Supplementary Information

Synthesis, characterization, and application of Riboflavin covalently-functionalized graphene oxide (RF-GO composite) for selective removal of Cd^{2+}

Fazal Muhammad Khoso[1], Mei-Yi Duan[1], Bi Yang[1], Guo-Cong Liu[2], Xi Zhu[3], Jin-Gang Yu[1,*]

[1]*College of Chemistry and Chemical Engineering, Central South University, Changsha, Hunan 410083, China*

[2]School of Chemistry and Materials Engineering, Huizhou University, Huizhou 516007, China

[3]*Chengdu Advanced Metal Materials Industry Technology Research Institute Co., Ltd., Chengdu 610300, China*

1. Adsorption kinetics

Equations S1 to S4 represent the mathematical expression of linear/nonlinear pseudo-first and pseudo-second-order kinetics, and intra-particle diffusion, respectively.

Linear pseudo-first-order equation:

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

Non-linear pseudo-first-order equation:

$$q_t = q_e(1-e^{-k_1 t}) \quad \text{(S2)}$$

Linear pseudo-second-order equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \text{(S3)}$$

Non-linear pseudo-second-order equation:

$$q_t = \frac{k_2 q_e^{\,2} t}{1 + k_2 q_e t} \quad \text{(S4)}$$

To whom correspondence should be addressed.
* JG Yu, E-mail: yujg@csu.edu.cn; Tel/Fax: +86-731-88879616.

Intra-particle-diffusion equation:

$$q_t = k_{id} t^{1/2} + C_{id} \quad \text{(S5)}$$

where qe (mg g^{-1}) is the adsorption capacity at equilibrium, qt (mg g^{-1}) is the adsorption capacity at time t. k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the pseudo-first and second-order rate constants, respectively. Where k_{id} represents intraparticle diffusion rate constant (mg g^{-1} $min^{-1/2}$) and C_{id} (mg g^{-1}) is regarded as a constant that characterizes the mass transfer over the boundary layer.

Table S1 Adsorption kinetic parameters for RF-GO composite towards Cd^{2+} adsorption.

Linear Pseudo-first-order model	k_1 (min^{-1})	0.0882
	R^2	0.969
	q_e (mg g^{-1})	11.75
Linear Pseudo-second-order model	k_2 (min^{-1})	0.000247
	R^2	0.995
	q_e (mg g^{-1})	20.22
Linear Intra-particle diffusion model	k_{1dif} (mg g^{-1}/$min^{1/2}$)	1.3753
	R_1^2	0.873
	q_e (mg g^{-1})	6.974
	K_{2dif} (mg g^{-1}/$min^{1/2}$)	0.0878
	R_2^2	0.839
	q_e (mg g^{-1})	17.94
Non-linear Pseudo-first-order model	k_1 (min^{-1})	0.09851
	R^2	0.632
	q_e (mg g^{-1})	18.12
Non-linear Pseudo-second-order model	k_2 (min^{-1})	0.00947
	R^2	0.913
	q_e (mg g^{-1})	19.29
Non-linear Intra-particle diffusion model	k_{dif} (mg g^{-1}/$min^{1/2}$)	0.62514
	R^2	0.794
	q_e (mg g^{-1})	11.88

2. Adsorption isotherms

Linear and non-linear forms of the classical (Langmuir, Freundlich) adsorption isothermal models were used to fit the experimental data of Cd^{2+} adsorbed on RF-GO composite.

i. Linear Langmuir model:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m k_L} \quad \text{(S6)}$$

ii. Non-linear Langmuir model:

$$q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \quad \text{(S7)}$$

where C_e (mg L^{-1}) is the equilibrium concentration; q_e (mg g^{-1}) is the amount of adsorbed adsorbate per specified amount of adsorbent; K_L (L mg^{-1}) is the Langmuir equilibrium constant and q_m (mg g^{-1}) is the amount of adsorbate required to form an adsorbed monolayer.

iii. Linear Freundlich isotherm model:

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e \quad \text{(S8)}$$

iv. Non-linear Freundlich isotherm model:

$$q_e = k_F C_e^{\frac{1}{n}} \quad \text{(S9)}$$

where C_e (mg L^{-1}) is the equilibrium concentration of adsorbent; q_e (mg g^{-1}) is the amount of adsorbent per unit mass; K_F (mg $L^{1/n}$ g^{-1} $mg^{-1/n}$) and n are two Freundlich constants: n represents the relative advantage of adsorption process; K_F is the affinity constant which is related to the adsorption capacity of the adsorbent and can also be defined as adsorption or distribution coefficient, indicating the amount of Cd^{2+} adsorbed on RF-GO composite at unit equilibrium concentration.

Table S2 Isothermal parameters for RF-GO composite towards Cd^{2+} adsorption

□	Parameters	Temperature				
		293 K	**298 K**	**303 K**	**308 K**	**313 K**
Linear Langmuir isotherm	k_L (L mg^{-1})	0.519	0.208	0.410	0.265	0.510
	q_m (mg g^{-1})	21.99	31.87	31.47	35.49	34.93
	R^2	0.971	0.991	0.993	0.979	0.988
Linear Freundlich	k_F (mg $L^{1/n}$ g^{-1} $mg^{-1/n}$)	0.364	0.400	0.441	0.430	0.478

isotherm						
	n	5.233	4.650	6.168	4.896	7.804
	R^2	0.444	0.849	0.715	0.742	0.765
Non-linear Langmuir isotherm	k_L (L mg^{-1})	0.204	0.167	0.265	0.200	0.388
	q_m (mg g^{-1})	24.19	32.89	32.77	36.93	35.67
	R^2	0.525	0.916	0.851	0.821	0.818
Non-linear Freundlich isotherm	k_F (mg L$^{1/n}$ g^{-1} mg$^{-1/n}$)	12.211	13.344	17.113	16.271	20.863
	n	7.008	5.145	7.078	5.611	8.330
	R^2	0.341	0.814	0.675	0.688	0.717

3. Thermodynamic parameters

The thermodynamics parameters such as Gibbs free energy change (ΔG), enthalpy change (ΔH), and entropy change (ΔS) were calculated by Eq. (S8), Eq. (S9) and (S10):

$$k_d = \frac{C_0 - C_e}{C_e} \times \frac{V}{m} \quad \text{(S10)}$$

$$\ln kd = \frac{-\Delta G}{RT} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad \text{(S11)}$$

$$\Delta G = \Delta H - T \times \Delta S \quad \text{(S12)}$$

where k_d (L mg^{-1}) is the thermodynamic equilibrium constant of adsorption; C_0 (mg L^{-1}) and C_e (mg L^{-1}) are the initial and equilibrium concentrations of Cd^{2+}, respectively; V (L) and m (g) represent the volume of Cd^{2+} solution and the mass of RF-GO composite respectively; R is molar gas constant (8.314 J mol^{-1} K^{-1}), and T (K) is the absolute temperature.

Table S3. Thermodynamic parameters for RF-GO composite towards Cd^{2+} adsorption (t= 60 min; pH=6; Dose= 5 mg).

Temperature	***ΔG* (KJ mol^{-1})**	***ΔH* (KJ mol^{-1})**	***ΔS* (J K^{-1} mol^{-1})**
293K	1.9085		
298K	1.2136		
303K	1.2122	16.955	52.016
308K	0.8124		
313 K	0.8256		