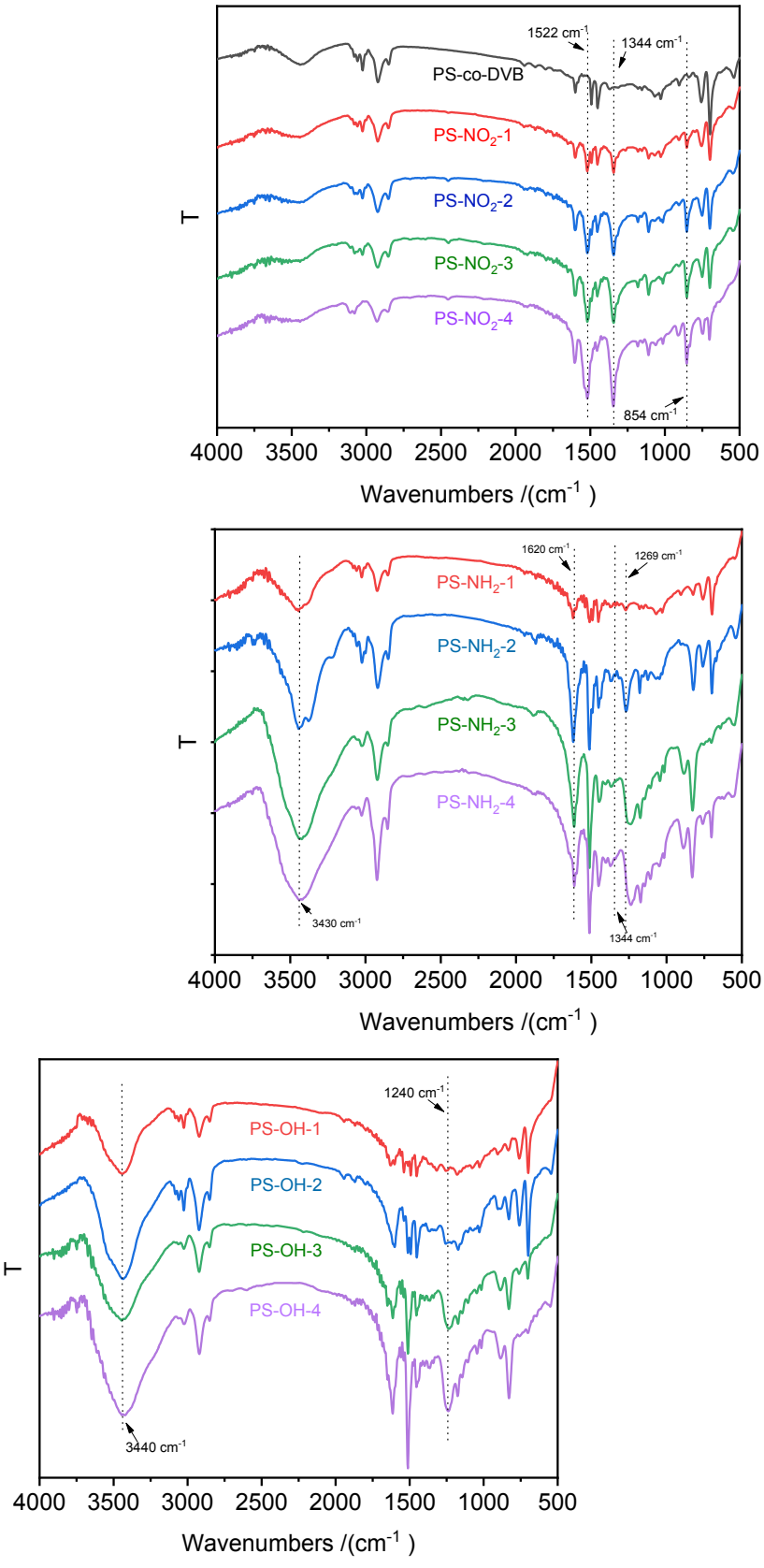

Fig. S2 The contact angles (CA) of the HCPS-OH resins with H_2O

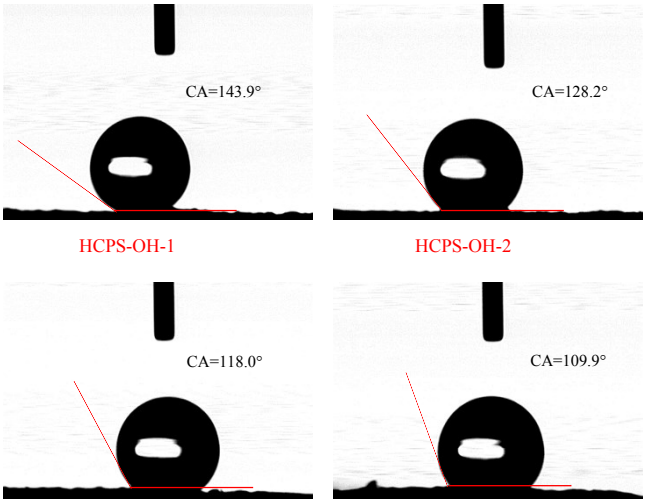

Fig. S3 XPS spectra of HCPS-OH resins

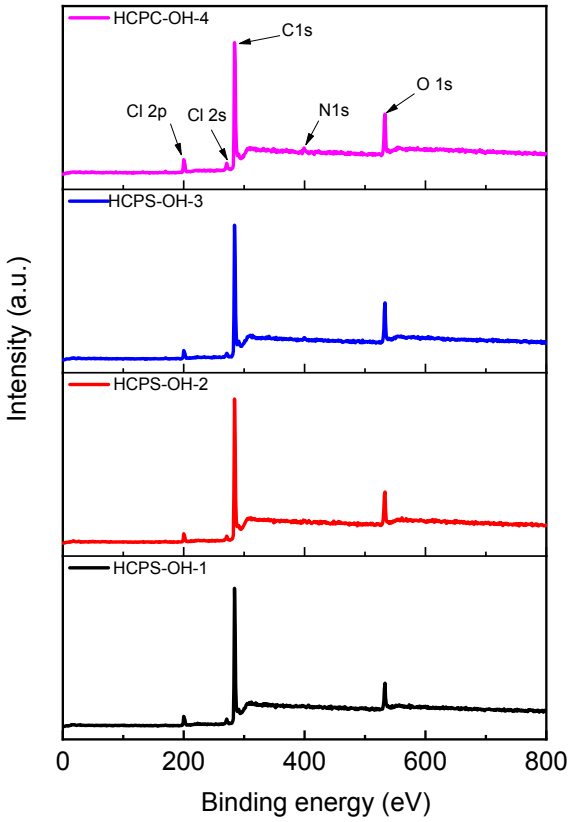

Fig. S4 Swelling ratio of the PS-OH resins in water and DCM

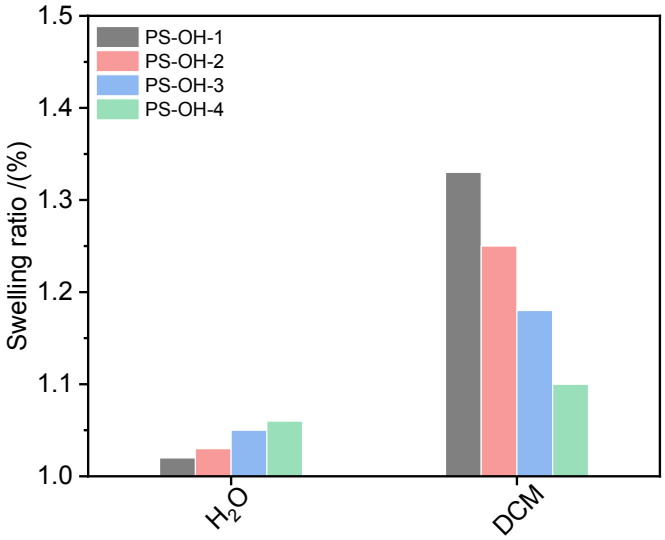

Fig. S5 Swelling ratio of the HCPS-OH resins in water (1), ethanol (2), acetone (3) and DCM (4)

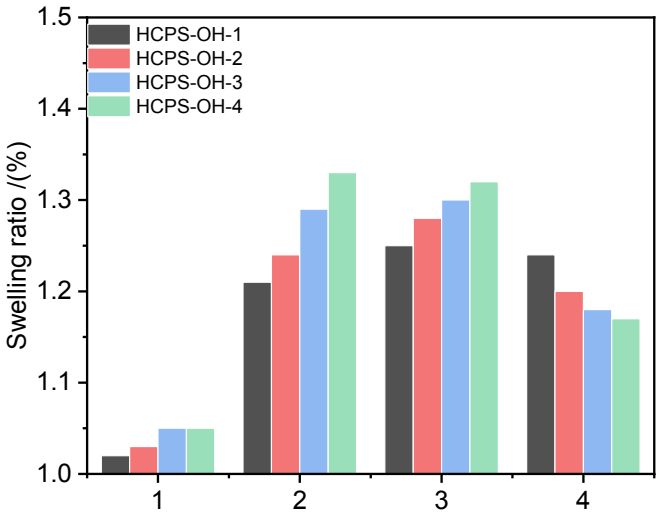

Fig. S6 The equilibrium isotherms of MB on (a) HCPS-OH-1, (b) HCPS-OH-2, (c) HCPS-OH-3, (d) HCPS-OH-4 at 298 K,308 K and 318 K

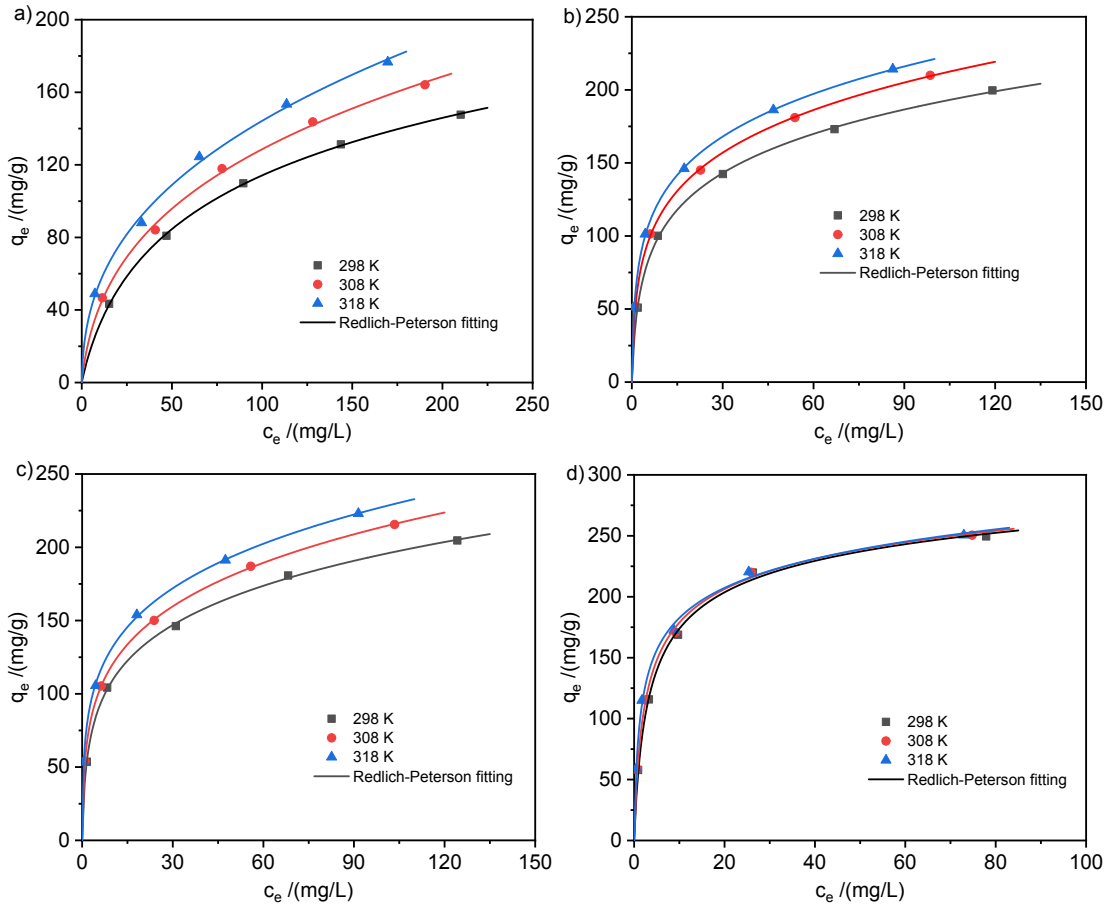

Fig. S7 Plot of lnK_c vs. 1/T for adsorption of MB on (a) HCPS-OH-1, (b) HCPS-OH-2, (c) HCPS-OH-3 and (d) HCPS-OH-4 at 298 K

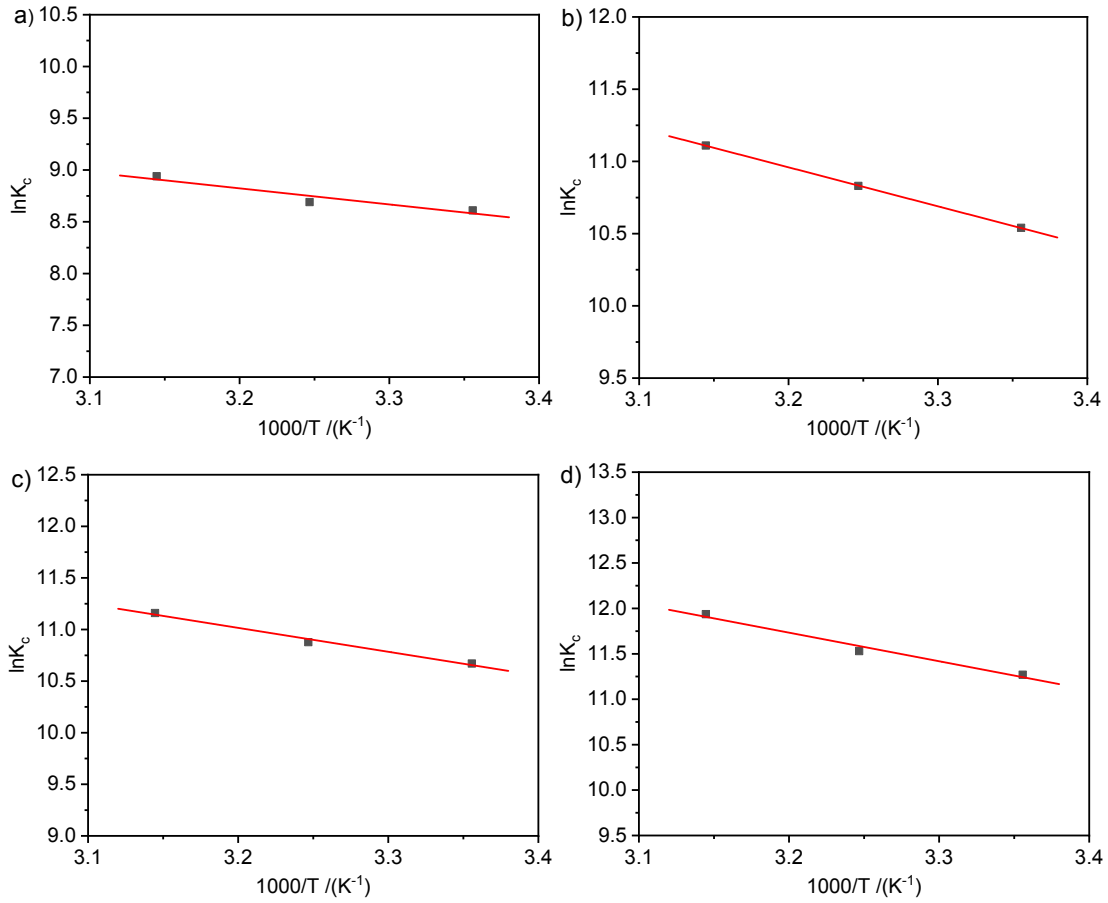

Fig. S8 The adsorption kinetic curves of MB on HCPS-OH-4 at 298 K, 308 K and 318 K

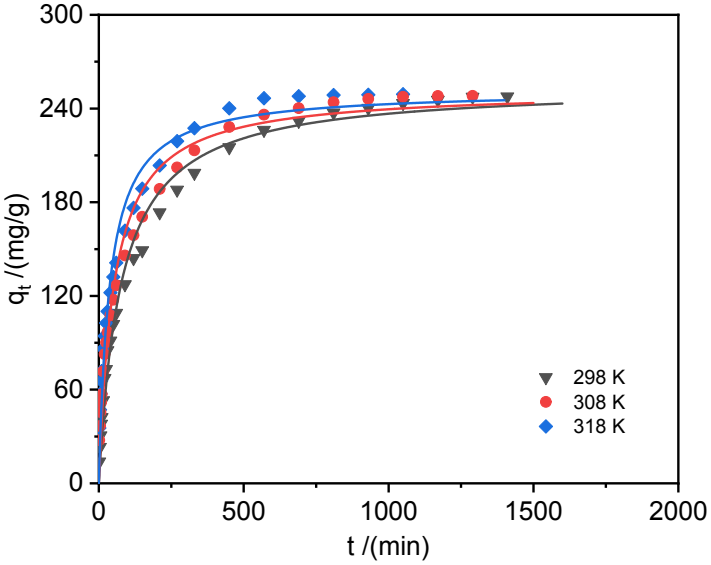

Fig. S9 Plotting of q_t versus $t^{1/2}$ on HCPS-OH-4 according to the intra-particle diffusion model

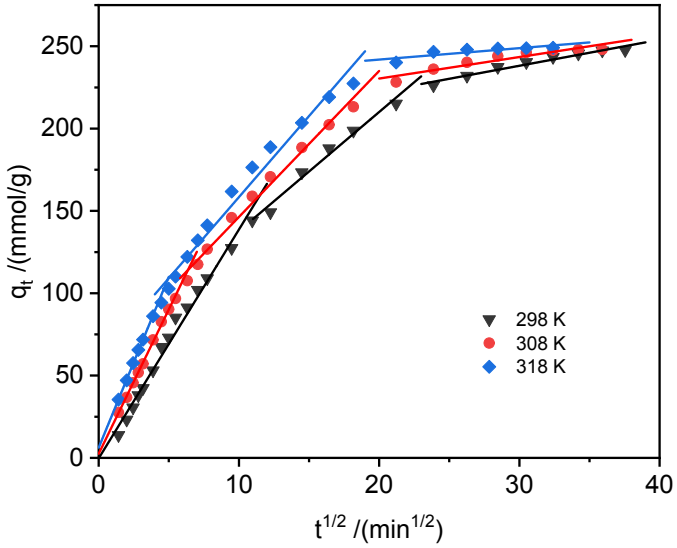

Fig. S10 Effect of KCl on MB removal (MB concentration: 500.5 mg/L, adsorbent dose: 0.100 g/25 ml, temperature: 298 K, contact time: 24 h)

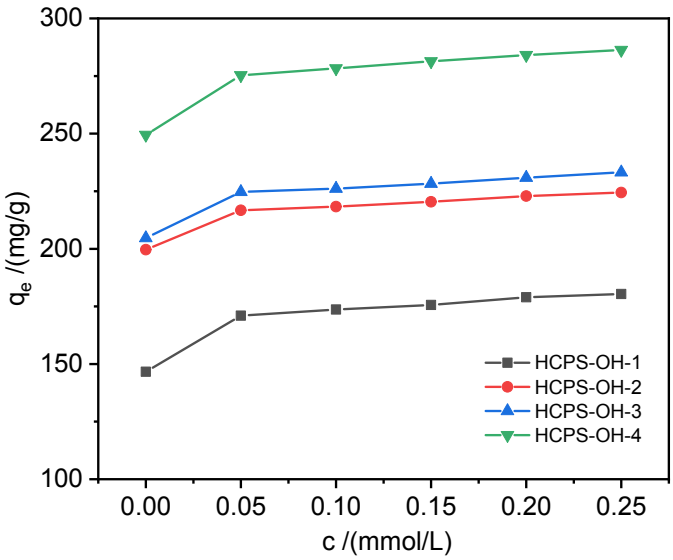

Fig. S11 The swelling capacity of HCPS-OH-1 (1), HCPS-OH-2 (2), HCPS-OH-3 (3) and HCPS-OH-4 (4) in 0.1 M NaOH solution

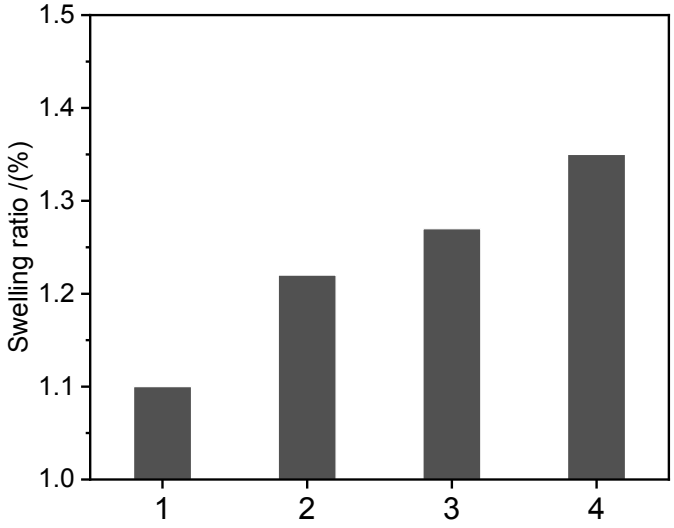

Fig. S12 Adsorption isotherms of (a) AN and (b) PNA on the HCPS-OH resins