

Supplementary Documents

Nano-MgO/pyro-hydrochar for enhancing adsorption of fluoride ion from aqueous solution: Performance, influencing factors, and mechanisms

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Text S1. Fabrication of nMgO/Py-HyC

6.0 g *Rhus typhina* powder was mixed with deionized water at a ratio of 1:5 and heated to 220 °C for 4 h. The obtained hydrochar was washed with deionized water and dried, then 1.0 g hydrochar and 8.3645 g $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ were mixed in 50 mL deionized water, stirred for 30 min, dried at 105 °C, and then pyrolyzed at 600 °C under N_2 for 2 h to obtain nMgO/Py-HyC.

Text S2. Characterization

nMgO/Py-HyC was characterized by scanning electron microscope (SEM, ZEISS, Sigma 300) equipped with energy-dispersive X-ray spectrometer (EDS), specific surface area and aperture analyzer (Micromeritics, ASAP 2020), X-ray diffraction (XRD, Rigaku, D/max-2500), Fourier transform infrared spectrometer (FTIR, Thermo Fisher Scientific, Nicolet 6700), and X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific, ESCALAB 250xi). XPS data were analyzed and fitted using Avantage (ThermoFisher Scientific, USA).

Text S3. Batch adsorption experiments

To obtain the adsorption isotherms and thermodynamics of fluoride ions on nMgO/Py-HyC, a batch adsorption experiment was carried out. The initial concentrations of the fluoride ion solutions were set to 100, 200, 300, 400, 500, 600, 700, and 800 mg/L. The pH was adjusted to 7.0 ± 0.1 using 0.1 mol/L NaOH and 5% HNO₃. In centrifuge tubes, 0.05 g of nMgO/Py-HyC was added to 50 mL of each fluoride ion solution, and the tubes were placed in a constant-temperature water bath shaker, shaking at 25 °C and 180 rpm for 48 h. Three replicates were set up for each concentration, and the solutions were filtered using a 0.22 µm polyethersulfone membrane for subsequent analysis.

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \quad (1)$$

In the formula, q_e represents the adsorption capacity of nMgO/Py-HyC for pollutants at equilibrium (mg/g); C_e denotes the equilibrium concentration of pollutants (mg/L); C_0 represents the initial concentration of pollutants (mg/L); V refers to the volume of the solution (L); m indicates the mass of nMgO/Py-HyC used (g).

$$\eta = \frac{C_0 - C_e}{C_e} \times 100\% \quad (2)$$

In the formula, η represents adsorption efficiency after reaching equilibrium, %; C_e denotes the equilibrium concentration of pollutants (mg/L); C_0 represents the initial concentration of pollutants (mg/L)

The adsorption isotherm data were fitted using the Langmuir and Freundlich models, and the corresponding nonlinear equations are presented in Table S1.

Table S1 Adsorption isotherm models and equations

Model type	Model equation
Langmuir	$q_e = \frac{K_L q_m C_e}{1 + K_L C_e}$
Freundlich	$q_e = K_F C_e^N$

Note: q_e represents the adsorption capacity of nMgO/Py-HyC for pollutants at equilibrium (mg/g); C_e denotes the equilibrium concentration of pollutants (mg/L); K_L represents Langmuir adsorption coefficient (L/mg); K_F represents Freundlich adsorption coefficient (L/mg); N represents Freundlich adsorption strength factor.

The adsorption isotherms were obtained at 25 °C, 35 °C, and 45 °C, respectively, the thermodynamic parameters of Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°), were calculated according to Van't Hoff equation and the Third Law of Thermodynamics.

$$\Delta G^\circ = -RT \ln K \quad (3)$$

$$\ln K = -\frac{\Delta G^\circ}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (4)$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \quad (5)$$

In the formula, ΔG° : change in Gibbs free energy of thermodynamic parameters during the adsorption process (kJ/mol); ΔH° : enthalpy change of adsorption (kJ/mol); ΔS° : adsorption entropy change (kJ/(mol·K)); K : adsorption equilibrium constant or distribution coefficient (L/mg); R : ideal gas constant, 8.314 J/(mol·K).

Samples were collected at specified time intervals of 1, 2, 4, 8, 12, 24, 48, 72, 96, and 120 h using an initial F^- concentration of 100 mg/L. The kinetic data were fitted using the pseudo-first-order, pseudo-second-order, Elovich, intraparticle-diffusion, and Boyd film-diffusion

models, and the corresponding equations are summarized in Table S2.

Table S2 Kinetic model types and equations

Model type	Model equation
Pseudo-first-order kinetics	$q_t = q_{e1}(1 - e^{-k_1 t})$
Pseudo-second-order kinetics	$q_t = \frac{k_2 q_{e2}^2 t}{1 + k_2 q_{e2} t}$
Elovich	$q_t = a + b \ln(t)$
Intra-particle diffusion	$q_t = k_p t^{0.5} + S$
Boyd/film diffusion	$B_t = -\ln\left(1 - \frac{q_t}{q_e}\right) - 0.4977$

q_t : adsorption amount at time t (mg/g); q_e : adsorption capacity at equilibrium (mg/g); k : adsorption rate g/(mg·h); k_p : intraparticle diffusion model constant (mg/(g·h)); S : intraparticle diffusion model constant; B_t : film diffusion constant.

For each batch adsorption experiment, 50 mg of nMgO/Py-HyC was added to 50 mL of fluoride solution in a 100 mL centrifuge tube, corresponding to an adsorbent dosage of 1.0 g/L. The tube was placed in a constant-temperature shaking incubator and agitated at 180 rpm and 25 °C for 48 h to attain adsorption equilibrium. After adsorption, the suspension was filtered through a 0.22 µm syringe filter, and the residual F⁻ concentration in the filtrate was determined by ion chromatography. The equilibrium adsorption capacity was calculated according to Eq. (1).

For the pH-effect experiments, the initial F⁻ concentration was fixed at 100 mg/L, and the initial solution pH was adjusted to 3, 5, 7, 9, 11, and 13. For the coexisting-ion experiments, the effects of NO₃⁻, SO₄²⁻, and HCO₃⁻ on F⁻ adsorption were investigated separately. The initial F⁻ concentration was maintained at 100 mg/L, while the concentration of each coexisting ion was set at 1, 5, or 10 mmol/L. A fluoride solution without an additionally introduced

coexisting ion was used as the control. The influence of ionic strength on F^- adsorption was evaluated by adjusting the $NaNO_3$ concentration to 0.02, 0.10, 0.20, and 0.30 mol/L. The initial F^- concentration was maintained at 100 mg/L, and the remaining adsorption conditions were unchanged. All experiments were conducted under otherwise identical conditions.

Text S4. Data analysis

The experimental data on adsorption isotherms were fitted using the Langmuir and Freundlich models via the nonlinear least-squares fitting method using OriginPro 2021 (OriginLab, Northampton, MA, USA). One-way ANOVA with Duncan's multiple range test was applied to determine significant differences at a threshold of $p < 0.05$ was performed using SPSS 25.0 (IBM Corporation, Armonk, New York, USA). All the data are presented as mean $\pm$ standard deviation (SD) derived from triplicate experiments.

Table S3 Parameters of adsorption isotherm models at different temperatures

Temperature (K)	Langmuir			Freundlich		
	$Q_{\max}$	K_L (L/mg)	R^2	K_F	1/n	R^2
	(mg/g)			(mg/g)/(mg/L) ⁿ		
298	469.64	0.004	0.99	10.92	0.55	0.96
308	391.96	0.008	0.97	23.91	0.43	0.91
318	248.06	0.020	0.95	39.85	0.29	0.96

Table S4 Thermodynamic parameters of adsorption of fluoride ions by nMgO/Py-HyC

Temperature (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/(mol · k))	R^2
298	−10.65			
308	−13.12	64.68	0.25	0.99
318	−15.70			

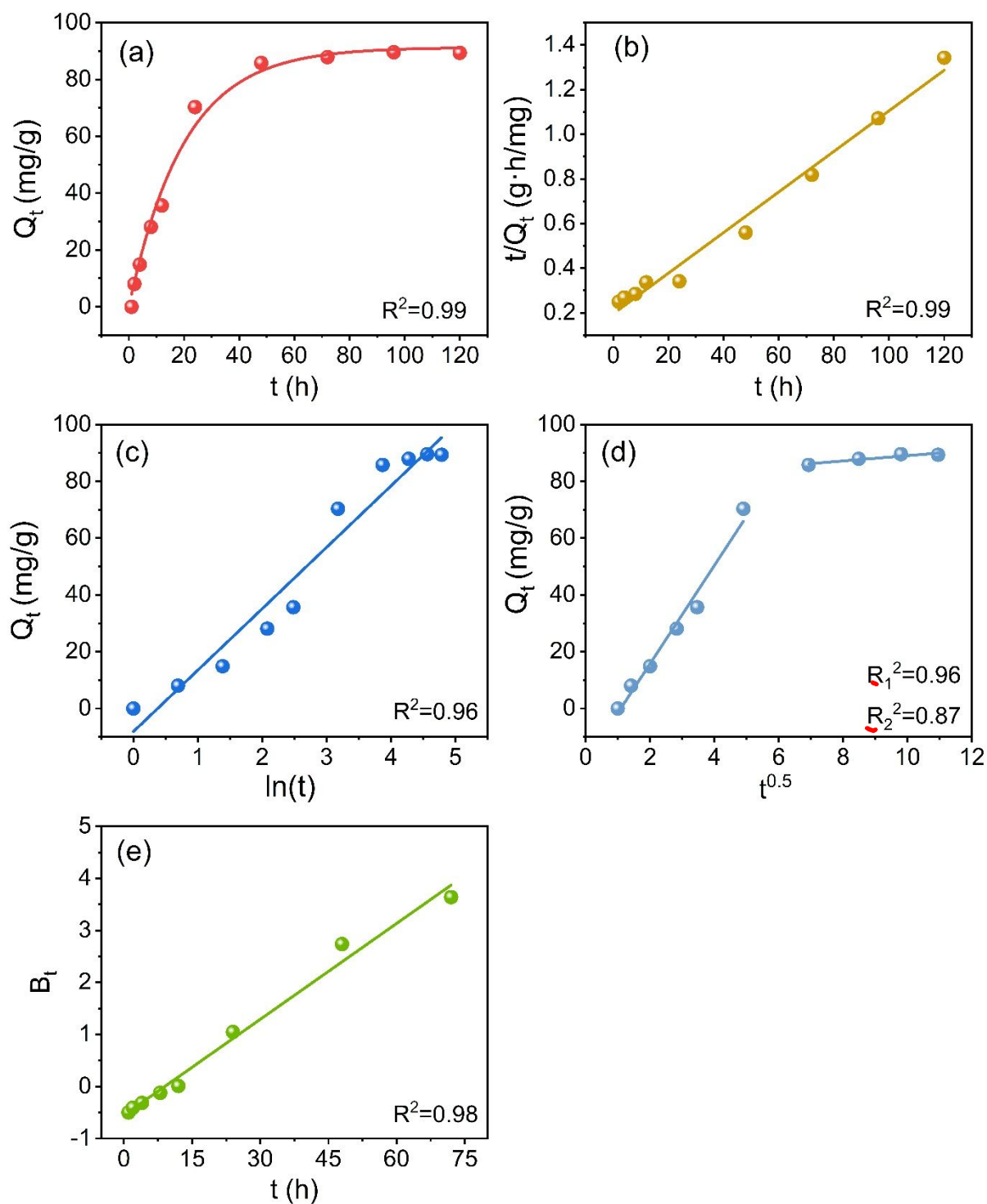


Figure S1. Kinetic model fitting for F^- adsorption onto nMgO/Py-HyC: **(a)** pseudo-first-order model; **(b)** pseudo-second-order model; **(c)** Elovich model; **(d)** intraparticle diffusion model; and **(e)** Boyd model

Table S5 Kinetic parameters of nMgO/Py-HyC for F⁻

Model type	Related parameter	R ²
Pseudo-first-order kinetics	$q_{e1} = 91.32 \text{ mg/g}$ $k_1 = 0.05$	0.99
Pseudo-second-order kinetics	$q_{e2} = 111.10 \text{ mg/g}$ $k_2 = 0.0005 \text{ g/(mg}\cdot\text{h)}$	0.99
	$k_{p1} = 14.98 \text{ mg/(g}\cdot\text{h)}$ $S_1 = -14.38$	0.99
Intra-particle diffusion	$k_{p2} = 14.03 \text{ mg/(g}\cdot\text{h)}$ $S_2 = -7.58$	0.90
	$k_{p3} = 0.59 \text{ mg/(g}\cdot\text{h)}$ $S_3 = 83.18$	0.66
Elovich Equation	$a = 14.85 \text{ mg/h}$ $b = 0.05 \text{ g/mg}$	0.96
Boyd/film diffusion	$k_f = 0.06 \text{ h}^{-1}$ $C = 0.05$	0.98

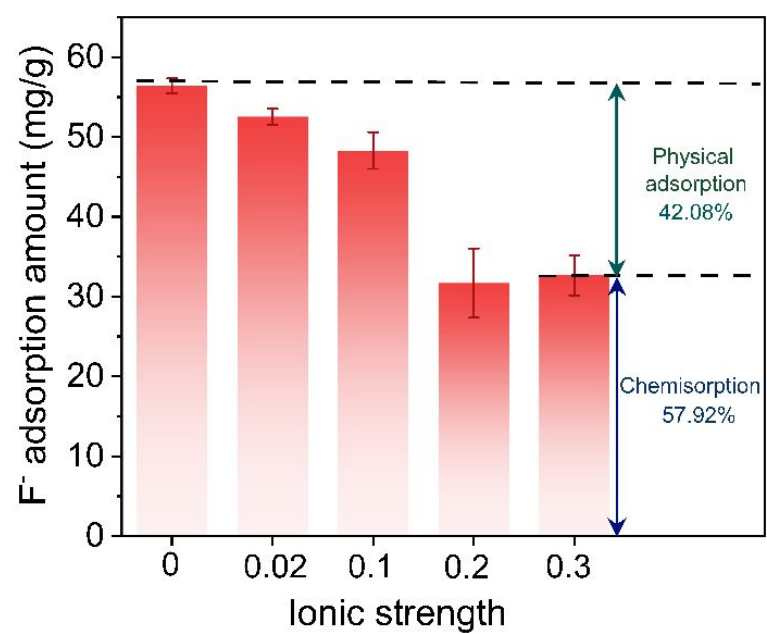


Figure S2. Effect of ionic strength on F^- adsorption by nMgO/Py-HyC

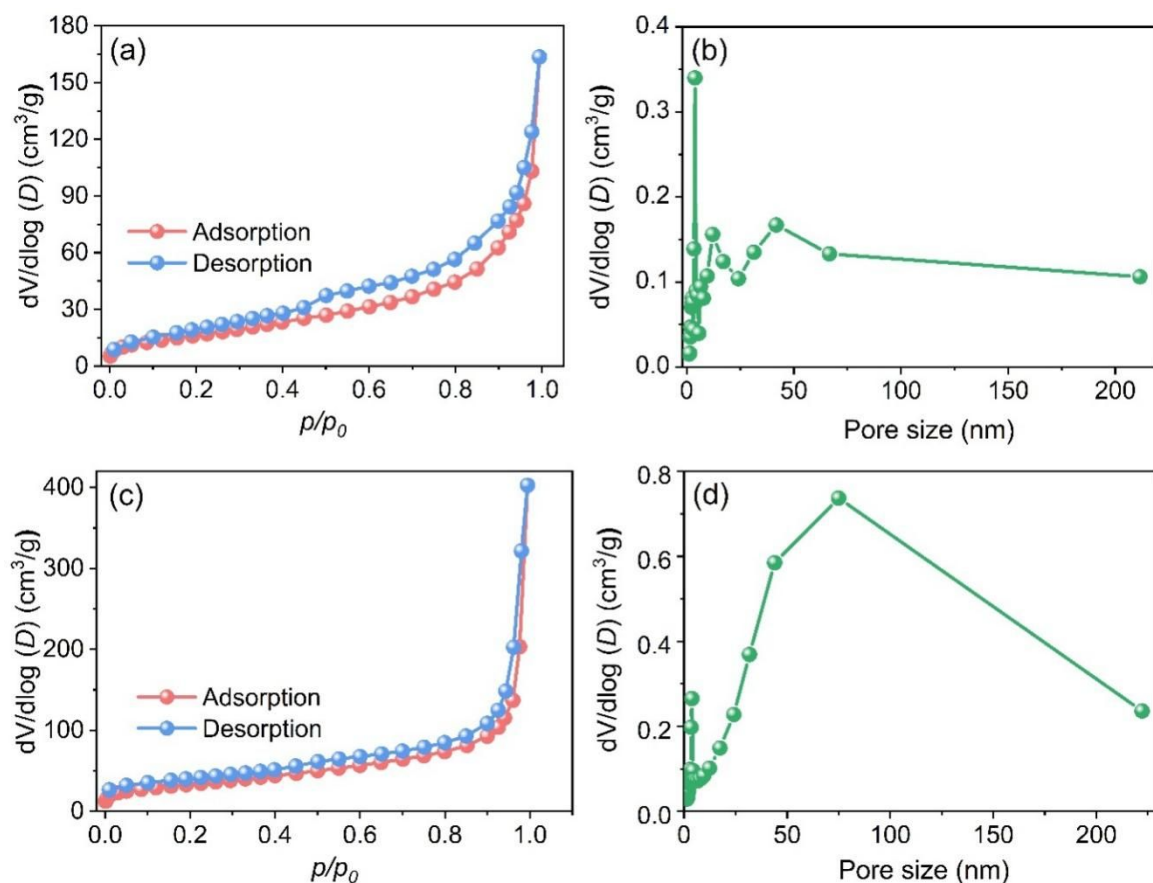


Figure S3. N_2 adsorption-desorption characteristics before and after $nMgO/Py-HyC$ adsorption of F^- : **(a)** isothermal curve before adsorption; **(b)** pore size distribution curve before adsorption; **(c)** isothermal curve after adsorption; **(d)** pore size distribution curve after adsorption

Text S5. Adsorption performance under the condition of Nanhu wetland water

Water was collected from the Nanhu Wetland in Changchun City, China, and its physicochemical characteristics are presented in Table S6. The collected water was spiked with F^- to an initial concentration of 100 mg/L. Subsequently, 50 mg of nMgO/Py-HyC was added to 50 mL of the fluoride-spiked wetland water in a 100 mL centrifuge tube. The adsorption experiment was conducted under the same conditions as those described in Text S4.

Table S6 Physicochemical characteristics of water collected from the Nanhu Wetland

Cl^-	PO_4^{3-}	S	CO_3^{2-}	Ca^{2+}	Mg^{2+}	DOC
(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
23	0.005	/	1.6	0.02	0.03	14

The F^- adsorption amount under actual Nanhu wetland water conditions was 81.0 ± 0.272 mg/g, comparable to that in synthetic fluoride solution (85.5 ± 0.126 mg/g; $p > 0.05$), indicating that nMgO/Py-HyC may maintain the performance in F^- adsorption in actual conditions.

Text S6. Life cycle assessment

A comparative life cycle assessment (LCA) was conducted for rice husk (RH) and spent coffee grounds (SCG)-based magnesium oxide (MgO) biochar composites (MgO/RH and MgO/SCG), and nMgO/Py-HyC using SimaPro 9. The functional unit was defined as the removal of 1 kg of fluoride (F^-), and the system boundary covered the major material- and energy-consuming processes involved in adsorbent preparation. Inventory data were obtained from laboratory records, relevant literature, and the ecoinvent 3.x database using the allocation, cut-off by classification system model. Environmental impacts were evaluated using the ReCiPe 2016 [H] method, including 18 midpoint impact categories and three endpoint damage categories: human health, ecosystems, and resources. For comparison, the impact of MgO/RH in each category was defined as 100%, and the impacts of MgO/SCG and nMgO/Py-HyC were expressed relative to this reference.

The environmental impacts of MgO modified biochar, including MgO/RH, MgO/SCG, and nMgO/Py-HyC, were evaluated by LCA at the midpoint and endpoint levels. Among the three materials, nMgO/Py-HyC exhibited the most favorable environmental performance, including global warming. Its normalized impacts were consistently lower than those of MgO/RH and MgO/SCG across all 18 midpoint categories (Fig. S4a). The endpoint assessment showed the same overall pattern (Fig. S4b). The impacts of MgO/RH were taken as 100%; the relative impacts of MgO/SCG on human health, ecosystems, and resources were approximately 56%, whereas those of nMgO/Py-HyC decreased to approximately 44%. Overall, nMgO/Py-HyC exhibited favorable life-cycle environmental performance and great potential for the sustainable treatment of fluoride-contaminated water.

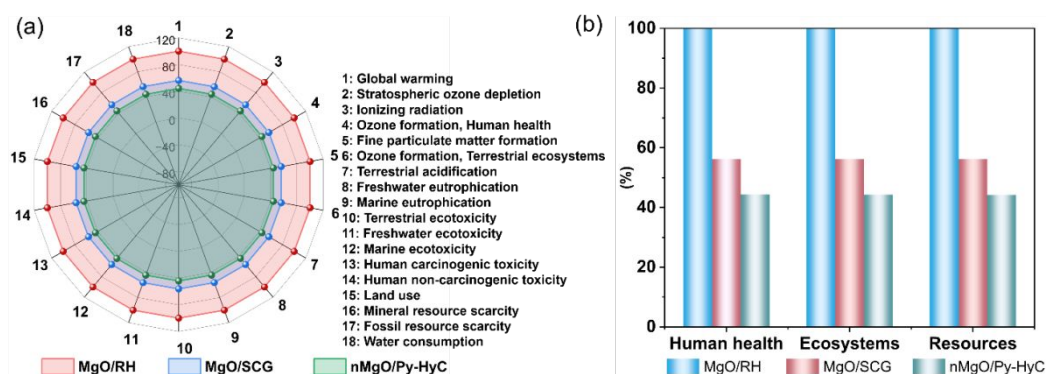


Figure S4. Comparative life-cycle environmental impacts of MgO/RH, MgO/SCG, and nMgO/Py-HyC: (a) normalized results for 18 midpoint impact categories; and (b) normalized endpoint damage results for human health, ecosystems, and resources.