

## ***Supporting information for***

### **Layered magnesium oxide for efficient removal of fluoride from groundwater**

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## Experiment section

### 1. Batch adsorption experiments

In the experiment to study the influence of different pH values, 0.05g of adsorbent was added to 0.05L of 10mg/L fluoride solution. The experimental conditions were set to 25°C, with an oscillation time of 24 h. The pH value of the fluoride solution was adjusted from 2 to 12 using 1mol/L NaOH and HNO<sub>3</sub> solutions.

In the study of anion adsorption competition, the concentration of 100 mg/L NaNO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, NaH<sub>2</sub>PO<sub>4</sub>, NaCl, NaHCO<sub>3</sub>, and Na<sub>2</sub>CO<sub>3</sub> anion solutions was prepared, and these solutions were added to a fluoride solution to study the influence of anions on fluoride adsorption.

During the kinetic experiment, the initial concentration of the fluorine solution was 10 mg/L, the volume of the fluoride solution was 0.15 L, the mass of the adsorbent was 0.15 g, the pH was maintained at 7, and the temperature was maintained at 25°C. The concentration of the residual fluorine solution was measured by sampling the supernatant at various intervals.

During the isotherm experiment, the mass of the adsorbent was 0.05 g, the volume of the fluoride solution was 0.05 L, the pH value was 7, the temperature was 25°C, the oscillation time was 12 h, and the initial concentration of the fluoride solution was changed in the range of 10-100 mg/L.

In the study of the regeneration performance test, 0.05 g of adsorbent was added to 0.05L of a 10mg/L fluoride solution. The temperature was maintained at 25°C, and the agitation time was 12 h. The pH value of the solution was 7, and the residual fluoride ion concentration was determined by sampling after adsorption. After filtration, the adsorbent was added to 50mL of a 0.001mol/L NaOH solution for desorption. It was then filtered and washed to neutrality after agitation for 8 hours. After drying, the adsorbent was calcined at 500°C for 2 hours for regeneration. This process was repeated three times for the adsorbent after each cycle of desorption and regeneration.

### 2. Formula and model equation in performance test

#### 2.1 Adsorption properties calculation formula

The calculation formulas of adsorption capacity ( $q_e$ ) and removal rate ( $R_F$ ) are shown in equation (1) and (2):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (1)$$

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

Where,  $C_0$  and  $C_e$  represent the initial fluoride concentration of fluoride in solution and the equilibrium concentration after adsorption, mg/L respectively.  $V$  stands for volume of fluoride solution, mL.  $m$  represents the mass of the adsorbent, g.  $R_F$  stands for fluoride removal rate, %.  $q_e$  is the adsorption capacity at equilibrium, mg/g.

## 2.2 adsorption isotherm model

The commonly utilized adsorption isotherm models in the process of adsorption encompass the Langmuir and Freundlich models [25,26]. For specific details, refer to equations (3) and (4).

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

$$q_e = K_F C_e^{\frac{1}{n}} \quad (4)$$

Where,  $C_e$  is the concentration of  $F^-$  at adsorption equilibrium, mg/L.  $q_e$  is the adsorption capacity of  $F^-$  at adsorption equilibrium, mg/g.  $q_m$  is the maximum adsorption capacity of  $F^-$ , mg/g.  $K_L$  is Langmuir constant related to adsorption free energy, L/mg.  $K_F$  is the Freundlich constant related to the relative adsorption capacity of the adsorbent, mg/g.  $n$  is the heterogeneous parameter corresponding to the adsorption strength, and the dimension is 1.

## 2.3 Adsorption kinetic equation

The commonly used kinetic models in the adsorption process are pseudo-first-order kinetic model, pseudo-second-order kinetic model and intra-particle diffusion model [27-29], for details, see equations (5), (6) and (7).

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

$$q_t = K_1 t^{0.5} + C_i \quad (7)$$

Where,  $q_t$  is the adsorption capacity at time  $t$ , mg/g.  $K_1$  is the equilibrium rate constant of the

pseudo-first-order kinetic model,  $\text{min}^{-1}$ .  $K_2$  is the equilibrium rate constant of the pseudo-second-order kinetic model,  $\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$ .  $K_i$  is the equilibrium rate constant of the in-particle diffusion model,  $\text{min}^{0.5}$ .  $C_i$  is the intercept of the Intra-particle diffusion model diffusion model.

## *Figures and Tables*

Table S1 Isotherm model parameters of MgO-3 adsorption fluoride

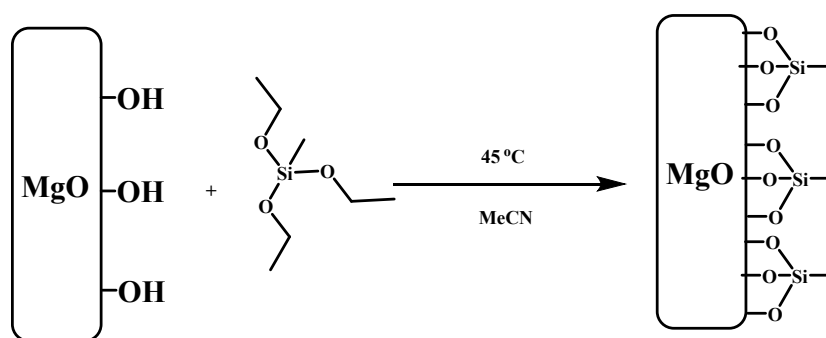
Model	Parameter	value
Langmuir Isotherm	$q_m/\text{mg}\cdot\text{g}^{-1}$	126.405
	$K_L/\text{L}\cdot\text{mg}^{-1}$	0.0090
	$R^2$	0.8914
Freundlich Isotherm	$K_F/\text{mg}\cdot\text{g}^{-1}$	2.5142
	$n$	1.4398
	$R^2$	0.8776
Experimental value	$q_e/\text{mg}\cdot\text{g}^{-1}$	69.600

Table S2 Model parameters of quasi-first-order, quasi-second-order and internal diffusion models

model	parameter	MgO-3	
		10 mg/L	30 mg/L
Pseudo-first-order dynamics model	$q_e/\text{mg}\cdot\text{g}^{-1}$	6.600	24.155
	$K_1/\text{min}^{-1}$	0.0065	0.0052
	$R^2$	0.9623	0.9947
Pseudo-second-order dynamics model	$q_e/\text{mg}\cdot\text{g}^{-1}$	10.6269	32.0512
	$K_2/\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$	0.0007	0.0001
	$R^2$	0.9984	0.9984
Intra particle diffusion model	$K_{i1}/\text{min}^{0.5}$	0.9215	1.7178
	$C_{i1}$	-1.6176	-1.9537
	$R_1^2$	0.9961	0.9997
	$K_{i2}/\text{min}^{0.5}$	0.5826	1.6316
	$C_{i2}$	0.8396	-1.2931
	$R_2^2$	0.9462	0.9892
	$K_{i3}/\text{min}^{0.5}$	0.0826	0.5062
	$C_{i3}$	7.5565	15.3270
Experimental value	$R_3^2$	0.9999	0.9963
	$q_e/\text{mg}\cdot\text{g}^{-1}$	9.728	28.710

Table S3 The effect of modified-MgO with different content methyltriethoxysilane on fluoride

adsorption.



Entry	Adsorbents	F removal rate (%)
1	MgO-3	92
2	MgO-3-org-Si-0.1	86
3	MgO-3-org-Si-0.5	71
4	MgO-3-org-Si-1	66
5	MgO-3-org-Si-1.5	59

Table S4 Different absorbed condition on MgO-3.

Temp. (°C)	Stirring rate (r/min)	Initial concentration (mg/L)	Adsorption capacity (mg/g)
25	150	10.98	69.9
35	150	10.98	75.6
45	150	10.98	79.3
50	150	10.98	79.6
45	300	10.98	79.9
45	600	10.98	82.5
45	800	10.98	82.4
45	600	12.62	91.3
45	600	14.84	102.7
45	600	16.86	114.1
45	600	21.96	116.8

The adsorption conditions: mass of adsorbent  $m = 0.05$  g, volume of fluoride solution  $V = 0.05$  L,  $\text{pH} = 7$ , oscillation time  $t = 10$  h.



Table S5 MgO-3 for fluoride adsorption in real wastewater.

Ion	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	F <sup>-</sup>	Na <sup>+</sup>	pH
pre-adsorption	53.2	3.69	15.46	4.49	4
after-adsorption	51.6	1.1	1.5	4.45	10
removal	3.02%	70.18%	90.29%	0.89%	-

The actual wastewater samples obtained from Jinchuan Company, which contain fluoride ions along with other ions such as chloride, sulfate, and sodium.

To validate the feasibility of our synthesized magnesium oxide material, we treated 100 mL of the sulfur-containing wastewater with 0.15 mg of the adsorbent at a pH of 4, without further adjustment. The adsorption experiment was conducted at a temperature of 25 °C, with a shaking speed of 150 rpm and a duration of 24 hours. The concentrations of each ion in the wastewater after adsorption are presented in the table below.

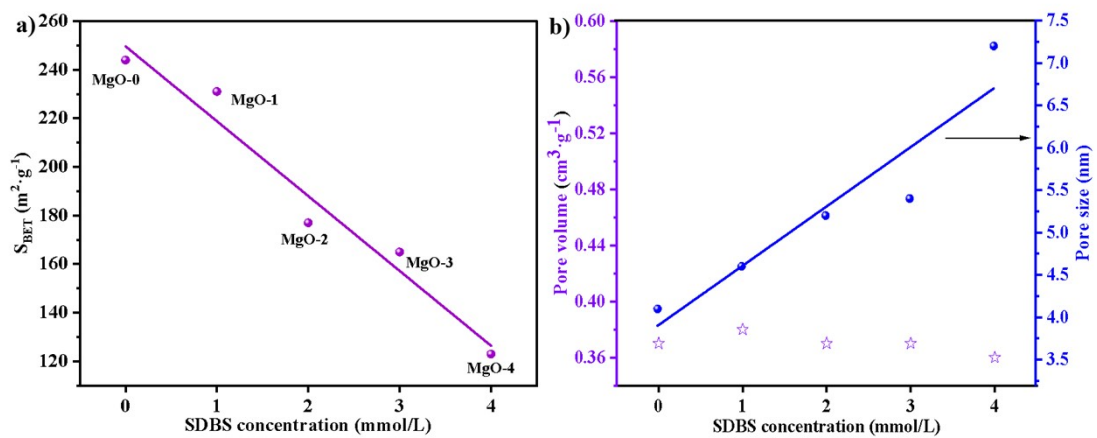


Fig.S1 Plot of SDBS concentration against with specific surface area (a), and pore size/volume (b).

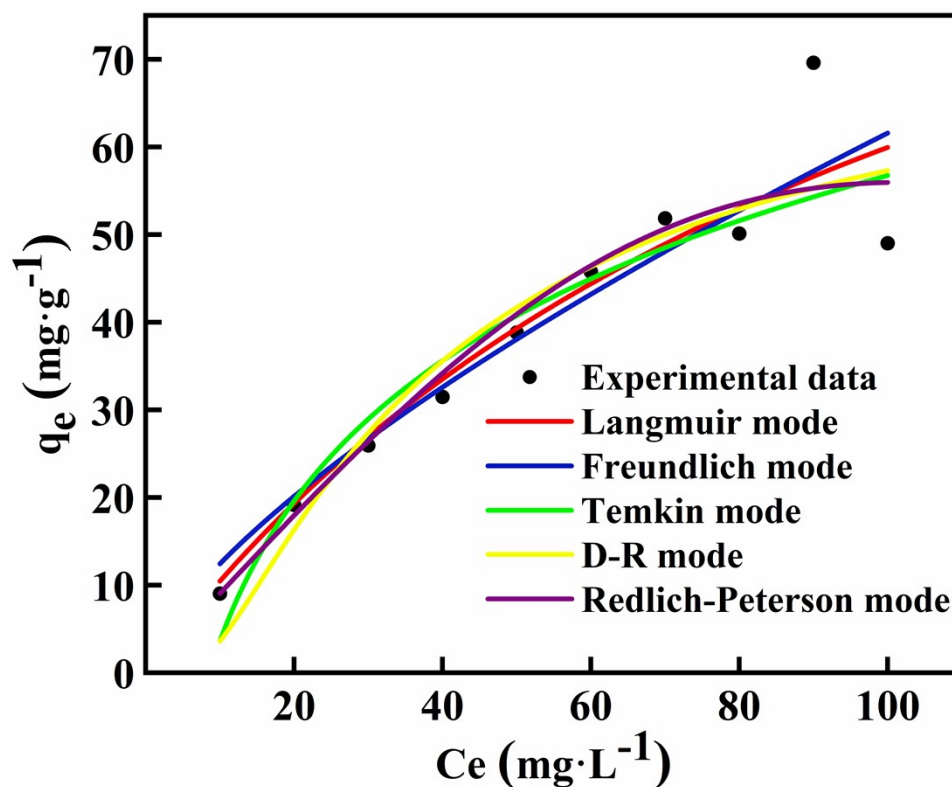


Fig. S2 Isothermal curve of MgO-3 adsorption of fluoride with different isotherm mode (dose =1 g/L, oscillation time =12 h, pH =7).

The Temkin isotherm model is indeed suitable for systems where there is a non-uniform distribution of adsorption energies due to interactions between adsorbate molecules on the adsorbent surface. However, as our material exhibits a uniform distribution of active sites, this model may not be the most appropriate for our system. The Dubinin–Radushkevich (D–R) isotherm model is designed for porous adsorbents and typically exhibits an S-shaped curve, which is not consistent with our material’s pore distribution characteristics. The Redlich–Peterson isotherm model is generally used for multicomponent adsorption, which does not align with our single-component fluoride adsorption system. Despite these considerations, we have tested the suggested models for completeness. The results show that the D–R model has a correlation coefficient of 0.9139, the Redlich–Peterson model has a correlation coefficient of 0.9929, and the Temkin model has a correlation coefficient of 0.9617. These coefficients indicate a good fit for the Redlich–Peterson and Temkin models, but we believe the D–R model is less applicable due to the nature of our adsorbent material.

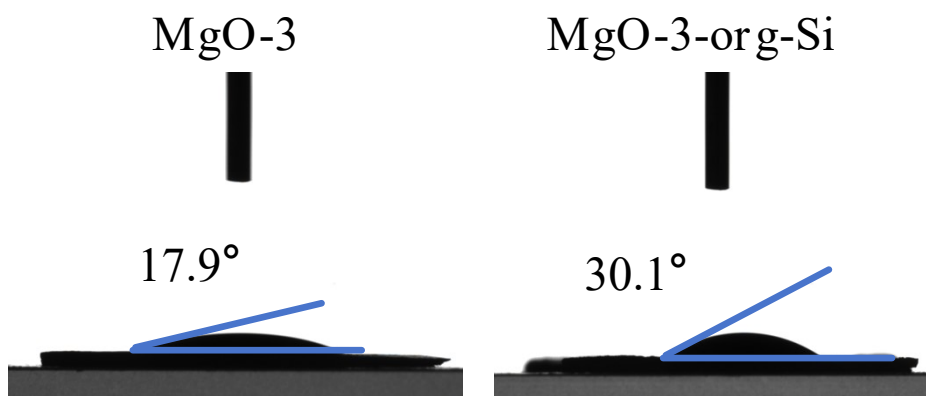


Fig.S3 Contact angle test of MgO absorbents.

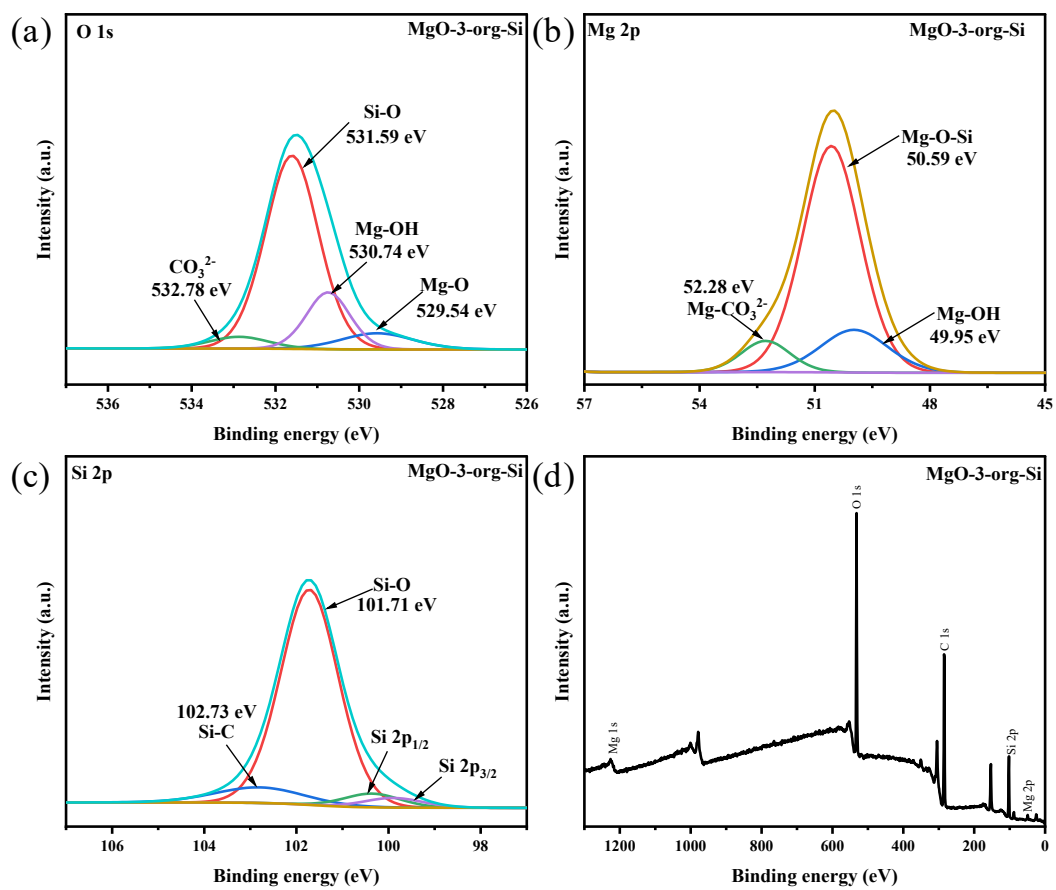


Fig. S4 XPS of modified-MgO with methyltriethoxysilane.

# Gas chromatography results

