



Preparation of 2D carbon ribbon/ Al_2O_3 and nitrogen-doped carbon ribbon/ Al_2O_3 by using MOFs as precursors for removing high-fluoride water

Lei HUANG^{1,2,3}, Zhi-hui YANG^{1,2}, LÜ-ji YAN¹, Sikpaam Issaka ALHASSAN¹,
Hai-yin GANG¹, Ting WANG¹, Hai-ying WANG^{1,2}

1. School of Metallurgy and Environment, Central South University, Changsha 410083, China;

2. National Engineering Research Center for Control and Treatment of Heavy Metal Pollution,
Central South University, Changsha 410083, China;

3. School of Environmental Science and Engineering, Guangzhou University, Guangzhou 510006, China

Received 20 June 2020; accepted 28 February 2021

Abstract: 2D carbon ribbon/ Al_2O_3 was synthesized with two-dimensional metal organic frameworks 2D-MOFs as precursors using the solvothermal and calcination methods. Batch experiments of adsorption parameters such as pH, liquid/solid ratio, adsorption kinetics, adsorption thermodynamics, and anions competitions were investigated to understand the adsorptive behavior of fluoride on carbon ribbon/ Al_2O_3 and nitrogen-doped carbon ribbon/ Al_2O_3 . The adsorption of fluoride on carbon ribbon/ Al_2O_3 could be described as the chemical and multilayer adsorption, while the adsorption of fluoride on nitrogen-doped carbon ribbon/ Al_2O_3 followed the chemical and monolayer adsorption phenomenon. The fluoride on nitrogen-doped carbon ribbon/ Al_2O_3 had a much faster adsorption rate of 3.1×10^{-7} m/s than carbon ribbon/ Al_2O_3 , which was 1.2×10^{-7} m/s. The nitrogen-doping on carbon ribbon enhances structural defects and improves the adsorption performance of fluoride. Also, the diacetylene linkages ($-\text{C}\equiv\text{C}-$) and pyridinic-N were studied to understand their influences on removing fluoride. The result indicates that carbon ribbon and nitrogen-doped ribbon could serve as good adsorbents for removing fluoride.

Key words: pyridinic-N; carbon ribbon; MIL-53(Al); adsorption; fluoride removal

1 Introduction

High fluoride concentration in water has a significant influence on the survival of both flora and fauna all over the world, especially in countries with erratic rainfall patterns and developing countries. There are several fluoride-bearing minerals in nature, such as biotite, sellaite, fluorspar, cryolite, topaz, tremolite, fluormica, epidote, and fluorapatite [1,2]. Mostly, dry areas suffer a higher concentration of fluoride than other regions, such as northern states in the United States, Australia, and North China. Moreover, semiconductors, zinc

metallurgy, aluminum metallurgy, iron and steel smelting, solar cell, and other companies that use fluoride as raw material all constitute major sources of fluoride emission [3–5]. Developing countries, especially China, India and Sri Lanka have many of these industries. As a result, over 200 million people worldwide are suffering from fluoride-related diseases, such as fluorosis, brain damage, thyroid disorder, infertility, Alzheimer's syndrome, and cancer [6].

Studies have shown that the level of fluoride in wastewater can be reduced by using many technologies: chemical precipitation and electrocoagulation, electroadsorption, membrane technology,

ion exchange, and adsorption [7–14]. Moreover, the adsorption technology is one of the most widely applied methods for removing fluoride since the adsorbents are easy-to-excess, relatively cheap, easy to operate in the factories, environmentally friendly with a good recovery rate. Different carbon materials have been used to investigate their ability to remove fluoride. These carbon materials could be divided into two types according to their structural morphologies: primary amorphous carbon material or sp^3 orbital hybridization, including activated carbon and biochar. Biochar derived from the *Luffa cylindrica* (LC), bone char prepared from pleco fish, charcoals/aluminum oxide, sucrose-derived porous carbon-doped $Zr_xLa_{1-x}OOH$ have been demonstrated to possess good fluoride removal capacity [15–22]. Furthermore, these carbon materials have a predominant sp^2 hybridized orbital, including graphene and carbon nanotube. Also, basic aluminum sulfate/graphene hydrogel, FeOOH-graphene oxide, hydroxyapatite/multi-walled carbon nanotubes, hierarchical AlOOH@reduced graphene oxide, nano-sized hydroxyapatite/graphene oxide sheets, single- and multi-walled carbon nanotubes have been reported as promising adsorbents for removing fluoride [23–29]. However, understanding how sp hybridized orbital of carbon materials bonds with fluoride ion has not been clearly defined [30]. Graphdiyne (GDY) as a carbonaceous allotrope is composed of diacetylene linkages and benzene rings, making it acquire a simultaneous hybridized and flat framework of sp and sp^2 orbitals [31]. Consequently, analogous-graphdiyne is a good strategy for removing fluoride in this study. Hence, synthesizing carbon ribbon with analogous-graphdiyne structure has a promising potential as an effective adsorbent for removing fluoride.

In this study, 2D carbon ribbon and nitrogen-doped carbon ribbon were successfully synthesized using 2D-MOFs. The carbon ribbon has a similar structure to analogous graphdiyne. The carbon ribbon material was applied to investigating the adsorption of fluoride. The adsorption behavior of the N-doped carbon ribbon was compared with that of carbon ribbon. The effects of pH, solid/liquid ratio, anions, adsorption kinetics, and adsorption thermodynamics were exhaustively studied. Moreover, different sp and sp^2 hybridized orbitals of carbon materials were also considered to

understand the main role of hybridized orbital in removing fluoride. The species of oxygen-N, graphitic-N, pyrrolic-N, and pyridinic-N in carbon ribbon were studied to identify the main adsorptive sites of the nitrogen.

2 Experimental

2.1 Chemical reagents

Terephthalic acid and 2-amino terephthalic acid were purchased from Aladdin Chemistry Co., Ltd. Aluminium nitrate and aluminium chloride were acquired from Sinopharm Co., Ltd. Furthermore, sodium fluoride, sodium bromide, sodium sulfate, sodium chloride, sodium phosphate, sodium nitrate, and sodium hydroxide were purchased from Sinopharm Co., Ltd. Ethyl alcohol and N, N-dimethyl formamide were purchased from Hengxing Chemical Reagent, and Sinopharm Co., Ltd, respectively. Hydrochloric acid was acquired from a specific company for pH adjustment. Additionally, ultrapure water was obtained by using the system of self-purification.

2.2 Preparation of MOFs

The MIL-53(Al) (Materials of Institute Lavoisier Framework, MIL) and MIL-53(Al)-NH₂ were synthesized as precursors under the solvothermal method. A certain amount of terephthalic acid (H₂BDC) and Al(NO₃)₃ were added into 20 mL of ultrapure water and 20 mL of absolute ethanol to dissolve the reactants with an ultrasonic cleaner for 30 min. The synthetic reaction was carried out in a mixed solution in a 60 mL polytetrafluoroethylene-lined autoclave, encapsulated, and reacted in an electric blast drying oven at 220 °C, and cooled at room temperature to obtain a pure white product. The product was then washed repeatedly 6 times with ultra-pure water and anhydrous ethanol. The supernatant was discarded, and the product was dried in a blast oven at 60 °C overnight, collected in the sample bag, and stored for further use. The MIL-53(Al)-NH₂ was prepared using a similar synthetic method, just by using N, N-dimethyl formamide as a solvent and 130 °C as reaction temperature. These samples were prepared for testing in the next step.

2.3 Synthesis of 2D-carbon ribbon/Al₂O₃

An appropriate amount of MIL-53 (Al) and

MIL-53(Al)-NH₂ materials were put in a porcelain boat, and then calcined at 1000 °C for 3 h at a heating rate of 600 °C/h with N₂ as a protective gas in a horizontal tube furnace. The 2D-carbon ribbon/Al₂O₃ and nitrogen-doped 2D-carbon ribbon/Al₂O₃ materials were stored for further characterization and defluorination experiments. The 2D-carbon ribbon/Al₂O₃ and nitrogen-doped 2D-carbon ribbon/Al₂O₃ materials were named as MIL-53/C and MIL-53-N/C, respectively.

2.4 Fluoride measurement

The adsorption experiment was carried out in batch modes to understand the behavior of MIL-53/C and MIL-53-N/C. As for the effect of pH, the 50 mL of 100 mg/L fluoride ion solution was put into a polyethylene bottle. The pH of the fluoride ion solution was adjusted to pH=1, 2, 3, 4, 5, 6, 7, 8, 9, 10 by using HCl and NaOH solution. 50 mg MIL-53/C and MIL-53-N/C were weighed into the polyethylene bottles at different pH mentioned above and then adsorbed in a water bath shaker at 30 °C. Regarding the liquid/solid ratios, 10, 20, 30, 40, and 50 mg of MIL-53/C and MIL-53-N/C were measured and added to the 0.01 wt.% fluoride ion solutions with the above-adjusted pH, respectively. They were further adsorbed into a water bath shaker at 30 °C for varying time of 5 min, 10 min, 20 min, 30 min, 40 min, 1 h, 2 h, 3 h, 6 h, 12 h, and 24 h. The reaction thermodynamics was carried out at different fluoride ion concentrations of 5, 10, 20, 45, 70, 100, 120, 150 and 200 mg/L and 30, 45 and 60 °C, respectively. The effects of five anions of NO₃⁻, SO₄²⁻, Cl⁻, Br⁻ and PO₄³⁻ were studied by measuring five groups of 500 mL solutions containing fluoride ion concentration of 100 mg/L. Concentrations of 10, 5, 2, and 1 mmol/L were prepared, and the adsorption conditions were kept the same to demonstrate the influence of anions on adsorption.

The fluoride ion composite electrode was used to measure the fluoride ion concentration in the solution. The measuring method was as follows: calibration of the fluoride ion composite electrode with fluoride ion standard solutions was done at concentrations of 1, 10, and 100 mg/L. The adsorbed solution was filtered. Firstly, 40 mL of the fluoride ion solution and 10 mL of the prepared total ionic strength buffer solution (TISAB) were

put into a small polytetrafluoroethylene bottle. The calibrated fluoride ion electrode was inserted into the solution and stabilized for 10–20 s after which the fluoride ion concentration was recorded using the equation shown as follows:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

where C_0 is the incipient concentration of fluoride (mg/L); C_t is the instant concentration of fluoride at a certain time t (mg/L), q_t is the adsorption capacity of fluoride over time t (mg/g), m is the mass of the adsorbing material (mg), and V is the volume of solution (mL).

2.5 Characterization of materials

The scanning electron microscope (SEM) and transmission electron microscope (TEM) with map-scanning energy dispersive spectrometer of 2D-carbon ribbon/Al₂O₃ and nitrogen-doped 2D-carbon ribbon/Al₂O₃ materials were used to characterize both adsorbents. The zeta potentials of 2D-carbon ribbon/Al₂O₃ and nitrogen-doped 2D-carbon ribbon/Al₂O₃ were obtained by using a zeta sizer Zano-ZS device (Malvern Instruments, UK) for the charge on materials. A pH detecting instrument (LeiCi, China) was used to monitor the pH of the solution. The X-ray diffraction measurements of 2D-carbon ribbon/Al₂O₃ and nitrogen-doped 2D-carbon ribbon/Al₂O₃ after and before adsorption were carried out with a Rigaku D/Max-RB diffractometer with Cu K_α radiation ($\lambda=0.15406$ nm, 35 kV, 40 mA) to determine the structure. Raman spectroscopy test with Ar⁺ ion laser beam at an excitation wavelength of 532 nm was done on these materials to provide insight into the orbital hybridization. The adsorption and connection of adsorption sites with fluoride on these materials were collected by the X-ray photoelectron spectroscopy (XPS) via Thermo Fisher-VG scientific measurements with an Al K_α X-ray as the excitation source. The distribution of pore size and specific surface area were obtained via N₂ adsorption and desorption measurement at 77 K using ASAP 2020 equipment (Micromeritics Instrument Corp, USA) to study 2D-carbon ribbon/Al₂O₃ and nitrogen-doped 2D-carbon ribbon/Al₂O₃. The infrared spectra of these materials were acquired by a Nicolet iS10 spectrometer (Thermo Fisher Scientific Instruments, PA, USA). The

thermogravimetry of 2D-carbon ribbon/ Al_2O_3 and nitrogen-doped 2D-carbon ribbon/ Al_2O_3 before and after adsorption was used to estimate the stability through a simultaneous thermal analyzer (STA-449F3) acquired from Germany Nierchi Instrument Manufacturing Co., Ltd.

3 Results and discussion

3.1 Materials characterization

As shown in Fig. 1, MIL-53/C appears to have a long ribbon shape, whereas the shapes of MIL-53-N/C are round and long. MIL-53/C and MIL-53-N/C both have similar nitrogen adsorption and desorption capacity, pore diameter, and specific surface area, as shown in Fig. 2. The nitrogen adsorption and desorption of MIL-53/C and MIL-53-N/C exhibited type IV with H1 hysteresis loop in Figs. 2 (a, b). N_2 molecules were adsorbed on the inner surface in a single layer to multiple layers, indicating the existence of mesopores in these materials [32]. MIL-53-N/C had much larger width than MIL-53/C within a relative pressure range of 0.1–0.9, suggesting that MIL-53-N/C possessed a much larger pore diameter. The average pore diameter of MIL-53/C was 3.770 nm, whereas that of MIL-53-N/C was 8.441 nm with hierarchical pores having diameters of 3.754 and 9.048 nm. Moreover, all the pore diameters of MIL-53-N/C appeared to be similar in shape to those of MIL-53/C, as shown in Figs. 2(c, d). Again, the pore diameter of MIL-53-N/C was measured to be

9.048 nm, contributing to the round shape. This generated a larger specific surface area for MIL-53-N/C ($209.75 \text{ m}^2/\text{g}$) than for MIL-53/C ($81.25 \text{ m}^2/\text{g}$).

3.2 Batch adsorption

3.2.1 Effect of pH

MIL-53/C and MIL-53-N/C were further investigated to comprehend the zeta potentials responsible for removing fluoride. Both MIL-53/C and MIL-53-N/C exhibited positive zeta potentials in Fig. 3(a) at $\text{pH} < 9$. The highest positive zeta potentials of MIL-53/C and MIL-53-N/C occurred at 52 and 63.9 mV, respectively. Moreover, the zero-point charge (pH_{PZC}) of MIL-53-N/C was a little higher than pH 10, whereas the zero-point charge (pH_{PZC}) of MIL-53/C was a little lower than pH 10 in Fig. 3(a). It could therefore be envisaged that the N atom significantly improved the positive zeta potentials of the materials. The effects of pH for fluoride removal using MIL-53/C and MIL-53-N/C as adsorbents were also studied. The fluoride removal efficiency of both adsorbents decreased with an increase in pH in Fig. 3(b). The fluoride removal efficiencies of MIL-53/C and MIL-53-N/C exceeded 73% and 81% when $\text{pH} < 3$, respectively. When pH was increased further, the fluoride removal efficiency in both adsorbents decreased steadily. Hence, the optimum adsorption occurred at $\text{pH} = 2$. Based on this, $\text{pH} = 2$ was chosen as the best fit for the next adsorption experiments.

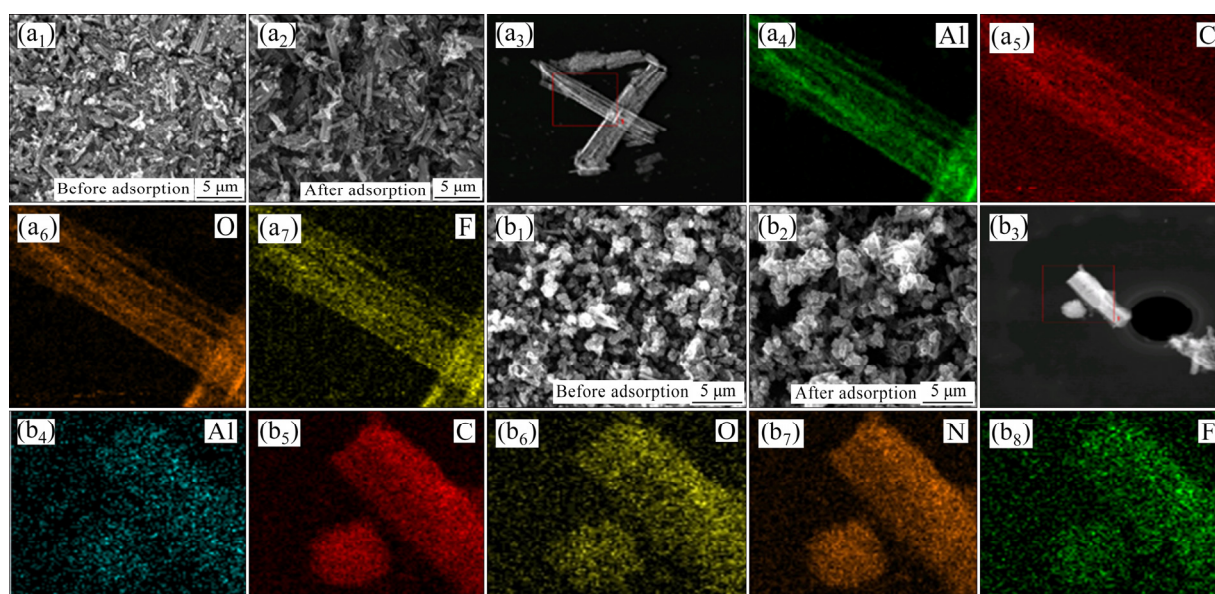


Fig. 1 SEM (a_1 , a_2 , b_1 , b_2) and TEM-EDS (a_3 – a_7 , b_3 – b_8) images of MIL-53/C (a_1 – a_7) and MIL-53-N/C (b_1 – b_8)

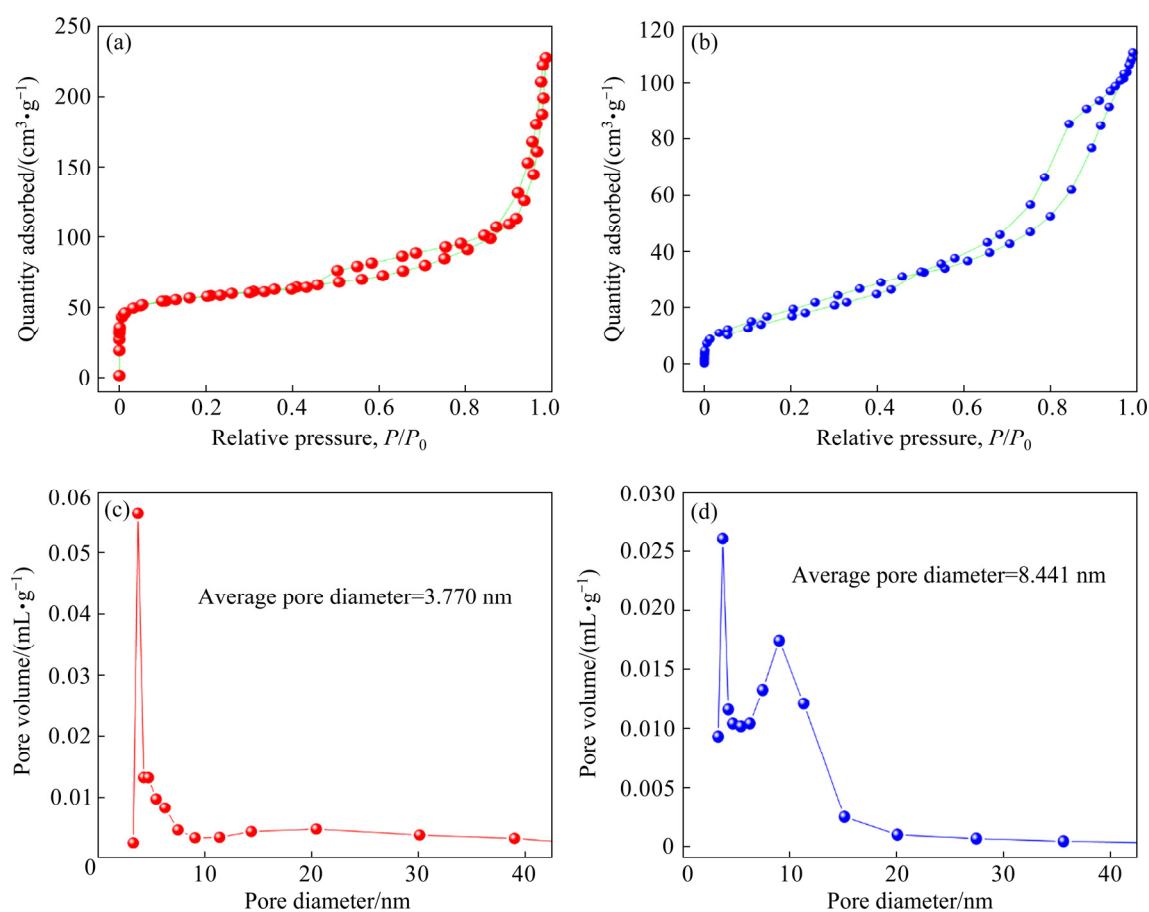


Fig. 2 Nitrogen adsorption and desorption curves of MIL-53/C (a), MIL-53-N/C (b) and pore diameter distribution of MIL-53/C (c) and MIL-53-N/C (d)

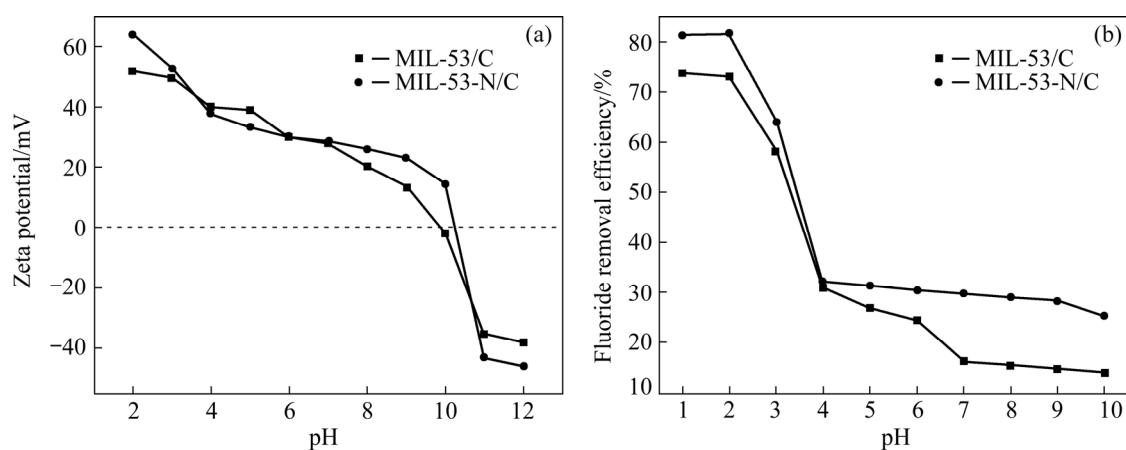


Fig. 3 Variation of zeta potential (a) and fluoride removal efficiency (b) with pH by using MIL-53/C and MIL-53-N/C

3.2.2 Liquid/solid ratio

Appropriate quantity should be considered to balance the adsorption capacity with the mass of adsorbent. The fluoride removal efficiency of MIL-53/C increased from 78%, 81.75%, 82.75%, 82.75%, to 82.88% as its mass increased from 10, 20, 30, and 40 to 50 mg, respectively. A similar trend was observed when MIL-53-N/C was used as

an adsorbent. The fluoride removal efficiency increased from 74.75%, 82.38%, 82.88%, 83.13%, to 83.25% when the following corresponding mass of the adsorbent was used: 10, 20, 30, 40, and 50 mg, respectively. When the quantity of the adsorbent in the solution was reduced beyond a certain threshold, it led to insufficient active sites for effective binding with fluoride ions. This

significantly affected the fluoride removal efficiency. At this point, the active sites of the adsorbent in the solution became saturated. However, when the solid/liquid ratio of the adsorption process was increased, the availability of more active sites on the adsorbent was obtained. Hence, the adsorption process was no longer limited by the active site of the adsorbent, but by the original concentration of fluoride ions in the solution. High liquid/solid ratio also significantly affected the full utilization of the adsorbent. As a result, 30 mg (0.6 g/L) and 20 mg (0.4 g/L) were selected as the adaptive masses for MIL-53/C and MIL-53-N/C, respectively.

3.2.3 Adsorption kinetics

The adsorption rates of both adsorbents (MIL-53/C and MIL-53-N/C) were studied and shown in Fig. 4. The adsorption rate was faster within the first 10 min, hence adsorbing about 69.83% of fluoride ions within the first 10 min as

presented in Fig. 4(a). However, when the time was extended to 180 min (3 h) the fluoride removal efficiency recorded a little increase to 82.63% by using MIL-53/C as an adsorbent. This showed that the adsorption capacity was not significantly influenced when the time was increased, thus attaining almost a negligible change after 180 min of contact time. Comparatively, both MIL-53/C and MIL-53-N/C had similar three steps in Fig. 4(c). Different kinetic models were simulated to understand the details distinguishing features between MIL-53/C and MIL-53-N/C. The pseudo-first-order model (Eq. (2)), pseudo-second-order model (Eq. (3)), external diffusion kinetic equation (Eq. (4)), intraparticle diffusion kinetic equation (Eq. (5)), Elovich equation (Eq. (6)), and mass transfer model (Eq. (7)) were all specified as follows [33,34]:

$$\lg(q_e - q_t) = \lg q_e - \frac{k_1 t}{2.303} \quad (2)$$

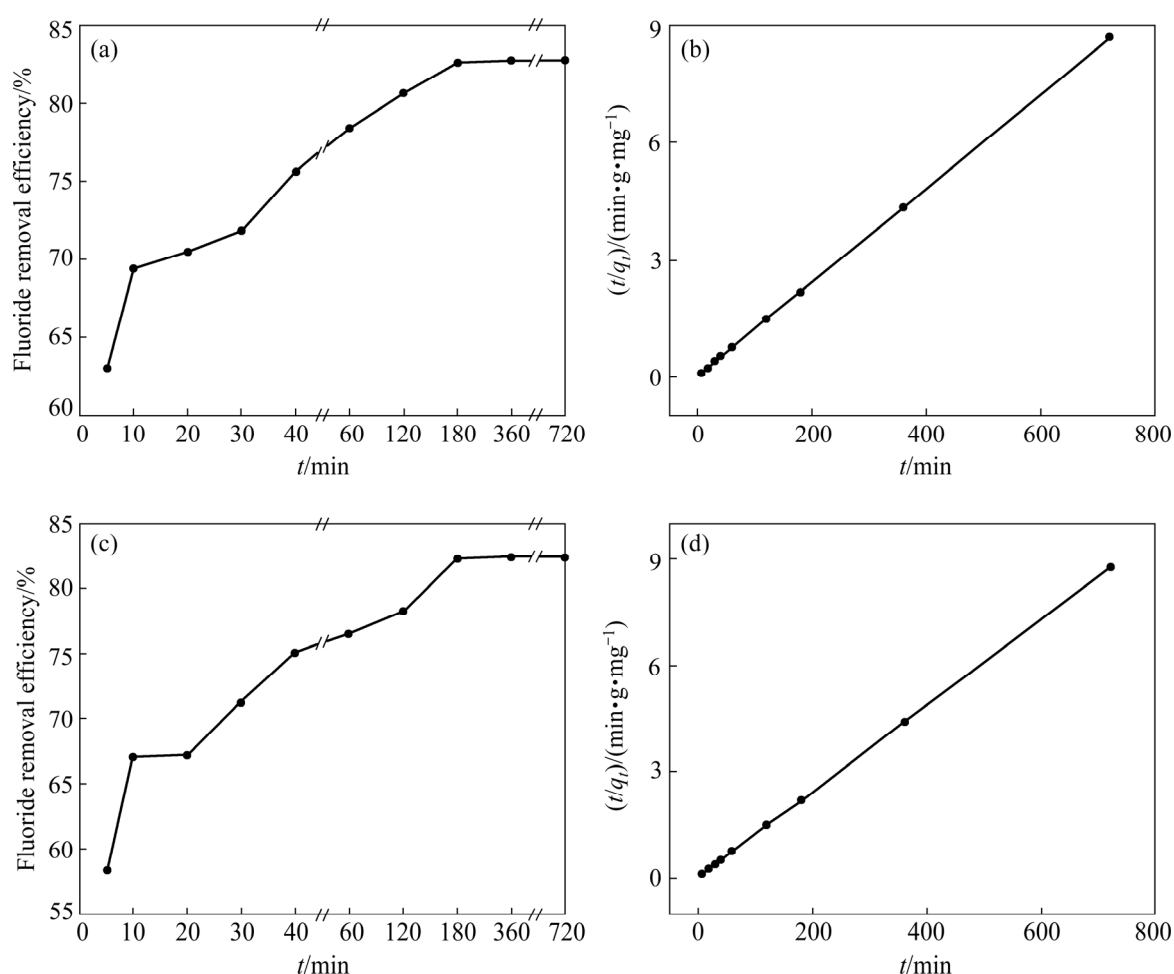


Fig. 4 Fluoride removal efficiencies by using MIL-53/C (a) and MIL-53-N/C (c) at different times, and adsorption kinetic curves (b, d) of removing fluoride by using pseudo-second-order model corresponding to (a) and (c), respectively

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

$$\ln \frac{C_t}{C_0} = -k_p t \quad (4)$$

$$q_t = k_{ID} t^{1/2} + C \quad (5)$$

$$q_t = A + 2.303 B \lg t \quad (6)$$

$$C = r \exp(-a t k_f) + z \quad (7)$$

In these equations, q_t , C_0 , and C_t have been defined as illustrated in Eq. (1). q_e (mg/g) is the equilibrium capacity. k_1 (min^{-1}), k_2 ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$), k_p (min^{-1}), k_{ID} ($\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-0.5}$), and k_f (m/s) are the kinetic parameters from the different kinetic models, respectively. C , A , r , and z are constants in the above equations. a is the correlation coefficient of specific surface area (m^2/m^3)

The kinetic parameters for both adsorbents of MIL-53/C and MIL-53-N/C were shown in Table 1. The correlation coefficients of MIL-53/C in decreasing order as obtained from the models were R_{PS}^2 (0.999) > R_{EE}^2 (0.969) > R_{PF}^2 (0.950) > R_{ID}^2 (0.891) > R_{ED}^2 (0.837). Similarly, the correlation coefficients of MIL-53-N/C were R_{PS}^2 (0.999) > R_{EE}^2

$$(0.951) > R_{PF}^2 (0.886) > R_{ID}^2 (0.847) > R_{ED}^2 (0.808).$$

As a result, the adsorption kinetics fitted very well with the pseudo-second-order model, which indicated that the rate-controlling step (rate-limiting step) was a chemisorption process as demonstrated in Figs. 4(b, d). The k_2 value of MIL-53-N/C (0.0031 $\text{g}/(\text{mg} \cdot \text{min})$) was less than that of MIL-53/C (0.0040 $\text{g}/(\text{mg} \cdot \text{min})$) in Table 1. Besides, another interesting observation was that the smaller the numerical value of k_2 is, the more the adsorption sites are acquired. This suggests that nitrogen-doping could improve the number of adsorption sites. The mass transfer model was employed to estimate the mass transfer velocity of both adsorbents of MIL-53/C and MIL-53-N/C. The result from the model showed that nitrogen-doping not only improved the adsorption sites but also enhanced mass transfer velocity (k_f : $3.1 \times 10^{-7} \text{ m/s}$ > $1.2 \times 10^{-7} \text{ m/s}$) in Table 1. Consequently, nitrogen-doping was responsible for increasing the velocity of adsorption and binding sites, hence contributing to the overall adsorption process of chemisorption.

3.2.4 Adsorption thermodynamics

Adsorbents of MIL-53/C and MIL-53-N/C

Table 1 Kinetic parameters of different models by using MIL-53/C and MIL-53-N/C

Model	Material	Parameter		
		k_1/min^{-1}	$q_e(\text{cal})/(\text{mg} \cdot \text{g}^{-1})$	R^2
Pseudo-first-order model	MIL-53/C	0.026	21.81	0.950
	MIL-53-N/C	0.025	25.60	0.886
Pseudo-second-order model		$k_2/(\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1})$	$q_e(\text{cal})/(\text{mg} \cdot \text{g}^{-1})$	R^2
	MIL-53/C	0.0040	83.195	0.999
	MIL-53-N/C	0.0031	82.919	0.999
External diffusion kinetic equation		k_p/min^{-1}		R^2
	MIL-53/C	0.0038		0.837
	MIL-53-N/C	0.0040		0.808
Intraparticle diffusion kinetic equation		$k_{ID}/(\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-0.5})$	C	R^2
	MIL-53/C	1.606	63.204	0.891
	MIL-53-N/C	1.831	59.671	0.847
Elovich equation		A	B	R^2
	MIL-53/C	55.274	5.336	0.969
	MIL-53-N/C	50.296	6.180	0.951
Mass transfer model		r	$k_f/(\text{m} \cdot \text{s}^{-1})$	z
	MIL-53/C	20.138	1.2×10^{-7}	17.454
	MIL-53-N/C	20.138	3.1×10^{-7}	17.454

Parameter a in mass transfer model is $2.10 \times 10^5 \text{ m}^2/\text{m}^3$ for MIL-53/C and $8.13 \times 10^4 \text{ m}^2/\text{m}^3$ for MIL-53-N/C; cal: Calculated

were investigated under different concentrations of fluoride to realize the adsorption thermodynamics, as shown in Figs. 5(a, b). When MIL-53/C was used as sorbent, the adsorption capacities were 299.17, 293.13, and 287.92 mg/g at 30, 45, and 60 °C, respectively. This indicates that the adsorption capacity decreases with an increase in temperature. Therefore, fluoride adsorption under this condition is an exothermic reaction in Fig. 5(a). Similarly, the adsorption capacities of MIL-53-N/C were 390.31, 382.50, and 370.94 mg/g at 30, 45, and 60 °C, respectively. This also further suggests an exothermic sorption process, as shown in Fig. 5(b). The following models were used for the thermodynamic studies: Langmuir model (Eq. (8)), Freundlich model (Eq. (9)), Temkin model (Eq. (10)), Dubinin–Radushkevich model (Eq. (11)) to simulate the adsorptive behavior of MIL-53/C and MIL-53-N/C as follows [35,36]:

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \quad (8)$$

$$q_e = k_F C_e^{1/n} \quad (9)$$

$$q_e = \frac{RT}{b_T} \ln(k_T T C_e) \quad (10)$$

$$\ln q_e = \ln q_{\max} - \beta \varepsilon^2 \quad (11)$$

where C_e is the equilibrium concentration of fluoride. $q_{\max}$ and b represent the thermodynamic parameters corresponding to the largest adsorption capacity and Langmuir isotherm constant, respectively. k_F and n are the Freundlich constants on behalf of adsorption capacity and adsorptive intensity. b_T and k_T are Temkin isotherm constant and Temkin isotherm equilibrium binding constant, respectively. Additionally, ε is the Polanyi potential, and β is the activity coefficient related to the average sorption free energy.

The adsorption thermodynamic parameters of MIL-53/C are shown in Table 2. The best-fitted model was the Freundlich model (R_F^2 (0.999) > R_L^2 (0.998) > R_T^2 (0.804) at 30 °C). Increasing the temperature resulted in a corresponding decrease in the value of k_F , indicating that increasing the temperature could inhibit the adsorption process. This phenomenon further suggests that the adsorption process is an exothermic reaction. Also, larger values of k_F induced higher binding capacities at lower temperatures, hence causing the binding ability to decline as the temperature went up as shown in Table 2.

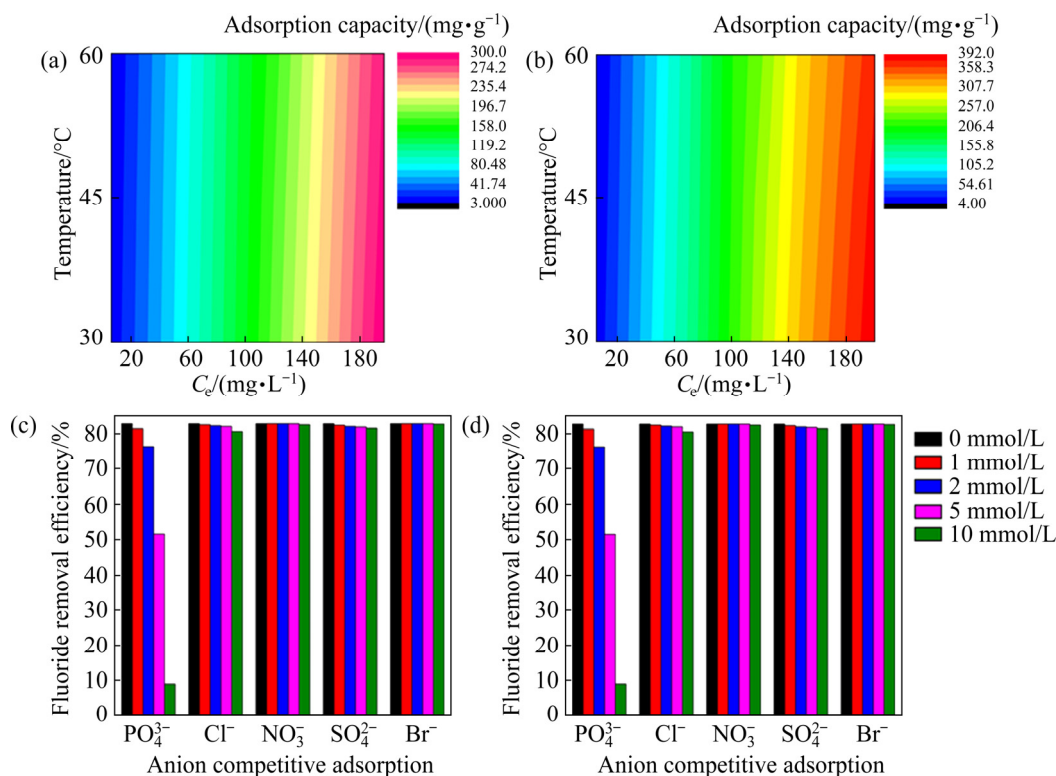


Fig. 5 Thermodynamic results of fluoride adsorption by using MIL-53/C (a) and MIL-53-N/C (b) at different temperatures and effect of anions on fluoride adsorption by using MIL-53/C (c) and MIL-53-N/C (d)

Table 2 Thermodynamic parameters of different models by using MIL-53/C and MIL-53-N/C at different temperatures

Absorbent	Temperature/ °C	Langmuir model			Freundlich model			Temkin model		
		$q_{\max}/$ ($\text{mg}\cdot\text{g}^{-1}$)	$b/$ ($\text{L}\cdot\text{mg}^{-1}$)	R_L^2	k_F	n	R_F^2	k_T	b	R_T^2
MIL-53/C	30	616.48	0.0004	0.998	1.04	0.94	0.999	0.0003	35.58	0.804
	45	441.00	0.0005	0.997	0.97	0.93	0.999	0.0003	37.86	0.806
	60	316.11	0.0006	0.996	0.87	0.91	0.999	0.0003	40.14	0.807
MIL-53-N/C	30	886.03	0.0005	0.998	2.53	1.05	0.997	0.0004	25.71	0.842
	45	620.37	0.0005	0.998	2.32	1.03	0.996	0.0003	27.29	0.844
	60	510.46	0.0008	0.997	2.10	0.91	0.996	0.0003	40.14	0.801

Furthermore, the fluoride ions adsorbed on MIL-53/C represented multilayer adsorption. Unlike the MIL-53/C adsorbent, the adsorption thermodynamics of MIL-53-N/C followed the Langmuir model as shown in Table 2 (R_L^2 (0.998) > R_F^2 (0.997) > R_T^2 (0.842) at 30 °C), indicating monolayer adsorption. The simulative adsorption capacity decreased with an increase in temperature. The simulative adsorption capacity of MIL-53/C was also lower than that of MIL-53-N/C under the same conditions in Table 2. Despite the monolayer adsorption, the increase in nitrogen-doping sites still showed higher adsorption ability. As a result, the nitrogen-doping site changed the multilayer adsorption to monolayer. However, it could also enhance the adsorption capacity of fluoride.

3.2.5 Effect of co-existing anions

The effects of co-existing anions in real water/wastewater such as PO_4^{3-} , Cl^- , NO_3^- , SO_4^{2-} , and Br^- were investigated under both adsorbents to understand their potential effect on fluoride adsorption. When all the five co-existing anions were applied on MIL-53/C, four of them, i.e., Cl^- , NO_3^- , SO_4^{2-} , and Br^- insignificantly influenced the fluoride removal efficiency at different concentrations from 1–10 mmol/L in Fig. 5(c). However, fluoride removal capacity decreased (82.75%, 81.38%, 76.38%, 51.50%, 9.00%) when PO_4^{3-} was added at different concentrations from 0 to 10 mmol/L in 100 mg/L fluoride solution. On the contrary, when the effects of Cl^- , NO_3^- , SO_4^{2-} , and Br^- on MIL-53-N/C were studied, an insignificant or negligible effect on fluoride removal efficiency was observed at different anion concentrations from 1–10 mmol/L in Fig. 5(d). Also, with regards to PO_4^{3-} , a similar effect was seen on MIL-53-N/C just as earlier reported on MIL-53/C. The fluoride

removal efficiencies were 82.38%, 81.50%, 78.25%, 53.25% and 11.50% at different concentrations of PO_4^{3-} from 0, 1, 2, 5 to 10 mmol/L in 100 mg/L fluoride solution. Despite the reduction of interference, PO_4^{3-} inhibited the adsorption of the materials. PO_4^{3-} is deemed to have a stronger combining capacity for competitive adsorption on the MIL-53/C and MIL-53-N/C, indicating its plausibility to hinder the adsorption of fluoride in real water samples. Therefore, the MIL-53/C and MIL-53-N/C could be good adsorbents for fluoride removal from wastewater even under several anions except for PO_4^{3-} .

3.3 Adsorption mechanism

The adsorbents were characterized to understand their adsorptive behavior. The XRD patterns of MIL-53/C and MIL-53-N/C are shown in Figs. 6(a, b) [37], respectively. The most obvious peak occurred around 2θ value of 23° , corresponding to the crystal face of (002) as analogous graphdiyne (JCPDS No.15-0806). Going forward, it also showed certain distinguishable diffraction peaks without higher intensity, confirming earlier propositions where analogous-graphdiyne had an amorphous structure. Considering Figs. 6(a, b), it was obvious that nitrogen-doping was a sure-way to improve the crystallinity of analogous graphdiyne for a better structure. Furthermore, the crystal structures of MIL-53/C and MIL-53-N/C were extremely stable with the changed pattern after adsorption.

The infrared spectrum peaks of MIL-53/C and MIL-53-N/C are the characteristic peaks of carbon ribbon and Al_2O_3 in Fig. 7, proving that crystallized carbon ribbon and amorphous Al_2O_3 are present in these materials. It also demonstrates the stability of

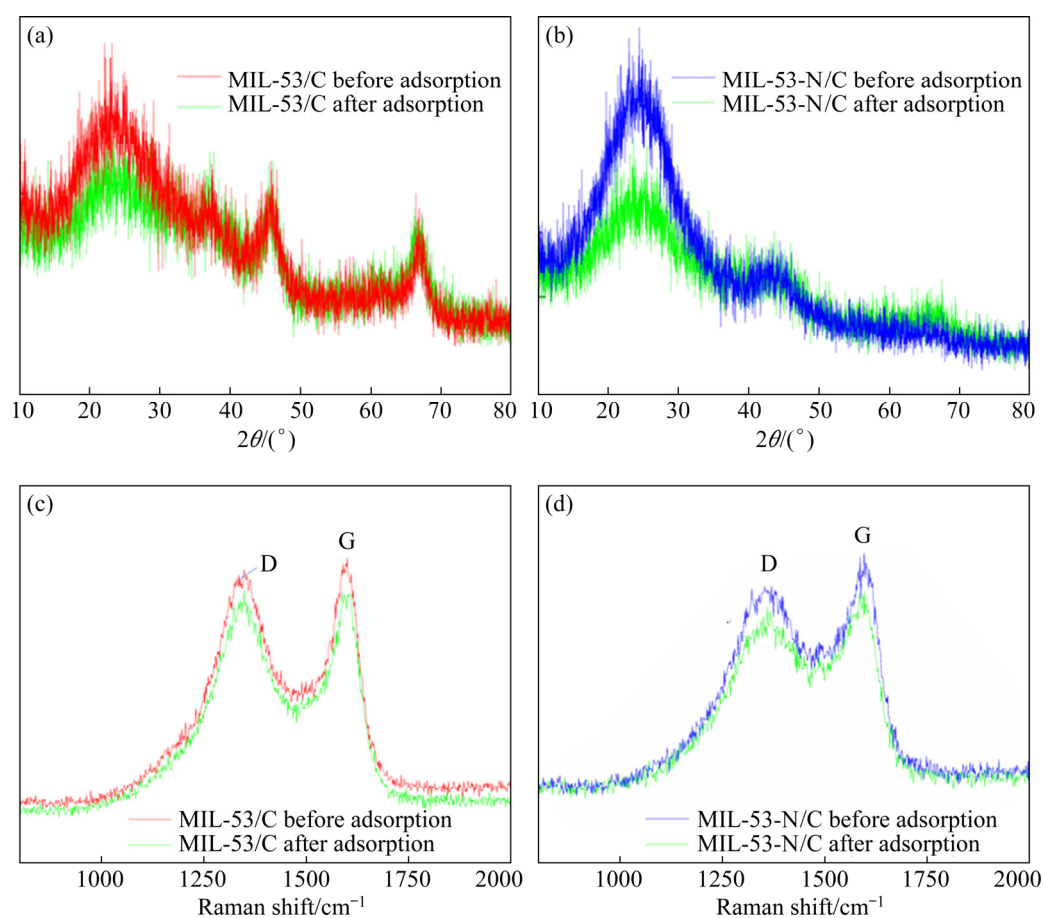


Fig. 6 XRD patterns of MIL-53/C (a) and MIL-53-N/C (b), and Raman spectra of MIL-53/C (c) and MIL-53-N/C (d) before and after adsorption

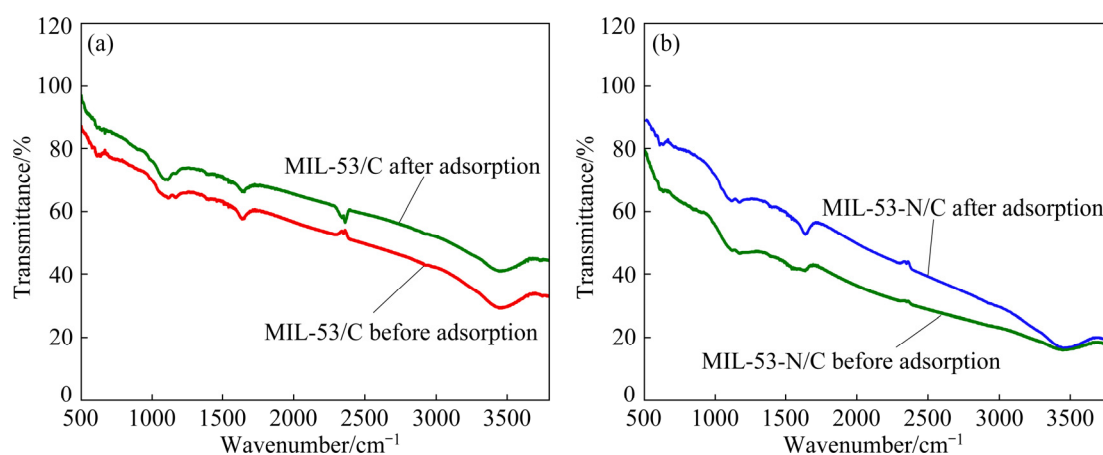


Fig. 7 Infrared spectra of MIL-53/C (a) and MIL-53-N/C (b) before and after adsorption

MIL-53/C and MIL-53-N/C from infrared spectra before and after adsorption. As shown in Fig. 6(c), the Raman spectra of MIL-53/C and MIL-53-N/C showed two prominent peaks at 1354 and 1597 cm^{-1} . Also, the D-bands of carbon ribbon/ Al_2O_3 and nitrogen-doped carbon ribbon/ Al_2O_3 are a result of the structural disorder, such as edges and

defects in carbon atoms, while the G-bands correspond to sp^2 carbon, leading to aromatic rings of the E_{2g} stretching vibration mode as reported before [38]. The nitrogen-doping enhanced the defects in the carbon ribbon between the intensity ratios (I_D/I_G) of the MIL-53/C (1.04) and MIL-53-N/C (1.13). Moreover, the defective carbon

content decreased a little after adsorbing fluoride due to the I_D/I_G ratios of the MIL-53/C (0.99) and MIL-53-N/C (1.06) in Figs. 6(c, d). Also, the EDS analysis results showed that the fluoride distribution adsorbed on both MIL-53/C and MIL-53-N/C was homogeneous (Fig. 1).

The peaks of Al 2p and O 1s before and after adsorption affected the binding energy on account

of adsorbing fluoride in Figs. 8(a–d). The peaks of fluoride are separately displayed in Figs. 8(e, f). Hence, Al_2O_3 plays an important role in the MIL-53/C and MIL-53-N/C for adsorbing fluoride. To estimate the impact on carbon ribbon and nitrogen-doped carbon ribbon [39], the carbon peaks were divided into four different peaks: C—C (sp , $-\text{C}\equiv\text{C}-$), C—C (sp^2), C=O, and C—Al in

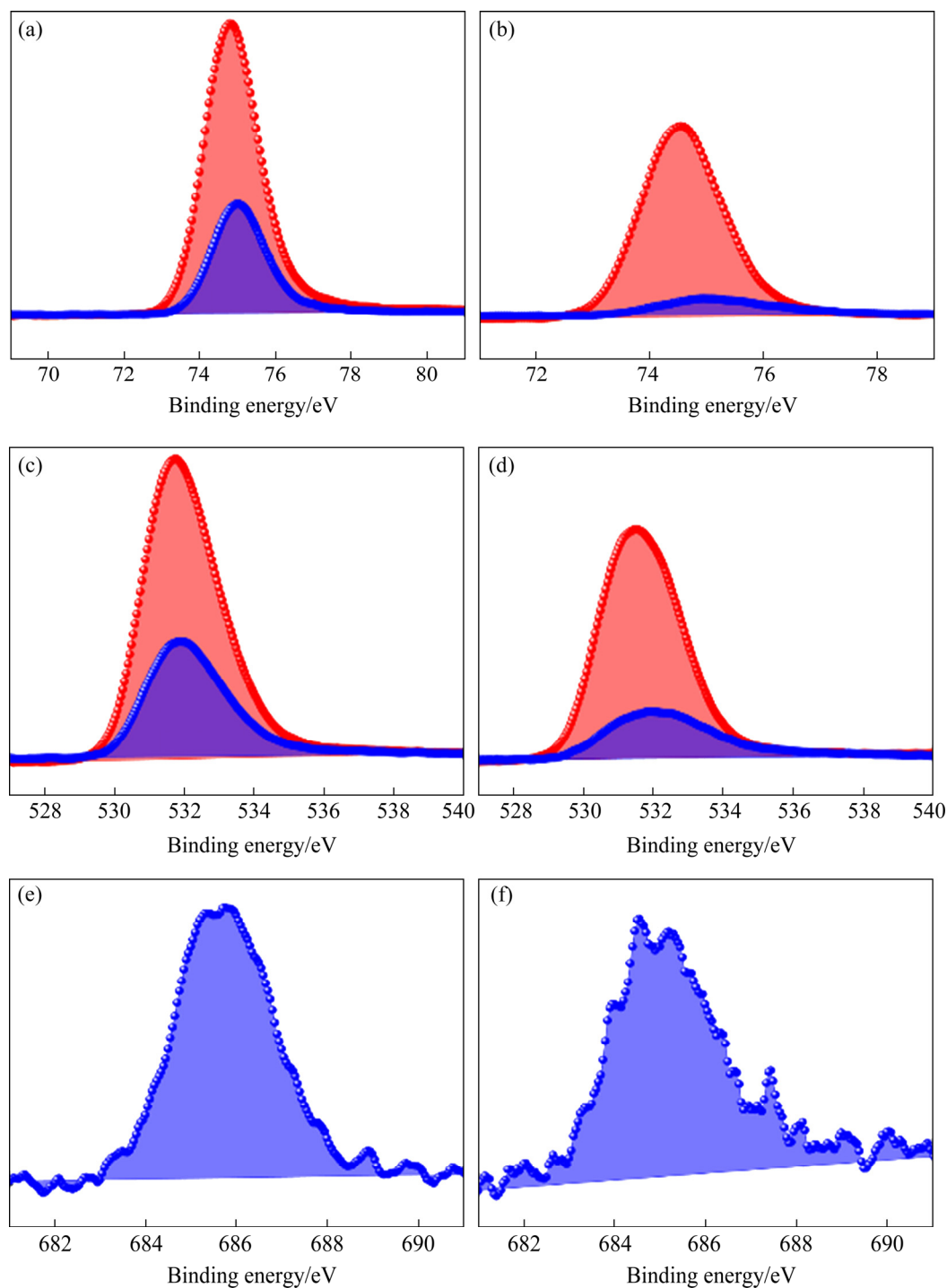


Fig. 8 X-ray photoelectron spectroscopy (XPS) patterns of MIL-53/C (a, c, e) and MIL-53-N/C (b, d, f) before and after adsorption: (a, b) Al 2p; (c, d) O 1s; (e, f) F 1s (Red represents before adsorption; blue represents after adsorption)

MIL-53/C material. The percentages of these peaks are shown in Figs. 9(a, b). The diacetylene linkages ($-\text{C}\equiv\text{C}-$) acted as the dominating adsorption sites for fluoride removal. Also, the carbon peaks for MIL-53-N/C adsorbent are $\text{C}-\text{C}$ (sp $-\text{C}\equiv\text{C}-$), $\text{C}-\text{C}$ (sp^2), $\text{C}=\text{O}$, $\text{C}-\text{Al}$, $\text{C}-\text{N}$, and $\text{C}=\text{N}$, respectively. Among these peaks, the diacetylene linkages ($-\text{C}\equiv\text{C}-$) and $\text{C}=\text{N}$ are responsible for the adsorption process in

Figs. 9(c, d). Furthermore, the N peaks correspond to oxygen-N, graphitic-N, pyrrolic-N, and pyridinic-N are demonstrated as shown in Figs. 9(e, f). The species of pyridinic-N have a positive effect on the adsorption of fluoride as shown in Fig. 10. Therefore, it should be noted that the diacetylene linkages ($-\text{C}\equiv\text{C}-$) and pyridinic-N are particularly suitable for removing fluoride.

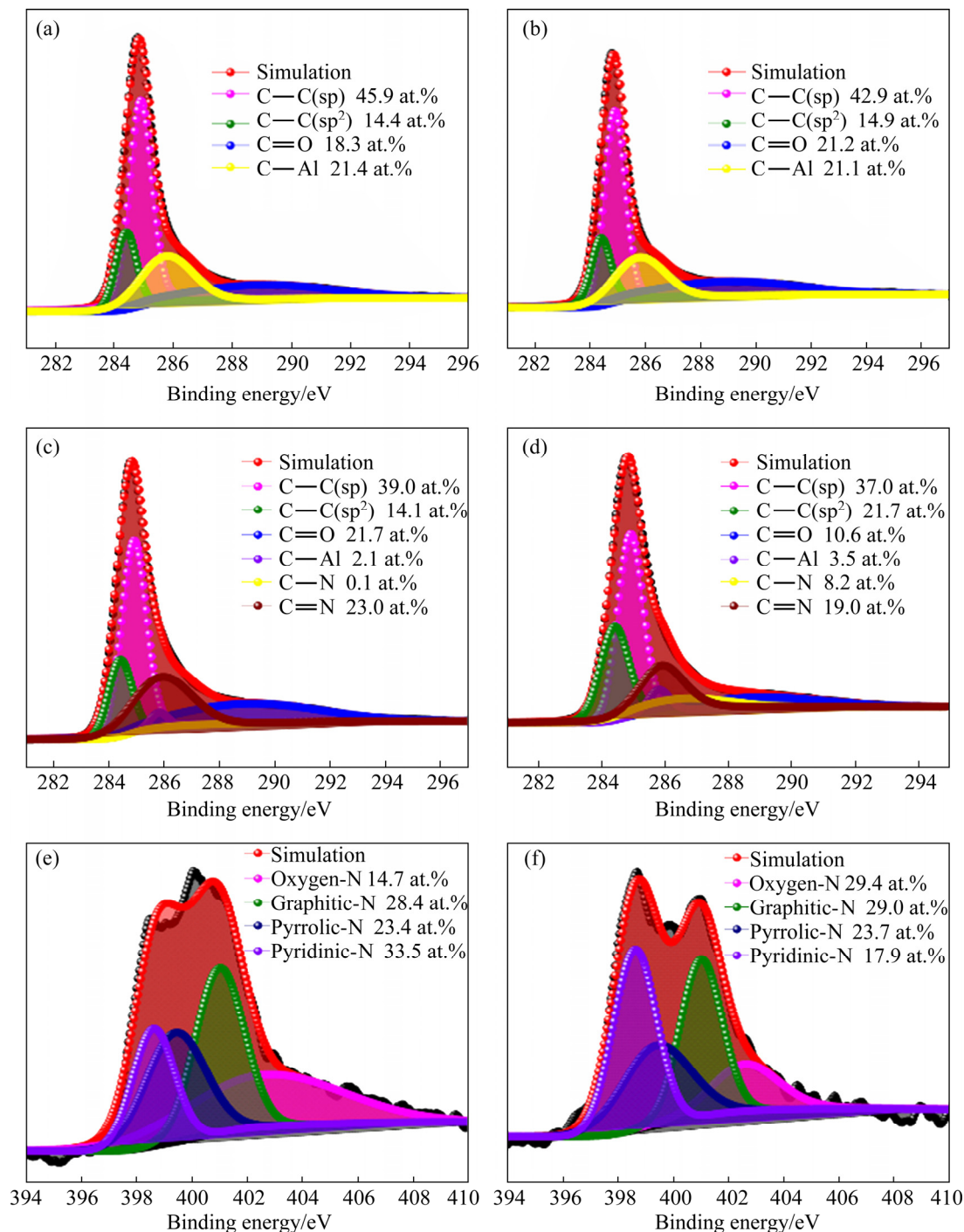


Fig. 9 XPS patterns of MIL-53/C (a, b) and MIL-53-N/C (c-f): (a, c) C 1s before adsorption; (b, d) C 1s after adsorption; (e) N 1s before adsorption; (f) N 1s after adsorption

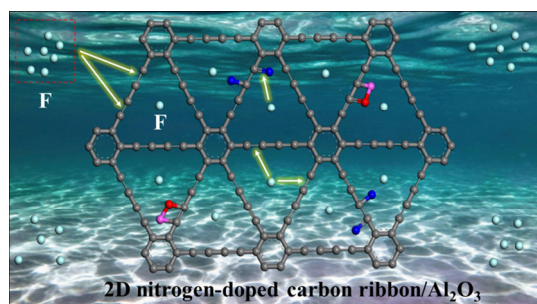


Fig. 10 Adsorption mechanism of removing fluoride by using MIL-53-N/C

4 Conclusions

(1) The adsorption of fluoride by MIL-53/C and MIL-53-N/C followed a chemisorption process. The adsorption on MIL-53/C was multilayer adsorption, whereas that of MIL-53-N/C was assumed to be monolayer adsorption. As such, the maximum adsorption capacity of MIL-53/C was recorded at 299.17 mg/g, whereas that of MIL-53-N/C was 390.31 mg/g.

(2) The best fit for removing fluoride occurred at pH=2 with an adaptive mass of 30 mg (0.6 g/L) and 20 mg (0.4 g/L) for MIL-53/C and MIL-53-N/C, respectively.

(3) The effect of four anions (Cl^- , NO_3^- , SO_4^{2-} , Br^-) had a negligible effect on both adsorbents on fluoride removal efficiency at different concentrations from 1–10 mmol/L except for high concentrations of PO_4^{3-} .

(4) In a nutshell, the experiment also showed that two peaks appeared as the diacetylene linkages ($-\text{C}\equiv\text{C}-$) and pyridinic-N played a significant role in fluoride removal. This study would serve as a foundation study on the application of carbon ribbon as a base material for removing fluoride.

Acknowledgments

The authors are grateful for the financial supports from the Key R&D Program of Hunan Province, China (No. 2018SK2026), the National Key R&D Program of China (No. 2018YFC1802204), and the National Natural Science Foundation of China (No. 51634010).

References

[1] LI C L, CHEN N, ZHAO Y N, LI R, FENG C P.

- Polypyrrole-grafted peanut shell biological carbon as a potential sorbent for fluoride removal: Sorption capability and mechanism [J]. *Chemosphere*, 2016, 163: 81–89.
- [2] MOHAN D, SHARMA R, SINGH V K, STEELE P, JR C U P. Fluoride removal from water using bio-char, a green waste, low-cost adsorbent: Equilibrium uptake and sorption dynamics modeling [J]. *Industrial & Engineering Chemistry Research*, 2012, 51(2): 900–914.
- [3] CUI H, QIAN Y, AN H, SUN C C, ZHAI J P, LI Q. Electrochemical removal of fluoride from water by PAOA-modified carbon felt electrodes in a continuous flow reactor [J]. *Water Research*, 2012, 46: 3943–3950.
- [4] JIN H Y, JI Z J, YUAN J, LI J, LIU M, XU C H, DONG J, HOU P, HOU S E. Research on removal of fluoride in aqueous solution by alumina-modified expanded graphite composite [J]. *Journal of Alloys and Compounds*, 2015, 620: 361–367.
- [5] HUANG L, YANG Z H, HE Y J, CHAI L Y, YANG W C, DENG H Y, WANG H Y, CHEN Y S, JOHN C. Adsorption mechanism for removing different species of fluoride by designing of core-shell boehmite [J]. *Journal of Hazardous Materials*, 2020, 394: 122555.
- [6] HUANG L, YANG Z H, ZHANG Z X, JIN L F, YANG W C, HE Y J, REN L L, WANG H Y. Enhanced surface hydroxyl groups by using hydrogen peroxide on hollow tubular alumina for removing fluoride [J]. *Microporous and Mesoporous Materials*, 2020, 297: 110051.
- [7] WANG F, ZUO Z C, LI L, HE F, LU F S, LI Y L. A Universal strategy for constructing seamless graphdiyne on metal oxides to stabilize the electrochemical structure and interface [J]. *Advanced Materials*, 2019, 31: 1806272.
- [8] HUANG L, YANG Z H, LI X R, HOU L J, ALHASSAN S I, WANG H Y. Synthesis of hierarchical hollow MIL-53(Al)- NH_2 as an adsorbent for removing fluoride: Experimental and theoretical perspective [J]. *Environmental Science and Pollution Research*, 2020, 28: 6886–6897.
- [9] RAGHAV S, NAIR M, KUMAR D. Tetragonal prism shaped Ni-Al bimetallic adsorbent for study of adsorptive removal of fluoride and role of ion-exchange [J]. *Applied Surface Science*, 2019, 498: 143785.
- [10] LIU J, LUO X W, SUN Y Q, TSANG D C W, QI J Y, ZHANG W L, LI N, YIN M L, WANG J, LIPPOLD H, CHEN Y H, SHENG G D. Thallium pollution in China and removal technologies for waters: A review [J]. *Environment International*, 2019, 126: 771–790.
- [11] WANG Q, CHEN P H, ZENG X, JIANG H L, MENG F F, LI X Q, WANG T, ZENG G S, LIU L L, SHU H Y, LUO X B. Synthesis of $(\text{ZrO}_2-\text{Al}_2\text{O}_3)/\text{GO}$ nanocomposite by sonochemical method and the mechanism analysis of its high defluoridation [J]. *Journal of Hazardous Materials*, 2020, 381: 120954.
- [12] NEHRA S, RAGHAV S, KUMAR D. Biomaterial functionalized cerium nanocomposite for removal of fluoride using central composite design optimization study [J]. *Environmental Pollution*, 2020, 258: 113773.
- [13] MUTLU I. Production and fluoride treatment of Mg-Ca-Zn-Co alloy foam for tissue engineering applications [J]. *Transactions of Nonferrous Metals Society of China*, 2018, 28: 114–124.
- [14] WU S B, KONG L T, LIU J H. Removal of mercury and fluoride from aqueous solutions by three-dimensional

- reduced-graphene oxide aerogel [J]. *Research on Chemical Intermediates*, 2016, 42: 4513–4530.
- [15] PRABHU S M, ELANCHEZHIAN S S, LEE G, MEENAKSHI S. Defluoridation of water by graphene oxide supported needle-like complex adsorbents [J]. *Journal of Inorganic and Organometallic Polymers and Materials*, 2016, 26: 834–844.
- [16] KUMAR H, PATEL M, MOHAN D. Simplified batch and fixed-bed design system for efficient and sustainable fluoride removal from water using slow pyrolyzed okra stem and black gram straw biochars [J]. *ACS Omega*, 2019, 4: 19513–19525.
- [17] LAI Y Q, YANG K, YANG C, TIAN Z L, GUO W C, LI J. Thermodynamics and kinetics of fluoride removal from simulated zinc sulfate solution by La(III)-modified zeolite [J]. *Transactions of Nonferrous Metals Society of China*, 2018, 28: 783–793.
- [18] ALKURDI S S A, AL-JUBOORI R A, BUNDSCHUH J, HAMAWAND I. Bone char as a green sorbent for removing health threatening fluoride from drinking water [J]. *Environment International*, 2019, 127: 704–719.
- [19] TCHOMGUI-KAMGA E, ALONZO V, NANSEU-NJIKI C P, AUDEBRAND N, NGAMENI E, DARCHEN A. Preparation and characterization of charcoals that contain dispersed aluminum oxide as adsorbents for removal of fluoride from drinking water [J]. *Carbon*, 2010, 48: 333–343.
- [20] DEBERITZ J, BELE K K, SCHADE K. Method of separating NaCl from a LiCl solution: WIPO patent, 1998019966 [P]. 1998–05–15.
- [21] MEDELLIN-CASTILLO N A, CRUZ-BRIANO S A, LEYVA-RAMOS R, MORENO-PIRAJÁN J C, TORRES-DOSAL A, GIRALDO-GUTIÉRREZ L, LABRADA-DELGADO G J, PÉREZ R O, RODRIGUEZ-ESTUPIÑAN J P, REYES L S Y, MENDOZA M S B. Use of bone char prepared from an invasive species, pleco fish (*Pterygoplichthys* spp.), to remove fluoride and cadmium(II) in water [J]. *Journal of Environmental Management*, 2020, 256: 109956.
- [22] PRABHU S M, KOILRAJ P, SASAKI K. Synthesis of sucrose-derived porous carbon-doped $Zr_2La_{1-x}OOH$ materials and their superior performance for the simultaneous immobilization of arsenite and fluoride from binary systems [J]. *Chemical Engineering Journal*, 2017, 325: 1–13.
- [23] CHEN Y Q, ZHANG Q K, CHEN L B, BAI H, LI L. Basic aluminum sulfate@graphene hydrogel composites: Preparation and application for removal of fluoride [J]. *Journal of Materials Chemistry A*, 2013, 1: 13101–13110.
- [24] KUANG L Y, LIU Y Y, FU D D, ZHAO Y P. FeOOH-graphene oxide nanocomposites for fluoride removal from water: Acetate mediated nano FeOOH growth and adsorption mechanism [J]. *Journal of Colloid and Interface Science*, 2017, 490: 259–269.
- [25] WANG X, SONG H, JIAO F, QIN W Q, YANG C R, CUI Y F, ZHANG Z Q, ZHANG J, LI H B. Utilization of wastewater from zeolite production in synthesis of flotation reagents [J]. *Transactions of Nonferrous Metals Society of China*, 2020, 30: 3093–3102.
- [26] DEGHANI M H, HAGIGHAT G A, YETILMEZSOY K, MCKAY G, HEIBATI B, TYAGI I, AGARWAL S, GUPTA V K. Adsorptive removal of fluoride from aqueous solution using single- and multi-walled carbon nanotubes [J]. *Journal of Molecular Liquids*, 2016, 216: 401–410.
- [27] SUN R H, ZHANG H B, QU J, YAO H, YAO J, YU Z Z. Supercritical carbon dioxide fluid assisted synthesis of hierarchical AlOOH@reduced graphene oxide hybrids for efficient removal of fluoride ions [J]. *Chemical Engineering Journal*, 2016, 292: 174–182.
- [28] PRABHU S M, ELANCHEZHIAN S S, LEE G, KHAN A, MEENAKSHI S. Assembly of nano-sized hydroxyapatite onto graphene oxide sheets via in-situ fabrication method and its prospective application for defluoridation studies [J]. *Chemical Engineering Journal*, 2016, 300: 334–342.
- [29] RUAN Z Y, TIAN Y X, RUAN J F, CUI G, IQBAL K, IQBAL A, YE H R, YANG Z Z, YAN S Q. Synthesis of hydroxyapatite/multi-walled carbon nanotubes for the removal of fluoride ions from solution [J]. *Applied Surface Science*, 2017, 412: 578–590.
- [30] GAO X, LIU H B, WANG D, ZHANG J. Graphdiyne: Synthesis, properties, and applications [J]. *Chemical Society Reviews*, 2019, 48: 908–936.
- [31] PILLAI P, LAKHTARIA Y, DHARASKAR S, KHALID M. Synthesis, characterization, and application of iron oxyhydroxide coated with rice husk for fluoride removal from aqueous media [J]. *Environmental Science and Pollution Research*, 2020, 27: 20606–20620.
- [32] LI Y Z, C ZHANG, JIANG Y P, WANG T J. Electrically enhanced adsorption and green regeneration for fluoride removal using $Ti(OH)_4$ -loaded activated carbon electrodes [J]. *Chemosphere*, 2018, 200: 554–560.
- [33] TAO W, ZHONG H, PAN X B, WANG P, WANG H Y, HUANG L. Removal of fluoride from wastewater solution using Ce-AlOOH with oxalic acid as modification [J]. *Journal of Hazardous Materials*, 2020, 384: 121373.
- [34] LI Y H, ZHANG P, DU Q J, PENG X J, LIU T H, WANG Z H, XIA Y Z, ZHANG W, WANG K L, ZHU H W, WU D H. Adsorption of fluoride from aqueous solution by graphene [J]. *Journal of Colloid and Interface Science*, 2011, 363: 348–354.
- [35] GAO H Y, HE Y H, ZOU J, XU N P, LIU C T. Tortuosity factor for porous FeAl intermetallics fabricated by reactive synthesis [J]. *Transactions of Nonferrous Metals Society of China*, 2012, 22: 2179–2183.
- [36] CHEN F, ZHANG M, MA L L, REN J G, MA P, LI B, WU N N, SONG Z M, HUANG L. Nitrogen and sulfur codoped micro-mesoporous carbon sheets derived from natural biomass for synergistic removal of chromium(VI): Adsorption behavior and computing mechanism [J]. *Science of the Total Environment*, 2020, 730: 138930.
- [37] WASSON A J, FUCHS G E. The effect of carbide morphologies on elevated tensile and fatigue behavior of a modified single crystal Ni-base superalloy [C]//*Proc Superalloys 2008*. Warrendale, PA: TMS, 2008: 489–497.
- [38] PAKORNCHOTE T, GEBALLE Z M, PINSOOK U, TAYCHATANAPAT T, BUSAYAPORN W, BOVORN-RATANATAKS T, GONCHAROV A F. Raman spectroscopy on hydrogenated graphene under high pressure [J]. *Carbon*, 2020, 156: 549–557.
- [39] UMPHREYS F J, HATHERLY M. Recrystallization and related annealing phenomena [M]. 2nd ed. Amsterdam: Elsevier, 2004.

以 MOFs 为前驱体制备二维碳带/ Al_2O_3 及氮掺杂碳带/ Al_2O_3 去除高氟废水

黄磊^{1,2,3}, 杨志辉^{1,2}, 严律己¹, Sikpaam Issaka ALHASSAN¹, 江海银¹, 王婷¹, 王海鹰^{1,2}

1. 中南大学 冶金与环境学院, 长沙 410083;

2. 中南大学 国家重金属污染防治工程研究中心, 长沙 410083;

3. 广州大学 环境科学与工程学院, 广州 510006

摘 要:以 2D-MOFs 为前驱体, 采用溶剂热法合成铝基金属有机骨架 MIL-53(Al), 采用煅烧法合成 2D 碳带/ Al_2O_3 。为了解氟在碳带/ Al_2O_3 和氮掺杂碳带/ Al_2O_3 上的吸附行为, 对吸附参数如 pH、液固比、吸附动力学、吸附热力学和阴离子竞争等进行研究。碳带/ Al_2O_3 对氟的吸附为化学吸附和多层吸附; 而氮掺杂碳带/ Al_2O_3 对氟的吸附为化学吸附和单层吸附。氮掺杂碳带/ Al_2O_3 对氟化物的吸附速率(3.1×10^{-7} m/s)比碳带/ Al_2O_3 对氟化物的吸附速率(1.2×10^{-7} m/s)快。氮掺杂增强碳带的缺陷结构, 提高对氟的吸附能力。此外, 研究二乙炔键($-\text{C}\equiv\text{C}-$)和吡啶 N 对除氟的影响。结果表明, 碳带和氮掺杂碳带均为良好的除氟吸附剂。

关键词:吡啶氮; 碳带; MIL-53(Al); 吸附; 除氟

(Edited by Wei-ping CHEN)