Supplementary Materials

Karst-inspired hierarchical Mg/Al layered double hydroxide with high entropy-driven for interception and storage

Hongyu Shi[1], Jun Qin[1, *], Qing Lv[1], Lijin Zhang[1], Qingxin Li[1], Bin Ou[1, 2], Xiaolang Chen[3, *]

1. Key Laboratory of Karst Georesources and Environment, Ministry of Education, College of Resources and Environment Engineering, Guizhou University, 550025 Guiyang, China;

2. Fuzhou Hongtai Investment Co., Ltd., 350001 Fuzhou, China;

3. Key Laboratory of Advanced Materials Technology Ministry of Education, School of Materials Science and Engineering, Southwest Jiaotong University, 610031 Chengdu, China

*Corresponding author, E-mail address: qi_njun@163.com (J. Qin); chenxl612@sina.com (X. Chen.).

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Text S1: Formula details

The removal efficiency (%) and phosphate adsorption capacity (mg g^{-1}) of three adsorbents were calculated using the following equations:

$$q_e=(C_0-C_e)V/m \quad (1)$$

$$q_t=(C_0-C_t)V/m \quad (2)$$

$$\eta=(C_0-C_e)V/C_0 \quad (3)$$

where C_0 (mg L^{-1}) represents the phosphate concentration before adsorption; C_e (mg L^{-1}) and C_t (mg L^{-1}) represent the phosphate concentration at equilibrium and time t, respectively; V (L) represents the solution volume and m (g) represents the mass of the adsorbent.

1.1. Adsorption kinetics

The adsorption kinetics is significant in further exploring the adsorption mechanism. Pseudo-first-order,[1] pseudo-second-order,[2] and Elovich [3,4] models were applied to fit the adsorption data. The equations are as follows：

$$\text{Pseudo-first-order equation: } q_t=q_e[1-exp(-K_1t)] \quad (4)$$

$$\text{Pseudo-second-order equation: } q_t=q_e^2K_2t/(1+K_2q_et) \quad (5)$$

$$\text{Elovich equation: } q_t=alnt+b \quad (6)$$

where q_t (mg g^{-1}) and q_e (mg g^{-1}) represent the amounts of phosphate adsorbed at time t and adsorption equilibrium, respectively; K_1 (min^{-1}) and K_2 (g mg^{-1} min^{-1}) represent the adsorption rate constants; a and b represent the rate constants fitted by the Elovich model.

1.2. Adsorption isotherms

Adsorption isotherms show the relationship between adsorption capacity (q_e) and the adsorption equilibrium concentration (C_e) under suitable reaction conditions. Langmuir,[5] Freundlich,[6] and Toth [7,8] models were applied to describe monolayer homogeneous, multilayer heterogeneous, and multilayer heterogeneous surface adsorption processes, respectively. The models can be expressed by the following equations:

$$\text{Langmuir model: } q_e=q_m K_L C_e/(1+K_L C_e) \quad (7)$$

$$\text{Freundlich model: } q_e=K_F C_e^{\,1/n} \quad (8)$$

$$\text{Toth model: } q_e=q_m C_e/[aT+C_e^{Z}]^{1/Z} \quad (9)$$

where q_m (mg g^{-1}) and K_L represent the maximum adsorption capacity of phosphate and the constant in the Langmuir related to the heat of adsorption, respectively; K_F and n represent the adsorption capacity and favorability of adsorption, respectively; Z represents the heterogeneity of the adsorbent surface, and aT represents the adsorption affinity.

1.3. Adsorption thermodynamics

To evaluate the spontaneity and thermostability of LDHs during adsorption process, three thermodynamic parameters (ΔG^0, ΔS^0, and ΔH^0) were calculated.[9] The equations are as follows:

$$\Delta G^0 = -RT\ln K \quad (10)$$

$$\Delta G^0=\Delta H^0-T\Delta S^0 \quad (11)$$

$$\ln K= -\Delta H^0/RT + \Delta S^0/R \quad (12)$$

where K (L mol^{-1}) and R (8.314 J K^{-1} mol^{-1}) are the thermodynamic equilibrium constant and the gas constant, respectively.

Table S1 Actual Mg-Al ratio of different LDHs.

Samples	Ratio	Mg element content(%)	Al element content(%)	[Mg]/[Al] (ICP-OES)
G-LDH	Mg^{2+}:Al^{3+}:Na^{+}=4:1:1	26.04	6.40	4.51
Rock-LDH	Mg^{2+}:Al^{3+}:Na^{+}=4:1:1	24.08	6.35	4.20
Karst-LDH		14.30	13.22	1.20

Table S2 BET data of adsorbents.

Samples	Specific Surface Area (m^2 g^{-1})	Pore Volume (m^3 g^{-1})	Average Pore Diameter (nm)
G-LDH	16.239	0.107	25.677
Rock-LDH	36.828	0.221	23.279
Karst-LDH	48.470	0.227	18.145

Table S3 Adsorption kinetics fitting parameters.

Samples	Pseudo-first-order			Pseudo-second-order			Elovich		
	q_e (mg g^{-1})	K_1 (min^{-1})	R^2	q_e (mg g^{-1})	K_2 (g mg^{-1} min^{-1})	R^2	a	b	R^2
G-LDH	6.345	0.927	0.320	6.599	0.193	0.681	0.501	4.368	0.986
Rock-LDH	14.201	0.660	0.602	14.664	0.077	0.899	1.059	9.800	0.919
Karst-LDH	60.457	0.310	0.947	62.790	0.008	0.982	6.384	32.081	0.810

Table S4 Adsorption isotherms fitting parameters.

Samples	T (K)	Langmuir isotherm equation			Freundlich isotherm equation			Toth equation			
		q_m (mg g^{-1})	K_L	R^2	K_F	$1/n$	R^2	q_m (mg g^{-1})	a_T	Z	R^2
G-LDH	298	16.14	0.012	0.956	1.342	0.400	0.982	39.25	0.025	0.357	0.978
	308	22.50	0.010	0.979	1.420	0.442	0.993	53.93	0.015	0.392	0.992
	318	24.81	0.013	0.968	2.275	0.388	0.982	61.15	0.031	0.347	0.983
Rock-LDH	298	38.36	0.013	0.893	2.954	0.422	0.976	123.76	0.039	0.291	0.962
	308	44.60	0.012	0.946	3.412	0.419	0.992	142.46	0.027	0.309	0.985
	318	49.96	0.012	0.979	4.146	0.400	0.996	153.78	0.026	0.314	0.996
Karst-LDH	298	105.54	0.860	0.750	61.402	0.119	0.990	435.00	$2.610*10^9$	0.081	0.959
	308	111.41	0.900	0.795	63.554	0.125	0.992	593.40	$3.066*10^9$	0.076	0.997
	318	114.30	1.980	0.711	67.794	0.119	0.998	1230.31	$4.411*10^{16}$	0.049	0.998

Table S5 Adsorption thermodynamic parameters.

Samples	T (K)	ΔG^0 (KJ mol^{-1})	ΔH^0 (KJ mol^{-1})	ΔS^0 (J K^{-1} mol^{-1})	$\%\zeta_H$	$\%\zeta_S$
G-LDH	298	-0.728	20.313	70.040	49.321	50.679
	308	-0.899			48.496	51.504
	318	-2.152			47.699	52.301
Rock-LDH	298	-2.683	13.330	53.655	45.466	54.250
	308	-3.142			44.649	55.351
	318	-3.760			43.861	56.139
Karst-LDH	298	-10.201	3.887	47.231	21.640	78.360
	308	-10.631			21.086	78.914
	318	-11.148			20.560	79.441

Table S6 Comparison of phosphate adsorption properties of Mg-Al LDH modified by different methods.

Adsorbents	Adsorbent characteristics and adsorption conditions	Actual maximum adsorption capacity (mg g^{-1})	Ref
Mg/Al hydroxides modified almond shell biochar	Mg/Al ratio=3 SSA: 4.51 m^2 g^{-1} PV: 0.023 cm^3 g^{-1} Dosage: 2.50 g L^{-1} C_0: 0-250 mg L^{-}	6.10	[10]
Mg-Al-LDH/BC	SSA: 77.32 m^2 g^{-1} PD: 16.377 nm C_0: 5-80 mg P L^{-1} T: 298K	36.19 (P)	[11]
Mg-Al-La LDH/Fe_3O_4/C	SA: 19.19 m^2 g^{-1} PV: 0.096 cm^3 g^{-1} PD: 20.637 nm Dosage: 0.6 g L^{-1} pH: 7 T: 328 K Co: 10-100 mg L^{-1}	106.21	[12]
Mg/Al-201	SA: 4.32 m^2 g^{-1} PD: 8.4 nm Dosage: 0.5 g L^{-1} T: 298 K	52.00	[13]
Mg-Al-CO_3LDH-Chitosancomposite	Dosage: 0.3 g L^{-1} pH: 5 Co: 10-120 mg L^{-1}	54.9	[14]
40% LDH/biochar composite	SA: 10.1 m^2 g^{-1} Dosage: 2.0 g L^{-1} Co: 50 mg P L^{-1}	13.23 (P)	[15]
Karst-LDH	SA: 48.47 m^2 g^{-1} PV: 0.227 cm^3 g^{-1} PD: 18.145 nm Dosage: 0.8 g L^{-1} Co: 25-300 mg L^{-}	127.17	This work

Note: SSA, PV, PD represent specific surface area, pore volume, pore diameter, respectively.

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