

Supporting Information

Graphene Oxide Covalently Functionalized with 5-Methyl-1,3,4-thiadiazol-2-amine for pH-Sensitive Ga³⁺ Recovery in Aqueous Solutions

Xi Zhu, Yong Guo *, Baozhan Zheng

College of Chemistry, Sichuan University, Chengdu 610065, China

To whom correspondence should be addressed.

* Y Guo, E-mail: guoy@scu.edu.cn;

1. Reagents and materials

Potassium permanganate (KMnO₄) and phosphoric acid (H₃PO₄, 85 wt.%) were bought from Sinopharm Group Chemical Reagent Co., Ltd. (Shanghai, China); Hydrochloric acid (HCl, 37 wt.%), sodium hydroxide (NaOH; AR, 97 wt.%), and concentrated sulfuric acid (H₂SO₄, 98 wt.%) were purchased from Chengdu Cologne Chemical Co. Ltd. (Chengdu, China); Flake graphite (80-90.5 wt.%) was supplied by Qingdao Braide Graphite Co., Ltd (Qingdao, China); 5-methyl-1,3,4-thiadiazol-2-amine (MTA, C₃H₅N₃S, 99 wt.%) , acetic acid (CH₃COOH, 99.5 wt.%) were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. (Shanghai, China); Hydrogen peroxide (H₂O₂, 30.0 wt.%) was bought from Shanghai Wokai Biotechnology Co., Ltd. (Shanghai, China); Indium(III) chloride (InCl₃, 99.99%), scandium(III) nitrate hydrate (Sc(NO₃)₃·H₂O; 99.9 wt.%) and gallium(III) nitrate hydrate (Ga(NO₃)₃·H₂O; 99.99 wt.%) were bought from Shanghai Run-Biotech Co., Ltd. (Shanghai, China); All chemicals were of analytical grade and used without further purification. Ultrapure water with a resistivity of 18.2 MΩ cm⁻¹ was produced from a Millipore Milli-Q water purification system (Millipore Trading Co., Ltd.; Shanghai, China).

2. FT-IR spectra of GO

As shown in **Figure S1**, the peaks at 3391.8 and 1721.2 cm^{-1} can be attributed to the stretching vibrations of the hydroxyl ($-\text{OH}$) and $\text{C}=\text{O}$ groups of GO, respectively. In addition, the peak at 1622.1 cm^{-1} can be assigned to the $\text{C}=\text{O}$ stretching vibrations of carboxyl groups, and the peak at 1567.9 corresponds to the aromatic skeletal vibrations, while the peaks at 1229.8 and 1037.5 cm^{-1} belong the $\text{C}-\text{O}$ and $\text{C}-\text{C}$ stretching vibrations, respectively.

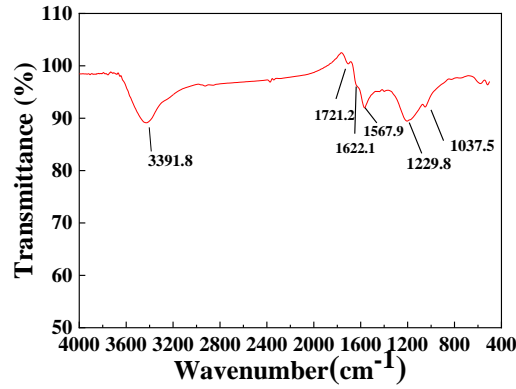


Figure S1 FT-IR spectra of GO.

3. Adsorption kinetic models

The linear pseudo-first-order rate and the linear pseudo-second-order rate equation are used to simulate the adsorption kinetics (**Equations (S1) and (S2)**):

$$\text{Linear pseudo-first-order model: } \ln(q_e - q_t) = \ln q_e - k_1 t \quad (\text{S1})$$

$$\text{Nonlinear pseudo-first-order model: } q_t = q_e (1 - e^{-k_1 t}) \quad (\text{S2})$$

$$\text{Linear pseudo-second-order model: } \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (\text{S3})$$

$$\text{Nonlinear pseudo-second-order model: } q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (\text{S4})$$

where q_e (mg g^{-1}) and q_t (mg g^{-1}) are the amounts of Ga^{3+} adsorbed by GO-MTA

composite at equilibrium state and at contact time t (min), respectively; k_1 (min^{-1}) and k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) are the specific adsorption rate constant of the pseudo-first-order model and the pseudo-second-order model, respectively.

4. Adsorption isothermal models

The linear/nonlinear Langmuir isothermal model and the linear/nonlinear Freundlich isothermal model are used to simulate the adsorption isotherms (**Equations (S5)–(S8)**):

$$\text{Linear Langmuir isothermal model: } \frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m k_L} \quad (\text{S5})$$

$$\text{Nonlinear Langmuir isothermal model: } q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \quad (\text{S6})$$

$$\text{Linear Freundlich isothermal model: } \ln q_e = \ln k_F + \frac{1}{n} \ln C_e \quad (\text{S7})$$

$$\text{Nonlinear Freundlich isothermal model: } q_e = k_F C_e^{\frac{1}{n}} \quad (\text{S8})$$

where C_e (mg L^{-1}) is the equilibrium concentration of Ga^{3+} ; q_e (mg g^{-1}) is the amount of Ga^{3+} adsorbed by GO-MTA composite at equilibrium state; q_m (mg g^{-1}) is the monolayer adsorption capacity; k_L (L mg^{-1}) is the Langmuir equilibrium constant; The two Freundlich constants, n represents the relative advantage of adsorption process, k_F ($\text{mg L}^{1/n} \text{g}^{-1} \text{mg}^{-1/n}$) is defined as adsorption or distribution coefficient which corresponds to the amount of Ga^{3+} adsorbed on GO-MTA composite at unit equilibrium concentration. The slope $1/n$ ranging between 0 and 1 could be used as a measure of adsorption intensity or surface heterogeneity, and a value close to zero suggests a more heterogeneous surface.

5. Adsorption thermodynamics

The change in the enthalpy (ΔH° , kJ mol^{-1}), the change in the entropy (ΔS° , J K^{-1})

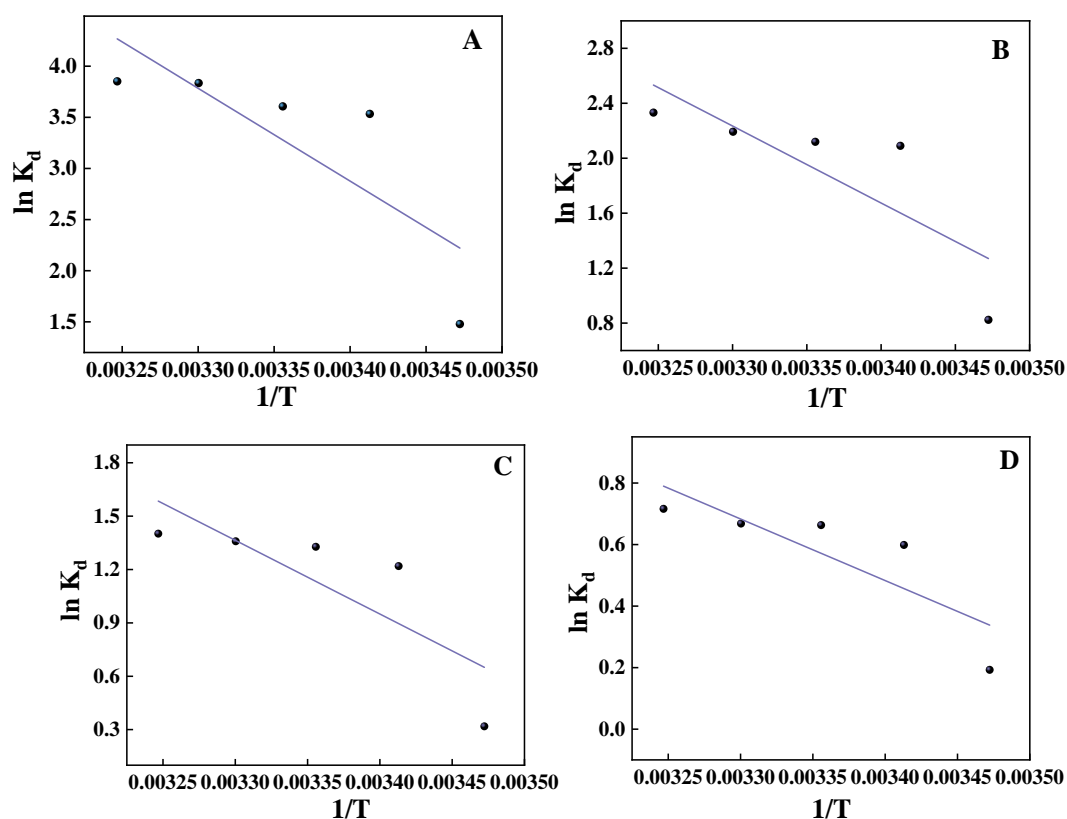
mol⁻¹) and the change in the Gibbs free energy (ΔG^o , kJ mol⁻¹) can be calculated by Equations (S9)–(S11).

$$k_d = \frac{C_0 - C_e}{C_e} \times \frac{V}{m} \quad (\text{S9})$$

$$\ln k_d = \frac{-\Delta G^o}{RT} = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad (\text{S10})$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \quad (\text{S11})$$

where k_d (L mg⁻¹) represents the thermodynamic equilibrium constant; V (L) and m (g) are defined as the volume of Ga³⁺ solution and the mass of GO-MTA composite, respectively; T (K) represents the absolute temperature; R (8.314 J mol⁻¹ K⁻¹) represents the ideal gas constant.



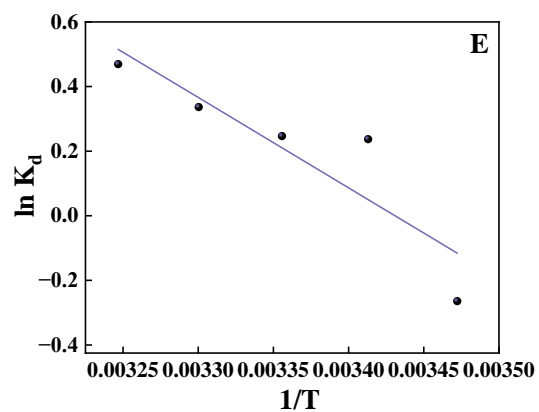


Figure S2 Experimental data and the fitted curve of $\ln K_d$ versus $1/T$ calculated from Van't Hoff plots of GO-MTA composite for Ga^{3+} with different concentration: (A) 10 mg L^{-1} ; (B) 20 mg L^{-1} ; (C) 30 mg L^{-1} ; (D) 40 mg L^{-1} ; (E) 50 mg L^{-1} .

Table S1 Adsorption thermodynamic parameters of GO-MTA composite for Ga³⁺.

C_0 (mg L ⁻¹)	T (K)	ΔG^\ominus (kJ mol ⁻¹)	R^2	ΔH^\ominus (kJ mol ⁻¹)	ΔS^\ominus (J mol ⁻¹ K ⁻¹)
10	288	-5.318	0.646	75.45	280.43
	293	-6.721			
	298	-8.123			
	303	-9.525			
	308	-10.927			
20	288	-3.040	0.658	46.57	172.24
	293	-3.040			
	298	-4.762			
	303	-5.623			
	308	-6.485			
30	288	-1.557	0.656	34.45	125.03
	293	-2.182			
	298	-2.808			
	303	-3.433			
	308	-4.058			
40	288	-0.809	0.698	16.66	60.66
	293	-1.113			
	298	-1.416			
	303	-1.719			
	308	-2.023			
50	288	0.277	0.802	23.27	79.82
	293	-0.122			
	298	-0.521			
	303	-0.920			
	308	-1.319			