Electronic Supporting Information

Coordination/cation exchangeable dual sites intercalated multilayered

T3C2Tx MXene for selective and ultrafast removal of thallium(I) from water

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Supporting Information 1. Adsorption models.¹⁻⁶

The adsorption processes were elucidated by the pseudo-first-order and pseudo-second-order kinetic models using:

$$\ln\left(1 - \frac{q_t}{q_e}\right) = \frac{k_l}{2.303}t\tag{1}$$

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

where $q_e \text{ (mg g}^{-1)}$ and $q_t \text{ (mg g}^{-1)}$ are the amounts of adsorption of thallium at the equilibrium time of t, respectively. The $k_l \text{ (min}^{-1)}$ and $k_2 \text{ (g mg}^{-1}\text{min}^{-1)}$ are the sorption rate constants of pseudo-first-order and pseudo-second-order, respectively. The k_l and k_2 are the slopes of linear fits to plots of $\log(q_e-q_t)$ versus t and t/qt versus t.

The adsorption isotherms of equilibrium are fitted by the Langmuir and Freundlich models described as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m k_l} + \frac{C_e}{q_m}$$
(3)

$$\ln q_e = \ln k_F + \frac{1}{n} C_e \tag{4}$$

where $q_e \text{ (mg g}^{-1)}$ and $q_m \text{ (mg g}^{-1)}$ are the amounts of adsorption of thallium and the maximum adsorption capacity. C_e is the equilibrium concentration of Tl⁺ and the k_L (L mg⁻¹) and k_F (mg1-(1/n)L^{1/n}g⁻¹) are the adsorption equilibrium constants of Langmuir and Freundlich models, respectively. Above all, the Langmuir indicates finite monolayer sorption, which occurs on a homogenous surface. And Freundlich models indicate multilayer sorption occurs on anon-ideal sorption on heterogeneous surfaces.

Thermodynamics of adsorption isotherms are calculated using:

$$\triangle G^0 = -RT \ln k_L \tag{5}$$

$$\ln k_L = \frac{\bigtriangleup S^0}{R} - \frac{\bigtriangleup H^0}{RT}$$
(6)

where *T* is the temperature, *R* is the universal gas constant (8.314×10⁻³ kJ mol⁻¹·K), and k_L is the Langmuir adsorption equilibrium constant (L mg⁻¹). Linear plots of standard Gibbs free energy change (ΔG) versus temperature were used to obtain values for the free standard enthalpy and entropy change as ΔH and ΔS , respectively.

The kinetic adsorption is also fitted by the Dubinin-Radushkevich (D-R) equation using :

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \tag{7}$$

where $q_e \pmod{g^{-1}}$ and $q_m \pmod{g^{-1}}$ are the amount of adsorption of thallium and the maximum adsorption capacity. The $\beta \pmod{(kJ^2)^{-1}}$ is the activity coefficient related to the mean free energy of adsorption and ε is the Polanyi potential.

The mean free energy of adsorption (E) is calculated using:

$$E = \frac{1}{\sqrt{2\beta}} \tag{8}$$

Supporting Information 2: Supplemental results.



Fig. S1. The EDS spectrum of $Ti_3C_2T_X$ NSs.



Fig. S2 The EDS spectrum of KOH@Ti $_3C_2T_x$ NSs.



Fig. S3 The kinetic adsorption fitted by the Dubinin-Radushkevich (D-R) (initial Tl⁺ concentration was 40 mg⁻¹, the KOH@Ti₃C₂T_x NSs dose was 0.5 g L⁻¹, pH = 6, T = 298K).



Fig. S4 Adsorption isotherms for Tl^+ removal by $Ti_3C_2T_x$ NSs at 288, 298 and 308 K.



Fig. S5 The Tl⁺ removal efficiency influenced by humic acid. (Initial Tl⁺ concentration was 1 mg L^{-1} , the KOH@Ti₃C₂T_x NSs dose was 0.5 g L^{-1} , pH = 6.0, T = 298 K).



Fig. S6 The EDS spectrum of KOH@Ti₃C₂T_X NSs after Tl⁺ adsorption.



Fig. S7 The XPS K 2p spectrum of KOH@Ti₃C₂T_x NSs after stirring in water.





Fig. S9 XRD patterns of pristine MXenes prepared by different treatments.



Fig. S10 XRD patterns of pristine MXenes after adsorption.



Fig. S11 The SEM of MXenes: (a) Ti_3AlC_2 , (b) $NaOH@Ti_3C_2T_X NSs$, (c) $NH_4OH@Ti_3C_2T_X$, NSs, (d) $KCl@Ti_3C_2T_X NSs$.



Fig. S12 (a-c) The N₂ adsorption-desorption isotherms of $Ti_3C_2T_x$ -B, $Ti_3C_2T_x$ NSs and $KOH@Ti_3C_2T_x$ NSs respectively.



Fig. S13 The FTIR spectrum of MXenes prepared by different treatments.



Fig. S14 The O 1s spectrum of MXenes prepared by different treatments: (a) NaOH@Ti₃C₂T_X,
(b) NH₄OH@Ti₃C₂T_X, (c) KCl@Ti₃C₂T_X, (d) Ti₃C₂T_X-B.



Fig. S15 The different adsorption configuration and corresponding adsorption energies of K^{+} and $$Tl^{+}$$ on OH-terminated $Ti_{3}C_{2}.$

Adsorbent	K		TI		
	Mass fraction (%)	Mole fraction (mmol g^{-1})	Mass fraction (%)	Mole fraction (mmol g^{-1})	
$Ti_3C_2T_X$	NA	NA	NA	NA	
KOH@Ti ₃ C ₂ T _X	1.71	0.44	NA	NA	
KOH@Ti ₃ C ₂ T _X -TI	0.94	0.24	11.81	0.58	
KCl@Ti ₃ C ₂ T _X	0.43	0.11	NA	NA	
KCl@Ti ₃ C ₂ T _X -TI	0.27	0.07	3.02	0.15	

Table S1 The K^+ and TI^+ content of MXenes were detected by ICP-MS.

Table S2 The parameters of Pseudo-first-order kinetics and Pseudo-second-order kineticsmodels for Tl⁺ adsorption on KOH@Ti₃C₂T_x NSs.

	Pseudo-first-order kinetics			Pseudo-second-order kinetics			
Adsorbent	k_l (1 min ⁻¹)	q_e (mg g ⁻¹)	R ²	k_2 (mmol· (g·min) ⁻¹)	q_e (mg g ⁻¹)	R ²	
KOH@Ti ₃ C ₂ T _x	2.34	163.1	0.978	0.03	157.3	0.991	

Temperature (K)	La	ngmuir model		Freundlich model		
	q_m (mg g ⁻¹)	K_L (L mmol ⁻¹)	R ²	n	$K_F(\text{mmol}(1-$	R ²
308	312.7	0.0214	0.991	2.5	17.6	0.933
298	238.1	0.0089	0.998	2.7	10.8	0.967
288	197.1	0.0159	0.997	4.2	8.3	0.967

Table S3 The equilibrium parameters of Langmuir and Freundlich models for Tl^+ adsorption on KOH@Ti₃C₂T_x NSs.

Table S4 The isothermal adsorption tests for different initial concentrations of Tl⁺.

Tl initial concentration (mg L ⁻¹)	0.5	1.0	5.0	9.9	19.5
Adsorption capacity $(mg g^{-1})$	1.99	3.98	19.88	35.19	66.93
Removal efficiency (%)	99.5	99.6	98.5	88.0	83.7

 $\label{eq:table S5} \ensuremath{\text{Table S5}}\xspace{1.5} The equilibrium parameters of Dubinin-Radushkevich isotherm model for Tl^+ adsorption on $KOH@Ti_3C_2T_x$ NSs. }$

	Dubinin-Radushkevich isotherm model						
Adsorbent	q_m (mmol g ⁻¹)	K (mol ² (kJ ²) ⁻¹)	E (kJ mol ⁻¹)	R ²			
KOH@Ti ₃ C ₂ T _x	3.35	0.0029	13.13	0.9831			

Temperatures (K)	$\ln k_L (\mathrm{L \ mg^{-1}}).$	riangle Go (kJ mol ⁻¹)
308	1.469	-3.52
298	0.592	-1.42
288	1.172	-2.81
$\Delta H^0 (\mathrm{kJ} \ \mathrm{mol}^{-1})$	65	.539
$\Delta S^0 (J \pmod{K}^{-1})$	0.	225

Table S6 Thermodynamic parameters for Tl^+ adsorption onto KOH@Ti₃C₂T_x NSs at different temperature.

Table S7 The concentration of different coexist ions calculated by ICP-MS and IC.

Compositions	TI(I)	K(I)	Ca(II)	Na(I)	Mg(II)	Cu(II)	Zn(II)	Pb(II)	NH ₄ (I)
Concentration (mg L ⁻¹)	0.13	2365	3.42	3571	0.96	0.04	4575	0.69	81769

Table S8 The concentration of COD and TOC calculated by TOC analyzer.

Compositions	COD	TOC
Concentration (mg L ⁻¹)	13561	325

Atomics (%)	С	Ti	Ο	K	T1
Before adsorption	20.23	23.77	47.62	8.35	0.03
After adsorption	28.8	21.07	44.19	0.89	5.05
Stirred in deionized water	21.12	22.24	48.57	7.98	0.09

Table S9 Semi-quantitative analysis of KOH@Ti $_3C_2T_X$ NSs using XPS.

Table S10 The Tl removal performance of KOH@Ti_3C_2T_X in the actual wastewater.

Adsorbent concentration (g L ⁻¹)	0.5	1	2	3	4
Tl Residual concentration ($\mu g L^{-1}$)	52.2	17.5	8.8	3.6	2.1
Removal efficiency (%)	60.2	86.6	93.3	97.3	98.4

 Table S11 Structural parameters of the adsorbents.

Adsorbent	Surface area (m^2, q^{-1})	Average pore size	Pore volume
	Surface area (III- g ·)	(nm)	$(cm^3 g^{-1})$
Ti ₃ C ₂ T _x -B	4.10	26.18	0.033
$Ti_3C_2T_x$	4.30	26.71	0.030
KOH@Ti ₃ C ₂ T _x	4.51	26.41	0.031

	Pseudo-first-order kinetics			Pseudo-second-order kinetics			
Adsorbent	k_l (min ⁻¹)	q_e (mg g ⁻¹)	R ²	k_2 (mmol· (g·min) ⁻¹)	q_e (mg g ⁻¹)	R ²	
KOH@Ti ₃ C ₂ T _x	1.81	215.1	0.986	0.0138	223.7	0.989	
NaOH@Ti ₃ C ₂ T _x	2.04	195.7	0.964	0.0171	204.9	0.987	
NH ₄ OH-Ti ₃ C ₂ T _x	2.28	160.0	0.975	0.0231	167.3	0.986	
KCl@Ti ₃ C ₂ T _x	2.01	67.7	0.989	0.0442	71.4	0.996	
$Ti_3C_2T_x$	1.58	45.96	0.814	0.0241	49.2	0.950	
Ti ₃ C ₂ T _x -B	1.54	32.36	0.839	0.0397	32.7	0.985	

Table S12 The parameters of Pseudo-first-order kinetics and Pseudo-second-order kinetics models for Tl⁺ adsorption on MXenes.

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