Supporting Information

Pb(II), Cu(II) and Cd(II) Removal using Humic Substances Based Double Network Hydrogel in Individual and Multicomponent Systems

Jianhong Ma, [ab] Jinming Luo, *[c] Yutang Liu, *[ab] Yuanfeng Wei, [d] Tao Cai, [ab] Xingwen Yu, [d] Hui Liu, [d] Chengbin Liu, [d] and John C. Crittenden [c]

[a] *College of Environmental Science and Engineering, Hunan University, Lushan South Road, Yuelu District, Changsha 410082, P. R. China*

[b] *Key Laboratory of Environmental Biology and Pollution Control (Hunan University), Ministry of Education, Lushan South Road, Yuelu District, Changsha 410082, P.R. China*

[c] *Brook Byers Institute for Sustainable Systems and School of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, 30332, United States*

[d] *State Key Laboratory of Chemo/Biosensing and Chemometrics, Hunan University, Lushan South Road, Yuelu District, Changsha 410082, P. R. China*

Corresponding author

Jinming Luo

Brook Byers Institute for Sustainable Systems and School of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, 30332, United States

E-mail address: jinming.luo@ce.gatech.edu (J. M. Luo)

Yutang Liu

College of Environmental Science and Engineering, Hunan University, Lushan South Road, Yuelu District, Changsha 410082, P. R. China

E-mail address: yt_liu@hnu.edu.cn (Y. T. Liu)

Cost analysis

The reference to the price of each material is mainly from Alibaba official website. The chemicals used in the experiment are shown below: humic substances (US\$ 0.3×10^3/t), acrylic acid (US\$ 1.5×10^3/t), sodium hydroxide (US\$ 0.3×10^3/t), urea (US\$ 0.4×10^3/t), potassium persulfate (US\$ 1.2×10^3/t), N, N-methylenebisacrylamide (US\$ 1.8×10^4/t), and hydrochloric acid (US\$ 3.5×10^3/t). According to the synthetic ratio, the cost of dried PAA/HS gel is approximately US\$ 2.0×10^3/t.

Selective adsorption

The selectivity of PAA/HS gel for the best removed meta ion (M_B(II)) over other metal ions can be appraised by the selectivity coefficient (M_B(II)/ M(II)), which is expressed as Eq. S1 and Eq. S2:

$$\beta_{M_B(II)/M(II)} = \frac{D_{M_B(II)}}{D_{M(II)}} \quad \text{(S1)}$$

$$D = \frac{C_0 - C_e}{C_e} \times \frac{V}{W} \quad \text{(S2)}$$

where $D_{MB(II)}$ and $D_{M(II)}$ are the distribution ratios (D) of the M_B(II) and other coexisted metal ions, respectively; C_0 (mg/L) and C_e (mg/L) are the concentrations of metal ions before and after adsorption, respectively; V (L) is the volume of solution and W (g) is the mass of adsorbent.

Adsorption models and thermodynamics.

The Langmuir, Freundlich and Langmuir-Freundlich mathematical forms can be described as the following non-linear equation (Eq. S3), (Eq. S4) and (Eq. S5), respectively:

$$Q_e = \frac{Q_m \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \quad \text{(S3)}$$

$$Q_e = K_F \cdot {C_e}^{1/n} \quad \text{(S4)}$$

$$Q_e = \frac{K_{LF} {C_e}^{1/n_{LF}}}{1 + a_{LF} {C_e}^{1/n_{LF}}} \quad \text{(S5)}$$

where C_e (mg/L) is the equilibrium concentration of metal ions, Q_e (mg/g) is the equilibrium sorption capacity, Q_m (mg/g) is the maximum monolayer metal ions coverage capacity per unit weight of adsorbent, K_L (L/mg), K_F ($mg^{1-n} \cdot L^n/g$), K_{LF} ((mg/g)·$(mg/L)^{n_{LF}}$) and a_{LF} ($(mg/L)^{n_{LF}}$) are the corresponding adsorption equilibrium constants, n and n_{LF} are the adsorption intensity and heterogeneity parameter, respectively.

The Dubinin-Radushkevish (D-R) isotherm is applied to estimate the adsorption energy. It is often expressed as (Eq. S6-8):

$$Q_e = Q_m exp(-k\varepsilon^2) \quad \text{(S6)}$$

$$\varepsilon = RT\ In\left(1 + \frac{1}{C_e}\right) \quad \text{(S7)}$$

$$E = (2k)^{-\frac{1}{2}} \quad \text{(S8)}$$

where Q_m (mol/g) is the D-R maximum adsorption capacity, k (mol^2/kJ^2) is the constant related to the adsorption energy, the Polanyi sorption potential ε (J/mol) is the amount of energy required to pull adsorbed molecule from its sorption site and E is the free energy (kJ/mol).

The separation factor (R_L) (Eq. S9):

$$R_L = \frac{1}{1 + K_L C_0} \quad \text{(S9)}$$

where K_L (L/mg) refers to the Langmuir constant and C_0 is the adsorbate initial concentration (mg/L). The R_L value indicates the adsorption nature to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

The isosteric heat of adsorption (ΔH_x) defined as the heat of adsorption determined at constant amount of adsorbate adsorbed is calculated using the Clausius-Clapeyron equation (Eq. S10):

$$\frac{d(lnC_e)}{dT} = -\frac{\Delta H_x}{RT^2} \quad \text{(S10)}$$

where C_e (mg/L) is the equilibrium adsorbate concentration in the solution, ΔH_x (kJ/mol) is the isosteric heat of adsorption, R (8.314 J/(mol·K)) is the ideal gas constant, and T (K) is the temperature in Kelvin. Generally, the ΔH_x values of adsorption at different surface coverage are used to explore the characterization of adsorption process, and the ΔH_x values would have been constant even with variation in surface loading if the adsorbent were a homogeneous surface.

Thermodynamic parameters such as free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) were according to van't Hoff equation (Eq. S11, S12):

$$\Delta G^0 = -RT \ln K^0 \qquad \text{(S11)}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad \text{(S12)}$$

where R (8.314 J/(mol·K)) is the ideal gas constant, T (K) is the temperature in Kelvin, and K^0 is the sorption equilibrium constant which can be calculated by plotting $\ln K_d$ versus C_e and extrapolating C_e to zero.

Adsorption kinetics

The elovich, pseudo-first-order, pseudo-second-order and intraparticle diffusion models were used to describe the experimental adsorption kinetic data. The mathematical equations of the elovich equation (Eq. S13), pseudo-first-order model (Eq. S14), pseudo-second-order model (Eq. S15) and intraparticle diffusion model (Eq. S16) are expressed:

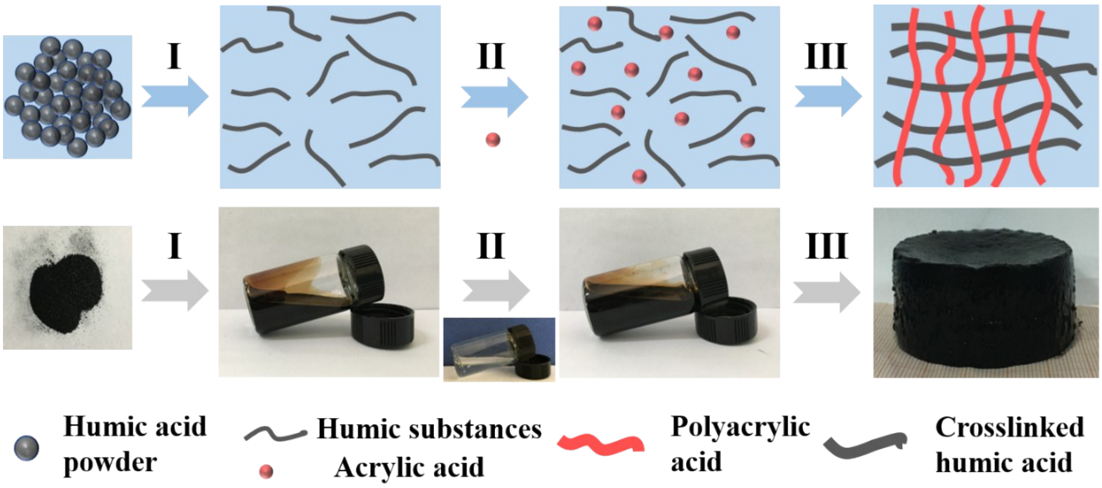
$$Q_t = \frac{1}{\beta} ln(\alpha\beta) + \frac{1}{\beta} lnt \qquad \text{(S13)}$$

$$Q_t = Q_e(1 - exp(-k_1 t)) \qquad \text{(S14)}$$

$$Q_t = Q_e\left(1 - \frac{1}{1 + q_e k_2 t}\right) \qquad \text{(S15)}$$

$$Q_t = k_p t^{0.5} \qquad \text{(S16)}$$

where α is the initial sorption rate constant (mg/g min); and the parameter β is related to the extent of surface coverage and activation energy for chemisorption (g/mg); Q_t (mg/g) is the sorbed quantity at time t; Q_e (mg/g) is the sorbed metal quantity at equilibrium; k_1 (L/min), k_2 (g/(mg·min)) and k_p (min^{-1}) are the corresponding adsorption rate constants.



Scheme S1. Preparation of PAA/HS gel. (I) Dissolution of HS powder, (II) preparation of sol containing HS solution, AA, MBA and KPS, (III) the gelation of the obtained sol.

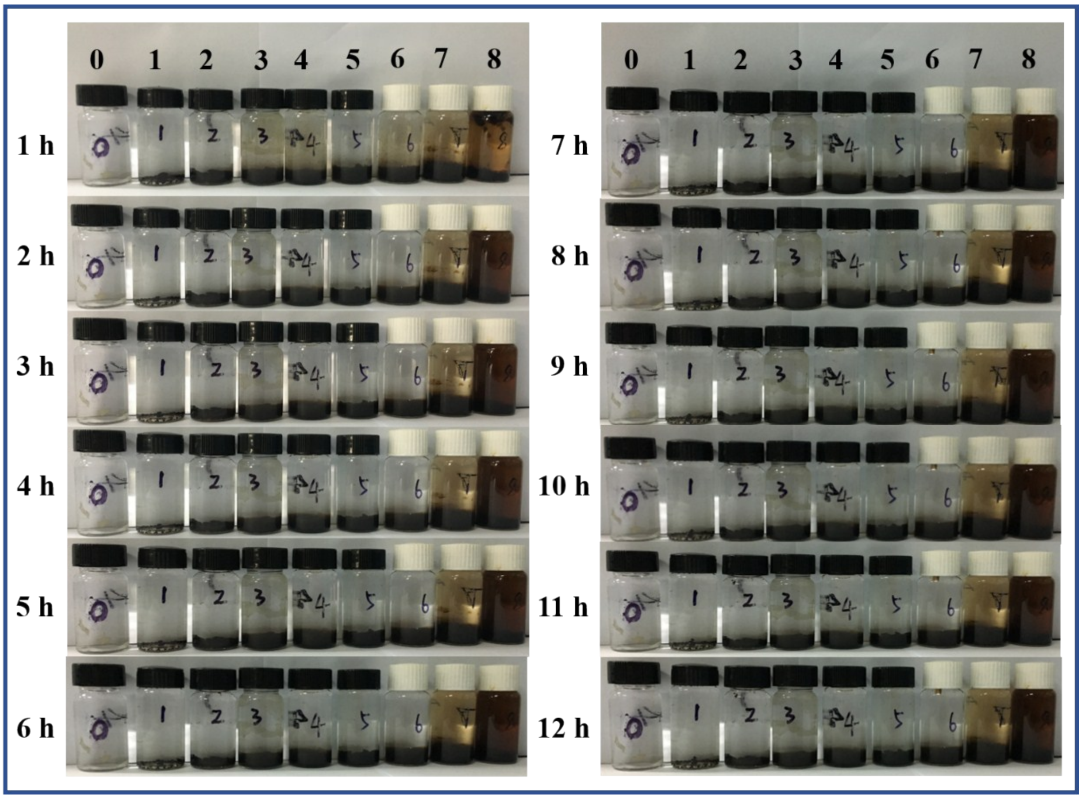


Fig. S1. The stability of PAA/HS gel in solutions with different pH values. The pH value of samples 0 to 8 are 5.98 (deionized water), 1.00, 3.00, 5.00, 5.98 (deionized water), 7.31 (tap water), 9.00, 11.00, and 13.00, respectively.

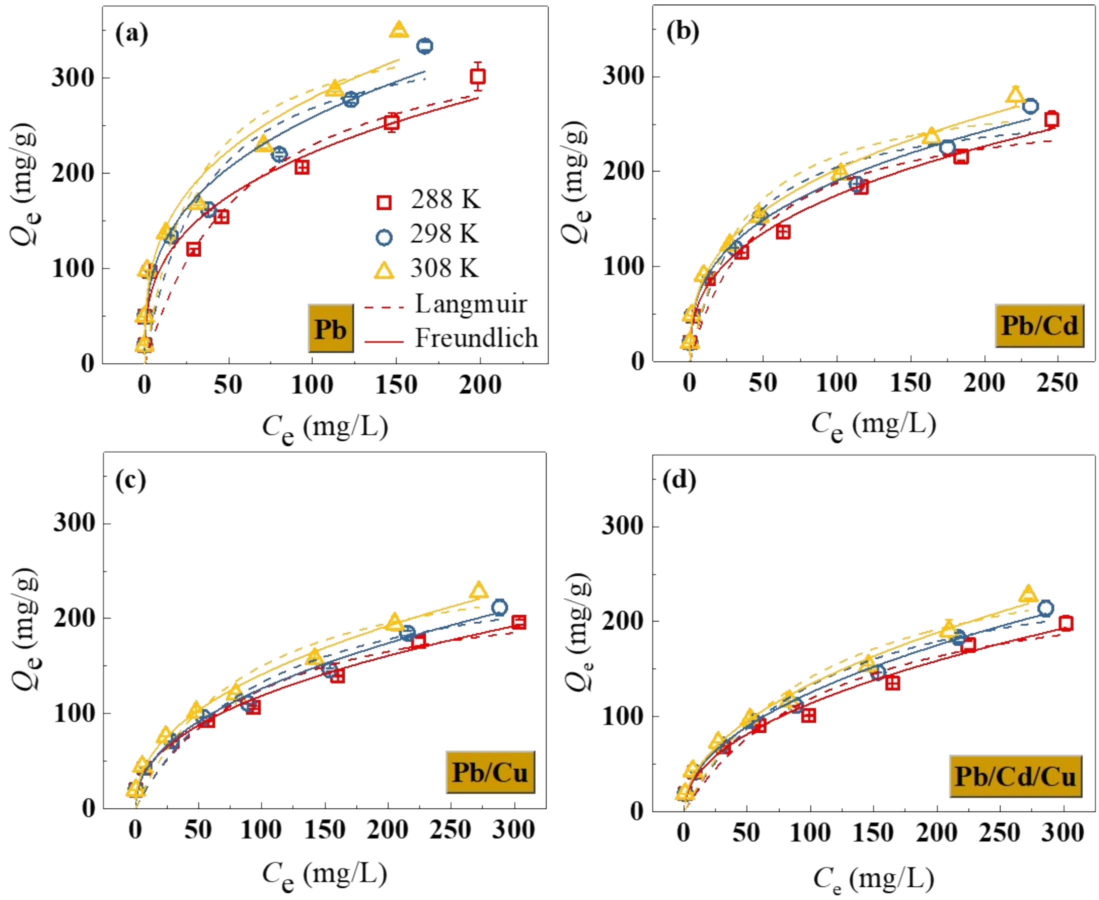


Fig. S2. Adsorption isotherms of Pb(II) on PAA/HS gel in the system of (a) Pb(II), (b) Pb(II)/Cd(II), (c) Pb(II)/Cu(II), and (d) Pb(II)/Cd(II)/Cu(II), $t_{contact}$ = 6 h, pH = 5.00 ± 0.01, m/V = 1 g/L.

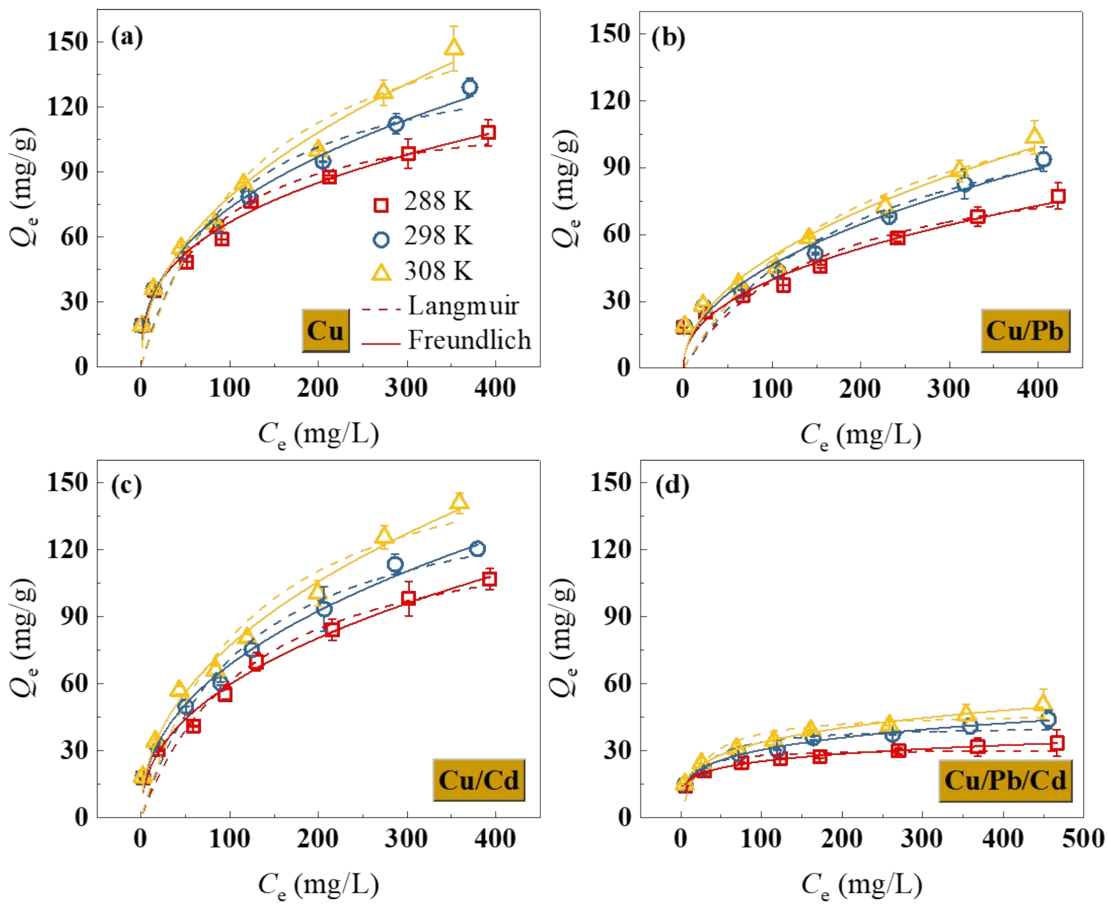


Fig. S3. Adsorption isotherms of Cu(II) on PAA/HS gel in the system of (a) Cu(II), (b) Cu(II)/Pb(II), (c) Cu(II)/Cd(II), and (d) Cu(II)/Pb(II)/Cd(II), $t_{contact}$ = 6 h, pH = 5.00 ± 0.01, m/V = 1 g/L.

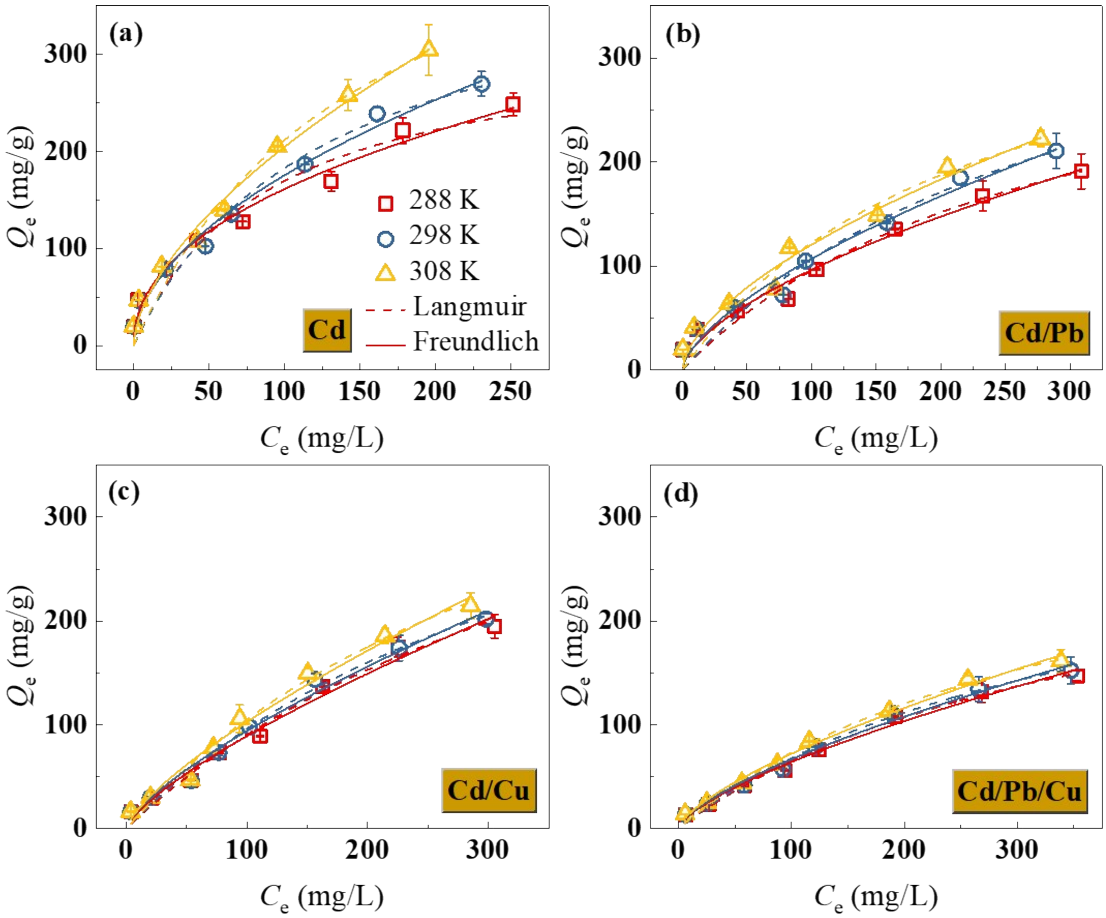


Fig. S4. Adsorption isotherms of Cd(II) on PAA/HS gel in the system of (a) Cd(II), (b) Cd(II)/Pb(II), (c) Cd(II)/Cu(II), and (d) Cd(II)/Pb(II)/Cu(II), $t_{contact}$ = 6 h, pH = 5.00 ± 0.01, m/V = 1 g/L.

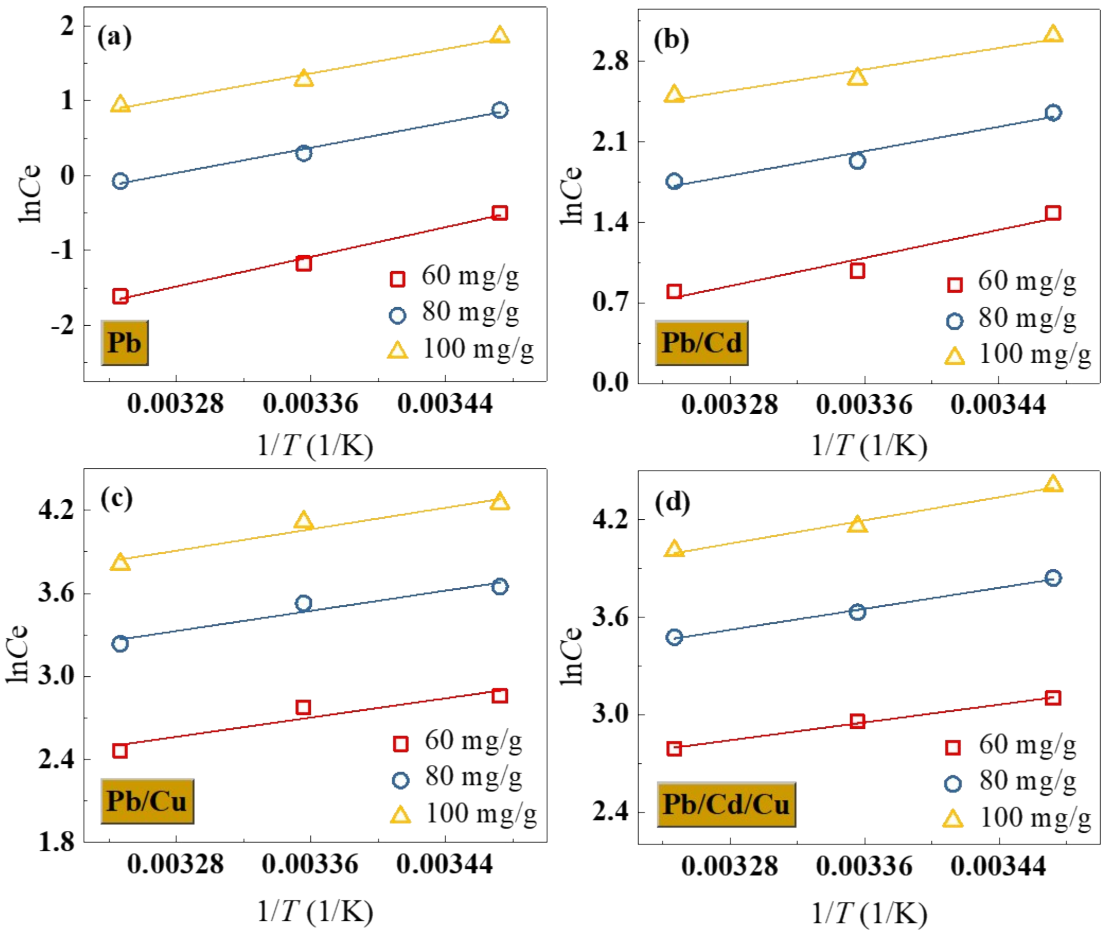


Fig. S5. Plot of lnC_e versus 1/T for Pb(II) adsorption on PAA/HS gel in the system of (a) Pb(II), (b) Pb(II)/Cd(II), (c) Pb(II)/Cu(II), and (d) Pb(II)/Cd(II)/Cu(II).

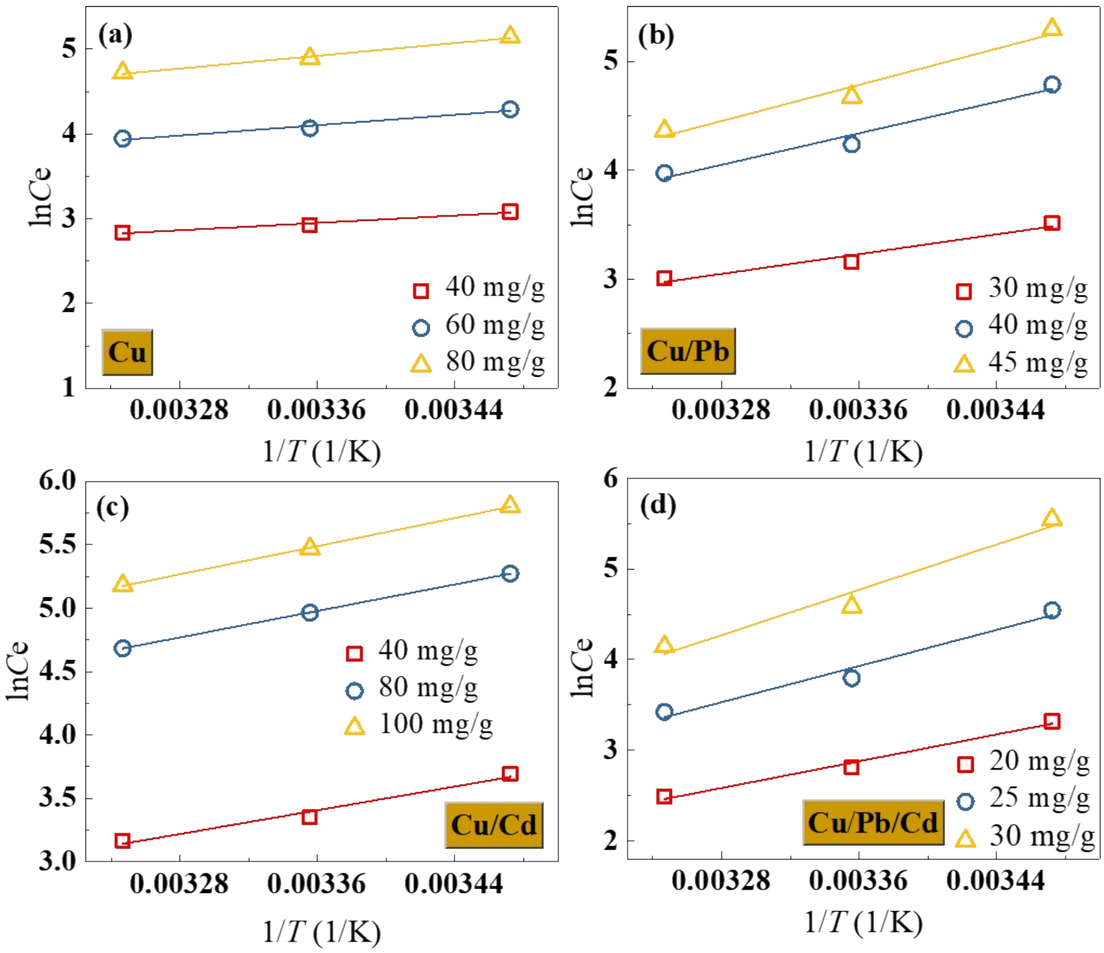


Fig. S6. Plot of lnC_e versus 1/T for Cu(II) adsorption on PAA/HS gel in the system of (a) Cu(II), (b) Cu(II)/Pb(II), (c) Cu(II)/Cd(II), and (d) Cu(II)/Pb(II)/Cd(II).

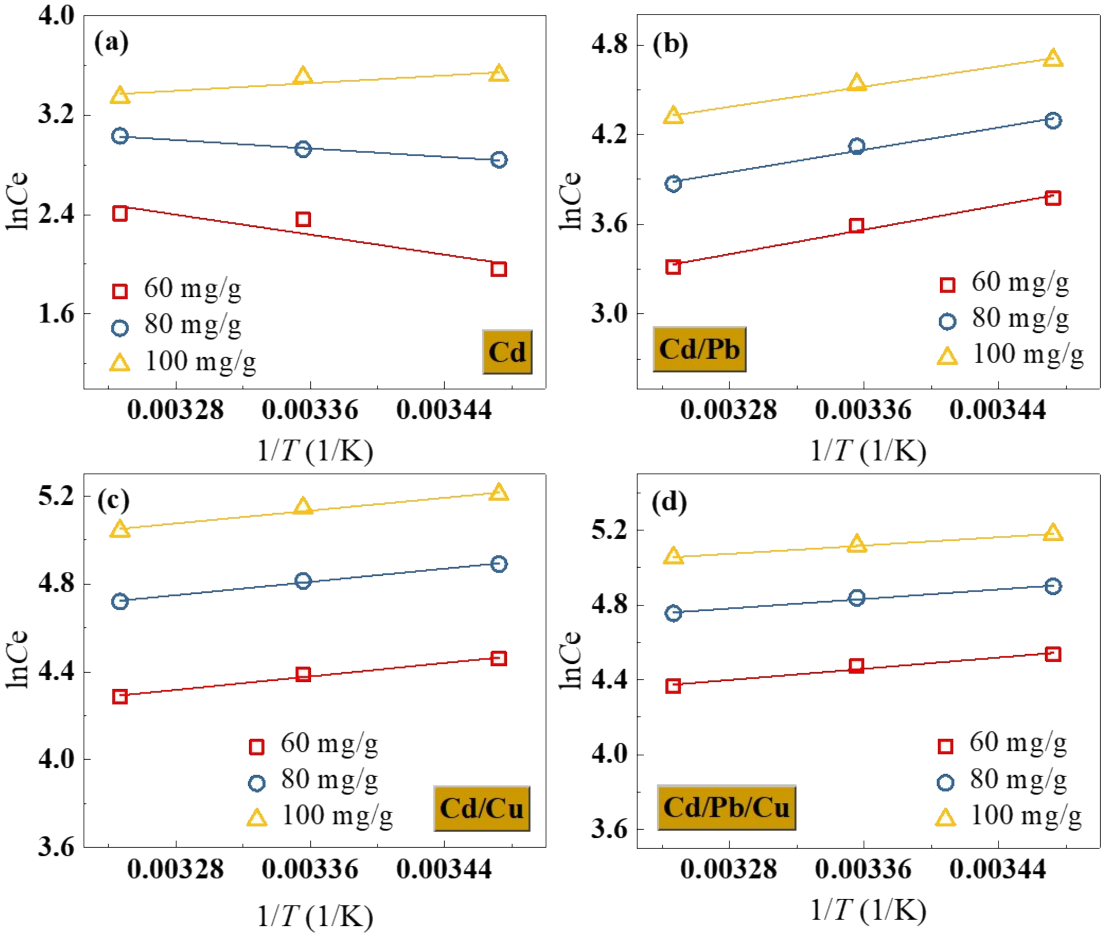


Fig. S7. Plot of lnC_e versus 1/*T* for Cd(II) adsorption on PAA/HS gel in the system of (a) Cd(II), (b) Cd(II)/Pb(II), (c) Cd(II)/Cu(II), and (d) Cd(II)/Pb(II)/Cu(II).

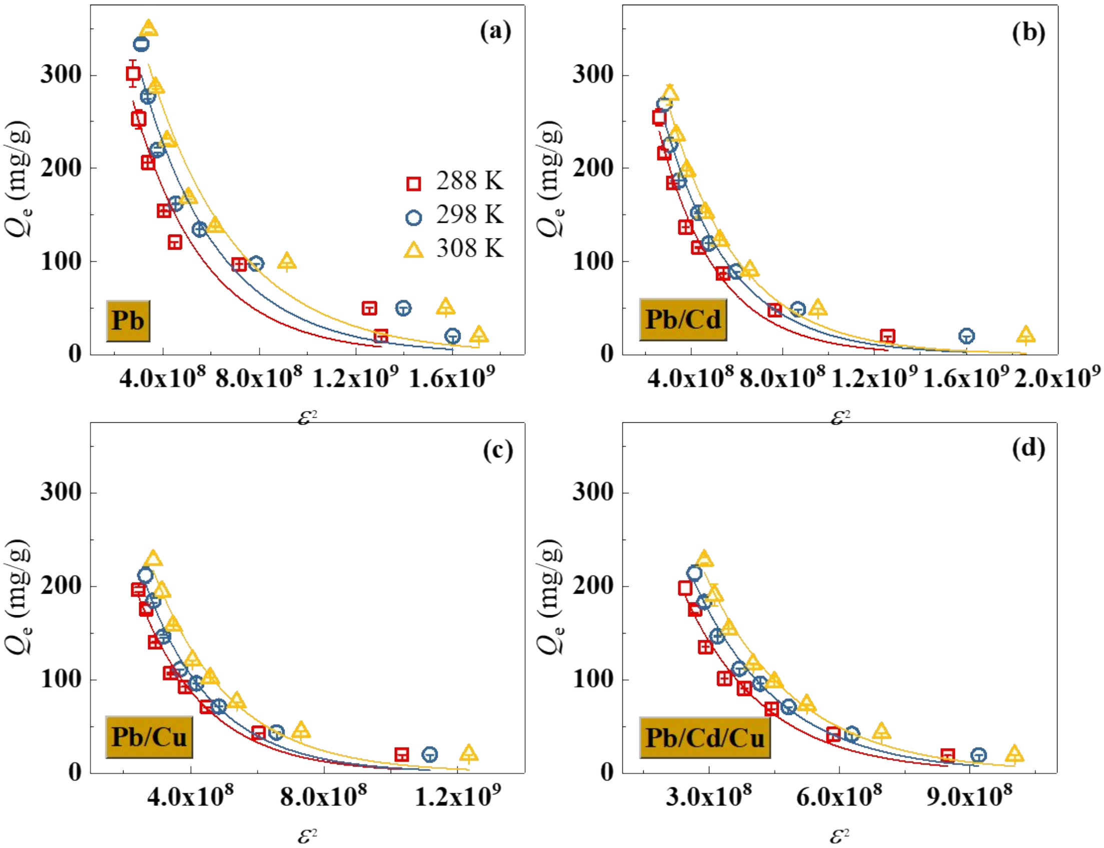


Fig. S8. Nonlinear curves of ε^2 vs. Q_e for adsorption of Pb(II) on PAA/HS gel in the system of (a) Pb(II), (b) Pb(II)/Cd(II), (c) Pb(II)/Cu(II), and (d) Pb(II)/Cd(II)/Cu(II).

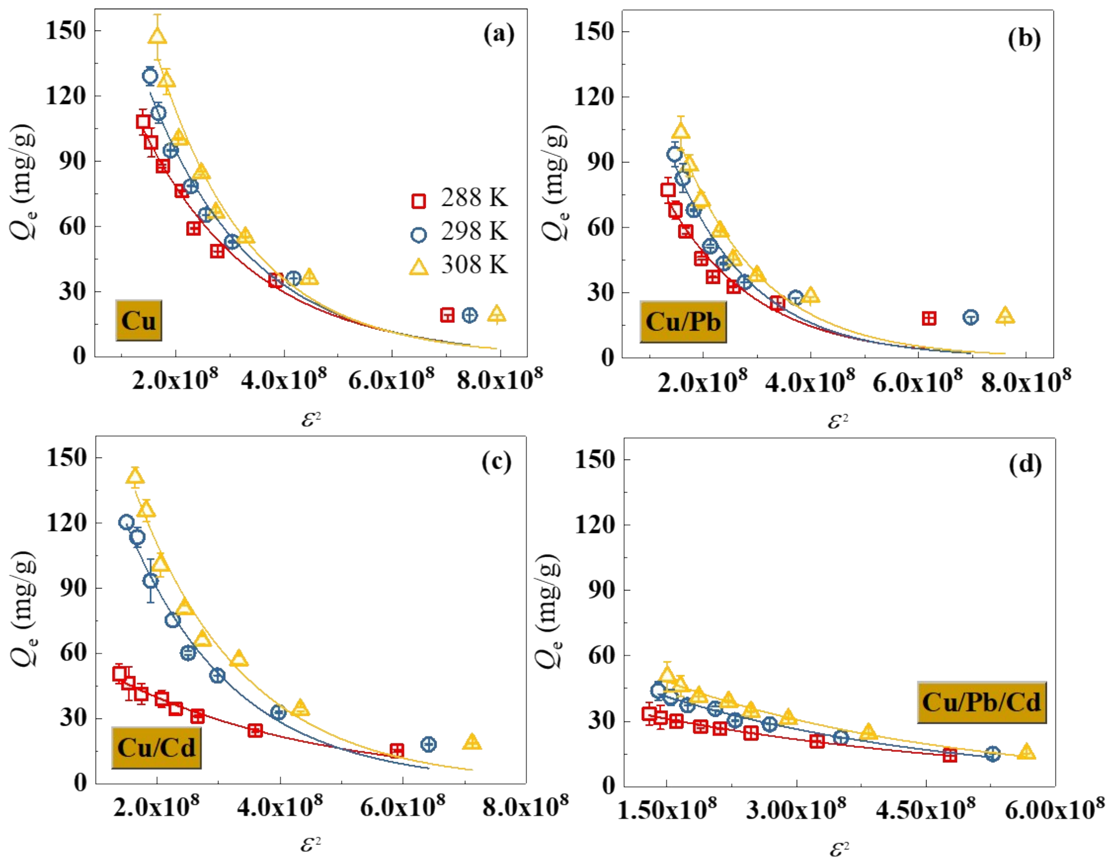


Fig. S9. Nonlinear curves of ε^2 vs. Q_e for adsorption of Cu(II) on PAA/HS gel in the system of (a) Cu(II), (b) Cu(II)/Pb(II), (c) Cu(II)/Cd(II), and (d) Cu(II)/Pb(II)/Cd(II).

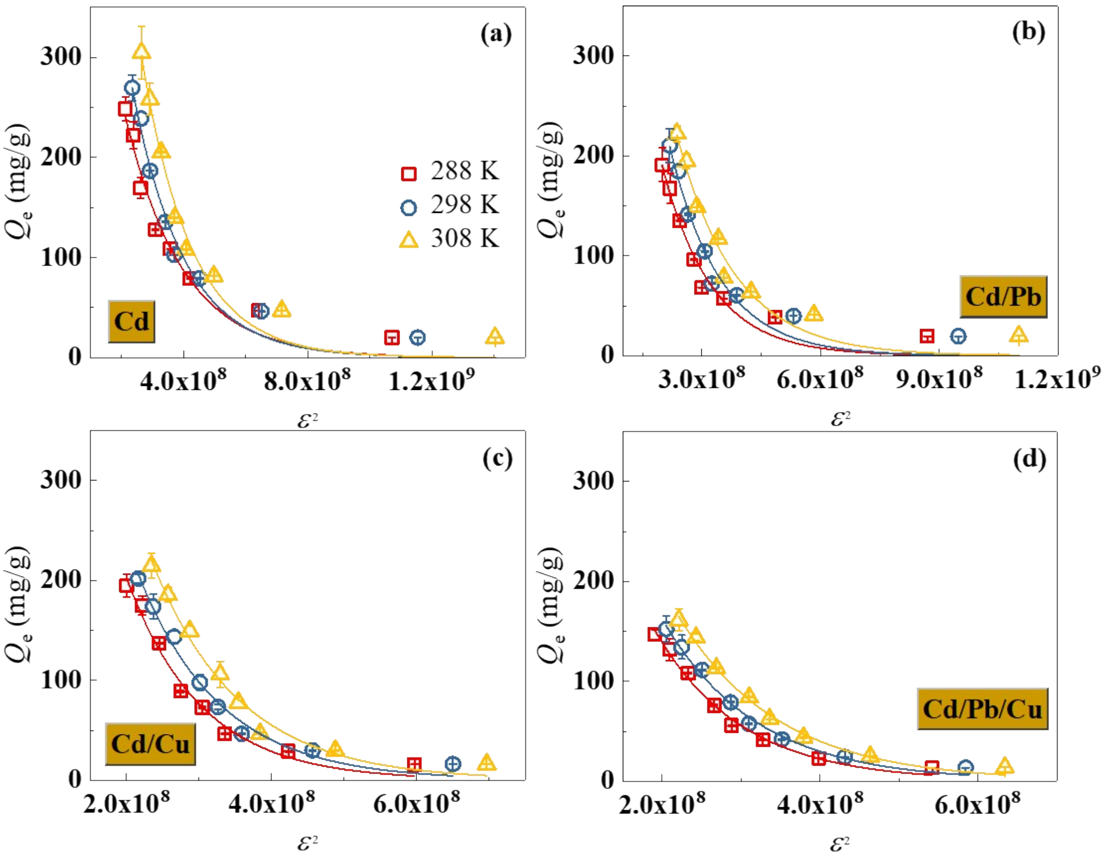


Fig. S10. Nonlinear curves of ε^2 vs. Q_e for adsorption of Cd(II) on PAA/HS gel in the system of (a) Cd(II), (b) Cd(II)/Pb(II), (c) Cd(II)/Cu(II), and (d) Cd(II)/Pb(II)/Cu(II).

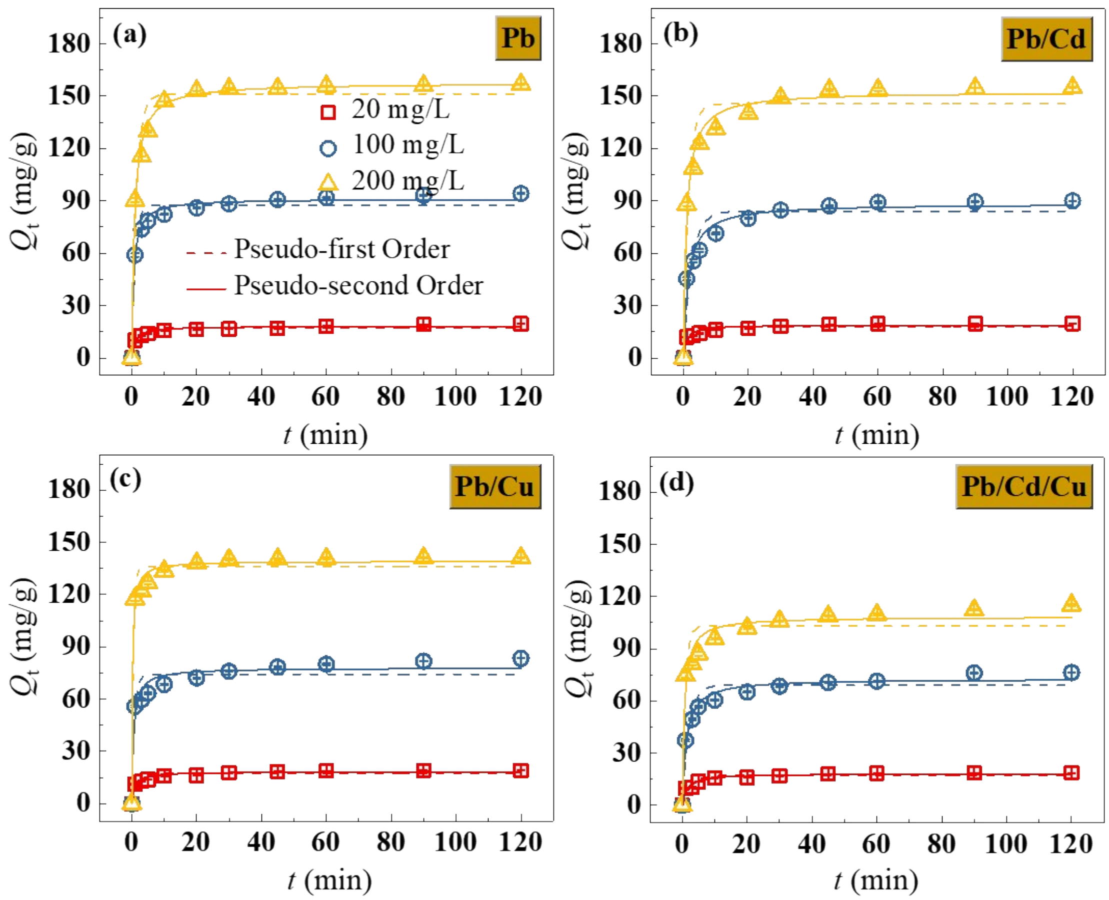


Fig. S11. Time-dependent adsorption of Pb(II) on PAA/HS gel in the system of (a) Pb(II), (b) Pb(II)/Cd(II), (c) Pb(II)/Cu(II), and (d) Pb(II)/Cd(II)/Cu(II), C_0 = 20/100/200 mg/L, T = 298 K, pH = 5.00 ± 0.01, m/V = 1 g/L.

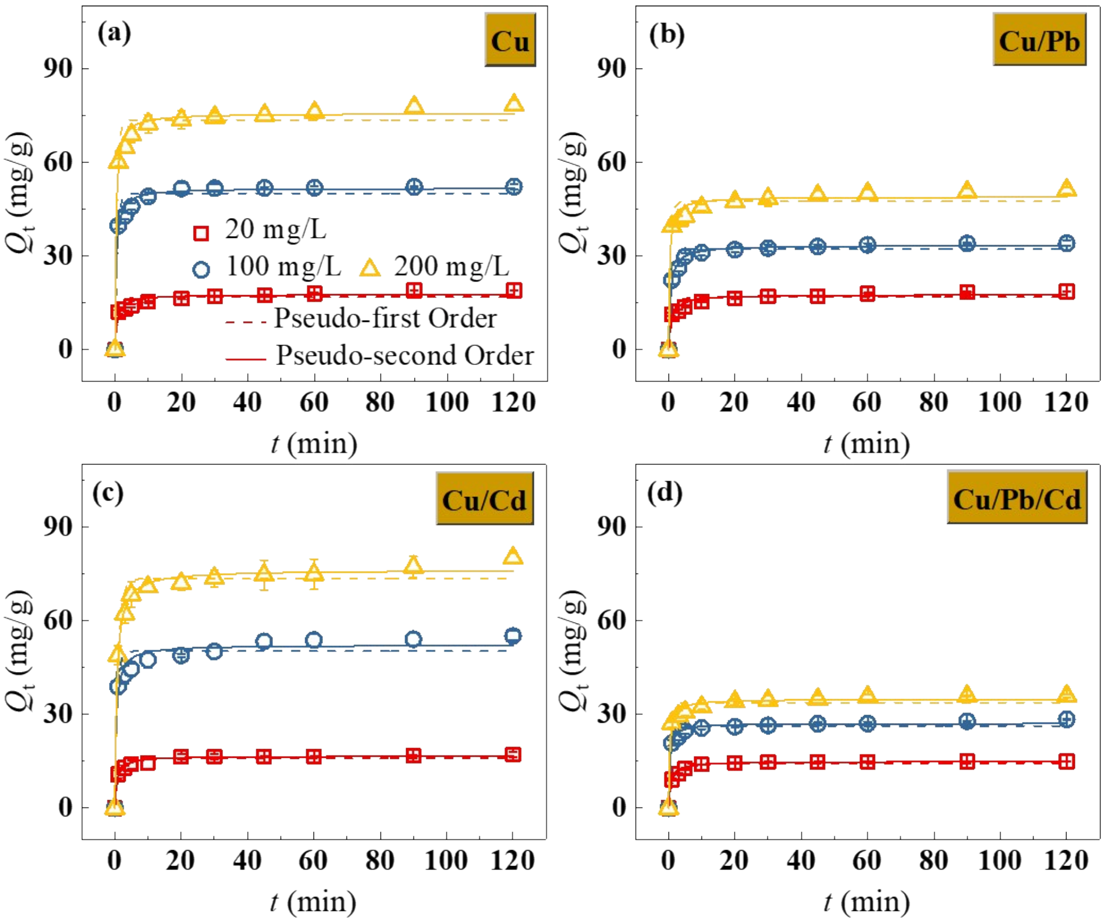


Fig. S12. Time-dependent adsorption of Cu(II) on PAA/HS gel in the system of (a) Cu(II), (b) Cu(II)/Pb(II), (c) Cu(II)/Cd(II), and (d) Cu(II)/Pb(II)/Cd(II), C_0 = 20/100/200 mg/L, T = 298 K, pH = 5.00 ± 0.01, m/V = 1 g/L.

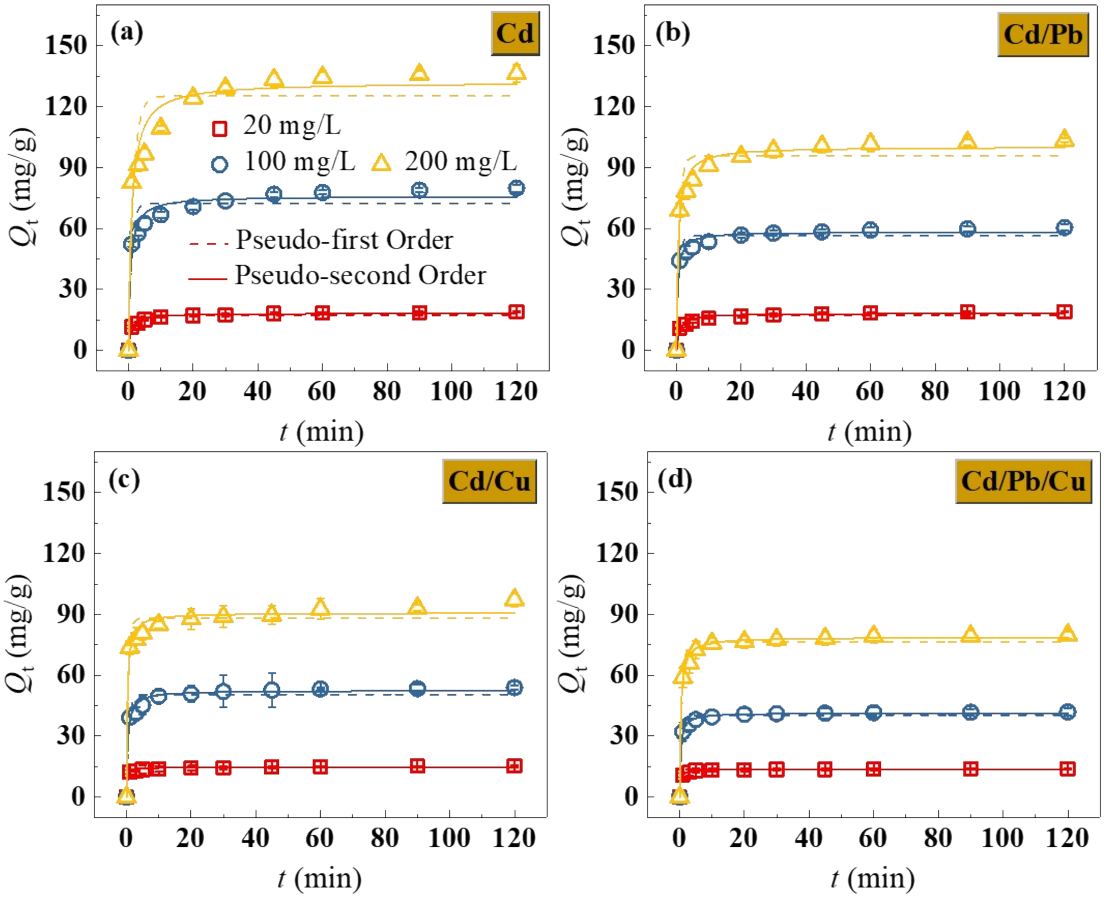


Fig. S13. Time-dependent adsorption of Cd(II) on PAA/HS gel in the system of (a) Cd(II), (b) Cd(II)/Pb(II), (c) Cd(II)/Cu(II), and (d) Cd(II)/Pb(II)/Cu(II), C_0 = 20/100/200 mg/L, T = 298 K, pH = 5.00 ± 0.01, m/V = 1 g/L.

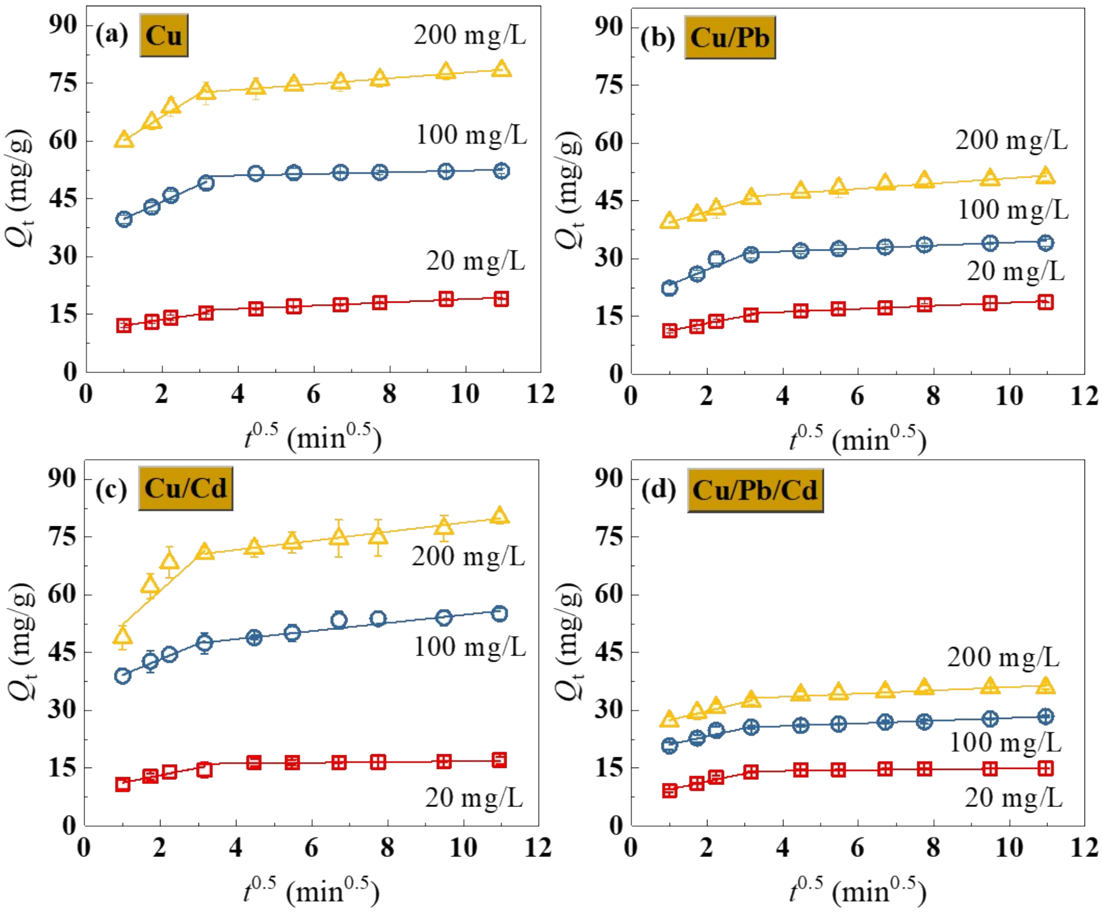


Fig. S14. Plots of Q_t versus $t^{0.5}$ for Cu(II) adsorption on PAA/HS gel in the system of (a) Cu(II), (b) Cu(II)/Pb(II), (c) Cu(II)/Cd(II), and (d) Cu(II)/Pb(II)/Cd(II), C_0 = 20/100/200 mg/L, T = 298 K, pH = 5.00 ± 0.01, m/V = 1 g/L.

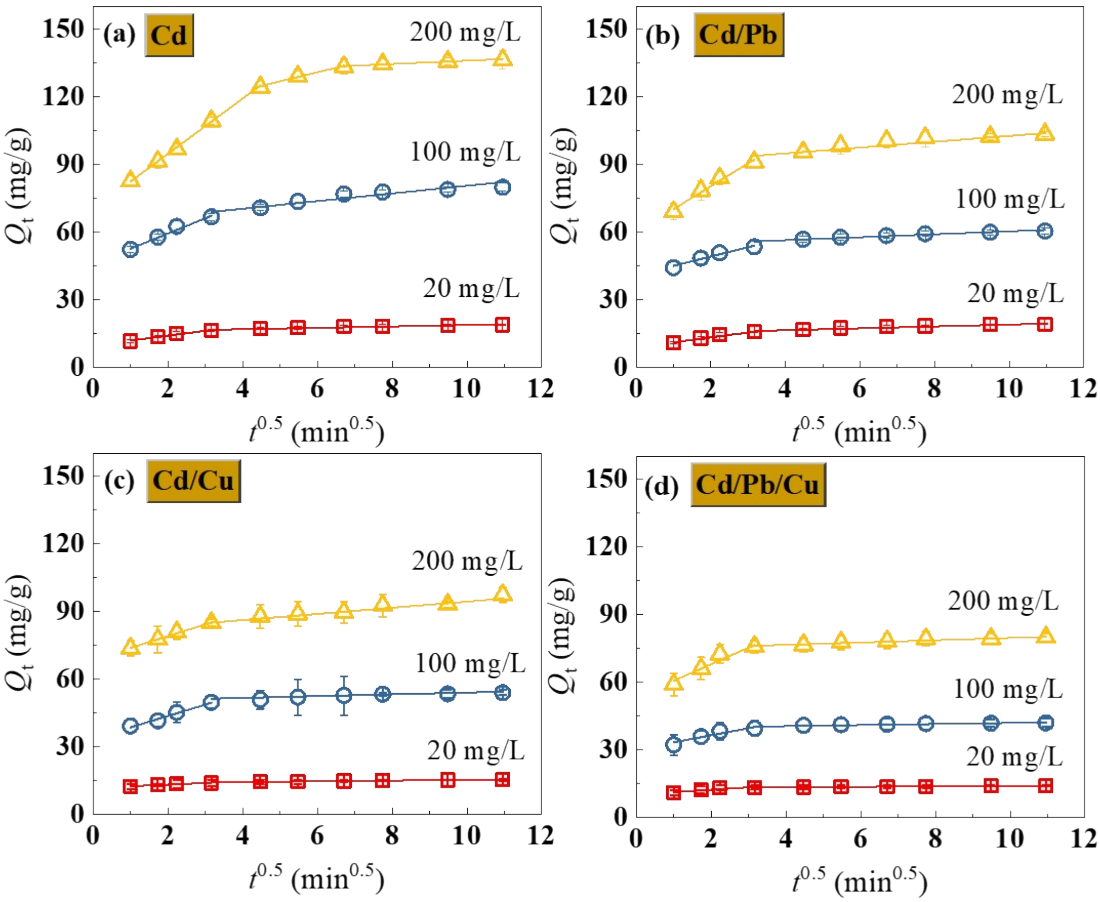


Fig. S15. Plots of Q_t versus $t^{0.5}$ for Cd(II) adsorption on PAA/HS gel in the system of (a) Cd(II), (b) Cd(II)/Pb(II), (c) Cd(II)/Cu(II), and (d) Cd(II)/Pb(II)/Cu(II), C_0 = 20/100/200 mg/L, T = 298 K, pH = 5.00 ± 0.01, m/V = 1 g/L.

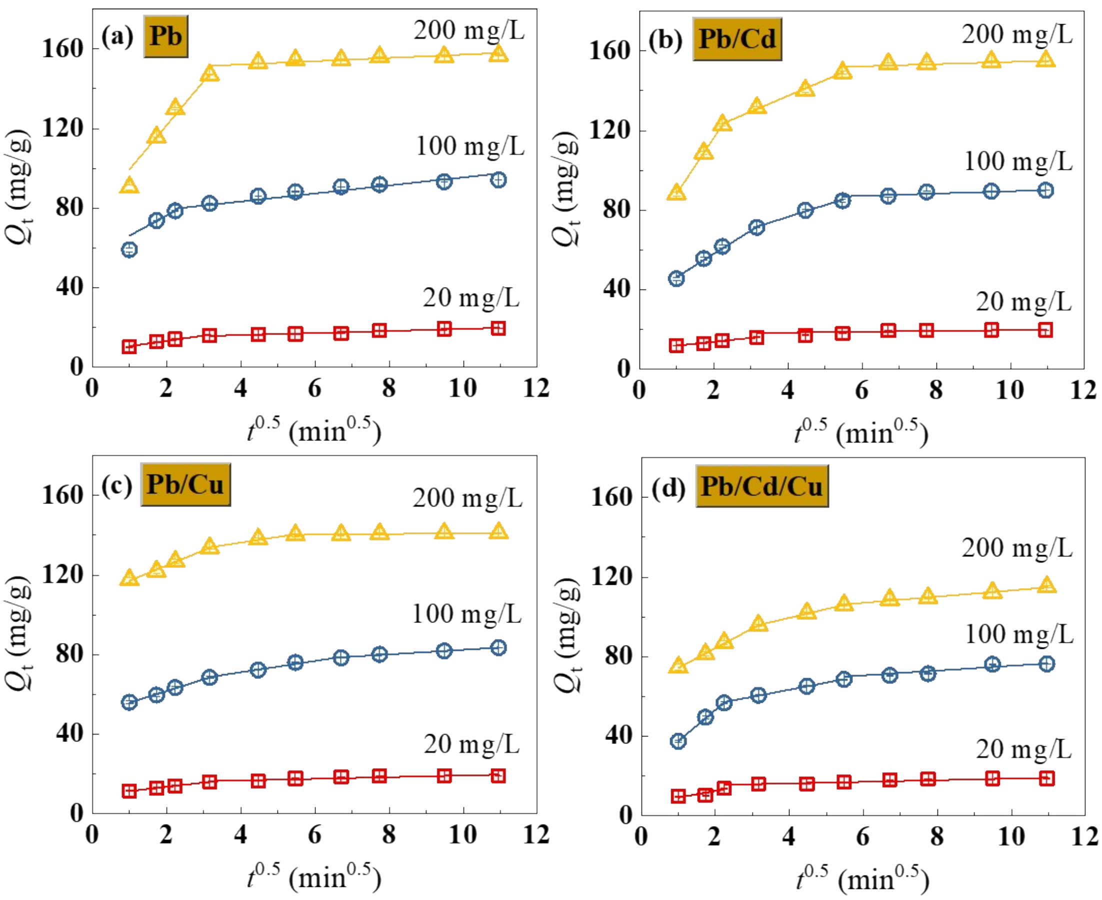


Fig. S16. Plots of Q_t versus $t^{0.5}$ for Pb(II) adsorption on PAA/HS gel in the system of (a) Pb(II), (b) Pb(II)/Cd(II), (c) Pb(II)/Cu(II), and (d) Pb(II)/Cd(II)/Cu(II), C_0 = 20/100/200 mg/L, T = 298 K, pH = 5.00 ± 0.01, m/V = 1 g/L.

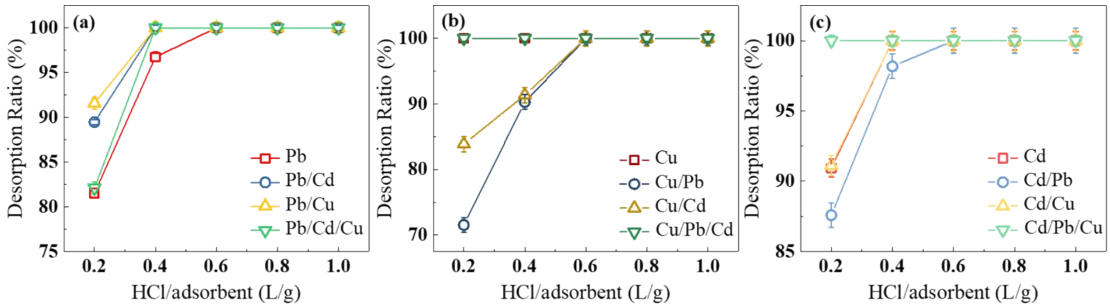


Fig. S17. The effect of HCl and adsorbent ratio (L/g) for the desorption of (a) Pb(II), (b) Cu(II) and (c) Cd(II) in individual and multicomponent systems.

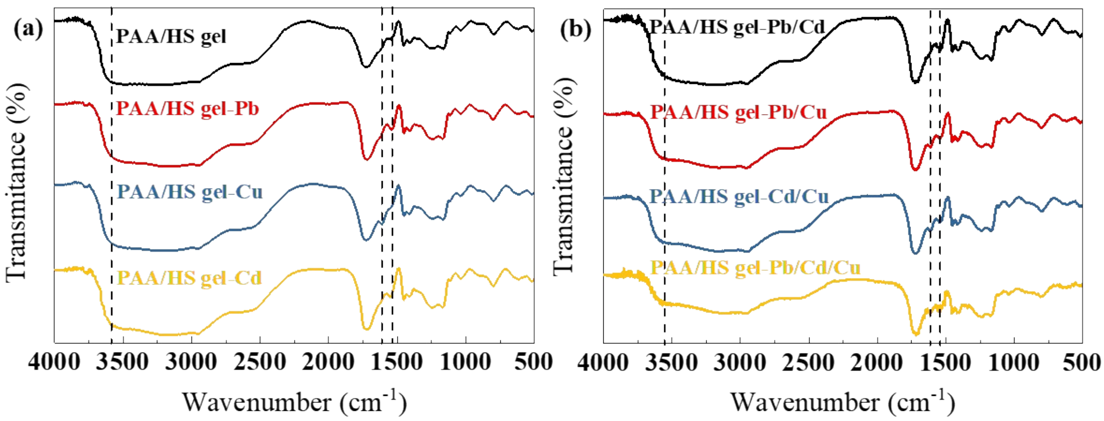


Fig. S18. FTIR spectra of the PAA/HS gel before and after adsorption of Pb(II), Cu(II), and Cd(II) in the individual (a) and multicomponent systems (b).

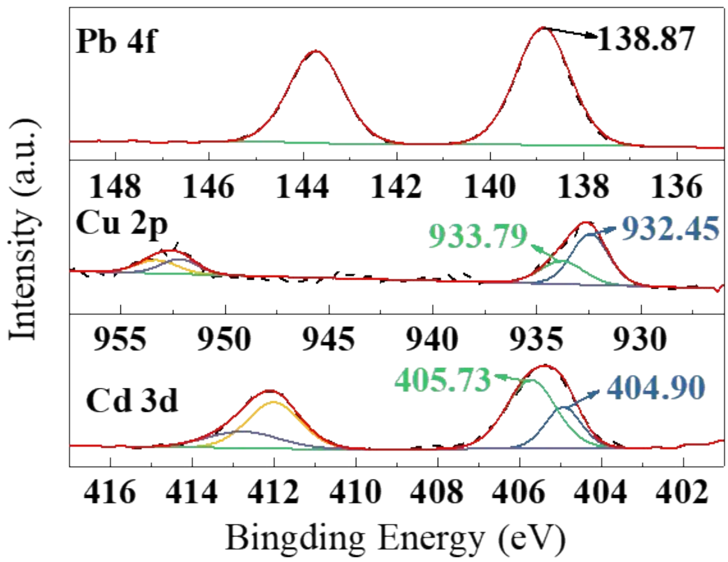


Fig. S19. Pb 4f, Cu 2p, and Cd 3d spectra of Pb(II), Cu(II), and Cd(II)-adsorbed PAA/HS gel.

Table S1 Comparison of preparation costs of various adsorbents.

Adsorbent	Cost (US$/t)	Reference
Activated carbon	7.50×10^{4}	[1]
Amino siloxane oligomer-linked graphene oxide	8.08×10^{3}	[2]
Thiol-functionalized polysilsesquioxane	1.64×10^{3}	[3]
Multi-walled carbon nanotubes	2.50×10^{6}	[4]
NH_2-Starch/PAA gel	7.00×10^{3}	[5]
PVA/PAA gel	2.50×10^{3}	[6]
Polyampholyte hydrogel	6.30×10^{3}	[7]
Jute/PAA gel	1.40×10^{3}	[8]
PSA–GO gel	6.93×10^{3}	[9]
PAA/HS gel	2.00×10^{3}	This work

Table S2 Moisture content of the raw and swollen PAA/HS gel.

	Raw gel	Swollen gel
Moisture content (%)	80.9	97.4

Table S3 The total organic carbon (TOC) of the solution with different pH value before and after immersing the material for 12 h.

Number	1	2	3	4	5	6	7	8
pH	1.00	3.00	5.00	5.98	7.31	9.00	11.00	13.00
0 h	1.070	0.5102	0.4370	0.2915	1.719	0.8373	0.6187	0.3561
12 h	*2.866*	0.9069	1.4820	1.0770	2.6580	1.2320	7.1580	32.310

Table S4 Selective adsorption of Pb(II), Cu(II), Cd(II), Ni(II), Mn(II), Fe(III), and Zn(II) on PAA/HS gel with different initial concentration.

Adsorbates	50 mg/L		100 mg/L		200 mg/L		300 mg/L	
	D	$\beta_{Pb(II)/M(II)}$	D	$\beta_{Pb(II)/M(II)}$	D	$\beta_{Pb(II)/M(II)}$	D	$\beta_{Pb(II)/M(II)}$
Pb(II)	5.36	–	3.06	–	1.34	–	0.82	–
Cu(II)	1.08	4.96	0.64	4.77	0.35	3.86	0.34	2.40
Cd(II)	0.52	10.41	0.43	7.07	0.40	3.38	0.57	1.45
Ni(II)	0.31	17.43	0.31	9.85	0.22	6.23	0.35	2.33
Mn(II)	0.00	/	0.00	/	0.00	/	0.00	/
Fe(III)	0.75	7.17	0.41	7.49	0.43	3.13	0.60	1.38
Zn(II)	0.19	27.73	0.19	15.83	0.20	6.84	0.31	2.67

Table S5 Isotherm parameters of Pb(II) adsorption onto PAA/HS gel.

Models	Parameters	Pb(II)			Pb(II)/Cd(II)			Pb(II)/Cu(II)			Pb(II)/Cd(II)/Cu(II)		
		288 K	298 K	308 K	288 K	298 K	308 K	288 K	298 K	308 K	288 K	298 K	308 K
Langmuir	Q_m (mg/g)	368.04	360.50	372.76	277.74	278.69	294.37	242.73	271.02	279.10	259.95	275.36	297.33
	K_L (L/mg)	0.0166	0.0291	0.0337	0.0209	0.0277	0.0278	0.0107	0.0096	0.0116	0.0085	0.0093	0.0091
	R^2	0.8255	0.8373	0.8347	0.9072	0.9109	0.9158	0.9264	0.9306	0.9342	0.9243	0.9461	0.9428
	R_L	0.108-0.751	0.064-0.632	0.056-0.597	0.087-0.705	0.067-0.643	0.067-0.642	0.157-0.824	0.172-0.839	0.147-0.811	0.191-0.855	0.177-0.843	0.181-0.846
Freundlich	K_F ($mg^{1-n}\cdot L^n/g$)	47.60	56.11	63.63	31.73	38.04	39.65	15.91	15.06	18.12	12.52	13.53	14.06
	n_F	2.9927	3.0117	3.1134	2.6943	2.8593	2.8250	2.2899	2.1646	2.2426	2.0858	2.0690	2.0414
	R^2	0.9416	0.9569	0.9574	0.9902	0.9871	0.9916	0.9871	0.9861	0.9905	0.9827	0.9932	0.9918
Langmuir-Freundlich	K_{LF} ((mg/g)·(mg/L)^{nLF})	47.61	56.11	63.64	31.73	38.02	39.62	15.91	15.05	18.10	12.51	13.51	14.04
	a_{LF} ((mg/L)^{nLF})	1.59E-04	1.68E-04	1.86E-04	4.02E-05	3.20E-04	3.11E-04	2.86E-05	1.27E-04	1.56E-04	1.04E-04	1.51E-04	1.22E-04
	n_{LF}	2.9914	3.0103	3.1121	2.6939	2.8558	2.8215	2.2894	2.1624	2.2401	2.0839	2.0663	2.0393
	R^2	0.9499	0.9583	0.9588	0.9982	0.9944	0.9929	0.9895	0.9892	0.9926	0.9892	0.9968	0.9931
D-R	Q_m (mg/g)	696.98	785.98	789.10	664.99	661.25	710.08	631.29	738.79	757.21	707.78	782.82	851.08
	k (mol^2/kJ^2)	3.40E-09	3.09E-09	2.72E-09	3.92E-09	3.42E-09	3.24E-09	4.92E-09	4.87E-09	4.33E-09	5.39E-09	5.05E-09	4.77E-09
	E (kJ/mol)	12.13	12.72	13.56	11.29	12.08	12.43	10.08	10.13	10.74	9.64	9.95	10.24
	R^2	0.9048	0.9265	0.9269	0.9737	0.9727	0.9775	0.9715	0.9705	0.9762	0.9673	0.9817	0.9789

Table S6 Isotherm parameters of Cu(II) adsorption onto PAA/HS gel.

Models	Parameters	Cu(II)			Cu(II)/Pb(II)			Cu(II)/Cd(II)			Cu(II)/Pb(II)/Cd(II)		
		288 K	298 K	308 K	288 K	298 K	308 K	288 K	298 K	308 K	288 K	298 K	308 K
Langmuir	Q_m (mg/g)	122.49	151.00	189.11	99.57	134.66	149.33	137.41	153.34	177.82	30.61	41.28	47.34
	K_L (L/mg)	0.0134	0.0103	0.0074	0.0065	0.0049	0.0048	0.0080	0.0086	0.0082	0.1002	0.0454	0.0385
	R^2	0.8908	0.9043	0.9117	0.7949	0.8613	0.8827	0.9307	0.9343	0.9245	0.8296	0.8090	0.8374
	R_L	0.130-0.788	0.163-0.829	0.212-0.871	0.236-0.885	0.289-0.911	0.294-0.912	0.200-0.862	0.188-0.853	0.196-0.859	0.020-0.333	0.042-0.524	0.049-0.565
Freundlich	K_F ($mg^{1-n}\cdot L^n/g$)	13.42	11.57	9.37	5.26	5.19	5.17	10.98	10.16	10.35	8.12	9.28	9.46
	n_F	2.8683	2.4899	2.1642	2.2774	2.1016	2.0254	5.5368	4.2054	3.9040	2.3098	2.3031	2.1947
	R^2	0.9802	0.9860	0.9770	0.8666	0.9400	0.9492	0.9919	0.9905	0.9923	0.9822	0.9887	0.9865
Langmuir-Freundlich	K_{LF} ($(mg/g)\cdot(mg/L)^{nLF}$)	13.42	11.56	9.36	5.25	5.19	5.17	8.12	9.25	9.45	11.24	10.16	10.33
	a_{LF} ($(mg/L)^{nLF}$)	7.34E-05	1.72E-04	9.41E-05	2.20E-05	6.08E-05	5.90E-05	5.36E-05	2.87E-04	1.48E-04	1.48E-01	5.86E-03	4.85E-03
	n_{LF}	2.8672	2.4873	2.1625	2.2770	2.1004	2.0241	2.3088	2.2979	2.1920	3.7417	4.1326	3.8429
	R^2	0.9862	0.9881	0.9823	0.8799	0.9480	0.9590	0.9986	0.9964	0.9938	0.9938	0.9895	0.9908
D-R	Q_m (mg/g)	205.93	271.33	359.24	162.82	240.33	275.56	72.60	284.54	339.69	44.50	64.45	75.79
	k (mol^2/kJ^2)	4.84E-09	5.27E-09	5.77E-09	6.03E-09	6.76E-09	6.55E-09	3.01E-09	5.76E-09	5.61E-09	2.40E-09	2.98E-09	3.01E-09
	E (kJ/mol)	10.16	9.74	9.31	9.10	8.60	8.74	12.89	9.32	9.44	14.43	12.95	12.88
	R^2	0.9553	0.9598	0.9521	0.8791	0.9001	0.9152	0.9695	0.9724	0.9666	0.9929	0.9794	0.9823

Table S7 Isotherm parameters of Cd(II) adsorption onto PAA/HS gel.

Models	Parameters	Cd(II)			Cd(II)/Pb(II)			Cd(II)/Cu(II)			Cd(II)/Pb(II)/Cu(II)		
		288 K	298 K	308 K	288 K	298 K	308 K	288 K	298 K	308 K	288 K	298 K	308 K
Langmuir	Q_m (mg/g)	322.16	412.76	537.43	365.21	437.28	400.74	499.90	479.90	520.12	310.73	318.64	336.77
	K_L (L/mg)	0.0111	0.0080	0.0065	0.0035	0.0032	0.0044	0.0022	0.0025	0.0025	0.0026	0.0027	0.0028
	R^2	0.9237	0.9546	0.9608	0.9467	0.9491	0.9474	0.9835	0.9863	0.9856	0.9912	0.9915	0.9933
	R_L	0.152-0.818	0.201-0.863	0.235-0.885	0.361-0.934	0.384-0.940	0.313-0.919	0.476-0.958	0.444-0.952	0.440-0.952	0.431-0.950	0.425-0.949	0.419-0.947
Freundlich	K_F ($mg^{1-n}\cdot L^n$/g)	20.11	15.47	13.36	5.66	5.46	7.42	2.89	3.27	3.41	2.64	2.79	3.00
	n_F	2.2116	1.8955	1.6868	1.6260	1.5486	1.6528	1.3434	1.3701	1.3519	1.4449	1.4497	1.4486
	R^2	0.9791	0.9817	0.9808	0.9669	0.9668	0.9672	0.9811	0.9827	0.9804	0.9881	0.9892	0.9921
Langmuir-Freundlich	K_{LF} ((mg/g)·(mg/L)^{nLF})	20.09	14.74	13.33	5.65	5.44	7.40	1.20	1.01	0.71	1.08	1.26	1.54
	a_{LF} ((mg/L)^{nLF})	1.16E-04	3.08E-03	9.42E-05	5.33E-05	5.00E-05	7.53E-05	2.26E-03	2.32E-03	1.83E-03	2.95E-03	3.10E-03	3.19E-03
	n_{LF}	2.2098	1.8306	1.6846	1.6242	1.5468	1.6506	1.0208	0.9585	0.8636	1.0740	1.1052	1.1461
	R^2	0.9799	0.9870	0.9869	0.9702	0.9701	0.9705	0.9883	0.9886	0.9886	0.9947	0.9923	0.9939
D-R	Q_m (mg/g)	769.63	1110.23	1589.88	949.19	1161.78	1090.89	1424.73	1409.76	1569.01	864.53	888.95	947.58
	k (mol^2/kJ^2)	5.45E-09	6.02E-09	6.28E-09	8.05E-09	7.84E-09	6.76E-09	9.74E-09	8.88E-09	8.37E-09	9.15E-09	8.49E-09	7.91E-09
	E (kJ/mol)	9.58	9.11	8.92	7.88	7.99	8.60	7.16	7.50	7.73	7.39	7.67	7.95
	R^2	0.9609	0.9705	0.9706	0.9541	0.9547	0.9564	0.9812	0.9838	0.9829	0.9896	0.9902	0.9927

Table S8 Comparison of potentially toxic metal ions sorption capacities with other humic substances sorbents.

Adsorbent	Solution conditions	Q_{max} (mg/g)			Reference
		Pb(II)	Cu(II)	Cd(II)	
HA/Ca-Mont	T = 298 K, pH = 5.0		12.633	12.443	[10]
Fe_3O_4/HA	T = 293 K, pH = 6.0	92.4	46.3	50.4	[11]
Solid HA	T = 293 K, pH = 5.0		23.04		[12]
ST-HA	T = 298 K, pH = 5.5	58.82			[13]
GA-HA/SA	T = 298 K		116.41		[14]
HA-Am-PAA-B	T = 303 K, pH = 5.0		96.15		[15]
PAA/HS gel	T = 298 K, pH = 5.0	360.5	151.0	412.76	This work

Table S9 The isosteric heat of Pb(II) adsorption (ΔH_x).

Q_e (mg/g)	ΔH_x (kJ/mol)			
	Pb(II)	Pb(II)/Cd(II)	Pb(II)/Cu(II)	Pb(II)/Cd(II) /Cu(II)
60	41.20	25.35	14.45	11.39
80	35.03	22.11	15.16	13.45
100	33.93	19.35	16.11	14.86

Table S10 The isosteric heat of Cu(II) adsorption (ΔH_x).

Q_e (mg/g)	ΔH_x (kJ/mol)	Q_e (mg/g)	ΔH_x (kJ/mol)	Q_e (mg/g)	ΔH_x (kJ/mol)	Q_e (mg/g)	ΔH_x (kJ/mol)
	Cu(II)		Cu(II)/Pb(II)		Cu(II)/Cd(II)		Cu(II)/Pb(II) /Cd(II)
40	9.06	30	18.85	40	19.44	20	30.68
60	12.73	40	30.03	80	21.72	25	41.44
80	15.63	45	34.47	100	23.03	30	51.96

Table S11 The isosteric heat of Cd(II) adsorption (ΔH_x).

Q_e (mg/g)	ΔH_x (kJ/mol)			
	Cd(II)	Cd(II)/Pb(II)	Cd(II)/Cu(II)	Cd(II)/Pb(II)/Cu(II)
60	-16.70	16.97	6.36	6.25
80	-7.04	15.55	6.28	5.31
100	6.40	14.09	6.09	4.63

Table S12 Values of thermodynamic parameters for Pb(II) adsorption.

Temperature (K)	Pb(II)			Pb(II)/Cd(II)			Pb(II)/Cu(II)			Pb(II)/Cd(II)/Cu(II)		
	ΔG^0 (kJ/mol)	ΔS^0 (J/(mol K))	ΔH^0 (kJ/mol)	ΔG^0 (kJ/mol)	ΔS^0 (J/(mol K))	ΔH^0 (kJ/mol)	ΔG^0 (kJ/mol)	ΔS^0 (J/(mol K))	ΔH^0 (kJ/mol)	ΔG^0 (kJ/mol)	ΔS^0 (J/(mol K))	ΔH^0 (kJ/mol)
288	-12.60	134.60	26.17	-7.27	80.89	15.99	-4.43	52.92	10.87	-4.03	41.06	7.87
298	-13.93			-8.19			-4.78			-4.22		
308	-15.29			-8.89			-5.49			-4.86		

Table S13 Values of thermodynamic parameters for Cu(II) adsorption.

Temperature (K)	Cu(II)			Cu(II)/Pb(II)			Cu(II)/Cd(II)			Cu(II)/Pb(II)/Cd(II)		
	ΔG^0 (kJ/mol)	ΔS^0 (J/(mol K))	ΔH^0 (kJ/mol)	ΔG^0 (kJ/mol)	ΔS^0 (J/(mol K))	ΔH^0 (kJ/mol)	ΔG^0 (kJ/mol)	ΔS^0 (J/(mol K))	ΔH^0 (kJ/mol)	ΔG^0 (kJ/mol)	ΔS^0 (J/(mol K))	ΔH^0 (kJ/mol)
288	-1.98	21.84	4.28	-0.22	26.25	7.30	-1.07	55.09	14.77	-1.44	32.21	7.82
298	-2.28			-0.60			-1.69			-1.84		
308	-2.42			-0.74			-2.17			-2.08		

Table S14 Values of thermodynamic parameters for Cd(II) adsorption.

Temperature (K)	Cd(II)			Cd(II)/Pb(II)			Cd(II)/Cu(II)			Cd(II)/Pb(II)/Cu(II)		
	ΔG^0 (kJ/mol)	ΔS^0 (J/(mol K))	ΔH^0 (kJ/mol)	ΔG^0 (kJ/mol)	ΔS^0 (J/(mol K))	ΔH^0 (kJ/mol)	ΔG^0 (kJ/mol)	ΔS^0 (J/(mol K))	ΔH^0 (kJ/mol)	ΔG^0 (kJ/mol)	ΔS^0 (J/(mol K))	ΔH^0 (kJ/mol)
288	-6.52	286.97	75.83	-7.11	86.94	18.04	-2.96	24.27	4.00	-1.50	25.56	5.87
298	-10.32			-7.62			-3.29			-1.71		
308	-12.22			-8.86			-3.44			-2.01		

Table S15 Constants for the kinetic adsorption data of Pb(II) on PAA/HS gel using different adsorption models.

Adsorbates	C_0 (mg/L)	$Q_{e,exp}$ (mg/g)	Elovich			Pseudo-first-order			Pseudo-second-order		
			α (mg/(g min))	β (g/mg)	R^2	$Q_{e,cal}$ (mg/g)	k_1 (L/min)	R^2	$Q_{e,cal}$ (mg/g)	k_2 (g/(mg min))	R^2
Pb(II)	20	19.54	5.88E+02	0.5399	0.9930	17.23	0.5799	0.9049	18.11	0.0516	0.9661
	100	94.18	9.40E+04	0.1481	0.9909	87.50	0.9662	0.9543	91.15	0.0175	0.9912
	200	156.87	3.25E+04	0.0754	0.9679	151.27	0.6569	0.9569	157.58	0.0073	0.9947
Pb(II)/Cd(II)	20	19.68	9.04E+02	0.5389	0.9935	17.93	0.6510	0.8633	18.88	0.0540	0.9480
	100	89.93	1.01E+03	0.0991	0.9897	84.02	0.3946	0.8985	88.38	0.0075	0.9685
	200	154.88	1.12E+04	0.0702	0.9879	145.52	0.6342	0.9260	152.52	0.0068	0.9831
Pb(II)/Cu(II)	20	19.08	1.04E+03	0.5669	0.9949	17.38	0.6704	0.8816	18.28	0.0575	0.9583
	100	83.44	4.27E+04	0.1628	0.9986	74.27	1.2089	0.8951	77.92	0.0217	0.9555
	200	141.17	1.72E+10	0.1844	0.9967	136.11	1.9497	0.9744	139.19	0.0306	0.9909
Pb(II)/Cd(II)/Cu(II)	20	18.66	2.17E+02	0.4832	0.9767	17.37	0.3823	0.8979	18.22	0.0365	0.9571
	100	76.31	1.44E+03	0.1278	0.9926	69.04	0.5007	0.9211	72.66	0.0111	0.9781
	200	115.07	3.82E+04	0.1132	0.9978	103.13	1.0503	0.8993	108.34	0.0139	0.9636

Table S16 Constants for the kinetic adsorption data of Cu(II) on PAA/HS gel using different adsorption models.

Adsorbates	C_0 (mg/L)	$Q_{e,exp}$ (mg/g)	Elovich			Pseudo-first-order			Pseudo-second-order		
			α (mg/(g min))	β (g/mg)	R^2	$Q_{e,cal}$ (mg/g)	k_1 (L/min)	R^2	$Q_{e,cal}$ (mg/g)	k_2 (g/(mg min))	R^2
Cu(II)	20	19.04	3.45E+03	0.6540	0.9981	16.84	1.0251	0.8807	17.73	0.0800	0.9505
	100	52.26	9.82E+06	0.3671	0.9908	50.11	1.4719	0.9606	51.73	0.0511	0.9896
	200	78.35	7.54E+07	0.2730	0.9972	73.67	1.6168	0.9691	75.72	0.0416	0.9910
Cu(II)/Pb(II)	20	18.72	1.72E+03	0.6175	0.9965	16.83	0.7643	0.8878	17.70	0.0664	0.9615
	100	34.12	7.53E+04	0.4288	0.9854	32.22	0.9912	0.9558	33.48	0.0505	0.9919
	200	51.15	8.98E+06	0.3841	0.9991	47.52	1.7063	0.9514	48.99	0.0627	0.9797
Cu(II)/Cd(II)	20	17.12	1.07E+04	0.7813	0.9872	15.93	0.9287	0.9368	16.64	0.0892	0.9847
	100	55.13	2.75E+05	0.2892	0.9985	50.25	1.3744	0.9320	52.21	0.0420	0.9724
	200	80.10	1.51E+05	0.1865	0.9823	73.48	0.9578	0.9672	76.28	0.0219	0.9934
Cu(II)/Pb(II)/Cd(II)	20	14.96	6.51E+03	0.8469	0.9750	14.35	0.7596	0.9501	14.95	0.0880	0.9923
	100	28.44	3.92E+06	0.6877	0.9959	26.32	1.4702	0.9639	27.13	0.1004	0.9892
	200	35.94	4.21E+06	0.5287	0.9981	33.79	1.5522	0.9574	34.87	0.0798	0.9859

Table S17 Constants for the kinetic adsorption data of Cd(II) on PAA/HS gel using different adsorption models.

Adsorbates	C_0 (mg/L)	$Q_{e,exp}$ (mg/g)	Elovich			Pseudo-first-order			Pseudo-second-order		
			α (mg/(g min))	β (g/mg)	R^2	$Q_{e,cal}$ (mg/g)	k_1 (L/min)	R^2	$Q_{e,cal}$ (mg/g)	k_2 (g/(mg min))	R^2
Cd(II)	20	18.90	4.87E+03	0.6625	0.9927	17.39	0.8296	0.9273	18.19	0.0733	0.9822
	100	79.90	3.43E+04	0.1649	0.9984	72.45	1.0638	0.9082	75.97	0.0205	0.9674
	200	136.40	6.91E+03	0.0779	0.9902	125.30	0.6565	0.8653	132.03	0.0077	0.9509
Cd(II)/Pb(II)	20	19.12	1.22E+03	0.5790	0.9968	17.37	0.6701	0.9065	18.23	0.0588	0.9725
	100	60.45	1.49E+06	0.2881	0.9979	56.35	1.4308	0.9499	58.35	0.0416	0.9839
	200	103.50	1.27E+05	0.1364	0.9951	96.05	1.0810	0.9341	100.27	0.0168	0.9826
Cd(II)/Cu(II)	20	15.29	3.35E+08	1.6202	0.9997	14.39	1.9242	0.9719	14.72	0.2844	0.9882
	100	53.95	6.11E+05	0.3048	0.9927	50.57	1.3470	0.9399	52.53	0.0415	0.9812
	200	97.30	2.87E+07	0.2134	0.9988	88.25	1.7298	0.9546	90.81	0.0358	0.9796
Cd(II)/Pb(II)/Cu(II)	20	13.99	6.22E+08	1.8001	0.9929	13.43	1.6335	0.9848	13.74	0.2606	0.9974
	100	41.95	9.20E+07	0.5212	0.9930	40.33	1.5304	0.9775	41.42	0.0737	0.9963
	200	79.90	2.01E+07	0.2455	0.9895	76.45	1.3772	0.9722	78.78	0.0329	0.9952

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