Comparison of fluorine removal performance and mechanism of spheroidal magnesium oxide before and after lanthanum modification

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Abstract
Firstly, spherical magnesium oxide was synthesized by simple magnesium salt and specific reaction conditions. Then, lanthanum-modified spherical magnesium oxide (LSMO) was prepared by impregnation of lanthanum salt. The adsorption mechanism of the adsorbent was investigated by XRD, SEM, XPS, and FT-IR. Through the study of fluorine removal performance, for the solution with fluoride ion concentration of 10 mg·L⁻¹, the fluorine removal efficiency of lanthanum-modified spherical magnesium oxide (15LSMO) (93.1%) with 15% impregnation mass ratio is higher than that of SMO (82.7%). In addition, in the pH range of 2–11 or in the presence of interfering ions, the fluoride removal effect of 15LSMO still meets the fluorine removal efficiency of more than 90%. The research enhanced the profound insights into the effect and mechanism of fluorine removal of lanthanum modified materials.

Keywords Spheroidal magnesium oxide · Lanthanum modified · Defluorination mechanism · Fluorine removal performance · Adsorption kinetics · Adsorption thermodynamics

Introduction
In the past decades, due to the excessive use of earth resources by human beings, fluoride ions infiltrated into groundwater caused by mineral exploitation, or fluoride wastewater produced by industrial production have posed great threats to nature and human beings themselves (Nur et al. 2014). The WHO has set fluoride concentrations in drinking water at less than 1.5 mg·L⁻¹ (Ayoob and Gupta 2006), while China has set fluoride concentrations at less than 1 mg·L⁻¹ (Zhang et al. 2021). Subsequently, scientists carry out a large number of experimental studies on fluorine removal, and developed various methods to effectively treat various fluorine-containing wastewater, such as chemical precipitation (Turner et al. 2005), adsorption (Maliyekkal et al. 2006), and ion exchange (Sairam Sundaram and Meenakshi 2009). Among them, adsorption method is the focus of fluorine removal research because of the advantages of simple operation and low cost.

The adsorption method includes carbon-based materials, natural minerals, metal materials, polymers and resins, and biological materials (He et al. 2020). Magnesium oxide as a metal material compared with traditional activated alumina with high selectivity and high efficiency in fluorine removal and become a new green adsorption material. On the nanometer scale, magnesium oxide has the advantages of high porosity and large specific surface area, and magnesium oxide has abundant structural defects, thus possessing more hydroxyl active sites (Maliyekkal et al. 2010). Of course, the excellent adsorption performance of magnesium oxide adsorbents has attracted widespread attention from scientists. Li et al. successfully prepared porous hollow magnesium oxide microspheres with a specific surface area of 130 m²·g⁻¹ and adsorption capacity of more than 120 mg·g⁻¹ by using magnesium chloride as magnesium source (Li et al. 2014). In addition, Xavy...
Based on the above research, we synthesized spheroidal magnesium oxide structures through different magnesium sources and different synthesis methods (Borgohain et al. 2020). Kuang et al. used magnesium acetate and spray drying to successfully prepare spherical magnesium oxide nanostructures, and they have excellent adsorption properties for Pb (II) and Cd (II) (Kuang et al. 2019). The above work is sufficient to prove the excellent adsorption performance of magnesium oxide and the simple preparation process, due to the size limitation; subsequent work will be affected, so a larger size magnesium oxide adsorbent is required. In this research, we successfully synthesized a spheroidal magnesium oxide with excellent fluorine removal performance, stable physical and chemical structure, and a diameter of 20–30 μm.

Based on the preparation of spheroidal magnesium oxide, in order to further optimize its fluorine removal performance, lanthanum modification on the surface of magnesium oxide has become our new goal. As a rare earth element, lanthanum has strong selectivity to fluoride ions due to its hard acidity and the hard alkalinity of fluoride (Zhang et al. 2016). In recent years, researchers have found many ways to modify materials by rare earth elements. He et al. successfully modified mesoporous alumina with lanthanum. Compared with mesoporous alumina (MA), La/MA significantly improved the fluorine removal performance, and the adsorption capacity was about 26.45 mg·g⁻¹ (He et al. 2019). In addition, Liu et al. prepared aluminum-cerium composite adsorbents by co-precipitation method and its maximum adsorption capacity is 27.5 mg·g⁻¹ (Liu et al. 2010). Compared with the co-precipitation method, which requires pH control, the impregnation method is more concise, and there is no report about the removal of fluoride by lanthanum-modified magnesium oxide. The current research contributes to deepen the understanding of the design, synthesis, and mechanism of fluorine adsorbents.

Based on the above research, we synthesized spheroidal magnesium oxide SMO and lanthanum-modified spheroidal magnesium oxide (LSMO). The defluorination effects of SMO and 15LSMO were compared and the adsorption capacities were 27.5 mg·g⁻¹ (Liu et al. 2010). Compared with the co-precipitation method, which requires pH control, the impregnation method is more concise, and there is no report about the removal of fluoride by lanthanum-modified magnesium oxide. The current research contributes to deepen the understanding of the design, synthesis, and mechanism of fluorine adsorbents.

The synthesis steps of spheroidal magnesium oxide include 10 g MgSO₄·7H₂O, 3 g urea, and 40 mL water that were mixed and stirred for 30 min, then placed in a reaction kettle, and reacted in an oven at 100°C for 12 h. The white precipitate was centrifuged and cleaned, and then dried at 80°C. Then, the white precipitate was calcined for 8 h at a heating rate of 1°C·min⁻¹ to obtain the spheroidal magnesium oxide adsorbent (SMO).

The synthesis steps of lanthanum-modified spheroidal magnesium oxide include 1 g SMO, La(NO₃)₃·6H₂O, and 10 mL water that were mixed and stirred for 12 h; the precipitation was centrifuged and cleaned, then dried in the oven, and then annealed at 400°C for 4 h; lanthanum-modified spheroidal magnesium oxide (LSMO) was obtained. LSMO with different doping amounts was obtained through different impregnation ratios (mass ratios of lanthanum nitrate and spheroidal magnesium oxide were 5%, 10%, 15%, 20%).

Characterization

The morphology and EDAS of SMO and LSMO were analyzed by a scanning electron microscope (FEI, Inspect F50). SMO and LSMO were characterized by an X-ray diffraction analyzer (XRD, Ultima IV). A Fourier transform infrared spectrometer (FT-IR, Nicolet 5700) was used to characterize the adsorption mechanism of the materials before and after adsorption. The specific surface area and pore size of the materials were analyzed by automatic specific surface and porosity analyzer (BET, Micromeritics 2020). X-ray photoelectron spectroscopy (XPS, Thermo K-alpha) was used to analyze the surface chemical properties of the materials before and after adsorption. The F⁻ ion concentration was measured by the fluoride ion selective electrode method (detection ion concentration range, 0.05–1900 mg·L⁻¹) (Tolkou et al. 2021).
Adsorption experiments

Add 1000 mL deionized water with 2.210 g NaF and configure it into 1000 mg·L⁻¹ fluoride ion stock solution and store it in refrigerator. The raw fluoride ion solution was diluted to fluoride ion solution of different concentrations; 1 g·L⁻¹ adsorption material was added to 10 mg·L⁻¹ fluoride ion solution and placed in a centrifugal tube, and stirred in an isothermal (25°C) shaker at 200 rpm for 180 min. After standing for 1 h, the supernatant was taken and the fluoride ion concentration was measured using F⁻ ion selective electrode (PF-202). The pH of fluoride ion solution was adjusted with 0.1 mol·L⁻¹ HCl and NaOH solution, and then the above fluoride removal experiment was repeated to understand the influence of pH on the material fluoride removal. Use KNO₃, Na₂SO₄, Na₂CO₃, KH₂PO₄, NaCl, and NaHCO₃; configuration is 100 mg·L⁻¹ to interference ion concentration of fluorine ion solution, in order to understand interference ions on the material in addition to the influence of fluorine. The remaining waste liquid was collected and filtered out of the adsorbent, and dried for 12 h at 100°C for further experiments. The total adsorption quantity Qₑ (mg·g⁻¹) of fluoride ion is calculated by formula (1):

\[
Q_e = \frac{(C_0 - C_e)V}{m}
\]

Fluoride removal rate (%) is calculated by Formula (2):

\[
R_F = \frac{C_0 - C_e}{C_0} \times 100\%
\]

C₀ and Cₑ respectively represent the initial concentration and equilibrium concentration of F⁻ in solution (mg·L⁻¹), and V and M respectively represent the volume of solution (L) and the mass of adsorbent (g).

In order to conduct adsorption isotherm studies, multiple initial F⁻ concentrations in the range of 1 to 200 mg·L⁻¹ of F⁻ mother liquor were used for adsorption equilibrium experiments. Other parameters were set as follows: 50 mL fluoride ion solution was added with 50 mg adsorbent, adsorption time was 180 min, initial pH range was 7, temperature range was 25°C, stirring speed was 200 rpm.

Isotherm models

In this research, two nonlinear isotherm equations (Langmuir, Freundlich) were tested and the adsorption mechanism was reasonably predicted (Tan et al. 2008; Yin et al. 2018; Tian et al. 2021).

Langmuir equation is shown in Formula (3):

\[
q_e = \frac{q_m K_L C_e}{1 + K_L C_e}
\]

\[q_e \text{ (mg·g}^{-1}\text{)} \] is the adsorption capacity, \(q_m \text{ (mg·g}^{-1}\text{)} \) is the saturated adsorption capacity, \(C_e \text{ is the equilibrium concentration of F}^-\text{, and } K_L \text{ (L·mg}^{-1}\text{)} \) is the Langmuir adsorption constant.

Freundlich equation is shown in Formula (4):

\[
q_e = K_F C_e^n
\]

\(K_F \text{ (mg·g}^{-1}\text{)·(mg·L}^{-1}\text{)}^{-1/n} \) is the binding energy constant, and \(1/n \) in Freundlich model is the heterogeneity factor (Cadaval et al. 2015).

Kinetic models

In this research, two nonlinear dynamics models (pseudo-first-order and pseudo-second-order) were tested using these nonlinear dynamics equations to analyze the adsorption rate and predict the determining steps of the adsorption rate (Ho 2000; Wang et al. 2018).

The pseudo-first-order dynamics equation is shown in Formula (5):

\[
q_t = q_e (1 - e^{-K_1 t})
\]

The pseudo-second-order kinetic equation is shown in Formula (6):

\[
q_t = \frac{K_2 q_e^2 t}{1 + K_2 q_e t}
\]

\(q_e \text{ and } q_t \) are the adsorption capacity of F⁻ at equilibrium and at time t (min), respectively. \(K_1 \text{ (min}^{-1}\text{)} \) is the pseudo-first-order adsorption rate constant, and \(K_2 \text{ (g·mg}^{-1}\text{·min}^{-1}\text{)} \) is the pseudo-second-order adsorption rate constant.

Results and discussion

Characterization

XRD analysis

In order to analyze the structural differences between SMO and LSMO, the samples were characterized by XRD. It can be seen from Fig. 1a that SMO has obvious diffraction peaks at 2θ = 38.1, 42.6, 62.1, and 78.3°. According to the literature and the standard card (PDF #45–0946), the above diffraction peaks belong to the (111), (200), (220), and (222) lattice planes of magnesium oxide, respectively, so the formation of magnesium oxide was confirmed (Sutradhar et al. 2011). But in the XRD spectrum of 15LSMO, the diffraction
peak at $2\theta = 38.1^\circ$ belonging to the (111) crystal plane is not obvious, which can be explained by the masking of impurity peaks. The three main diffraction peaks of 15LSMO are well matched with SMO, and no new diffraction peaks are generated. It is inferred that the lanthanum salt formed by impregnation and calcination of lanthanum nitrate has a smaller proportion than the magnesium oxide carrier.

It can be seen from Fig. 1b that both materials have obvious diffraction peaks at $2\theta = 32.8, 37.9, 50.7, 58.6, 62.1, 68.2, 68.8,$ and $72.0^\circ$. According to the literature and the standard card (PDF #44-1482), the above diffraction peaks belong to the (100), (101), (102), (110), (111), (103), (200), and (201) lattice planes of magnesium hydroxide, respectively (Ding et al. 2001). Therefore, it is shown that magnesium oxide is basically converted into magnesium hydroxide after adsorption.

**Microscopic study**

In order to observe the morphology of the formed SMO and LSMO, the product was characterized by SEM. According to Fig. 2a, Fig. 2b, and Fig. 2c, we found that the magnesia precursor powder was calcined to form a spheroidal oxide packaged by flake magnesia. According to Fig. 2e, Fig. 2f, and Fig. 2g, we found that the size of the morphology did not change after loading. Figure 2d and Fig. 2f are the EDS spectra and element ratio table of SMO and 15LSMO, in which the diffraction peak of $2\sim 3$ eV is caused by the gold spraying treatment of the material. Figure 2i is the scanning distribution map of 15LSMO lanthanum, which can prove that lanthanum is uniformly distributed on the SMO surface.

In order to further study the morphological characteristics of SMO, the SMO was characterized by TEM, and the characterization results are shown in Fig. 3. Figure 3a and Fig. 3c are the TEM images of the assembled spherical magnesia scattered flake magnesia. In Fig. 3c, it can be found that there are many pores on the surface of flaky magnesia, which are caused by the escape of carbon dioxide and water during calcination. At the same time, these pores also mean that SMO has a larger specific surface area. The inset in Fig. 3a is the SAED image corresponding to flaky magnesium oxide, showing that the flaky magnesium oxide has a polycrystalline and crystal structure; the crystal plane corresponds to the XRD pattern. Figure 3b is the edge TEM image of SMO. It can be seen that the morphology of the flake-shaped magnesium oxide matches the SEM image of Fig. 2a. Figure 3d is the TEM photo of 15LSMO. Compared with Fig. 3b, there is an additional layer of flocs on the surface, and the superimposed structure of flaky magnesium oxide in Fig. 2b cannot be observed.

**BET analysis**

The microstructure of SMO and 15LSMO is further analyzed by BET characterization. Figure 4 shows the N$_2$ adsorption and desorption isotherms of SMO and 15LSMO, and the corresponding pore size distribution curves. According to the classification of the article, the isotherm of SMO belongs to type IV, H3-type hysteresis loop; the isotherm of LSMO also belongs to type IV, H3-type hysteresis loop (Sing 1985). The hysteresis ring of type IV isotherm is its remarkable feature, which represents the condensation of the mesoporous capillary, which is a typical mesoporous adsorbent; the H3-type hysteresis ring represents the abundant fissure-type pores in it. Among them, the difference between the hysteresis loops in Fig. 4a and Fig. 4c is mainly caused by the modification of lanthanum to generate new slit pores and block the old slit pores. At the same time, Table 1 shows the BET data of SMO and 15LSMO, based on the SEM images of SMO and 15LSMO with higher resolution; it is inferred that the relative specific surface area of the flocs on the surface of the material is larger than that of the magnesium oxide bulk, and the flocs do not greatly affect the pores of magnesium oxide, so the specific surface area of...
15LSMO will be slightly larger than SMO. From the comparison of the pore size distribution diagrams, it is inferred that the material floes affected the pore size of magnesium oxide to decrease from 4 to 3 nm, while the pore size of the flocs itself was 17 nm.

**FT-IR analysis**

In order to explain the fluorine removal mechanism of the materials, the two materials were characterized by infrared before and after the fluorine removal. The results are shown in Fig. 5. Figure 5a is the infrared spectrum of SMO before and after fluorine adsorption. The peaks at 3430 cm⁻¹ and 1640 cm⁻¹ before adsorption belong to the stretching vibration of the OH band and the bending vibration of the H-OH band formed by the adsorbed water in the air (Zhang et al. 2015). The strong peak near 3699 cm⁻¹ after fluorine adsorption is attributed to the $\nu_{\text{A}_2\delta\text{(OH)}}$ lattice vibration caused by the formation of Mg(OH)$_2$ (Niu et al. 2006). Moreover, after adsorption, the peak intensity at 3430 cm⁻¹ is greatly reduced, which proves that the substitution of OH is part of the mechanism of fluoride ion adsorption. The peaks at 1470 cm⁻¹, 1129 cm⁻¹, and 868 cm⁻¹ before adsorption belong to the antisymmetric stretching vibration peak, the
symmetric stretching vibration peak, and the out-of-plane bending vibration absorption peak of \( \text{CO}_3^{2-} \), respectively (Xu and Zeng 2003). After fluorine adsorption, the disappearance of the 1129 cm\(^{-1}\) peak indicates that carbonate also plays a role in replacing fluoride ions. The range of 400–800 cm\(^{-1}\) basically belongs to the infrared characteristics of the metal bond. The peaks at 640 cm\(^{-1}\) and 438 cm\(^{-1}\)

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**Table 1** BET data of the prepared samples

| Sample  | Specific surface area (m\(^2\)g\(^{-1}\)) | Pore diameter (nm) | Pore volume (cm\(^3\)g\(^{-1}\)) |
|---------|----------------------------------------|-------------------|----------------------------------|
| SMO     | 216.76                                 | 4.04              | 0.23                             |
| 15LSMO  | 232.41                                 | 17.05             | 0.66                             |

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Fig. 3  a The TEM image of scattered sheets of magnesium oxide and inside a shows the corresponding SAED pattern. b The TEM image of edge of SMO. c The high magnification TEM image of dispersed magnesium oxide flakes. d The TEM image of 15LSMO

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Fig. 4  a, b N\(_2\) adsorption–desorption isotherm and the corresponding pore size distribution of the SMO. c, d N\(_2\) adsorption–desorption isotherm and the corresponding pore size distribution of the 15LSMO
The significant infrared characteristics of MgO before adsorption are the tensile vibration of Mg-F (Jin et al. 2015). It is proved that the fluorine removal mechanism of magnesium oxide is the result of the combined action of hydroxyl, carbonate, and metal bond adsorption.

Figure 5b shows the infrared spectra of 15LSMO before and after fluorine adsorption. We can find that the continuous double peak at 1463 cm\(^{-1}\) is the typical infrared characteristic of lanthanum carbonate (Sun et al. 2020). Compared with the one before the adsorption in Fig. 5a, the extra peak at 1069 cm\(^{-1}\) before the adsorption in Fig. 5b is the infrared characteristic of lanthanum carbonate. The split with the peak near 1100 cm\(^{-1}\) and 1463 cm\(^{-1}\) indicates the presence of non-equivalent carbonate ions, which verifies the successful loading of lanthanum on the other hand, and the peak near 1100 cm\(^{-1}\) disappears after adsorption, which is similar to the carbonate ion in Fig. 5a. The peak
at 3697 cm\(^{-1}\) after adsorption is attributed to the \(A_{2u}(\text{OH})\) lattice vibration caused by the formation of Mg(OH)\(_2\) and La(OH)\(_3\). Before adsorption, 418 cm\(^{-1}\) is the infrared characteristic of MgO, while the peaks near 609 cm\(^{-1}\) belong to the infrared characteristics of MgO and La\(_2\)O\(_3\) (Chowdhury et al. 2016; Khalil et al. 2021), while the peak at 455 cm\(^{-1}\) after adsorption is the infrared characteristic of MgO covered with F, and the peak at 566 cm\(^{-1}\) is the formation of the bond between metal and F (Mg-F and La-F). In summary, we found that lanthanum nitrate impregnation and calcination mainly formed lanthanum carbonate and lanthanum oxide, and the defluorination mechanism of SMO and 15LSMO was basically similar.

**XPS analysis**

In order to further study the fluorine removal mechanism of the material, XPS characterization was performed on the material before and after fluorine adsorption. Figure 6 and Fig. 7 are the relevant XPS spectra of SMO and 15LSMO, respectively. From Fig. 5a and Fig. 6a, we can find that a new peak of 684.9 eV belonging to F1s appeared after adsorption, which clearly proves the effective adsorption of fluorine by the material (Sugama et al. 1998). Figure 6b and Fig. 7b are the C1s spectra before and after the adsorption of SMO and 15LSMO; the peak values are 284.8 eV (after calibration) and 289.8 eV, 284.8 eV, and 289.8 eV are organic carbon and carbonate, respectively peak (Jia et al. 2013; Mao et al. 2022; Powell 1989). Carbonate is the thermal decomposition of urea in the raw material and the supply of air atmosphere. After adsorption, the binding energy of carbonate is reduced to 289.2 eV, and the proportion is also reduced, which means the combination and consumption of carbonate and F. Figure 6c and Fig. 7c are the O1s spectra before and after the adsorption of SMO and 15LSMO, with a total of 529.7 eV, 530.8 eV, 532.3 eV, and 533.1 eV peaks. A total of 529.7 eV belongs to the lattice oxygen atom combined with metal (Wuttke et al. 2008; Powell 1989). The peaks at 530.8 eV and 533.1 eV belong to the metal hydroxide and the hydroxyl group of adsorbed water, respectively (Benedetti et al. 2011; Newberg et al. 2011; Powell 1989). The peak at 532.3 eV is due to the presence of oxygen in carbonate.
(Descostes et al. 2000; Wang et al. 2017; Powell 1989). In Fig. 6c and Fig. 7c, the metal oxides were converted to metal hydroxides after adsorption, and the peaks of oxygen atoms in carbonates were also reduced. In Fig. 6c, the peak of metal hydroxide increases to 531.2 eV after adsorption, which is the result of fluoride ion adsorption. In Fig. 7c, the peak of H2O before adsorption may be caused by the lanthanum impregnation process. Figure 6d and Fig. 7d are the F1s spectra of SMO and 15LSMO after adsorption, of which 684.9 eV, 686.2 eV, and 689.2 eV belong to metal fluoride MFn, metal hydroxide fluoride MOH-F, and metal fluoride cover (MFn)n, respectively (Wang et al. 2017; Li et al. 2016; Powell 1989). Figure 6e and Fig. 7e are the Mg2p spectra before and after the adsorption of SMO and 15LSMO. Both have peaks near 49.2 eV and 50.3 eV before adsorption, of which 49.2 eV is the Mg-OH peak, and 50.3 eV is Mg-O Peak (Wuttke et al. 2008; Li et al. 2014; Powell 1989). After adsorption, the binding energy of the peak of Mg-OH increased to 49.5 eV, which was due to the adsorption of fluorine, and the peak of Mg-OH was transformed into the peak of Mg-OH-F. The peak proportion of Mg-OH also increases, which is consistent with the O1s spectral results. The peak of Mg-O (50.3 eV) was deduced to be converted to the peak of Mg-F (50.5 eV) after adsorption (Powell 1989). Figure 7f shows La3d spectrum before and after 15LSMO adsorption. The main peaks of La3d5/2 and La3d3/2 before adsorption are located at 835.7 eV and 852.5 eV, respectively, and the corresponding satellite peaks are located at 839.0 eV and 855.8 eV, respectively. These peaks confirm the presence of La2O3. After adsorption, the binding energy of La3d5/2 and La3d3/2 became higher, which was inferred to be caused by the formation of new binding bonds between La and F (Wu et al. 2017).

### Effect of La impregnation ratio

Figure S1 shows the fluorine removal efficiency of SMO and LSMO with different impregnation mass ratios. In the range of impregnation ratio from 10 to 20%, the fluorine removal balance tends to be balanced, and the fluorine removal rate reaches more than 90%. Among them, the material with the impregnation rate of 15% (15LSMO) has the highest
(93.1%) and fastest defluorination efficiency. Therefore, it can be considered that the impregnation rate of 15% is the best covering efficiency of lanthanum on the SMO surface. In other words, flocculation on the surface of LSMO with impregnation rate greater than 15% begins to affect the fluorine removal efficiency, and 15LSMO is used as the analysis model in the experiment accordingly (He et al. 2019). Besides, in the adsorption experiments, we found that the pH of the solution increased slightly after adsorption, which is consistent with the fluorine removal mechanism of the hydroxyl substitution of the adsorbent. The corresponding SEM images are shown in Fig. S2.

**Kinetic and thermodynamic study**

The Langmuir adsorption isotherm is assumed to be a homogeneous adsorption process, while the Freundlich adsorption isotherm is suitable for the equation of a heterogeneous system. As shown in Fig. 8, two models are used to fit the adsorption process of SMO and 15LSMO. The relevant parameters are shown in Table 2. The experimental results of the two materials are closer to the Langmuir adsorption isotherm, indicating that the adsorption on the surface of the adsorbent is homogeneous adsorption. However, theoretically, the maximum adsorption capacity of SMO is greater than 15LSMO, indicating that lanthanum-supported materials are more advantageous for low-concentration fluorine removal.

In order to further study the changes of the adsorption capacity of the two materials with time, the pseudo-first-order kinetic equation and the pseudo-second-order kinetic equation were used for kinetic simulation. The experimental diagram of the fitted adsorption kinetics is shown in Fig. 9. Table 3 is the relevant data of the fitting results of the kinetic

**Fig. 8** The plots of Langmuir and Freundlich isotherm model for F- adsorption over (a) SMO and (b) 15LSMO under different concentration of F—(C0 = 1–200 mg·L−1, pH = 7.0, dosage 1 g·L−1)

**Table 2** Langmuir and Freundlich adsorption isotherm parameters for fluoride on SMO and 15LSMO

| Equations | Langmuir model |
|-----------|----------------|
| Parameter | \( q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \) |

| Parameter | \( q_m \) (mg·g−1) | \( K_L \) (L·mg−1) | \( R^2 \) |
|-----------|-----------------|-----------------|-------|
| SMO       | 171.368         | 0.0666          | 0.977 |
| 15LSMO    | 168.689         | 0.0939          | 0.977 |

| Freundlich model |
|------------------|
| \( q_e = K_F C_e^n \) |

| Parameter | \( K_F \) (mg·g−1) | \( n \) | \( R^2 \) |
|-----------|-----------------|-----|-------|
| SMO       | 18.581          | 2.012 | 0.901 |
| 15LSMO    | 22.836          | 2.128 | 0.917 |

**Fig. 9** The plots of pseudo-first-order and pseudo-second-order kinetic model for F- adsorption over (a) SMO and (b) 15LSMO (C0 = 10 mg·L−1, pH = 7.0, dosage = 1 g·L−1)
model. The correlation coefficient of the pseudo-second-order kinetic models of the two materials is higher, and the fitted adsorption capacity value is closer to the actual value, indicating that the surface chemistry of the materials is the main limiting step of the adsorption rate, and the adsorption mechanism of the materials is mainly chemical adsorption. (Table 4)

### Effect of pH and interfering anions

To investigate the effect of pH on the adsorption performance of the material, set the pH value from 1 to 12, a constant adsorbent dosage of 1 g·L\(^{-1}\), an initial fluorine concentration of 10 mg·L\(^{-1}\), and a contact time of 180 min. Figure 10 shows the relationship between the fluorine removal efficiency of the material and the pH of the solution. The results show that the material exhibits extremely high stability under acidic conditions, and the material only dissolves in the solution when pH = 1. Excessive free hydroxyl ions will affect the substitution of fluoride ions and hydroxyl active sites on the surface of the material, but when the pH = 12, the fluorine removal efficiency is greatly affected. The fluorine removal performance does not change much in the pH range of 2–11. According to the comparison of the results of SMO and 15LSMO, it is speculated that the acid and alkali resistance of the material is derived from the presence of magnesium oxide.

### Table 3 Kinetic parameters for fluoride adsorption on SMO and 15LSMO

| Equations | Pseudo-first-order kinetic model | Pseudo-second-order kinetic model |
|-----------|---------------------------------|----------------------------------|
| \( q_t = q_e (1 - e^{-K_1 t}) \) |                                   | \( q_t = \frac{K_2 q_e t}{1 + K_2 t} \) |
| Parameter | \( K_1 \) (min\(^{-1}\)) | \( q_e \) (mg·g\(^{-1}\)) | \( R^2 \) | \( K_2 \) (g·(mg·min\(^{-1}\))) | \( q_e \) (mg·g\(^{-1}\)) | \( R^2 \) |
| SMO       | 0.215                           | 7.71                             | 0.941 | 0.029                           | 8.28                             | 0.998 |
| 15LSMO    | 0.51                            | 8.93                             | 0.975 | 0.107                           | 9.21                             | 0.999 |

### Table 4 Comparison of fluorine adsorption capacity of similar adsorbents

| Adsorbents | Specific surface area (m\(^2\)·g\(^{-1}\)) | Particle diameter (μm) | Adsorption capacity (mg·g\(^{-1}\)) | References |
|------------|-------------------------------------------|------------------------|--------------------------------------|------------|
| Porous MgO nanostructure | 10.5–171.2 | / | 5716–15,691 | (Borgohain et al. 2020) |
| Porous MgO nanoplate | 47.4 | / | 185.5 | (Jin et al. 2016) |
| Porous hollow MgO microsphere | 130 | 5–7 | >120 | (Li et al. 2014) |
| Hollow MgO sphere | / | 2 | >182.4 | (Zhang et al. 2021) |
| Nanomagnesia | / | / | 267.82 | (Maliyekkal et al. 2010) |
| LAA | 235 | / | 16.9 | (Shi et al. 2013) |
| Ce/MA | 257.37 | / | 14.29 | (He et al. 2019) |
| La/MA | 236.86 | / | 26.45 | |
| Al-Ce hybrid adsorbent | 60.1 | 0.1–0.3 | 27.5 | (Liu et al. 2010) |
| SMO | 216.76 | 20–30 | 171.34 | This work |
| 15LSMO | 232.41 | 20–30 | 168.39 | |

Fig. 10 Effect of initial pH on fluoride adsorption capacity of SMO and 15LSMO (dosage = 1 g·L\(^{-1}\), C\(_0\) = 10 mg·L\(^{-1}\), contact time = 180 min)

To investigate the influence of interference ions on the adsorption performance of the material, set a constant adsorbent dosage of 1 g·L\(^{-1}\), initial fluorine concentration of 10 mg·L\(^{-1}\), interference ion concentration of 100 mg·L\(^{-1}\), and contact time of 180 min. The results are shown in Fig. 11. The results show that the interference
After the defluorination experiment, the adsorbent was centrifugally washed and dried, washed three times with 1 mol·L⁻¹ NaOH solution, and then the defluorination performance of the adsorbent was re-tested, and the above process was repeated five times. The results are shown in Fig. S3. The results showed that SMO and 15LSMO lost 80% of the fluorine removal performance in the initial state during the fifth regeneration, but the excellent regeneration efficiency of the adsorbents could still be demonstrated.

**Conclusion**

In this paper, magnesia precursor powder is calcined to generate SMO, and then LSMO is prepared by impregnation method. According to the fluorine removal experiment research, it is found that 15LSMO has better fluorine removal efficiency, and then a series of characterization analysis comparisons are carried out through SMO and 15LSMO. BET results show that 15LSMO has a larger specific surface area and average pore size than SMO. SEM results show that lanthanum is successfully supported on the surface of the material. FT-IR and XPS spectroscopy results show that the fluorine removal mechanism of SMO and 15LSMO is OH⁻ substitution, metal chemical adsorption (M-F), electrostatic attraction, and carbonate substitution. The kinetic fitting results show that the adsorption rates of SMO and 15LSMO are closer to chemical adsorption, and the adsorption isotherm fitting results show that the adsorption process of SMO and 15LSMO is closer to the homogeneous adsorption process. After pH fluctuation and interfering ion influence experiment, for the initial fluorine concentration of 10 mg/L, the highest fluorine removal efficiency of SMO can reach 82.7%, and the lowest is 77.3%. The fluorine removal efficiency of 15LSMO can meet the fluorine removal efficiency of more than 90% when the pH is less than 11, and it can meet the international standard of 1.5 mg·L⁻¹. Furthermore, in regeneration experiments, 15LSMO exhibited excellent regeneration ability. In summary, 15LSMO is therefore a green, renewable, and economical adsorbent candidate material.

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**Declarations**

**Ethics approval and consent to participate** Not applicable.

**Consent for publication** Not applicable.

**Competing interests** The authors declare no competing interests.

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