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Supporting Information

Green Synthesis of Porous β-Cyclodextrin Polymer for Rapid and Efficient Removal of Organic Pollutants and Heavy Metal Ions from Water

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Synthesis of CS-EDTA

After drying in vacuum, a total of 1 g of chitosan was dissolved in 20 mL of 10 vol. % aqueous acetic acid solution and then diluted five times with methanol. After that 4.77 g of EDTA anhydride (18.6 mmol) suspended in methanol was added to this solution and stirred vigorously for about 24 h at room temperature. The precipitate was further mixed with ethanol and stirred for another 16 h. It was then washed with NaOH solution (pH 11) to eliminate unreacted EDTA. The precipitate was washed with deionized water, 0.1 M HCl, again deionized water, and ethanol. At last, the product was dried under vacuum for 48 h and stored in a desiccator.

Synthesis of P-CDSA

β-CD (1 g, 0.88 mmol), SA (0.335 g), and K_2CO_3 (1.5 g, 10.85 mmol) were suspended in 4.5 mL of deionized H_2O and sonicated for 10 min. PFP (0.25 mL, 2.57 mmol) and MeTHF (40 mL) were added to a 100 mL pressure vessel equipped with a magnetic stir bar. The mixed β-CD solution was then added dropwise to the MeTHF solution and the contents were bubbled with N_2 for 5 min. The N_2 inlet was removed, the pressure vessel sealed, and the mixture placed on a hot stirring plate (80 °C) and stirred at 500 rpm for 48h. The yellow solid was filtered and washed with 1 M HCl until CO_2 evolution stopped to remove the residual K_2CO_3. The recovered yellow solid was washed with H_2O and C_2H_5OH for several times. The product was filtered and dried under high vacuum for 24h at room temperature.

Synthesis of P-CDMCC

β-CD (1 g, 0.88 mmol), MCC (0.335 g), and K_2CO_3 (1.5 g, 10.85 mmol) were suspended in 4.5 mL of deionized H_2O and sonicated for 20 min. PFP (0.3 mL, 3.08 mmol) and MeTHF (40 mL) were added to a 100 mL pressure vessel equipped with a magnetic stir bar. The mixed β-CD solution was then added dropwise to the MeTHF solution and the contents were bubbled with N_2 for 5 min. The N_2 inlet was removed, the pressure vessel sealed, and the mixture placed on a hot stirring plate (80 °C) and stirred at 500 rpm for 48h. The yellow solid was filtered and washed with 1 M HCl until CO_2 evolution stopped to remove the residual K_2CO_3. The recovered yellow solid was washed with H_2O and C_2H_5OH for several times. The product was filtered and dried under high vacuum for 24h at room temperature.

Synthesis of P-CDAL

β-CD (1 g, 0.88 mmol), AL (0.335 g), and K_2CO_3 (1.5 g, 10.85 mmol) were suspended in 4.5 mL of deionized H_2O and sonicated for 10 min. PFP (0.3 mL, 3.08 mmol) and MeTHF (40 mL) were added to a 100 mL pressure vessel equipped with a magnetic stir bar. The mixed β-CD solution was then added dropwise to the MeTHF solution and the contents were bubbled with N_2 for 5 min. The N_2 inlet was removed, the pressure vessel sealed, and the mixture placed on a hot stirring plate (80 °C) and stirred at 500 rpm for 48h. The brown solid was filtered and washed with 1 M HCl until CO_2 evolution stopped to remove the residual K_2CO_3. The recovered brown solid was washed with H_2O and C_2H_5OH for several times. The product was filtered and dried under high vacuum for 24h at room temperature.

Synthesis of P-CD

β-CD (1 g, 0.88 mmol), K_2CO_3 (1.5 g, 10.85 mmol), PFP (0.25 mL, 2.57 mmol) and MeTHF (40 mL) were added to a 100 mL pressure vessel equipped with a magnetic stir bar. The contents were bubbled with N_2 for 5 min. The N_2 inlet was removed, the pressure vessel sealed, and the mixture placed on a hot stirring plate (80 °C) and stirred at 500 rpm for 48h. The brown solid was filtered and washed with 1 M HCl until CO_2 evolution stopped to remove the residual K_2CO_3. The recovered yellow solid was washed with H_2O and C_2H_5OH for several times. The product was filtered and dried under high vacuum for 24h at room temperature.

Synthesis of EPI-CDP

β-CD (0.300 g, 2.64 mmol) was dissolved in aqueous NaOH (6.5 M, 5.00 mL) and epichlorohydrin (2.50 mL, 32.4 mmol) was added to this solution dropwise while stirring vigorously at 60 °C. The reactant turned into a yellow gel within 1 h and was socked in deionized H_2O for 30 min. The solid was then washed and filtered with deionized H_2O and C_2H_5OH for several times. The product was dried under high vacuum for 24 h at room temperature to give EPI cross-linked β-CD polymer (EPI-CDP) as a white powder.[1]

Measurement of molecular weight

MCC

The cellulose samples were dissolved in a standard reagent of 1 mol L^{-1} copper(II)-ethylenediamine (Cuen), and then intrinsic viscosity measurements were completed using an Ubbelodhe viscometer. The calculated molecular weight of microcrystalline cellulose is 4.9×10^4.

CS

The chitosan samples were dissolved in reagent of 0.2 mol L^{-1} NaCl and 0.3 mol L^{-1} CH_3COOH. Then intrinsic viscosity measurements were completed using an Ubbelodhe viscometer. The calculated molecular weight of chitosan is 3.4×10^5.

SA

The sodium alginate samples were dissolved in reagent of 0.1 mol L^{-1} NaCl. Then intrinsic viscosity measurements were completed using an Ubbelodhe viscometer. The calculated molecular weight of sodium alginate is 4.1×10^5.

Degree of substitution

The degree of substitution of EDTA is measured by back titration. the sample of CS-EDTA was firstly immersed in an excess 0.1 M HCl solution for 2h to make sure all the carboxylate groups were converted into carboxylic acid. Then the sample was rinsed with deionized water, methanol successively and dried in vacuum at 60℃ overnight. The amount of free carboxylic acid groups on CS-EDTA was determined by a typical back titration procedure: 100 mg of CS-EDTA was stirred in 100 mL of 0.01 M NaOH aqueous solution for 2 h. Under a gentle stirring, the excess NaOH in the solution was back-titrated by a 0.01 M HCl solution to reach the neutral point (determined by a pH meter, LICHEN PH-100B).

The calculated degree of substitution of EDTA is 31%.

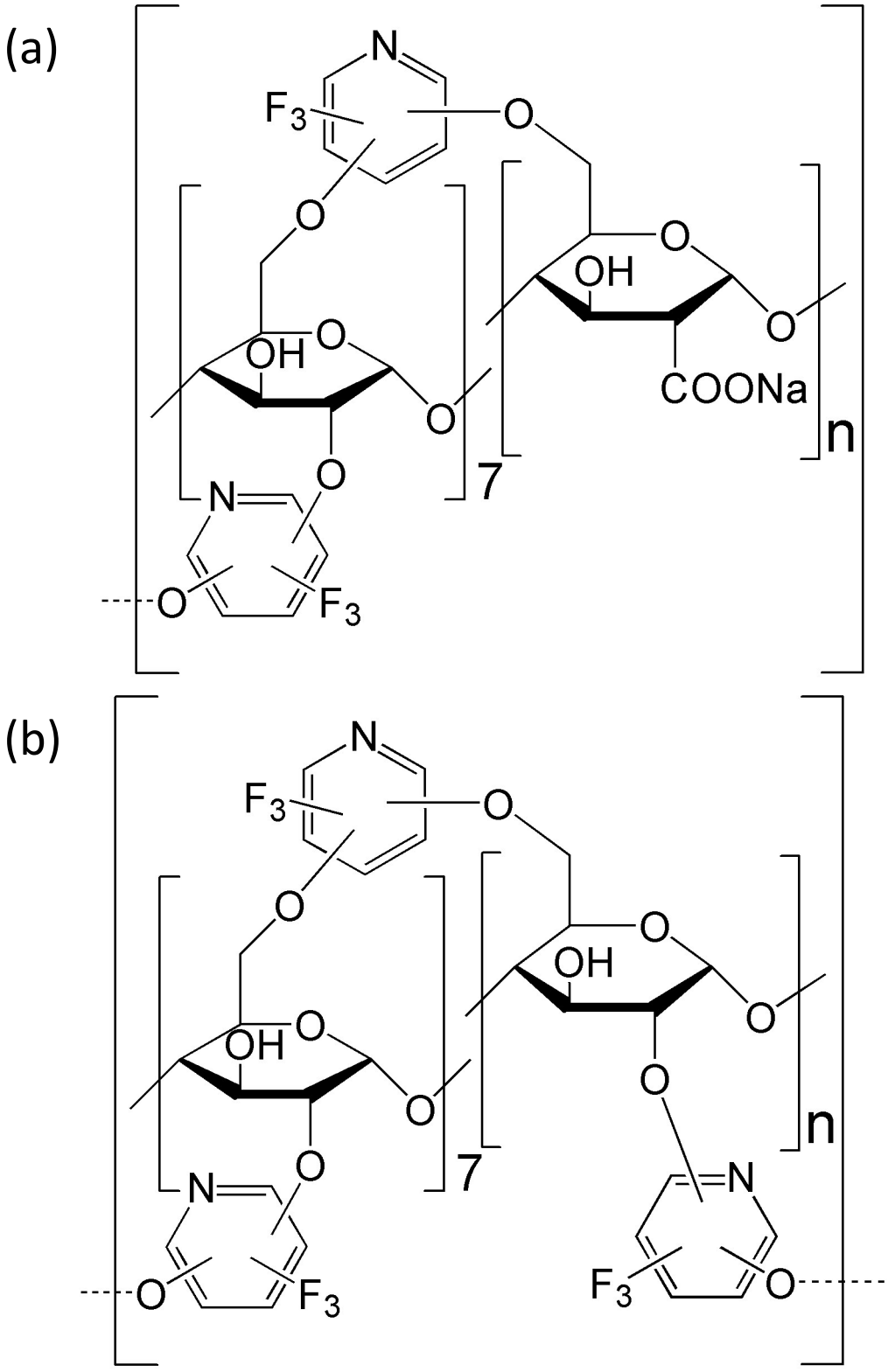

Fig. S1 Structures of (a) P-CDSA and (b) P-CDMCC.

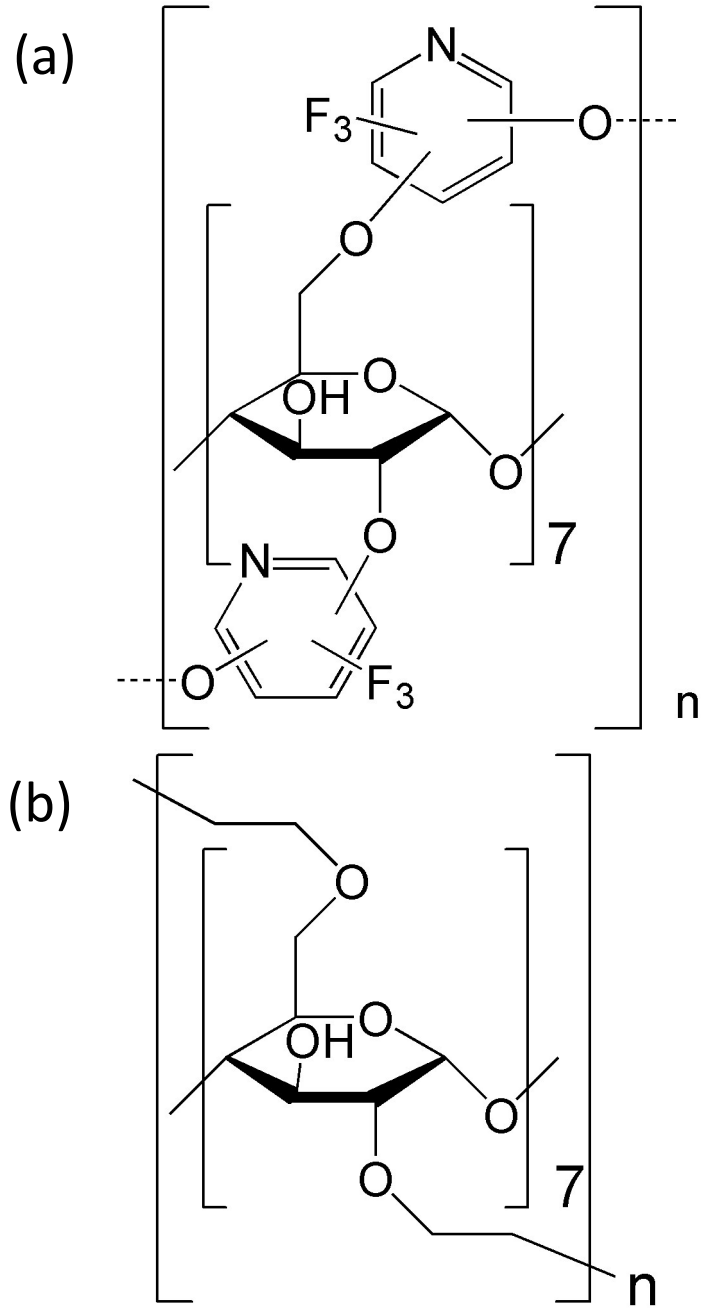

Fig. S2 Structures of (a) P-CD and (b) EPI-CDP.

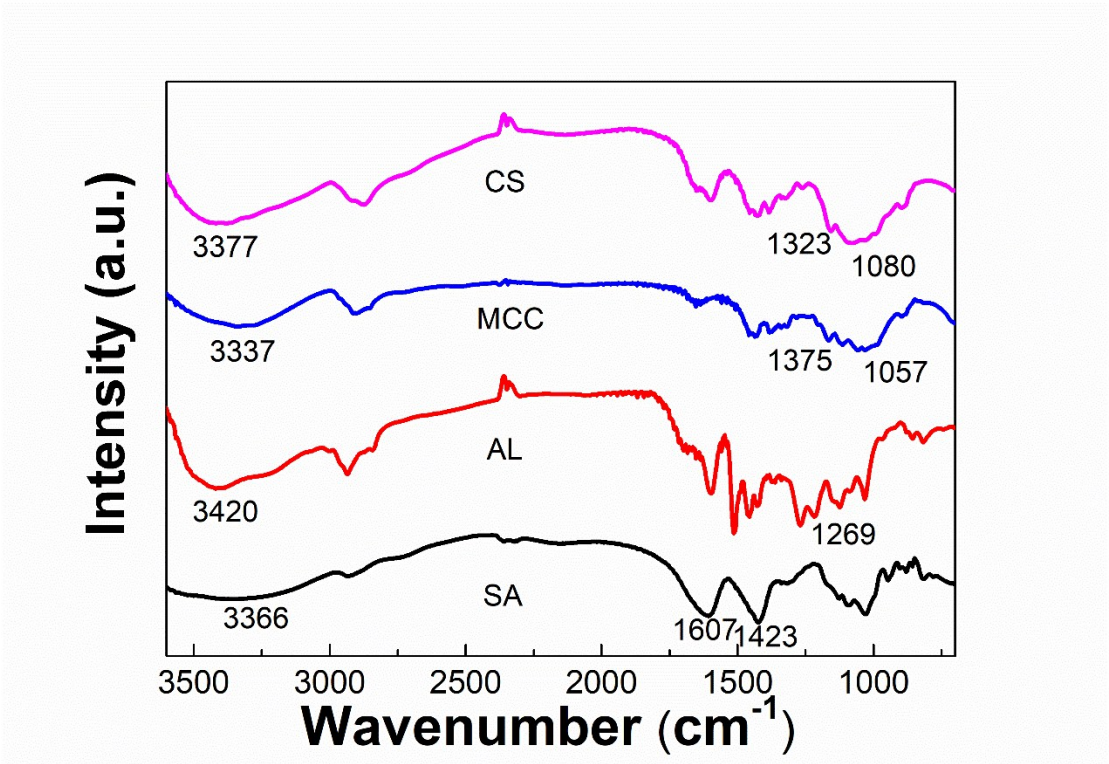

Fig. S3 The FT-IR spectrum of chitosan (CS), microcrystalline cellulose (MCC), alkali lignin (AL), and sodium alginate (SA).

Table S1 Synthesis conditions of a series of hierarchical porous polymers.

Product	Reactants	Solvents	Temperature
P-CDEC	β-CD, CS-EDTA, PFP	MeTHF, H_2O	80 °C
P-CDSA	β-CD, SA, PFP	MeTHF, H_2O	80 °C
P-CDMCC	β-CD, MCC, PFP	MeTHF, H_2O	80 °C
P-CDAL	β-CD, AL, PFP	MeTHF, H_2O	80 °C
P-CD	β-CD, PFP	MeTHF, DMF	80 °C
P-CDEC2	β-CD, CS-EDTA, PFP	MeTHF, H_2O	90°C
P-CDEC3	β-CD, CS-EDTA, PFP	MeTHF, DMF	80 °C
P-CDP	β-CD, TFP	THF, DMF	85°C
P-CDEC4	β-CD, CS-EDTA, TFP	MeTHF, H_2O	80 °C
P-CDEC5	β-CD, CS-EDTA, TFP	MeTHF, H_2O	90 °C
P-CDEC6	β-CD, CS-EDTA, TFP	MeTHF, DMF	80 °C
P-CDEC7	β-CD, CS-EDTA, PFP	THF, DMF	80 °C
P-CDEC	β-CD, CS-EDTA, TFP	THF, DMF	80 °C

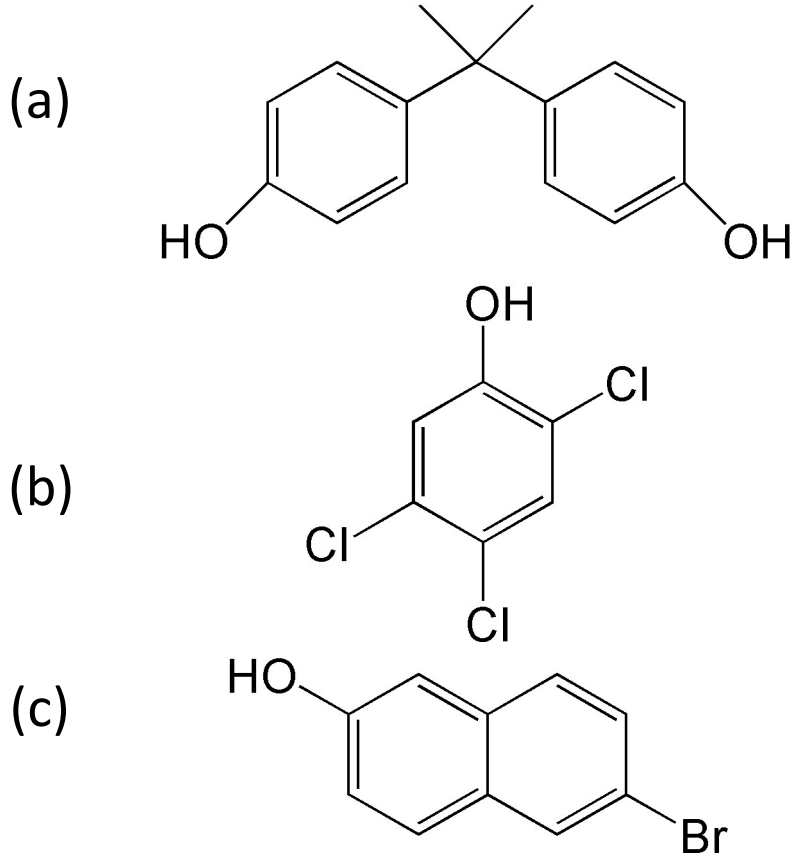

Fig. S4 Structures of (a) BPA, (b) TCP, and (c) BNP.

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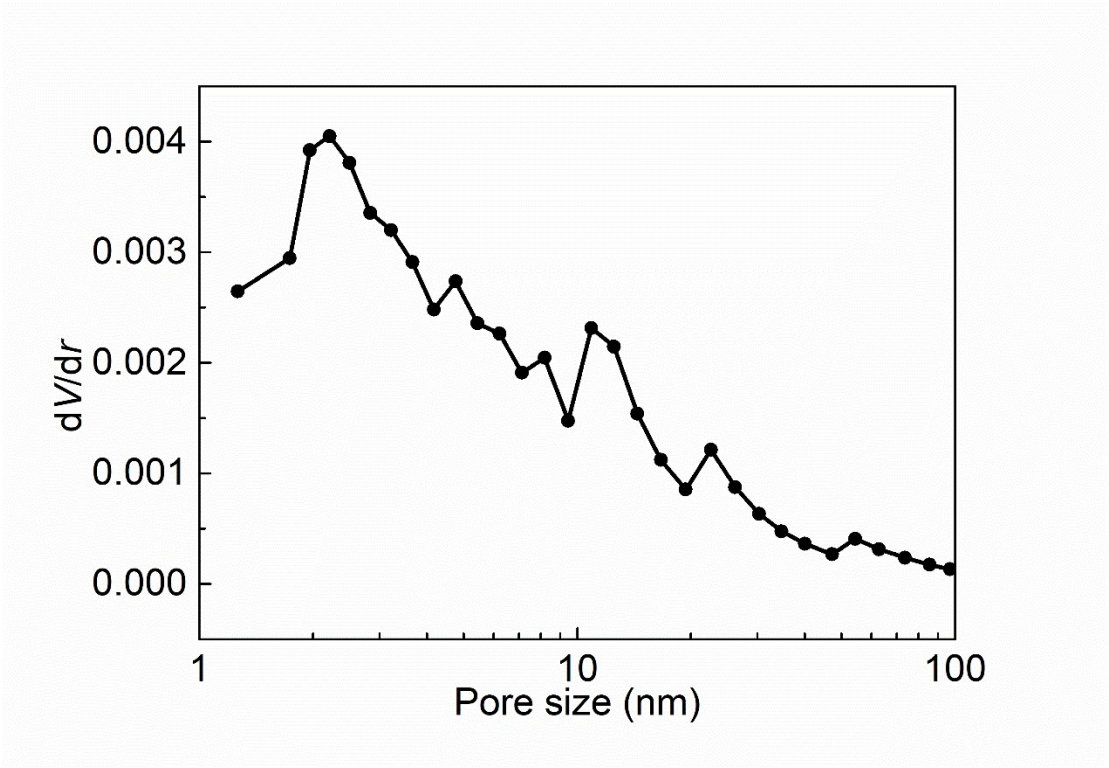


Fig. S5 Pore size distribution of P-CDEC (1-100nm).

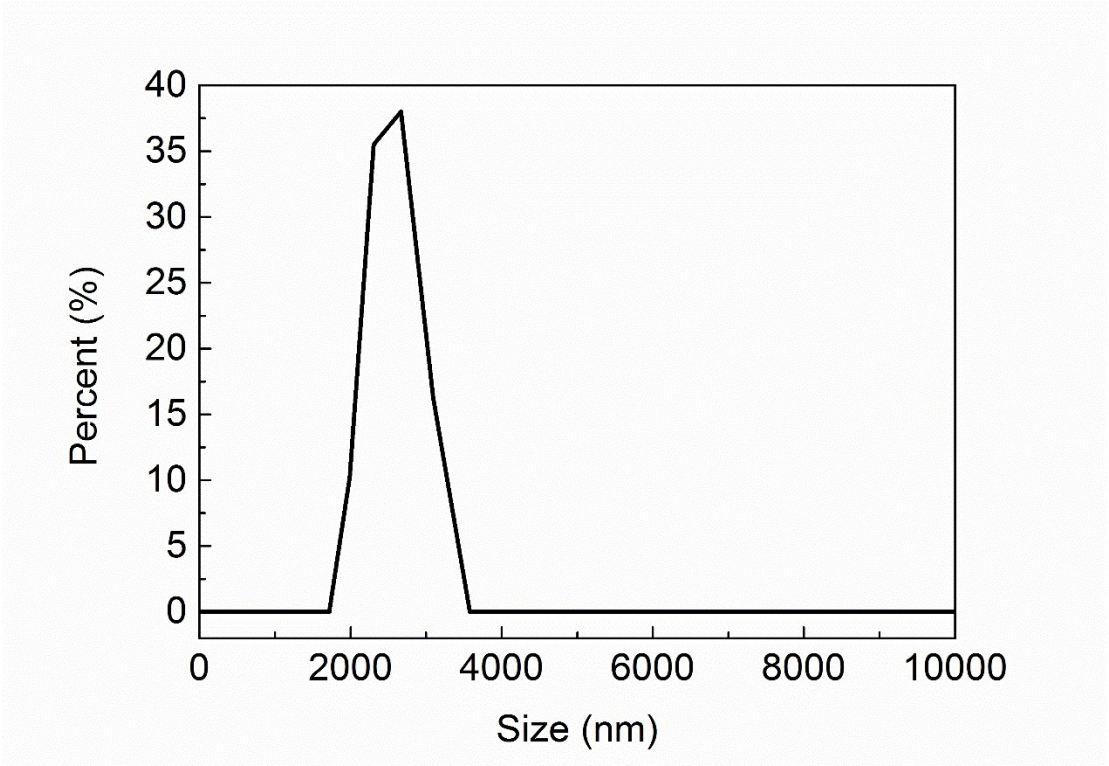


Fig. S6 Size image of P-CDEC.

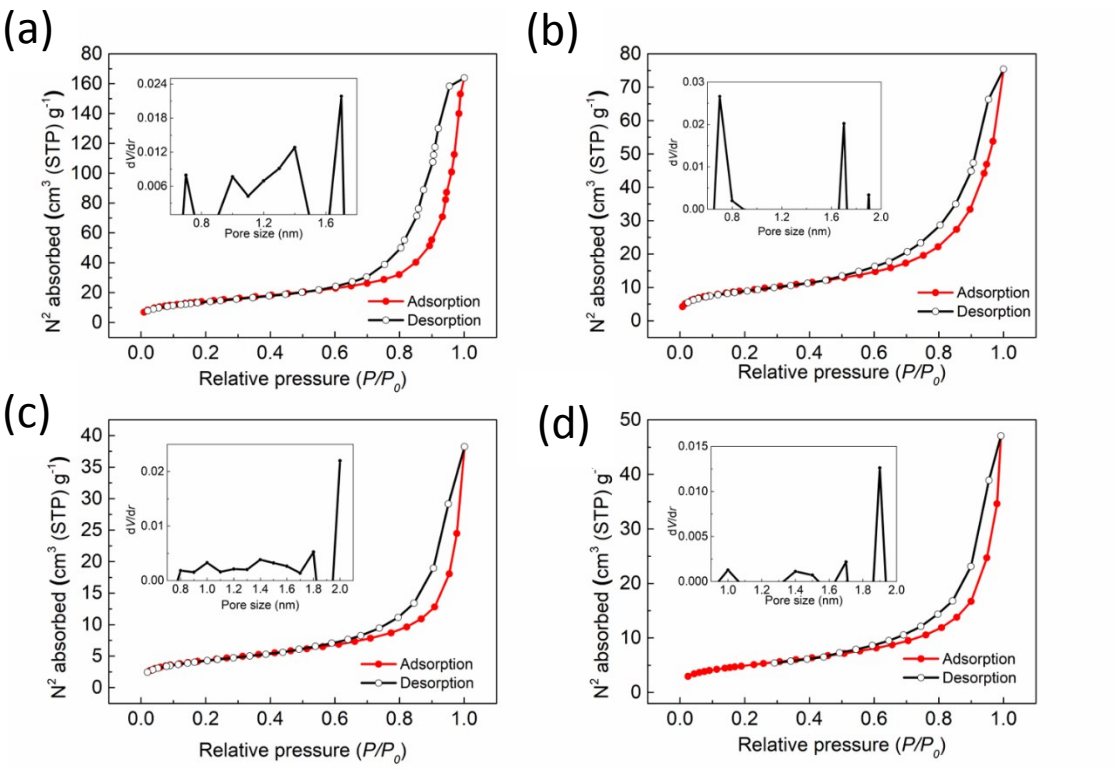


Fig. S7 N_2 adsorption-desorption isotherms and pore size distribution (inset) of (a) P-CDSA, (b) P-CDMCC, (c) P-CDAL, and (d) P-CD measured at 77 K. The Brunauer–Emmett–Teller specific surface areas of (a) P-CDSA, (b) P-CDMCC, (c) P-CDAL, and (d) P-CD are 51.5 $m^2 g^{-1}$, 32.4 $m^2 g^{-1}$, 15.6 $m^2 g^{-1}$, and 17.8 $m^2 g^{-1}$ respectively.

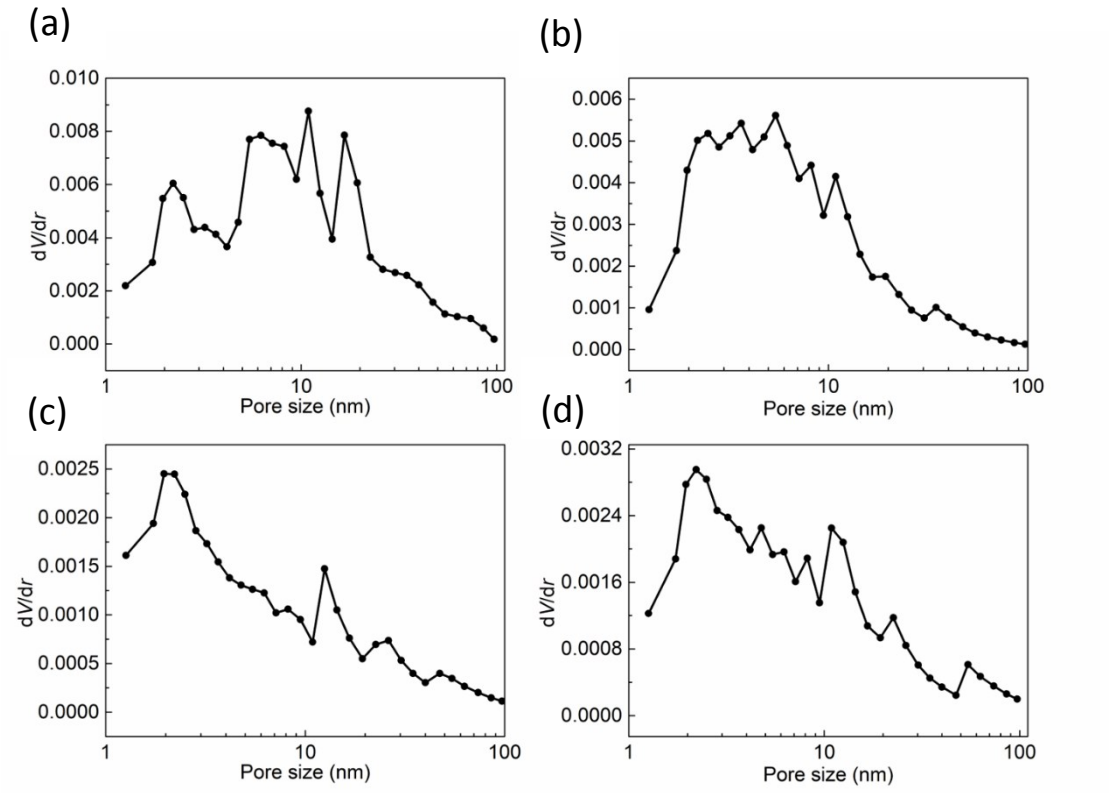


Fig. S8 Pore size distribution of (a) P-CDSA, (b) P-CDMCC, (c) P-CDAL, and (d) P-CD (1-100nm).

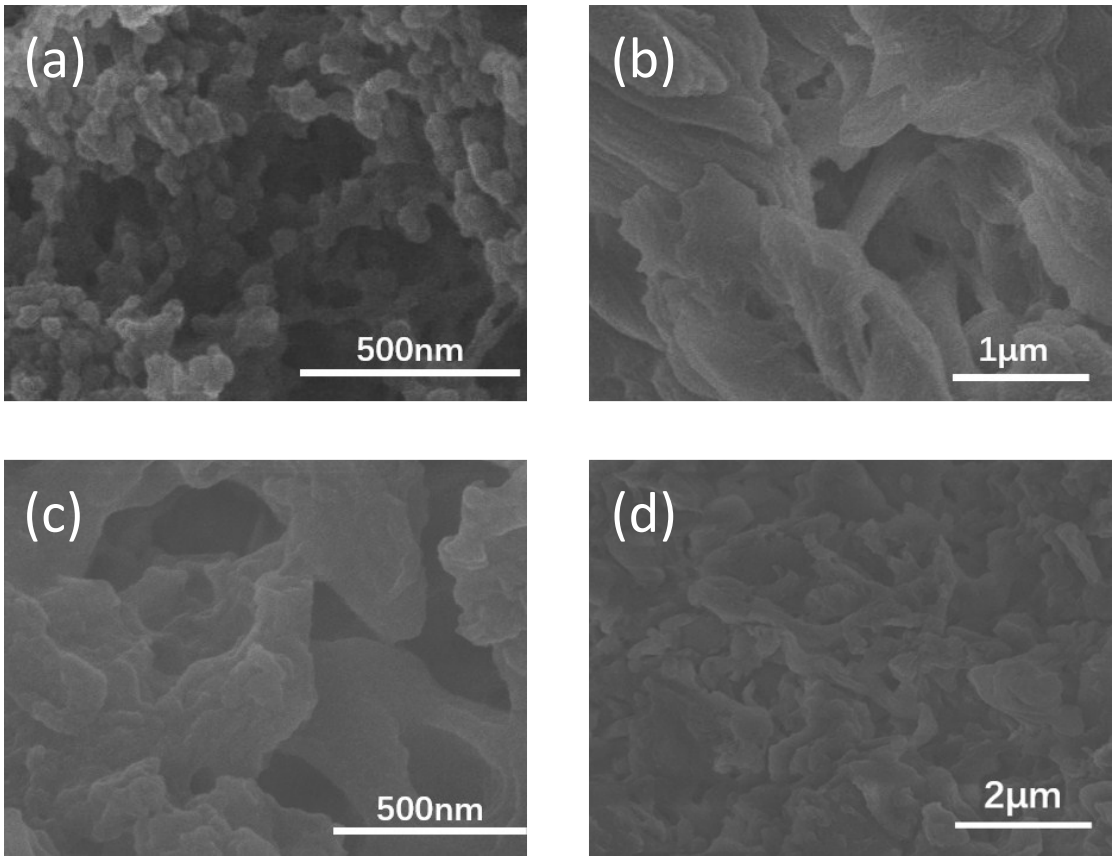
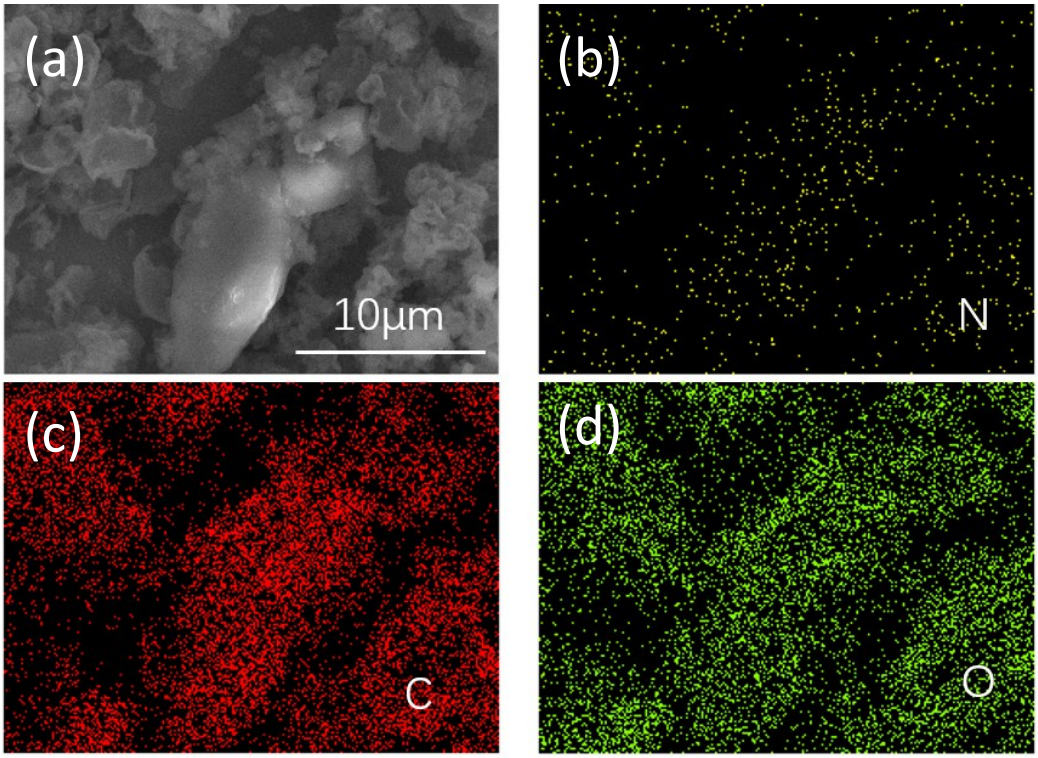
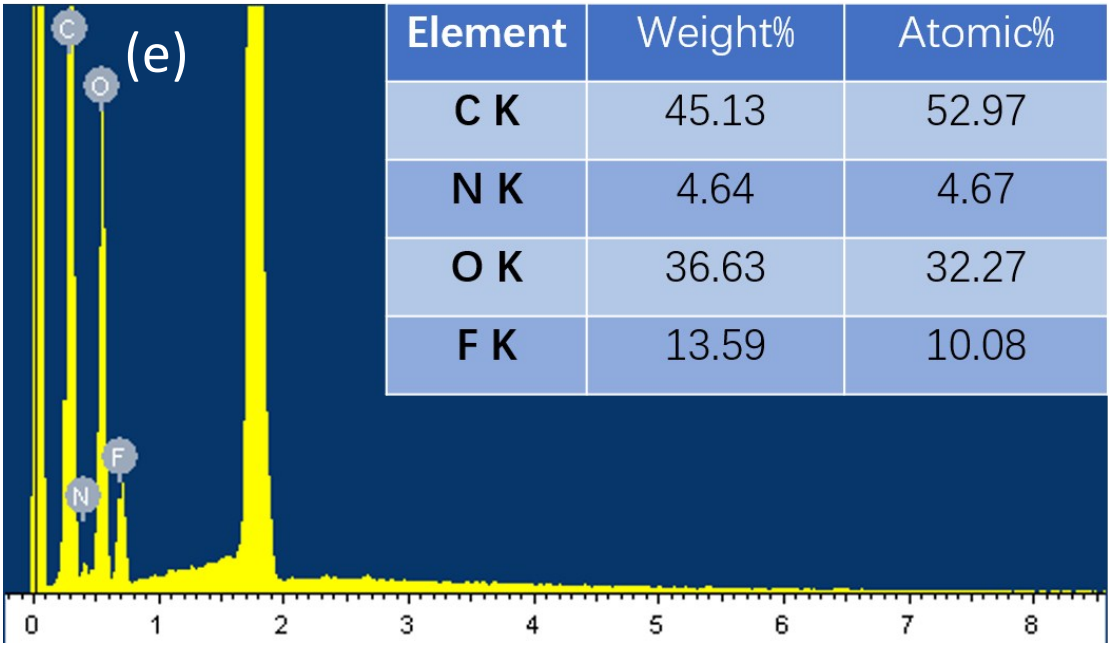


Fig. S9 SEM images of (a) P-CDSA, (b) P-CDMCC, (c) P-CDAL, and (d) P-CD.





Element	Weight%	Atomic%
C K	45.13	52.97
N K	4.64	4.67
O K	36.63	32.27
F K	13.59	10.08

Fig. S10 (a) TEM of P-CDEC. X-ray mapping of N, C and O are shown in (b) (c) and (d). (e) EDX spectra of P-CDEC.

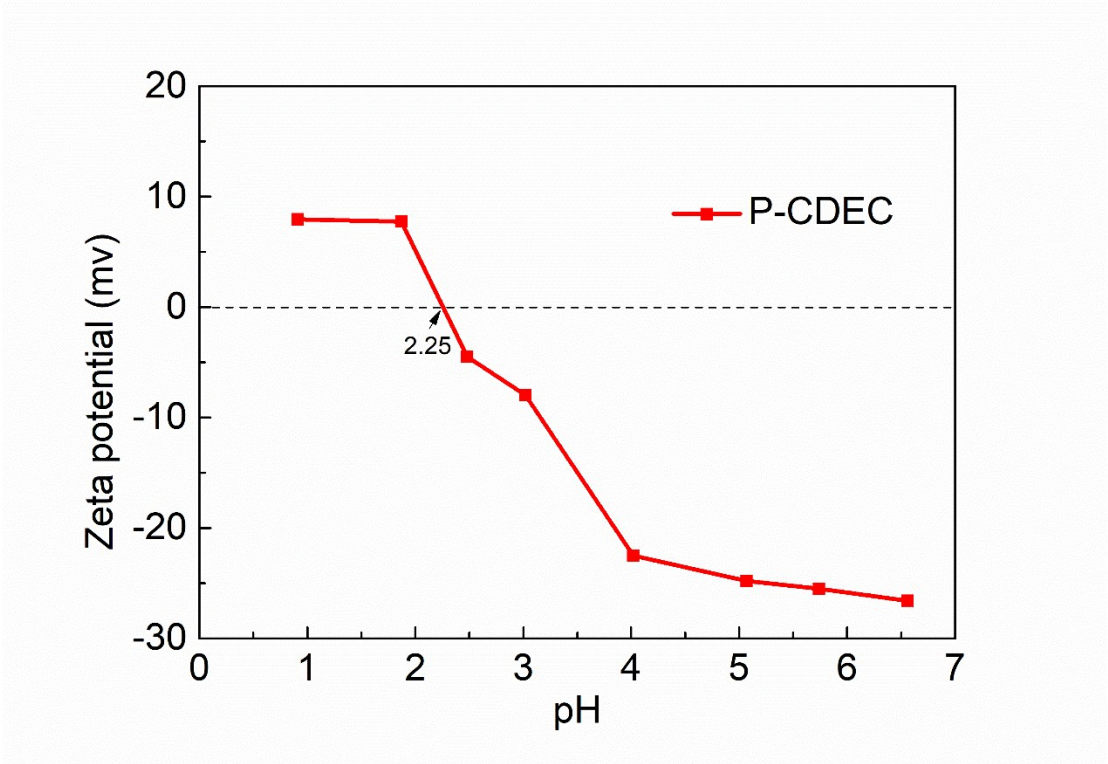


Fig. S11 Zeta potentials of P-CDEC as a function of solution pH.

Table S2 Parameters of adsorption kinetics of pollutants onto P-CDEC fitted by pseudo-second-order model.

Pollutants	q_e (mg g^{-1})	k_2 (g mg^{-1} min^{-1})	R^2
Pb(II)	24.7	18.64	0.9998
Ni(II)	23.5	0.95	0.9978
Cu(II)	24.5	1.30	0.9998
BPA	10.6	1.60	0.9998
TCP	9.2	4.93	0.9998
BNP	10.4	5.33	0.9998

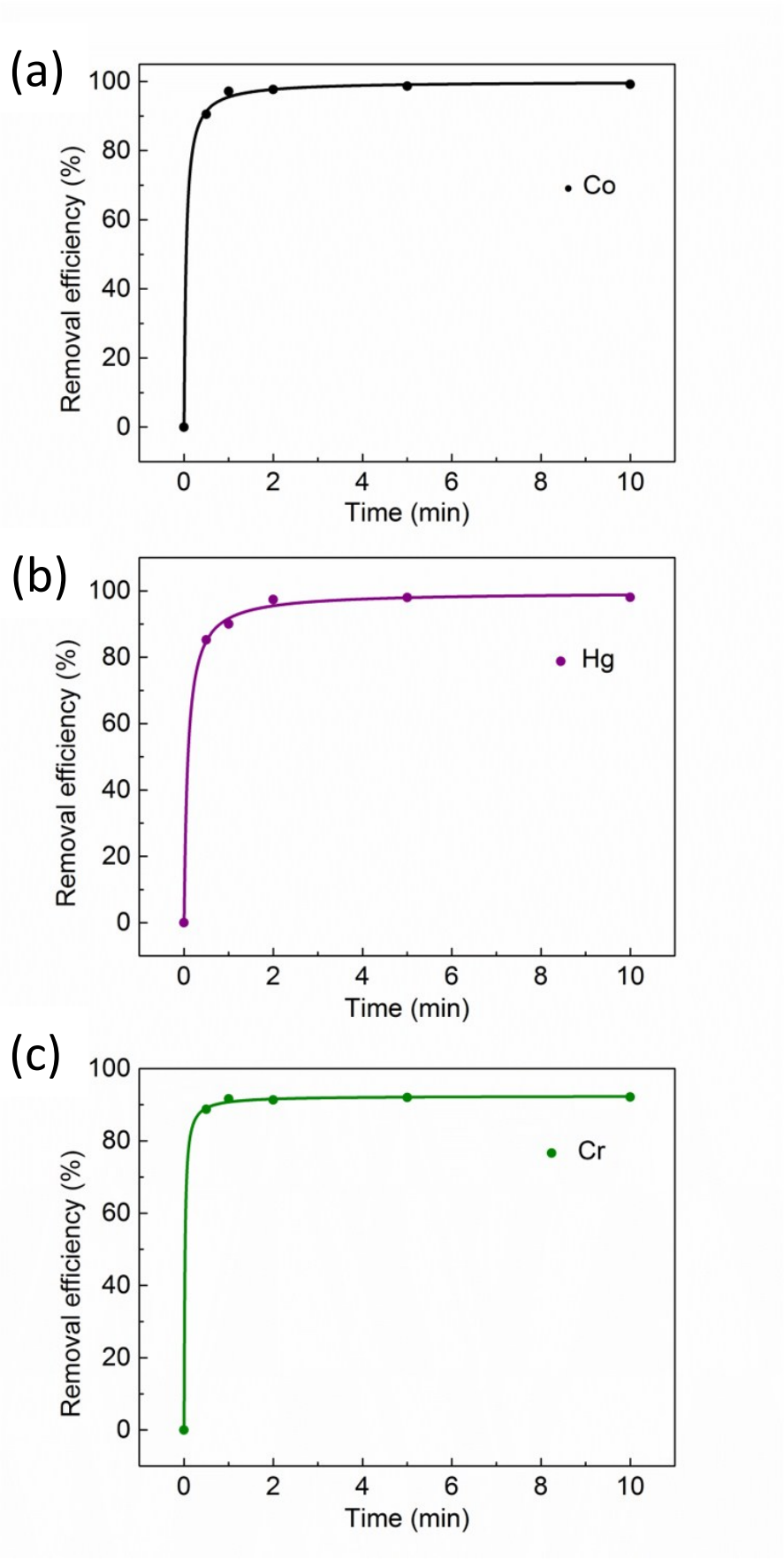


Fig. S12 Time-dependent removal of (a) Co(II), (b) Hg(II), and (c) Cr(II) by P-CDEC in batch

adsorption experiments.

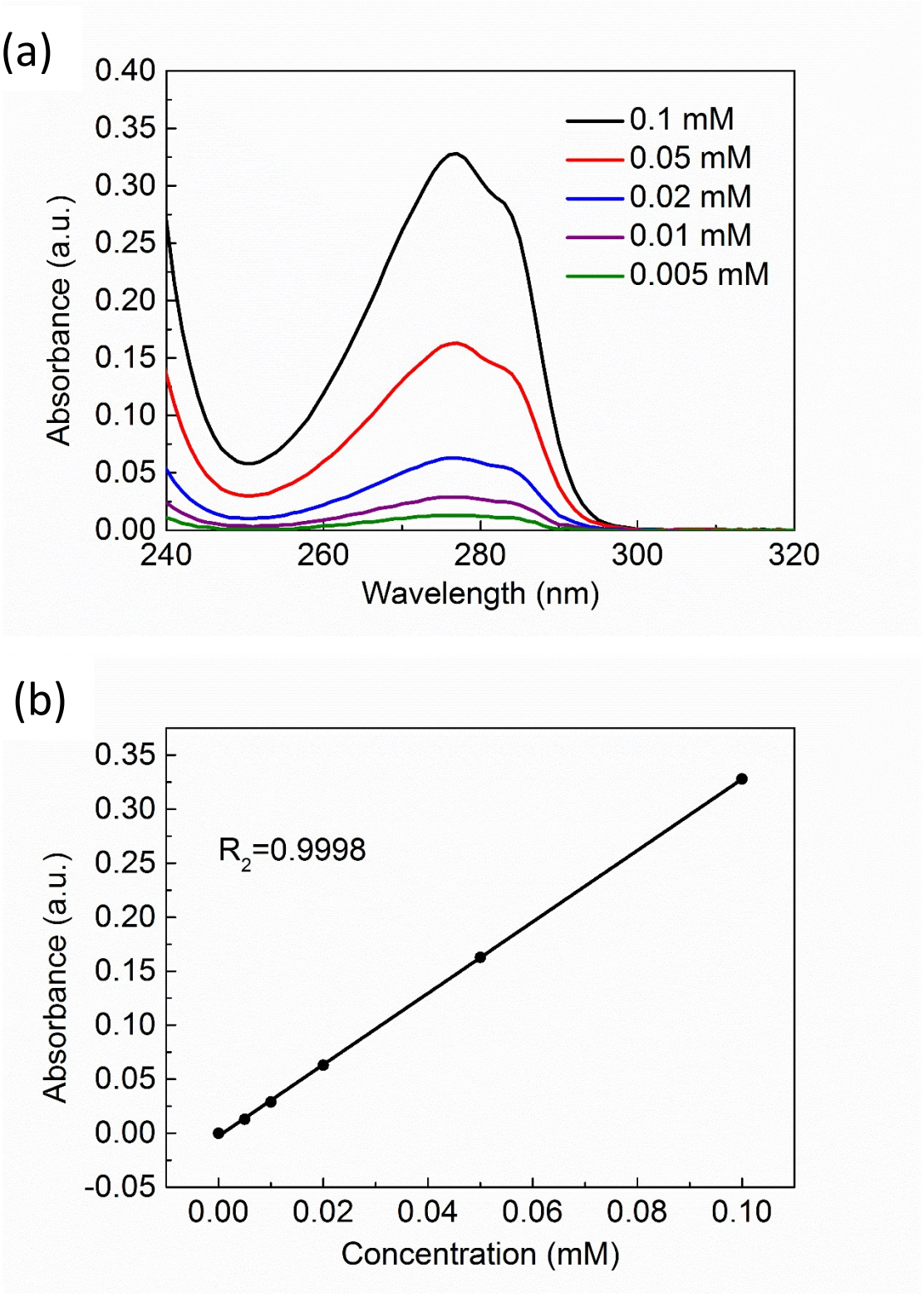


Fig. S13 (a) UV-Vis spectra of BPA of different concentrations. (b) Standard curve plotted based on the absorbance at 277 nm.

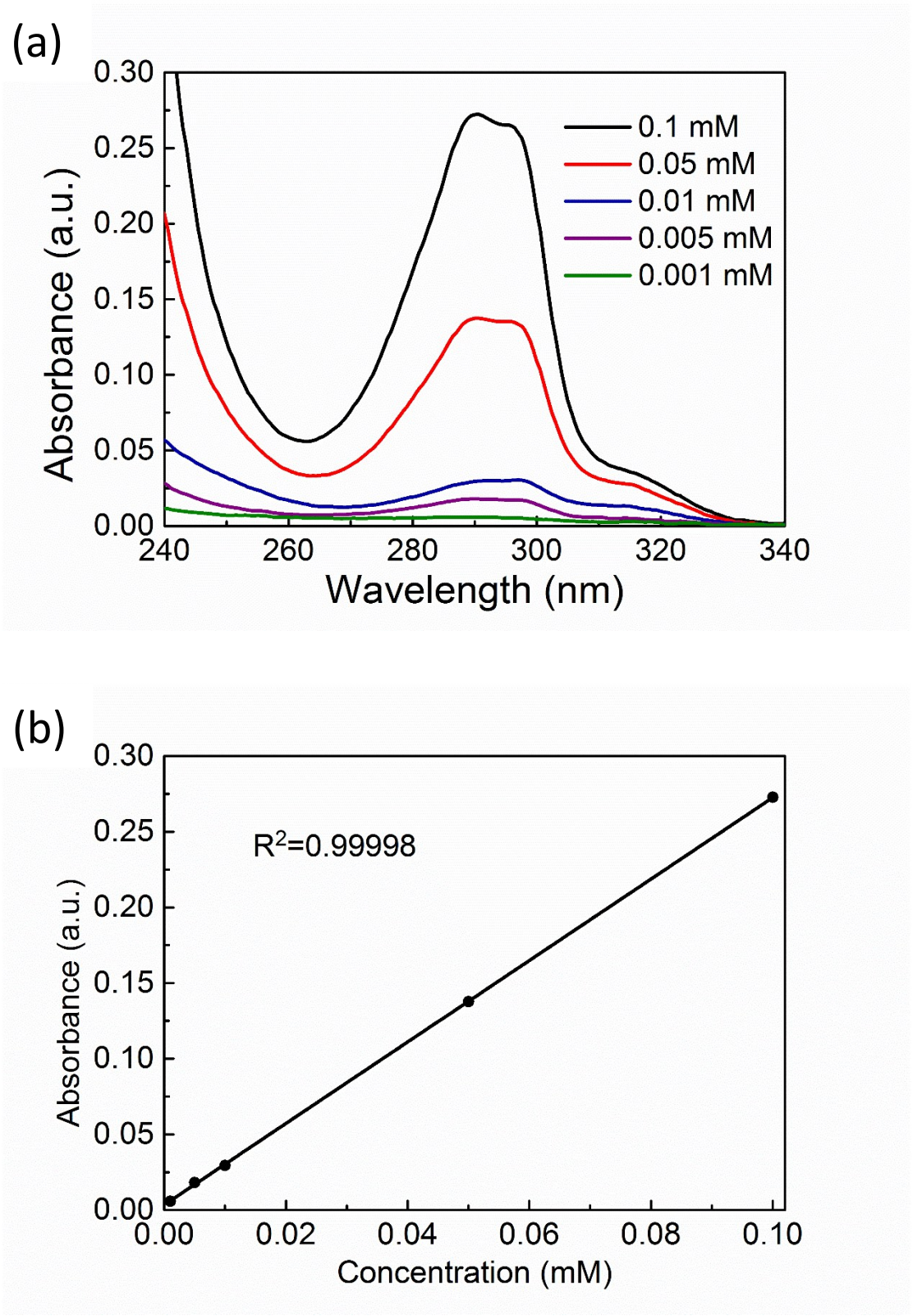


Fig. S14 (a) UV-Vis spectra of TCP of different concentrations. (b) Standard curve plotted based on the absorbance at 290.5 nm.

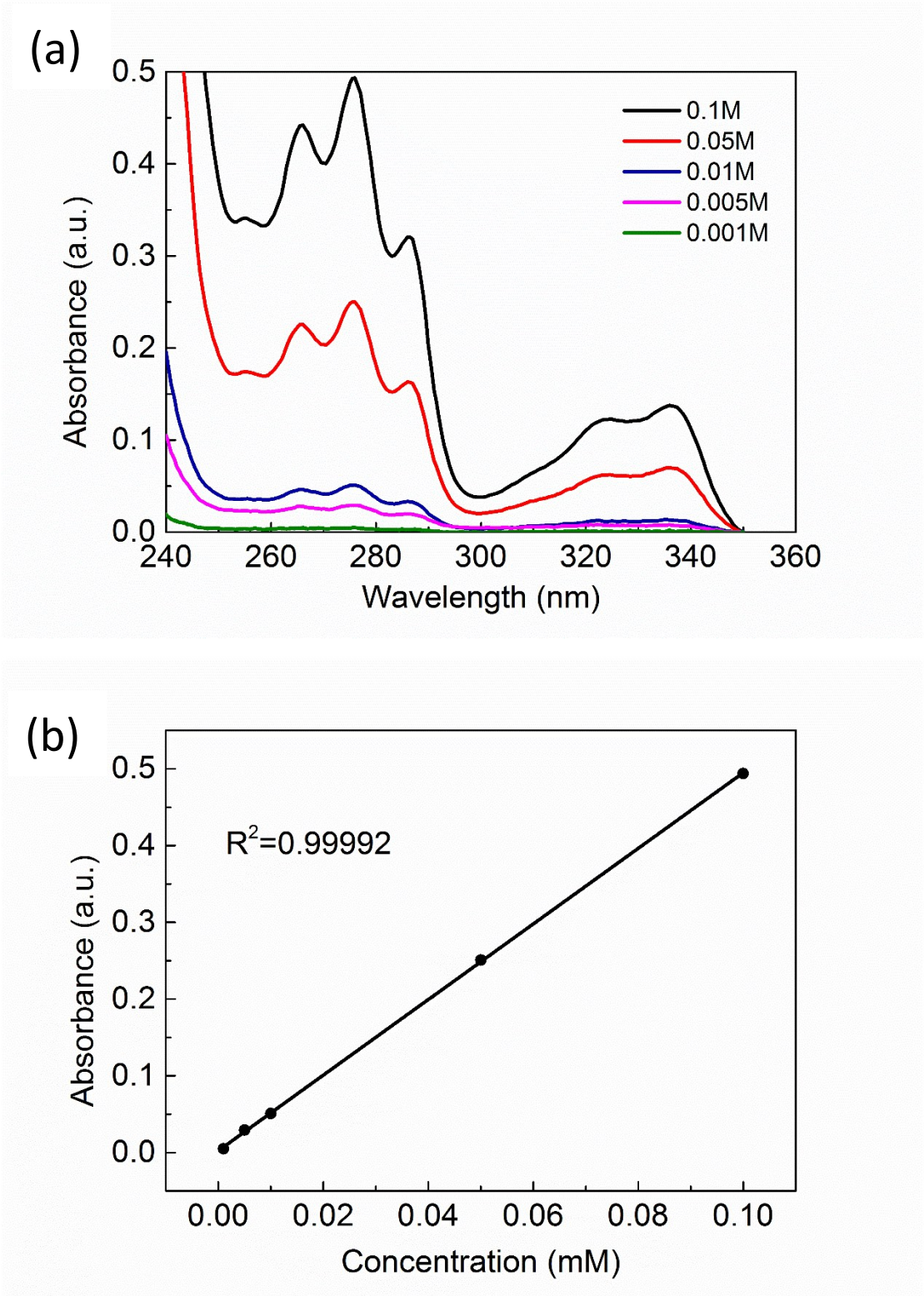


Fig. S15 (a) UV-Vis spectra of BNP of different concentrations. (b) Standard curve plotted based on the absorbance at 275.5 nm.

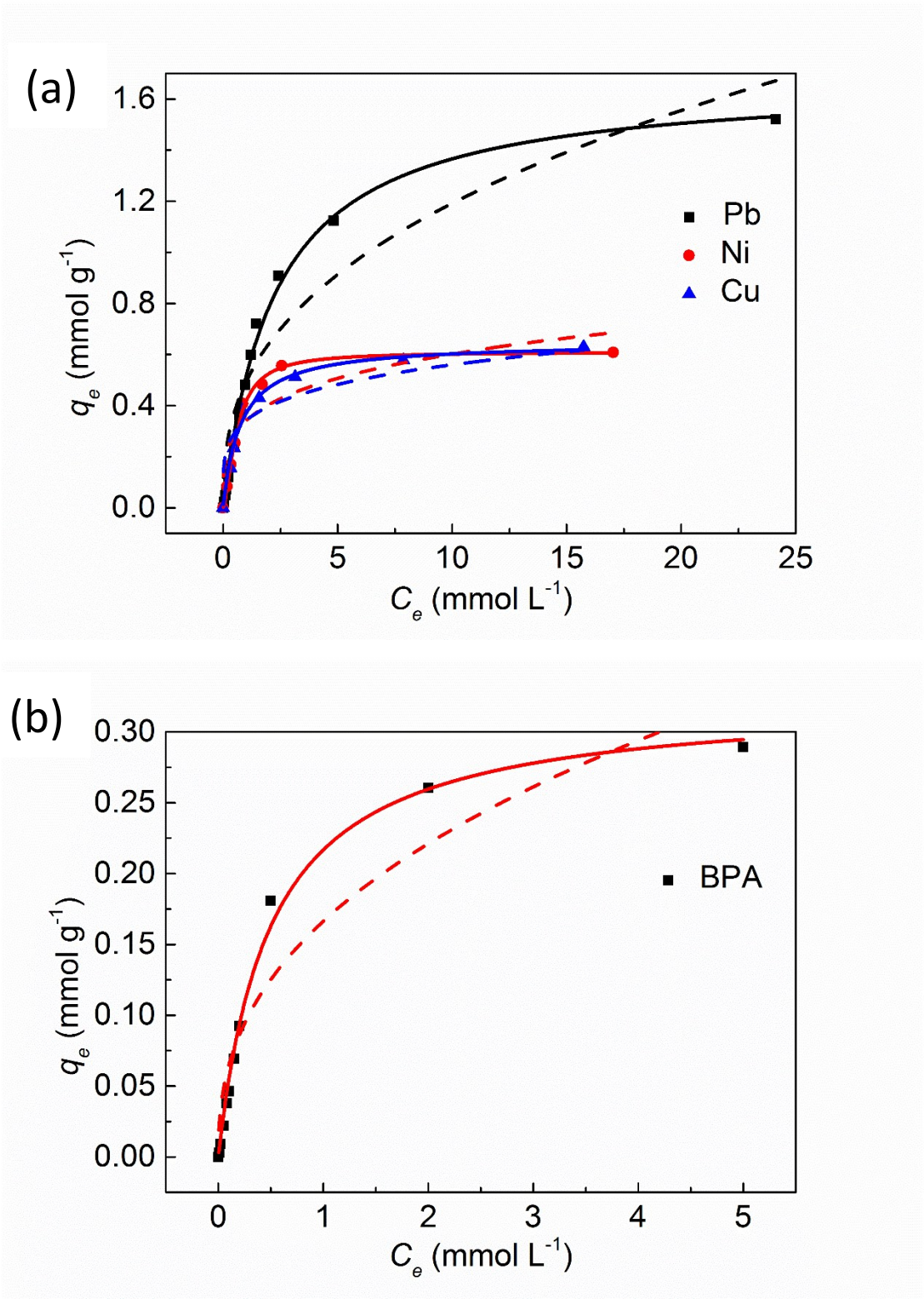


Fig. S16 Adsorption isotherms of metals (a) and BPA (b) on P-CDEC, fitting by Langmuir and Freundlich models. The solid line represents Langmuir models, the dash line represents Freundlich models.

Table S3 Adsorption capacity ($\mathbf{q_e}$) of P-CDEC in different initial concentrations ($\mathbf{C_0}$) of pollutants

Pollutants	C_0 (mmol L^{-1})	q_e (mmol g^{-1})
Pb (II)	4.8	1.12
	24.1	1.52
Ni (II)	2.5	0.56
	17	0.61
Cu (II)	3.1	0.51
	15.7	0.63
BPA	2	0.26
	5	0.29

Table S4 Isotherm parameters of Langmuir and Freundlich models for metals and organic pollutants adsorption

Pollutants	Langmuir model			Freundlich model		
	q_m (mmol g^{-1})	K_L (L mg^{-1})	R^2	K_F (mmol g^{-1})	n_F	R^2
Pb(II)	1.675	0.442	0.993	0.493	2.6	0.883
Ni(II)	0.471	6.341	0.984	0.341	4.1	0.673
Cu(II)	0.648	1.324	0.965	0.343	4.7	0.799

Adsorption Isotherms

The Langmuir and Freundlich,[2] as two well-known and widely used models, were employed to fit the adsorption equilibrium data of heavy metal ions and organic pollutants on P-CDEC. The Langmuir model is based on homogeneous adsorption. The binding sites have the same adsorption affinity and no interactions between adsorbates. The Langmuir equation is:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (1)$$

where q_e (mg g^{-1}) is the equilibrium adsorption capacity of the adsorbate, q_m (mg g^{-1}) is the maximum adsorption capacity of adsorbent, and C_e (mg L^{-1}) is the equilibrium concentration of the adsorbate, while K_L (L mg^{-1}) is the Langmuir adsorption constant.

The Freundlich model expects the adsorption on a heterogeneous surface without saturation of adsorbent binding sites:

$$q_e = K_F C_e^{1/n_F} \quad (2)$$

where q_e (mg g^{-1}) is the equilibrium adsorption capacity of the adsorbate, K_F (mg g^{-1}) is a unit capacity coefficient C_e (mg L^{-1}) is the equilibrium concentration of the adsorbate, and n_F is the Freundlich parameter related to the degree of system heterogeneity.

Figs. S15a and S15b illustrate that, compared with the Freundlich model, the Langmuir model is fitter with the experimental data for both heavy metal ions and organic pollutants. This is further confirmed by its correlation coefficients R^2 values (Table S4). It might indicate homogeneous distribution of adsorption active sites for metal ions and organic pollutants.

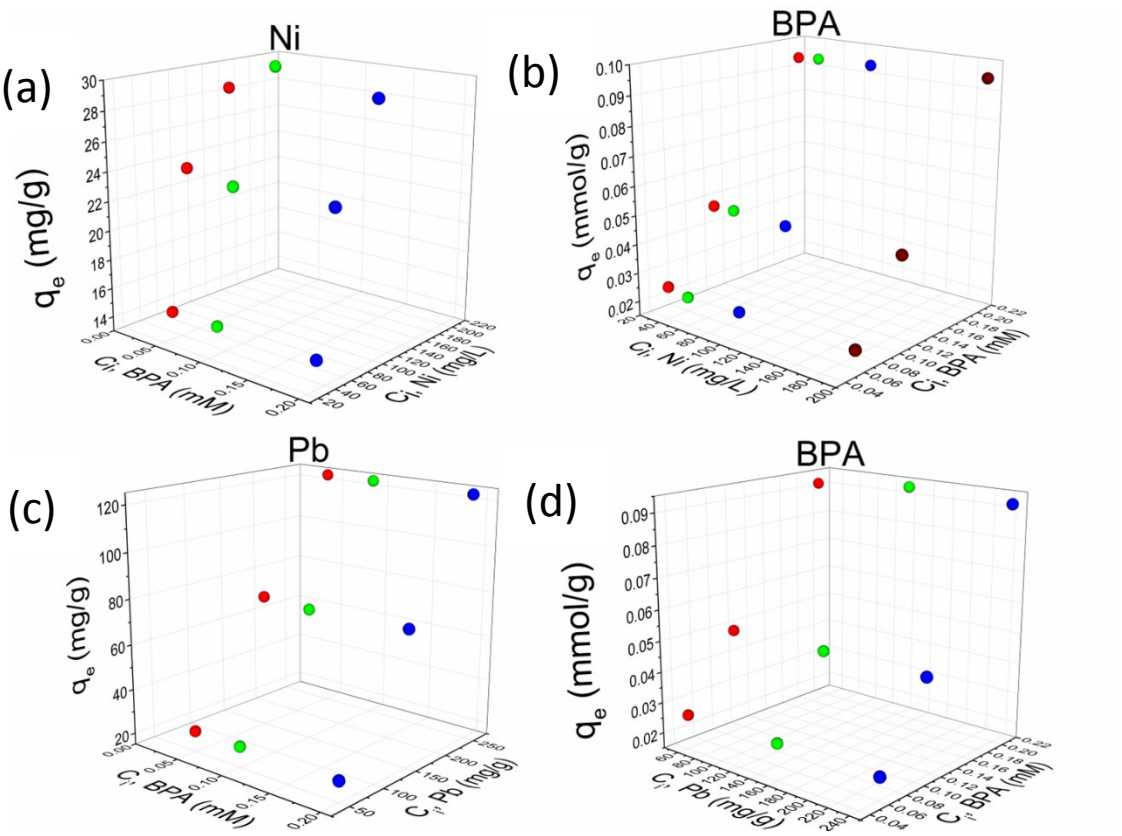


Fig. S17 Simultaneous adsorption of Cu(II), MB, SO, and CV on P-CDEC using binary solutions. Experimental conditions: 25 °C, pH 4.5, adsorbent dose 2 g L^{-1}, and contact time 20min. The initial concentrations: for Ni(II) 30 mg L^{-1} (red), 50 mg L^{-1} (green), 100 mg L^{-1} (blue), 200 mg L^{-1} (brown); for Pb(II) 50 mg L^{-1} (red), 150 mg L^{-1} (green), 250 mg L^{-1} (blue); for BPA 0.05mM (red), 0.1mM (green), 0.2mM (blue).

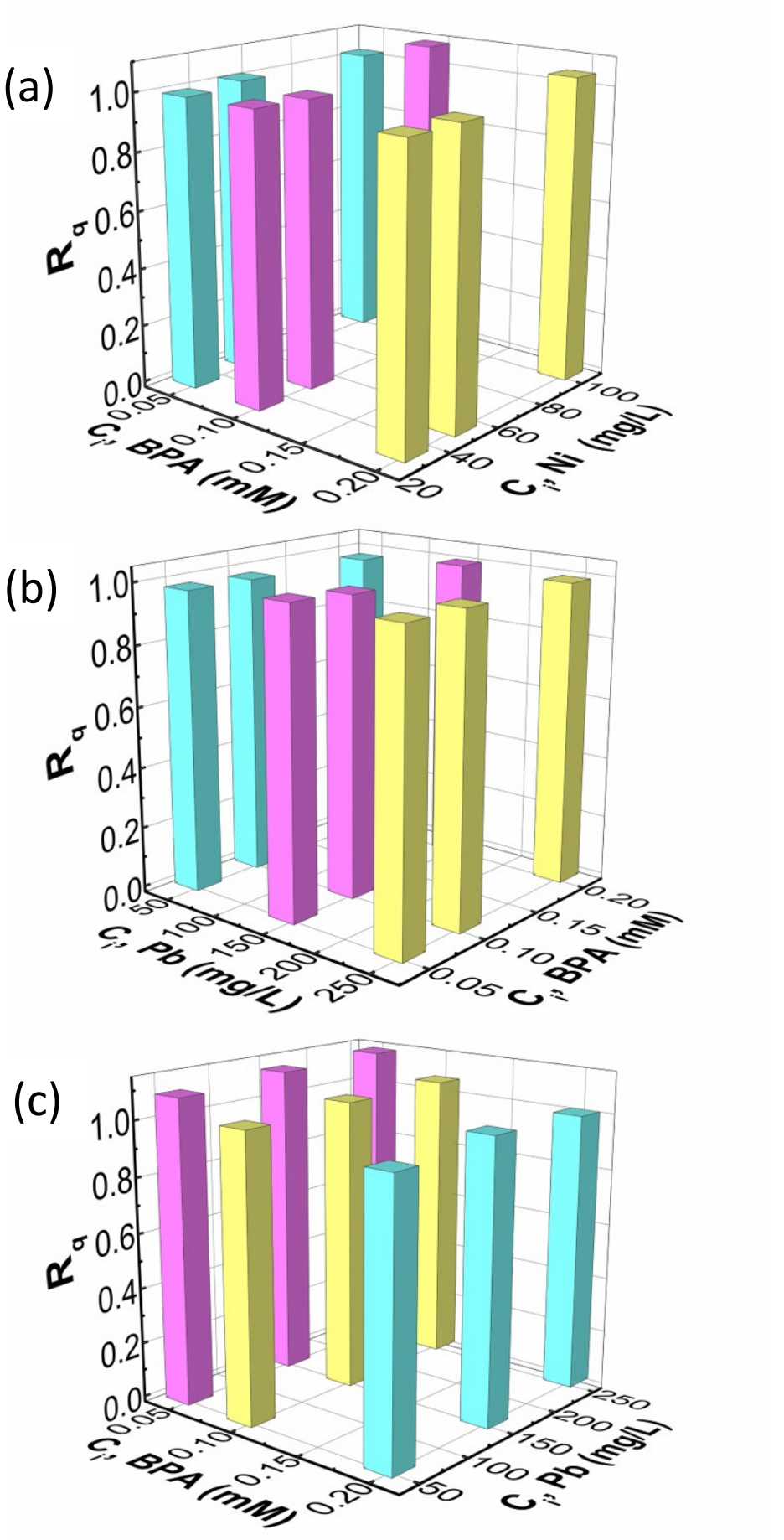

(a)
R_q
1.0
0.8
0.6
0.4
0.2
0.0
$C_{i,1}$ BPA (mM)
0.05
0.10
0.15
0.20
$C_{i,2}$ Ni (mg/L)
20
40
60
80
100
(b)
R_q
1.0
0.8
0.6
0.4
0.2
0.0
$C_{i,1}$ Pb (mg/L)
50
100
150
200
250
$C_{i,2}$ BPA (mM)
0.05
0.10
0.15
0.20
(c)
R_q
1.0
0.8
0.6
0.4
0.2
0.0
$C_{i,1}$ BPA (mM)
0.05
0.10
0.15
0.20
$C_{i,2}$ Pb (mg/L)
50
100
150
200
250

Fig. S18 Simultaneous adsorption studies P-CDEC. R_q versus the initial concentration of binary solutions for the simultaneous removal of BPA, Ni(II) and Pb(II) using P-CDEC. The initial concentrations: for Ni(II) 30 mg L^{-1} (cyan), 50 mg L^{-1} (magenta), 100 mg L^{-1} (yellow); for Pb(II) 50 mg L^{-1} (cyan), 150 mg L^{-1} (magenta), 250 mg L^{-1} (yellow); for BPA 0.05mM (magenta), 0.1mM (yellow), 0.2mM (cyan). (Dose, 2 g L^{-1}; pH 4.5)

(1) Zhao, F.; Repo, E.; Yin, D.; Meng, Y.; Jafari, S.; Sillanpää, M. EDTA-cross-linked β-cyclodextrin: an environmentally friendly bifunctional adsorbent for simultaneous adsorption of metals and cationic dyes. *Environ. Sci. Technol.* **2015**, *49*, 10570-10580.

(2) Wong, Y.; Szeto, Y.; Cheung, W.; McKay, G. Equilibrium studies for acid dye adsorption onto chitosan. *Langmuir* **2003**, *19*, 7888-7894.