Supporting Information

Effect of Buffer on Direct Lithium Extraction Process of Tibetan Brine by Formed Titanium-based Lithium Ion Sieves

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Table S1. A summary of effect of adding buffer on lithium adsorption process by titanium-based lithium ion sieves

Adsorbent	Initial concentration of Li^+ (g/L)	Buffer	Initial pH value	Adjusted pH value	Adsorption condition	Adsorption capacity of Li^+ (mg/g)	Increasing ratio of adsorption capacity (%)	Recovery ratio of Li^+ (%)	Reference
H_2TiO_3	1.950 (brine)	Ammonia	-	10.1	25 ℃, 6 h	16.68	-	-	[1]
H_2TiO_3	1.56 (brine)	$Ca(OH)_2$	2.8	8.8	25 ℃, 5 g/L, 24 h	~33	94.1	10	[2]
H_2TiO_3	1.63 (brine)	$NaHCO_3$ NaOH	6.7	6.5 ~8	25 ℃, 20 g/L, 24 h	32.6 31.5	- -	40 38.6	[3]
PVB-HTO (H_2TiO_3)	0.2 (Simulated brine)	Ammonia	7.2	9.2	30 ℃, 10 g/L, 5 h	~12	60	50	[4]
P-HTO-NF ($H_4Ti_5O_{12}$)	1.0 (Simulated brine)	NaOH	8	11	25 ℃, 1 g/L, 12 h	59.1	61.9	20	[5]
$H_4Ti_5O_{12}$	0.166 (Simulated brine)	KOH	-	13	25 ℃, 2 g/L, 4 h	16.83	-	20	[6]
H_2TiO_3	0.093 (Shale gas produced water)	$KHCO_3$	7.0	6.4	30 ℃, 3 g/L, 24 h	18.32	-	59	[7]
PSF-HTO (H_2TiO_3)	0.025 (Geothermal water)	NaOH	8.8	12	60 ℃, 1 g/L, 2 h	22.66	~126.6	88.7	[8]
PVC-HTO (H_2TiO_3)	0.025 (Geothermal water)	NaOH	-	12	55 ℃, 2 g/L, 12 h	~9	-	~70	[9]

According to Table S1, when NaOH, $NH_3 \cdot H_2O$, $Ca(OH)_2$ and KOH were added in the brine or simulated brine, the pH value of the solution increased greatly due to the addition of a large amount of OH^-, while the pH value of the solution basically remained unchanged after the addition of $NaHCO_3$ and $KHCO_3$. In addition, except geothermal water and shale gas produced water that with low concentration of Li^+, the recovery ratio of Li^+ in the brine or simulated brine was poor.

Table S2. Effect of the buffer on the pH value of Tibetan Brine

Buffer	/	NaOH	$NaHCO_3$	$NH_3 \cdot H_2O$	$Ca(OH)_2$	$KHCO_3$
pH value	8.26	9.84	7.84	9.74	12.20	7.70

Table S3. Main cations content and physical properties of Tibetan Brine and Tibetan Brine-$NaHCO_3$

Type	Main cations content, mg/L					pH value	viscosity, mPa/S
	Li^+	Mg^{2+}	K^+	Na^+	Ca^{2+}		
Tibetan Brine	879.4	3778.5	5997.3	26901	268.3	8.26	1.93
Tibetan Brine-$NaHCO_3$	877.3	3643.2	5985.1	30903	210.6	7.84	1.99

Table S4. Fitting results of lithium adsorption on HTO-P in Tibetan Brine-$NaHCO_3$ and Tibetan Brine by different isotherm models

Isotherm model	parameter	Tibetan Brine-$NaHCO_3$	Tibetan Brine
Langmuir	q_m, mg/g	28.82	22.22
	K_L, mg/g	0.0044	0.0027
	R^2	0.998	0.993
Freundlich	K_F, L/g	2.70	0.78
	n	3.14	2.24
	R^2	0.975	0.971
D-R	q_0, mg/g	23.63	15.35
	β, mol^2/J^2	0.00621	0.00687
	R^2	0.993	0.970

Table S5. Fitting results of lithium adsorption on HTO-P in Tibetan Brine-$NaHCO_3$ and Tibetan Brine by different kinetic models

Kinetic model	Parameter	Tibetan Brine-$NaHCO_3$	Tibetan Brine
PFO	q_e, mg/g	21.168	13.366
	k_1, 1/h	0.406	0.392
	R^2	0.981	0.915
PSO	q_e, mg/g	22.256	14.735
	k_2, g/(mg·h)	0.038	0.025
	R^2	0.993	0.995
MO	q_e, mg/g	21.914	13.996
	k_1', 1/h	0.116	0.0759
	k_2', g/(mg·h)	0.022	0.0161
	R^2	0.990	0.992

Table S6. O 1s peak parameters of HTO-P, HTO-P(Li)-$NaHCO_3$ and HTO-P(Li)

Adsorbent	Peak					
	O-Ti		HO^-/Li-O^-		H_2O	
	Binding energy (eV)	Atomic ratio	Binding energy (eV)	Atomic ratio	Binding energy (eV)	Atomic ratio
HTO-P	530.10	74.19%	531.60	21.85%	532.80	3.96%
HTO-P(Li)-$NaHCO_3$	529.88	46.47%	531.21	46.89%	532.74	6.64%
HTO-P(Li)	529.91	55.83%	531.36	33.05%	532.50	11.11%

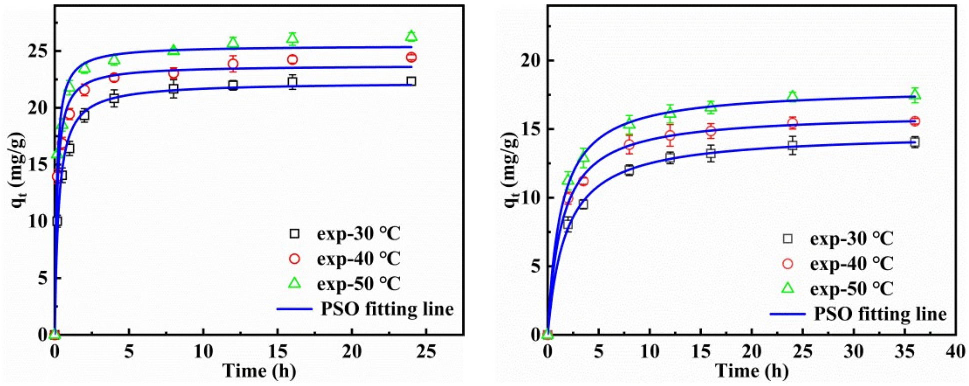

Fig. S1 Adsorption rate curves of Li^+ on HTO-P in (a) Tibetan Brine-$NaHCO_3$ and (b) Tibetan Brine under different adsorption temperatures

Table S7. Fitting results of lithium adsorption on HTO-P in Tibetan Brine-$NaHCO_3$ and Tibetan Brine under different adsorption temperatures by PSO model

Temperature, ℃	Tibetan Brine-$NaHCO_3$			Tibetan Brine		
	q_e, mg/g	k_2, g/(mg·h)	R^2	q_e, mg/g	k_2, g/(mg·h)	R^2
30	22.256	0.038	0.993	14.735	0.025	0.995
40	23.749	0.061	0.986	16.171	0.046	0.998
50	25.489	0.067	0.987	17.991	0.043	0.999

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