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Supporting Information

for

Dendrimer-modified carbon nanotubes for the removal and recovery of heavy metal ions from water

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Kinetic and adsorption model equations, comparison of various adsorbents for Pb^{2+} and Cd^{2+} adsorption with previously reported literature

Kinetic study

The pseudo-first order (Equation S1) and pseudo-second order (Equation S2) models are expressed as follows [1]:

$$\ln(q_e - q_t) = -k_1 t \quad \text{(S1)}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \text{(S2)}$$

where q_t and q_e are the amount of metal ion adsorbed per unit mass of adsorbent at time t and equilibrium (mg/g), and k_1 (1/min), and k_2 (g/mg·min) are the equilibrium rate constants. The kinetic results were also evaluated using the average relative error (ARE) as given following equation:

$$\mathrm{ARE} = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{q_{e,exp} - q_{e,cal}}{q_{e,cal}}\right| \quad \text{(S3)}$$

where $q_{e,exp}$ and $q_{e,cal}$ values are determined by experiment and theory, respectively.

Freundlich and Langmuir models

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \quad \text{(S4)}$$

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}} \quad \text{(S5)}$$

where, q_e (mg/g), C_e (mg/L), and q_{max} (mg/g) are the equilibrium adsorption capacity, equilibrium concentration, and maximum adsorption capacity, respectively; K_F (mg/g(L/mg)$^{1/n}$) and n are the Freundlich constants; K_L (L/mg) is the Langmuir constant.

Thermodynamic parameters

Thermodynamic parameters including changes of Gibbs free energy (Δ*G*), enthalpy (Δ*H*), and entropy (*ΔS*) of the adsorption can be calculated by experimental data at different temperature values following equations:

$$\Delta G = -RT\ln K_e \quad \text{(S6)}$$

$$\ln K_e = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad \text{(S7)}$$

where R is the gas constant (8.314 J/mol·K), K_e is the thermodynamic equilibrium constant (L/mol), and T is the absolute temperature (K). Values of K_e may be obtained using the following equation:

$$K_e = \frac{q_e}{C_e} \quad \text{(S8)}$$

where q_e (mg/g) and C_e (mg/L) are the equilibrium concentration of metal ions on the CNTs-G5 and liquid phase, respectively.

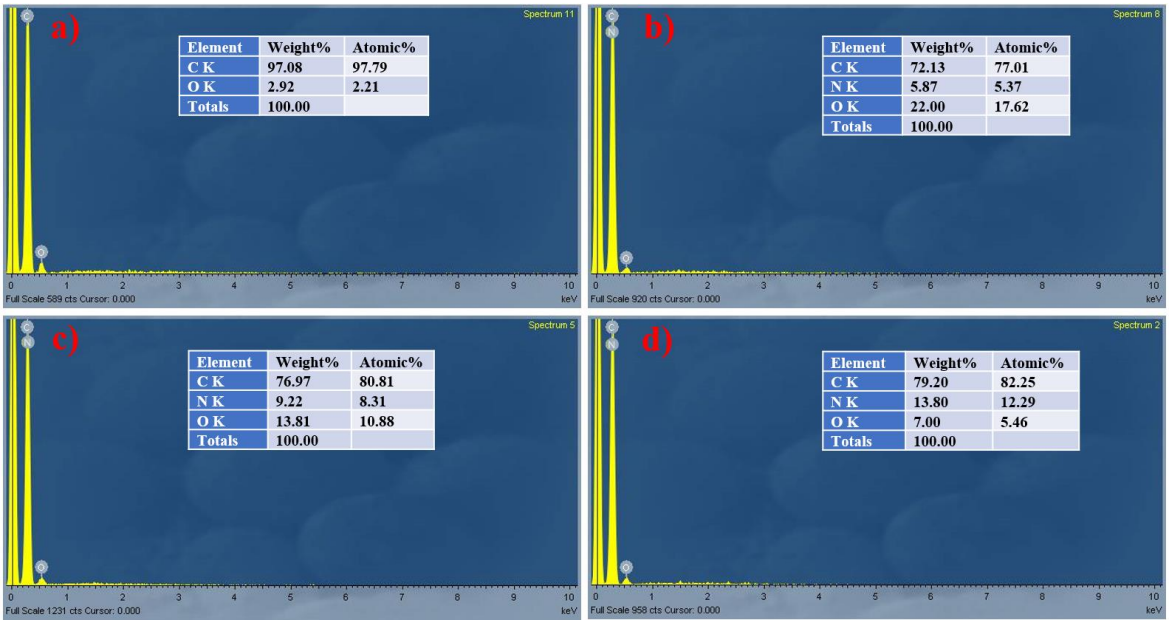

Figure S1: EDX analysis of (a) CNTs, (b) CNTs-G1, (c) CNTs-G3, and (d) CNTs-G5.

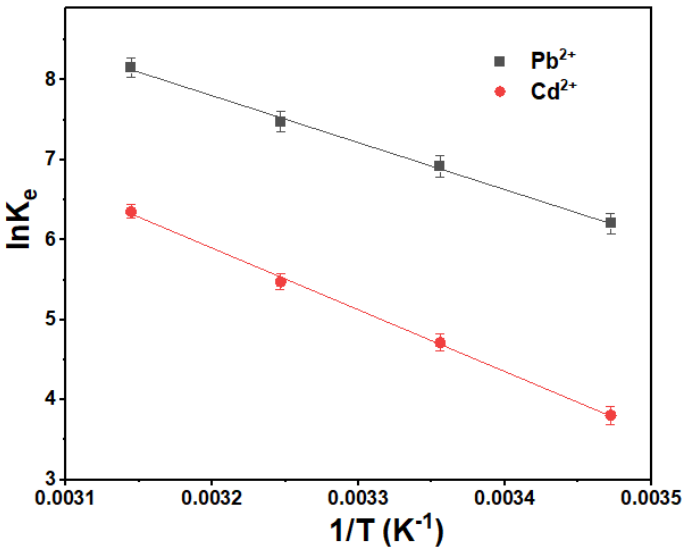

Figure S2: Plot of lnK_e versus 1/T for determination of reaction enthalpy (ΔH) and entropy (ΔS) of metal ions adsorption onto the CNTs-G5.

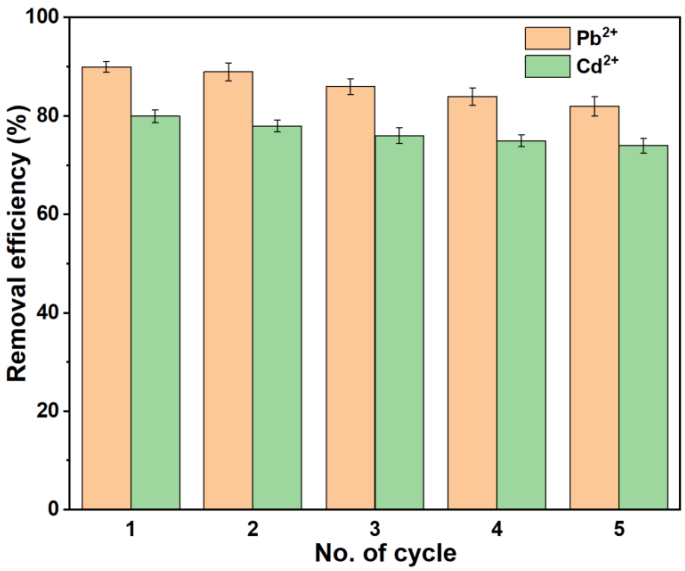

Figure S3: Recyclability results of CNTs-G5 for metal ion removal.

Table S1: Equilibrium rate constants, amounts adsorbed at equilibrium, and correlation coefficients for the adsorption of metal ions on CNTs-G5.

Metal ion	*C* (mg/L)	$q_{e,exp}$ (mg/g)	Pseudo-first order				Pseudo-second order			
			$q_{e,cal}$ (mg/g)	$k_1 \times 10^4$ (1/min)	ARE	R^2	$q_{e,cal}$ (mg/g)	$k_2 \times 10^4$ (g/mg·min)	ARE	R^2
Pb^{2+}	40	38.9±2.13	20.3	148.1	0.221	0.9785	39.0	301.1	0.073	0.9981
	60	41.9±2.24	19.4	147.9	0.311	0.9703	42.1	231.9	0.043	0.9926
	80	60.3±2.15	35.2	278.2	0.265	0.9615	61.4	151.4	0.094	0.9925
Cd^{2+}	40	34.3±2.34	19.8	190.1	0.145	0.9585	34.7	236.4	0.074	0.9960
	60	38.8±3.04	28.6	143.1	0.161	0.9740	37.9	139.9	0.091	0.9983
	80	55.8±3.67	41.6	145.9	0.194	0.9718	56.2	136.0	0.088	0.9973

Table S2: Adsorption isotherms constants for the adsorption of metal ions onto CNTs-G5.

Isotherm model	Equation	Parameter	Pb^{2+}	Cd^{2+}
Freundlich	$\ln q_e = \ln K_F + \frac{1}{n} ln C_e$	K_F (mg/g(L/mg)$^{1/n}$)	40.7158	32.5129
		$1/n$	0.1003	0.1142
		R^2	0.6985	0.7066
		ARE	0.346	0.354
Langmuir	$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}}$	K_L (L/mg)	595.6731	0.8439
		q_{max} (mg/g)	80.7102	66.8003
		R^2	0.9984	0.9997
		ARE	0.067	0.056

Table S3: Comparison of various adsorbents for Pb^{2+} and Cd^{2+} adsorption.

Materials	Environmental aspect	q_{max} for Pb^{2+} (mg/g)	q_{max} for Cd^{2+} (mg/g)	Recyclability	Reference
oxidized multiwalled carbon nanotubes (O-MWCNTS	requires oxidants	5.73	3.34	N/A	[2]
CNT/starch/Fe_3O_4	physical deposition, use of metals	50.36	44.72	high (7 cycles)	[3]
waste biomass–based biochar and alginate-based biopolymer	physical, mixing, low stability	55	36.8	N/A	[4]
nitric acid-modified coconut shell carbon (MHBC)	high temperature	160.41	47.46	high (5 cycles)	[5]
Caragana korshinskii biochar (CB)	high temperature	220.94	42.43	N/A	[6]
cerium oxide modified activated carbon (Ce/AC)	high temperature, use of metals	4.17	5.88	N/A	[7]
CNTs-G5	mild solvent, no oxidants and metals	80.7102	66.8003	high (5 cycles)	this study

Table S4: Determination of thermodynamic parameters for the adsorption of metal ions

Metal ions	*T* (K)	K_e (L/mol)	Δ*H* (kJ/mol)	Δ*S* (J/K·mol)	Δ*G* (kJ/mol)	R^2
Pb^{2+}	288	494.8757	48.894	221.345	−14.857	0.9981
	298	1006.4484			−16.557	
	308	1761.7712			−17.898	
	318	3474.6344			−19.524	
Cd^{2+}	288	44.9053	64.234	254.591	−9.110	0.9984
	298	111.5431			−11.289	
	308	238.4793			−13.109	
	318	574.4604			−15.214	

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