Original Research

Highly efficient fluoride removal from water using 2D metal-organic frameworks MIL-53(Al) with rich Al and O adsorptive centers

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ABSTRACT

In this study, metal-organic framework MIL-53(Al) was synthesized and studied to understand the different mechanisms between normal MIL-53(Al) and 2D metal-organic framework MIL-53(Al) for removing fluoride. Comparatively, the 2D MIL-53(Al) had two-dimensional linear morphology rather than block shape, indicating more expose adsorptive sites than normal MIL-53(Al). The batch adsorption experiments were applied to investigate the performance of 2D MIL-53(Al), including pH, adsorption kinetics, and thermodynamics. The 2D MIL-53(Al) (75.50 mg/g) showed better adsorption capacity than normal MIL-53(Al) (35.63 mg/g). The adsorption process of 2D MIL-53(Al) followed the pseudo-first-order model and Langmuir model. The adsorption mechanism of this material was further studied by using experimental characterization and density functional theory calculations in detail. The main adsorptive sites were Al and O in the 2D MIL-53(Al), and the relationship between fluoride binding with Al and O was HF2 -> HF -> F-. The species of fluoride were HF2, HF, F at different pH and concentrations. Hence, this study provides a significant way on the application of two-dimensional materials for removing fluoride.

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1. Introduction

Fluoride is anionic primary pollution from drinking water in many developing countries, such as China, India, South Africa, Bangladesh, and Mexico [1]. It harms a lot of poor people who are unable to treat their drinking water to recommended permissible limits, causing fluorosis of bone, dental fluorosis, Alzheimer's disease, and cancer [2]. High concentrations of fluoride could be produced by industrial wastewater. Many technologies such as membrane treatment, precipitation, and adsorption have been developed to remove fluoride from water [3–8]. At present, adsorption is the most significant and widely scaled-up technology. However, the critical factor of adsorption is adsorbent. At present, researches on series of new adsorbents such as perovskites, metal-organic frameworks are important research interests.

Metal-organic frameworks are many kinds of crystal structure materials formed by combining metal sites with organic ligands [9,10]. There are different types of metal-organic frameworks. Therefore, metal-organic frameworks have always been applied in many fields, such as UiO-66(Zr) for removing fluoride, other ions [11–18]. Based on researches on adsorbing fluoride, metal elements Al, La, Fe, and Zr have been dominant adsorptive sites for removing fluoride. Many kinds of metal-organic frameworks have been investigated to adsorb fluoride before [19]. MIL-96(Al), CAU-6, UiO-66(Zr), MIL-88A(Fe), MIL-53(Fe), MIL-100(Fe), MIL-101(Fe), MOF-801(Zr), lanthanum-based metal-organic framework, and aluminum fumarate metal-organic framework had been investigated as adsorbents. Thereinto, aluminum fumarate metal-organic framework with a large adsorption capacity of about 600 mg/g [20–32]. Hence, it is evident from this literature that metal-organic
Frameworks have good application prospects. However, existing literature suggests that the adsorption capacities of other metal-organic frameworks are generally lower than 100 mg/g, except for the aluminum fumarate metal-organic framework. Hence, the adsorption capacity still needs to be improved.

Adsorption mainly depends on the accessible active sites. Synthesizing a material with “naked” sites is a crucial strategy in the field of adsorption. The naked sites will help increase accessible active sites that correspond to the adsorption capacity of adsorbents. A similar strategy was applied in our previous researches, where we designed core-shell boehmite and hollow lanthanum-aluminum perovskite, which had higher adsorption capacities of fluoride [33,34]. Different synthesis methods of the metal-organic framework were investigated to prepare various metal-organic frameworks. First, these metal-organic frameworks MIL-53(Al) under different synthesis methods were studied and compared. Furthermore, complete self-assembly of MIL-53(Al) and two-dimensional metal-organic framework MIL-53(Al) were investigated, and their structure and morphology were compared. The combination of organic ligands and metal sites in the metal-organic framework benefitted from charge dispersal, which enhanced the ability to remove fluoride at a wider pH. Finally, adsorption experiments and Density Functional Theory (DFT) calculations were carried out to understand the mechanism of adsorbing fluoride. The adsorption crystal plane and the adsorption sites were confirmed by using DFT modeling. Also, adsorbents were characterized before and after adsorption to confirm the adsorption behavior.

2. Experimental

2.1. Synthesis methods of MIL-53(Al)

According to the molar weight ratio, 5 mmol terephthalic acid and 5 mmol aluminum nitrate nonahydrate were mixed and added in 20 mL ultrapure water/20 mL of anhydrous ethanol. It was transferred to an autoclave and reacted in a drying oven at 170 °C for 24 h. Then it was cooled at room temperature to obtain a pure white product called MIL-53(Al)-1.

MIL-53(Al)-1 synthesis was used as the base case and compared to sorbents obtained by modified synthesis from this base on the synthesis process, the following solvents were used: 40 mL of absolute ethanol, 40 mL of methanol, and 40 mL of N,N-dimethylformamide through the solvothermal synthesis method. After drying, they were named MIL-53(Al)-2, MIL-53(Al)-3, and MIL-53(Al)-4. In addition, based on the MIL-53(Al)-1 synthesis method, the reaction time was extended to 72 h, and the prepared material was named MIL-53(Al)-5. Similarly, the reaction temperature was increased to 220 °C, and the sample was named MIL-53(Al)-6.

Finally, according to the traditional method of synthesis reported before [35], 27.72 mmol aluminum nitrate nonahydrate and 13.87 mmol terephthalic acids were mixed and added to 40 mL ultra-pure water. They were reacted in a drying oven at 220 °C for 72 h. The sample was named MIL-53(Al)-7.

2.2. Material characterization

The materials were investigated by different characterization methods. Detailed descriptions of the characterization methods had been clearly explained in S1.

2.3. Batch of adsorption experiments

The adsorption capacity of fluoride was calculated as follows:

\[ q_{t} = \frac{(C_{0} - C_{t}) \cdot V}{m} \]  

\[ q_{e} = \frac{C_{0} \cdot V - C_{t} \cdot (V + V_{ad})}{m} \]  

The study applied different models to investigate the adsorption thermodynamic behavior: a. the Langmuir model (Eq. (3)), b. the Freundlich model (Eq. (4)), c. the Temkin model (Eq. (5)), d. the Dubinin-Radushkevich model (Eq. (6)) [36–38].

\[ q_{e} = \frac{q_{max} \cdot b_{t}}{1 + b_{t} \cdot C_{t}} \]  

\[ q_{e} = K_{f} \cdot C_{t}^{1/n} \]  

\[ q_{e} = \frac{RT}{b_{t}} \cdot \ln(K_{T} \cdot T_{C}) \]  

\[ \ln(q_{e}) = \ln(q_{m}) - \beta C^{2} \]  

Moreover, different kinetic models were also conducted to further evaluate the adsorption kinetic behavior of 2D-MIL-53(Al). These kinetic models are as follows: a. pseudo-first-order model (Eq. (7)), b. pseudo-second-order model (Eq. (8)), c. Elwood model (Eq. (9)), d. intraparticle diffusion kinetic model (Eq. (10)), e. external diffusion kinetic model (Eq. (11)), f. mass transfer model (Eq. (12)) [39–42].

\[ \log(q_{e} \cdot q_{t}) = \log(q_{e}) - \frac{k_{f} \cdot t}{2.303} \]  

\[ t = \frac{C}{K_{T} \cdot C_{0}^{2} + C} \]  

\[ \ln(q_{e} / C_{0}) = -K_{p} \cdot t \]  

\[ C = \exp(-k_{a} \cdot t) + C \]  

The batch of adsorption studies was conducted in duplicate to minimize the errors. The parameters in Equations 1–12 are reflected as follows:

- \( q_{t} \) (mg/g): the adsorption capacity at a certain time;
- \( q_{e} \) (mg/g): the amount of equilibrium capacity;
- \( V \) (L): the initial volume of fluoride solution;
- \( V_{ad} \) (L): the accumulated added volume of sodium hydroxide and hydrochloric acid;
- \( C_{0} \): initial fluoride concentration;
- \( C_{e} \): equilibrium fluoride concentration;
- \( C_{t} \): fluoride concentration at a definite time;
- \( m \): the mass of adsorbent (g);
- \( q_{max} \): the maximal loading capacity;
- \( b \): the Langmuir isotherm constants;
- \( K_{f} \): the Freundlich constants;
- \( b_{t} \) and \( K_{T} \): the Temkin isotherm constant and Temkin isotherm equilibrium binding constant;
- \( \beta \): the Polanyi potential;
The activity coefficient related to sorption average free energy (\(\text{mol}^2/\text{J}^2\)):

\[
\begin{align*}
K_1 &= (\text{min}^{-1}), \\
K_2 &= (\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}), \\
K_3 &= (\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-0.5}), \\
K_4 &= (\text{min}^{-1}), \ r, \ \text{and} \ z: \ \text{the kinetic constants of the different kinetics models.}
\end{align*}
\]

2.4. Density functional calculation

The material structures were built and calculated using density functional theory with the castep module in this study. The calculating parameters of generalized-gradient approximation, Perdew-Burke-Ernzerh, ultra-fine quality were put into use to understand correlation effects and electrical exchange. Brillouin zone sampling of electronic states was carried out on a \(4 \times 5 \times 1\) Monkhorst-Pack grid. The cut-off energy of plane-wave was 610 eV. The adsorptive and energetic spectrum analysis was performed using VASP models.

The structure of normal MIL-53(Al) was consistent with the reported morphological characteristics of MIL-53(Al) [46,47]. It was investigated as the dominating adsorbing material for removing fluoride.

3. Results and discussion

3.1. Materials characterization

The adsorption efficiencies of MIL-53(Al) under different preparation methods were discussed and included in S3. The adsorption performance of MIL-53(Al) synthesized under the seven adjustment schemes were MIL-53(Al)-1 (75.50 mg/g), MIL-53(Al)-2 (65.00 mg/g), MIL-53(Al)-3 (69.60 mg/g), and MIL-53(Al)-4 (72.50 mg/g), MIL-53(Al)-5 (50.27 mg/g), MIL-53(Al)-6 (40.34 mg/g), MIL-53(Al)-7 (35.63 mg/g). The MIL-53(Al)-1 had the best performance, while MIL-53(Al)-7 had the worst performance for removing fluoride. As shown in Fig. 1, the two-dimensional linear morphology of MIL-53(Al)-1 was named 2D-MIL-53(Al). The EDS energy spectrum analysis of surface scanning electron microscopy showed that the distribution of adsorbed fluoride and the distribution of O and Al were consistent after adsorbing fluoride. The original judgment was that 2D-MIL-53(Al) had a relatively dominant ability to absorb fluoride. On the other hand, the scanning electron microscopy results of sample MIL-53(Al)-7 were similar to the reported morphological characteristics of MIL-53(Al) [46,47]. It also showed many block particles. Hence, the name of sample MIL-53(Al)-7 was defined as normal MIL-53(Al). Similarly, the EDS energy spectrum analysis of normal MIL-53(Al) found that the distribution of fluoride after adsorption was also consistent with the distribution of O and Al on the material.

In order to further analyze the difference between 2D-MIL-53(Al) and normal MIL-53(Al), both adsorbents were characterized with a transmission electron microscope, as shown in Fig. S1. The shape of 2D-MIL-53(Al) showed a rectangular block appearance and width of approximately 5 \(\mu\)m with 500 nm diameter two-dimensional nanowires in Fig. S1, similar to the unshaped assembly particle of normal MIL-53(Al). Hence, it can be considered that 2D-MIL-53(Al) was an incompletely assembled two-dimensional material with good adsorption properties.

The structure of normal MIL-53(Al) was consistent with the structure reported before in Fig. S2 [48,49]. The crystal plane showed narrow and sharp peaks, which indicated good crystallinity and a high crystal-forming degree of normal MIL-53(Al). However, the X-ray diffraction peaks of 2D-MIL-53(Al) were broad and short at the same degree, with the main peaks in the normal MIL-53(Al) appearing, and the remaining corresponding peaks did not appear. The intensity of other corresponding peaks in 2D-MIL-53(Al) was very weaker and much shorter, and some crystal peaks did not appear at all. Therefore, 2D-MIL-53(Al) can be considered as a two-dimensional morphology metal-organic framework with low crystallinity. It was investigated as the dominating adsorbing material for removing fluoride.

3.2. Batch of adsorption

3.2.1. Effect of pH and liquid-solid ratio

First of all, the increase in pH led to decreasing the potential in Fig. 2(a). But at the same time, it can be seen that the metal-organic framework 2D-MIL-53(Al) showed a positive charge in most pH values, which promoted the adsorption and enhanced binding with the strongly electronegative fluoride. The potential value was 49.00 mV as the highest at pH 1. At pH 12, the potential value of the adsorbent was 0.60 mV, but finally became a negative value (-50.10 mV) at pH 13. It can be immediately inferred that the zero point potential of the 2D-MIL-53(Al) was between 12 and 13, suggesting that 2D-MIL-53(Al) displayed positive charges in the range of pH 1 – 12. It also confirmed our earlier conclusion that positively charged 2D-MIL-53(Al) has the potential to adsorb and remove fluoride in a wide pH range. This result provides the idea for designing a higher positive charge of adsorbing materials that could make for removing fluoride.

The 2D-MIL-53(Al) had excellent fluoride removal efficiencies at a wide pH range, as shown in Fig. 2(b). The adsorption efficiencies were 93.25%, 83.94%, 75.63%, 76.13%, 78.38% at pH 1, 2, 3, 7, 12, respectively. The adsorption efficiencies were pretty good and similar in the pH range of 3 – 11, meanwhile, maximum adsorption efficiency happened at pH 1 and 2. However, the adsorption efficiency at pH = 12 was slightly higher than at pH 3 – 11, but the adsorption efficiency was lower than pH = 1, 2. This may be caused by the higher positive charge of 2D-MIL-53(Al) at pH = 1, 2. In addition, HF is the main species at pH = 1, 2. It indicated that the metal-organic framework 2D-MIL-53(Al) structure had excellent fluoride removal ability in a wide pH range. Therefore, the pH = 7 was directly selected as the most suitable pH for removing fluoride since adsorption was still very high at pH = 7.

Here, these 0 – 4 g/L metal-organic framework 2D-MIL-53(Al)/100 ppm fluoride solutions were studied as shown in Fig. S5. The liquid-solid ratios of adsorption efficiencies at 0.5 g/L, 1 g/L, 1.5 g/L, 2 g/L, 4 g/L were 66.38 mg/g, 75.06 mg/g, 77.13 mg/g, 77.31 mg/g, 79.56 mg/g, respectively. It could be noticed that the increase in adsorption efficiency was just little after 1 g/L. Hence, 1 g/L metal-organic framework 2D-MIL-53(Al)/100 ppm fluoride solution was chosen as the appropriate liquid-solid ratio and was used for further adsorption experiments.

3.2.2. Adsorption isotherm

The adsorption data were fitted into the different thermodynamic models that obtained adsorption thermodynamic data to understand the conjugation of the particles and adsorption heat in Fig. S6, Fig. S7, and Table 1. It showed a complete simulated adsorption thermodynamic process of metal-organic framework 2D-MIL-53(Al). When the concentration of the initial fluoride solution was 5 ppm, the adsorption capacities at 30 °C, 40 °C, and 50 °C were 3.94 mg/g, 3.38 mg/g, and 3.00 mg/g, respectively. After increasing the concentration of the initial fluoride solution to 200 ppm, the adsorption capacities at 30 °C, 40 °C, and 50 °C were...
**Fig. 1.** The Scanning Electron Microscope and Energy Dispersive Spectrum analysis of 2D-MIL-53(Al), (a): Scanning Electron Microscope; (b): Scanning Electron Microscope that corresponded to Energy Dispersive Spectrum; (c): O; (d): Al; (e): F; (f): superposition of all; The Scanning Electron Microscope and Energy Dispersive Spectrum analysis of Normal MIL-53(Al) (g): Scanning Electron Microscope; (h): Scanning Electron Microscope that corresponded to Energy Dispersive Spectrum; (i): O; (j): Al; (k): F; (l): superposition of all.

**Fig. 2.** (a): The zeta potential-pH diagram of 2D-MIL-53(Al); (b): the effect of pH about 2D-MIL-53(Al) adsorbing fluoride.

**Table 1**
The different thermodynamic coefficients of 2D-MIL-53(Al) at different temperatures.

| Temperature(°C) | Langmuir model | Freundlich model | Temkin model |
|----------------|----------------|-----------------|--------------|
|                | $q_e = \frac{q_{max}bC_e}{1 + bC_e}$ | $q_e = K_Fc^{1/n}$ | $q_e = \frac{K_T}{2T}[\ln(K_T/G_e)]$ |
| $R^2$ | $q_{max}$ (mg g$^{-1}$) | $b$ (L mg$^{-1}$) | $R^2$ | $K_F$ (mg$^{-1}$L$^{-1}$mg$^{-1}$) | $N$ | $R^2$ | $K_T$ | $b_T$ |
| 30 | 0.996 | 1941.33 | 0.0003 | 0.995 | 3.147 | 1.38 | 0.774 | 0.00012 | 16.46 |
| 40 | 0.987 | 303.23 | 0.0010 | 0.984 | 0.918 | 1.07 | 0.872 | 0.00021 | 63.65 |
| 50 | 0.983 | 240.46 | 0.0013 | 0.979 | 0.905 | 1.06 | 0.874 | 0.00021 | 68.11 |
124.94 mg/g, 119.56 mg/g, and 114.25 mg/g, respectively. Therefore, it can be concluded from the adsorption isotherm of fluoride by the metal-organic framework 2D-MIL-53(Al) was an exothermic process in Fig. S6.

The thermodynamic parameters obtained by the simulation of thermodynamic models were shown in Table 1. The correlation coefficients of Langmuir model at 30 °C, 40 °C, and 50 °C were 0.996, 0.987, 0.983, respectively, and the correlation coefficients of the Freundlich model at 30 °C, 40 °C, and 50 °C were 0.995, 0.984, 0.979, respectively. The correlation coefficients from the Langmuir model were higher than the correlation coefficients of the Freundlich model at the same temperature, indicating that the bond fluoride with 2D-MIL-53(Al) was single layer adsorption [50,51]. Moreover, the maximum adsorption capacity simulated by the Langmuir model decreased with increasing temperature, indicating that the 2D-MIL-53(Al) adsorbed fluoride through an exothermic process [52,53]. The separation coefficient constant R_{s} at 30 °C, 40 °C, and 50 °C were 0.97, 0.91, 0.88 by using equation (51), respectively. It can be seen that the adsorption separation constants were between 0 and 1, indicating that the adsorption of fluoride on 2D-MIL-53(Al) was favorable. Also, a decreasing separation coefficient constant (R_{s}) further confirmed that temperature rise was unfavorable for the adsorption of fluoride. Hence, it belonged to an exothermic process [54,55]. From Fig. S7(a), it can be concluded that the adsorption capacity increased with the improvement of initial fluoride concentrations. When the concentration of the initial fluoride solution was 3000 ppm, the adsorption capacity also reached 1035.63 mg/g. The adsorption efficiency under different initial fluoride concentrations was shown in Fig. S3. When the concentration of fluoride solution was less than 600 ppm, the adsorption efficiency was above 60%. On the contrary, the adsorption efficiency reached 78.75% at a concentration of 5 ppm fluoride solution. The adsorption efficiency dropped to 71.58% when the initial concentration was also increased to 150 ppm. The adsorption efficiency continued to decrease when the fluoride solution was above 600 ppm. It can be inferred that the adsorbent 2D-MIL-53(Al) kept high fluoride adsorption percentages under low concentrations. It was necessary to use multistep adsorption to make up for the deficiency of adsorption percentages. The adsorption capacity of 100 ppm fluoride solution at different temperatures was shown in Fig. S4. The adsorption capacities at 30 °C, 40 °C, 50 °C, and 60 °C were 74.35 mg/g, 66.38 mg/g, 64.31 mg/g, and 60.69 mg/g, respectively. It was further confirmed that the adsorption was unfavorable at higher temperatures since the isotherm studies revealed that it was an exothermic process. Furthermore, these adsorption capacities by different types of metal-organic frameworks that were reported before have been shown in Table S1.

### 3.2.3. Adsorption kinetics

Adsorption kinetics is an important factor for studying the adsorption equilibrium time to obtain the dynamic behavior of fluoride with 2D-MIL-53(Al). In Fig. 3, the adsorption capacity in the first 5 min was 16.95 mg/g, which increased to 28.55 mg/g after 1 h. When the adsorption time extended, the adsorption capacity increased to reach 73.80 mg/g until 10 h. From Fig. 3 and Fig. S8, it can be seen that these simulated lines of the pseudo-first-order kinetic model were the most suitable, indicating that the adsorption rate was significantly influenced by the concentrations of fluoride solutions [56,57]. The specific kinetic parameters were listed in Table 2. From the correlation coefficients of kinetic models, the adsorption process also agreed with the internal diffusion kinetic model. It can be inferred that the long nanowire-like morphology was beneficial to the diffusion process of adsorption since the external diffusion process showed little effect on adsorption. It can be inferred that the higher concentrations of fluoride solutions, the longer it took for reaching the adsorption equilibrium. Therefore, the adsorption kinetics of metal-organic framework 2D-MIL-53(Al) was controlled by these concentrations of fluoride solution as the limiting speed of adsorption kinetics, and the adsorption process was affected by the internal diffusion mechanism to some extent. These other models that were considered and inappropriate were discussed in S4.

#### 3.2.4. Effect of co-existing anions

The effects of Br\(^{-}\), SO\(_4\)\(^{2-}\), NO\(_3\) \(^{-}\), Cl\(^{-}\), PO\(_4\)\(^{3-}\) anions were studied with different concentrations of 1 mmol/L-10 mmol/L as shown in Fig.S9. The unit of mol/L had been changed to ppm in S5. Under the influence of Br\(^{-}\), SO\(_4\)\(^{2-}\), NO\(_3\) \(^{-}\), Cl\(^{-}\), PO\(_4\)\(^{3-}\) at the concentration of 10 mmol/L, the adsorption capacities were 70.85 mg/g, 72.4 mg/g, 70.75 mg/g, 70.65 mg/g, 55.85 mg/g. It was concluded that the order of their effects on adsorption was as follows: PO\(_4\)\(^{3-}\) > Cl\(^{-}\) > NO\(_3\) > Br\(^{-}\) > SO\(_4\)\(^{2-}\). Except for PO\(_4\)\(^{3-}\) anion, other anions had nearly negligible influences on removing fluoride. The adsorption capacities were 61.75 mg/g, 59.00 mg/g, 57.65 mg/g, 55.50 mg/g with different concentrations of PO\(_4\)\(^{3-}\) anions: 1 mmol/L, 2 mmol/L, 5 mmol/L, and 10 mmol/L. The anions of PO\(_4\)\(^{3-}\) possibly had competitive adsorption with F\(^{-}\), reducing the adsorption capacity of fluoride. This finding implied that wastewater containing high concentrations of PO\(_4\)\(^{3-}\) would not be suitable by using 2D-MIL-53(Al) for removing fluoride.

#### 3.2.5. Regenerative process

Three reagents were tested to regenerate the material. Sulfuric acid, alum, and water were investigated and shown in Fig. S10(a). The regeneration efficiencies were 82.88%, 89.53%, and 74.85%, respectively. It can be concluded that the regeneration efficiency of alum was relatively better, so it was selected as the reagent for recycling the material. As shown in Fig. S10(b), the adsorption efficiencies were 79.32%, 89.53%, 85.89%, and 82.47% by using different concentrations of alum: 0.001 mol/L, 0.005 mol/L, 0.01 mol/L, 0.05 mol/L, and 0.1 mol/L to regenerate. The best concentration was 0.005 mol/L. Hence, it was applied. The study of different regeneration times found that the regeneration efficiencies recovered to 74.49%, 86.47%, 86.99%, 89.21%, 89.38%, 89.53% at 5 min, 0.5 h, 1 h, 2 h, 6 h, and 12 h. Regeneration speed was very fast, and good regeneration consequence was acquired within 2 h, which was chosen as the best regeneration time as shown in Fig. S11(a). After recycling, the material was able to use up to 5 cycles. These different cycles with their respective adsorption capacities were: (1) 89.53%, (2) 85.27%, (3) 83.22%, (4) 81.18%, (5) 79.86% as shown in Fig. S11(b). With the increase of cycles, the recovery of adsorption efficiencies a slightly decreasing trend. Therefore, the metal-organic framework 2D-MIL-53(Al) was an excellent adsorbent with good adsorption capacity for several regenerations.

### 3.3. Adsorption mechanism

#### 3.3.1. Experimental mechanism

From Fig. 4, it can be observed that the surface roughness of metal-organic framework 2D-MIL-53(Al) before adsorption was 210.64 nm. After adsorption, the surface roughness of the metal-organic framework 2D-MIL-53(Al) was sharply reduced to 64.58 nm. The adsorbent had filling effects on the surface, and the adsorption of fluoride was filled in the folds of the metal-organic framework 2D-MIL-53(Al). The fold morphology played a very critical role in the adsorption process. It can be seen that the main diffraction peak of 2D-MIL-53(Al) still existed after adsorption, indicating that the crystal structure of the material was not
destroyed after removing fluoride in Fig. 5(a). The 2D-MIL-53(Al) still maintained a good crystal structure after regeneration. It can also be concluded from Fig. 5(b) that the crystal diffraction of normal MIL-53(Al) was relatively high, with narrower and sharper X-ray diffraction peaks, and the main characteristic peak shape of X-ray diffraction also existed after adsorbing fluoride, indicating that its crystal structure was not affected. After regeneration, the crystal form remained relatively high, but the half-width of the diffraction peak widened. It can be seen that the regeneration of metal-organic framework normal MIL-53(Al) crystal had a weaker effect on the crystal form, which may be due to the influence of alum.

The thermal stability test of metal-organic framework 2D-MIL-53(Al) can be used to judge the influence of fluoride adsorption on

Table 2
The kinetic parameters from different models by using 2D-MIL-53(Al).

| Model                        | Function                              | k (min⁻¹) | R²     |
|------------------------------|---------------------------------------|-----------|--------|
| Pseudo-first-order model     | log (qₜ - qₜₐ) = log qₑ - k₁t / C₀     | 0.0037    | 0.9966 |
| Pseudo-second-order model    | t⁻¹ = k₂qₑ⁻¹ / qₜ                         | 0.0002    | 0.9757 |
| Elovich Equation             | A = 1 / k₂qₑ⁻¹ + Bqₑ⁻¹                  | 12.7329   | 0.8976 |
| Intraparticle Diffusion      | Cₜ = C₀ - kₙ₁t⁻¹                          | 8.7383    | 0.9887 |
| Kinetic Equation             | Cₜ = C₀ - kₙ₂t                           | 15.8839   |        |
| External Diffusion Kinetic   | Cₜ = C₀ - kₙ₃t                          | 12.7329   | 0.8976 |

Fig. 3. (a): the adsorption kinetics; (b): pseudo-first-order model by using 2D-MIL-53(Al).

Fig. 4. The Atomic Force Microscope of 2D-MIL-53(Al) before adsorption and after adsorption.
materials. The thermal stability of 2D-MIL-53(Al) was mainly divided into two stages: the first stage, the decrease in thermal weight came from the water molecules and air hid in the pores of the metal-organic framework before 200 °C in Fig. S12(a). In the second stage, the ligands of the metal-organic framework decomposed rapidly by releasing a large amount of CO₂ and water vapor [58]. As shown in Fig. S12(a), the mass percentage from 200 °C to 900 °C dropped from 94.18% to 42.44%, and the mass loss remained 51.74% when the weightless test sample was 2D-MIL-53(Al). When the weightless test sample was adsorbed on metal-organic framework 2D-MIL-53(Al)–F, the mass percentage from 200 °C to 900 °C reduced from 99.96% to 52.61%, and the mass loss stood at 47.35%. Due to the adsorption of fluoride, the proportion of mass lost after adsorption was lower, which further confirmed that adsorption had taken place. In addition, the in-situ temperature test was applied to detect the slight temperature change during the adsorption process of metal-organic framework 2D-MIL-53(Al), as shown in Fig. S12(b). The temperature of fluoride-containing solution before adsorption was 25.30 °C. During the adsorption process, the temperature continuously increased to 25.50 °C. The conclusion of adsorption thermodynamics was further affirmed by the slight change of temperature in the adsorption process, indicating that the adsorption was an exothermic process.

The infrared spectrum between 1400 cm⁻¹ and 1700 cm⁻¹ corresponded to the vibration peaks of the carboxyl functional group, which about 1436 cm⁻¹ matched with the metal-oxygen cluster bond at the peak of 763 cm⁻¹. The infrared spectrum between 1400 cm⁻¹ and 1700 cm⁻¹ also corresponded to the vibration peaks of the carboxyl functional group, which about 1436 cm⁻¹ matched with the symmetrical stretching vibration peak of the carboxyl group. The peak at 1511 cm⁻¹ and 1581 cm⁻¹ corresponded to the asymmetric stretching vibration peaks of the carboxyl group. The 1700 cm⁻¹ originated from the infrared stretching vibration peak of terephthalic acid in a certain free state, indicating that 2D-MIL-53(Al) had a certain free terephthalic acid. The vibration peak around 3400 cm⁻¹ corresponded to the hydroxyl vibration peak. The transmittance of the peak decreased after adsorption, indicating that the corresponding vibration amplitude decreased after adsorbing fluoride, and the transmittance of the peak recovered after regeneration. The corresponding characteristic peak of fluoride appeared at 686.19 eV when metal-organic framework 2D-MIL-53(Al) was adsorbed, indicating that the fluoride adsorption was bound to metal-organic framework 2D-MIL-53(Al) material [61,62]. After regeneration, the corresponding characteristic peaks of fluoride in the full spectrum disappeared, demonstrating that the use of alum regeneration was a very effective way. The Al peaks of X-ray photoelectron spectroscopy before adsorption, after adsorption, and regeneration were 74.59 eV, 75.04 eV, and 74.95 eV, respectively. The Al peak shifted to the right towards higher energy after adsorption. After regeneration, the Al peak shifted to the left, but it did not completely return to the original position due to the effect of aluminum in the alum. In Fig. 6, the characteristic peaks of oxygen before adsorption, after adsorption, and regeneration were 532.10 eV, 532.09 eV, and 532.19 eV, respectively. After adsorption of fluoride, the characteristic peak of oxygen shifted to the left towards the lower energy peak, and the characteristic peak of oxygen shifted to the higher energy peak after the regeneration of the O peak. The main reason could also be the presence of oxygen atoms on the alum.

3.4. Computational mechanism

Detailed calculations of density functional theory were made to understand the role of adsorption at the molecular level between fluoride with MIL-53(Al). First, the main adsorption crystal planes were selected as (1 1 2), (0 1 1), (0 1 1), and (2 0 0). Furthermore, these four crystal planes were selected as the adsorptive crystal plane of metal-organic framework MIL-53(Al), calculating the corresponding crystal plane energy according to equation (13), as shown in Table 3. The values of adsorption crystal planes (1 1 2), (1 0 1), (0 1 1) and (2 0 0) were 0.01724 eV, 0.03688 eV, 0.04094 eV, and 0.02614 eV, respectively. The adsorption surface energies were in the following order: γ(1 1 2) < γ(2 0 0) < γ(1 0 1) < γ(0 1 1). Therefore, the stability of adsorption crystal plane in decreasing order: (1 1 2) > (2 0 0) > (1 0 1) > (0 1 1). Hence, the crystal plane (1 1 2) was chosen as the dominant adsorption crystal plane to study the adsorption of fluoride. According to calculate fluoride species, fluoride had three species: H₂F⁻, F⁻, and HF₂ in water. Combined with the above-mentioned optimal adsorption crystal plane (1 1 2), the dominant adsorptive sites on the 2D-MIL-53(Al) material were Al and O, as shown in Fig. 7.

Al atoms and O atoms combined more strongly with different species of fluoride, as presented in Fig. 7. The aluminum sites in the binding energies of metal-organic framework MIL-53(Al) bounded with F⁻, HF, and HF₂ were −320.2 kJ/mol, −264.4 kJ/mol, and −463.5 kJ/mol, respectively. The relationship between fluoride species binding ability was as follows: HF₂ > HF > F⁻. The binding
energies of oxygen sites with $F^-$, HF, and HF$_2$ were $-300.0$ kJ/mol, $-231.7$ kJ/mol, and $-434.6$ kJ/mol, respectively. It can be seen that the binding ability of oxygen sites with fluoride species was also HF$_2$ > HF > $F^-$. Furthermore, aluminum sites had a much stronger binding ability with fluoride species than oxygen sites. The metal-organic framework 2D-MIL-53(Al) showed good adsorption capacity for all species of fluoride. Therefore, it exhibited a superior capacity for removing fluoride at a wide pH range.

4. Conclusions

Metal-organic framework 2D-MIL-53(Al) is a good adsorbent due to its unique features and high adsorption capacities. In this study, we compared different synthesis methods for obtaining 2D-MIL-53(Al) with high fluoride efficiency removal from water. Both experimental characterizations and DFT calculations were applied to study the properties of the material and its adsorption mechanism. The XRD crystallinity of the sample 2D-MIL-53(Al) was not as good as normal MIL-53(Al). However, its adsorption capacities were

| Crystal face | (1 1 2) | (1 0 1) | (0 1 1) | (2 0 0) |
|--------------|--------|--------|--------|--------|
| Surface Energy/eV | 0.01724 | 0.03688 | 0.04094 | 0.02614 |

Fig. 6. The XPS spectra of 2D-MIL-53(Al) (a): full spectrum; (b): Al 2p; (c): O 1s; (d): F 1s.

Table 3
These surface energies of MIL-53(Al) model with adsorptive faces by using theoretical calculation.

Fig. 7. The change of bonding energy by using MIL-53(Al) for removing fluoride.
high at a wide range of pH 1–12. The 10 h was enough to reach the adsorption equilibrium, and the adsorption process was affected by the concentrations of fluoride solution and internal diffusion. Adsorption was a single-layer exothermic process and was slightly interfered with by PO_4^{3-} ion. Various regeneration experiments with 2D-MIL-53(Al) after adsorption showed that the alum had superior regeneration performance at a regeneration time of 2 h with the optimal concentration of 0.005 mol/L. The adsorption mechanism showed that the surface roughness of 2D-MIL-53(Al) significantly reduced after adsorbing fluoride, and the structure was very stable. Density Functional Theory (DFT) calculations confirmed that the crystal plane (1 1 2) of the metal-organic framework was the dominant crystal plane. It was also confirmed that Al and O were the major adsorptive sites of the material. The adsorption energy about the three species of fluoride at the adsorption sites of Al and O were HF_2 > HF > F^-. Furthermore, the cost of MIL-53(Al) is almost 21.939 USD/100 g from Sinopharm Group, China. Therefore, this study provides an effective method for achieving higher adsorption capacity at wide pH.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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