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Abstract: Excessive fluoride in mine water has become a major concern because it can cause detrimental effects to human health. Nevertheless, the removal efficiency of traditional adsorbents is far from satisfactory. Herein, La and Fe bimetallic supported zeolite was synthesized by co-precipitation method, for efficient defluoridation. The defluoridation performance of La-Fe zeolite was studied by a batch adsorption experiment and dynamic adsorption column test. Results indicated that the removal efficiency of F<sup>-</sup> was 99.04% under the optimal conditions (4 h, adsorbent dosage 8.0 g/L, agitation rate 200 rpm/min, temperature 298K and pH = 6 ± 1) that were determined through the batch adsorption experiments.  $CO_3^{2-}$  and  $HCO_3^{-}$  can inhibit the defluorination effect of La-Fe zeolite. The adsorption of fluoride ions on La-Fe zeolite can be well described by the Langmuir adsorption model, and the maximum fluoride ion adsorption capacity is 2.64 mg/g. The test of dynamic adsorption column shows that the adsorption efficiency of F<sup>-</sup> by La-Fe zeolite on was higher than 85% for continuous adsorption of 9 h, indicating that La-Fe zeolite has good practical applications. The mechanism analysis indicated that the adsorption of fluoride ion by La-Fe modified zeolite involves both ion exchange and complexation, which belongs to the physicochemical process.

Keywords: adsorption; La-Fe zeolite; fluoride ion; concentration; mechanism

# 1. Introduction

Hazards of fluoride to human body consist of chronic fluorosis and acute fluorosis [1]. The chronic fluoride poisoning has a strong irritation and corrosive attack to the skin mucous membrane, and it can dehydrate and dissolve tissue proteins by corroding or penetrating the skin. Generally speaking, it is rare for humans to cause acute fluorosis, while it can cause salivation, vomiting, diarrhea and abdominal pain, etc. in large animals because of acute fluorosis [2]. Moderate fluoride intake is beneficial to dental health, but excessive intake of fluoride is expected to cause dental fluorosis and serious bone problems [3]. It could not only affect the health of teeth and skeleton but also lead to cancer due to the accumulation over a long time [4]. As a big coal utilization country, China mines more than 4 billion tons every year. The mine water produced in the process of coal mining usually shows the phenomenon of excessive fluorine. If the mine water with excessive fluorine is discharged directly without treatment, it will lead to fluorine pollution in the surrounding water bodies (groundwater, surface water etc.). In addition, discharge of fluorinated mine water also leads to pollution to a great extent. The World Health Organization (WHO) stipulates that the content of fluoride in drinking water should not exceed 1.0 mg/L, and the industrial wastewater discharge standard requires that the content of fluoride ion should be below 1.5 mg/L [5]. Thus, it is urgent to develop environmentally sound and efficient technologies to remove excessive fluoride from water.

So far, a large amount of techniques have been put forward to remove fluoride ions effectively from water, including adsorption [6], precipitation [7], ion exchange [8] and electrolysis [9], etc. Meenakshi overviewed the advantages and limitations about the existing



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technologies for fluoride removal [10]. Among the mentioned technologies, the adsorption method has been regarded as one of the promising approaches for water defluoridation [11]. In addition, different adsorbents such as zeolite [12], activated alumina [13], hydroxyapatite [14], and activated carbon [15] were used to achieve the goal of defluoridation. Pan et al. [16] designed a novel nanocomposite adsorbent HZO-201 for preferable and sustainable defluoridation from NOM-rich water. HZO-201 can treat >3000 BV of the acidic effluent per run at pH 3.5, compared to only ~4 BV with D201. Zhang et al. [17] synthesized the nanocomposite HZO@HCA by encapsulating hydrated zirconia nanoparticles (HZO NPs) in hyper-cross-linked polystyrene anion exchanger (HCA) combined with tertiary amine groups. The synthesized fluorinated groundwater can pass through the HZO@HCA fixed bed and finally produce ~80 bed volume (BV) effluent to meet the drinking water standards (<1.5 mg/L). Thus, developing a highly efficient and selective adsorbent for fluoride ions removal from wastewater is highly needed.

Among the available adsorbents, zeolite was extensively researched and used in water defluoridation because of its extensive sources, stable defluorination ability, and long lifespan [18]. Typically, natural zeolite is crystalline microporous aluminosilicates, which is composed of silicon and aluminum oxide tetrahedron sharing oxygen vertices [19]. Silicon has one more positive charge than aluminum, so the framework of aluminum has a net negative charge, and it is balanced by commutable cation. However, the pores of natural zeolite are usually blocked by impurities, and its adsorption performance is limited [19]. Therefore, natural zeolite usually required further treatment or modification to improve their adsorption properties. It has been shown that loading multivalent active component metal ions on natural zeolite can improve its adsorption capacity. Therefore, cations with strong exchange properties such as La, Fe, Al, Ti, etc., have been used to exchange the positive ions in the pores of natural zeolite and the framework [19,20], which is identified as an effective method to improve the adsorption ability. Liu et al. [21] studied the removal of humic acid (HA) by encapsulating natural zeolite with titanium dioxide. Compared with natural zeolite, 80% of the bulk organic matter could be removed by the zeolite/ $TiO_2$ within 5 min of adsorption. Camacho et al. [22] studied the adsorption of arsenic on natural clinoptilolite and MnO<sub>2</sub>-modified clinoptilolite-Ca, and the study showed that the removal efficiency of trace arsenic by MnO<sub>2</sub>-modified clinoptilolite-Ca was doubled. Among the hetero atoms that can be loaded into the zeolite framework, oxides formed by transition metal elements have become preference because of the low cost, high selectivity, and halogen resistance [23]. Fe proves to be easier to incorporate into zeolite frameworks than other transition metal elements [24]. It was found that  $Fe^{3+}$  could involve in the zeolite framework preferably because of the similar behavior like  $Al^{3+}$  [25]. In addition, lanthanum-based adsorbents have excellent physical and chemical properties and affinity for hydroxide radical on the surface, and have a powerful affinity for fluoride ions [26]. In addition, La has some advantages indicating being low cost, nontoxic and environmentally friendly compared with other rare earth elements [27]. In previous studies, there were a few examples of zeolite modification with both La and Fe, and most of the zeolites were modified by monometallic La or Fe. In the present study, the modification with La and Fe has achieved considerable results, and La is a precious metal, which reduces the cost compared with the modified zeolite with the single metal La. When the dosage was 10 g/L, the pH was 6.94, and the temperature was 313 K, the maximum adsorption capacity of the modified zeolite synthesized by Sun et al. [18] for fluoride in simulated zinc sulfate was 2.31 mg/g. Samatya et al. [20] studied the removal effect of La-ZEO on fluoride ions, and the results showed that the maximum adsorption capacities of La-ZEO-1, La-ZEO-2, and La-ZEO-3 were 2.63, 2.37, and 2.55 mg/g, respectively. In contrast, the optimal pH environment of this experiment was about 7. Under the condition of 318 K and dosage of 8 g/L, the maximum adsorption capacity of modified zeolite to simulated mine water was 2.64 mg/g, which was more economical and environmentally friendly.

In this study, La and Fe bimetallic supported zeolite was synthesized by co-precipitation method in one step, and the method and process of removing fluoride ions from mine

water by modified zeolite were explored. The optimal preparation process of La and Fe bimetallic zeolite was determined by static adsorption experiment, and the defluorination efficiency of the modified adsorbent was explored by conditional experiments and the dynamic adsorption process, which proved the key factors affecting its defluorination. The mine water was simulated by the NaF solution prepared in laboratory. The regeneration experiment was implemented to study the utilization effect of modified zeolite as well as explore the practical applicability of modified zeolite.

# 2. Materials and Methods

# 2.1. Materials

Ferric chloride hexahydrate (FeCl<sub>3</sub> · 6H<sub>2</sub>O, AR) and aluminum sulfate (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> · 18H<sub>2</sub>O, AR) were purchased from Xilong Chemical Co., Ltd. (Guangdong, China). Lanthanum chloride heptahydrate (LaCl<sub>3</sub> · 7H<sub>2</sub>O, AR) and sodium citrate (Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>OH · nH<sub>2</sub>O, 99%) were provided by Macklin (Shanghai, China). Glacial acetic acid (C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>, 99.5%) was supplied by Modern Oriental Technology Development Co., Ltd. (Beijing, China). Sodium fluoride (NaF, AR) and ammonium hydroxide (H<sub>5</sub>NO, AR) were furnished by Aladdin. Natural zeolite was purchased from Henan, China. The interior of natural zeolite is generally composed of silicon-oxygen tetrahedron and aluminum-oxygen tetrahedron, with a large number of regular pore structures, which makes it have a certain specific surface area.

pH meter (PHSJ-5) was purchased from Shanghai INESA Scientific Instrument Co., Ltd., Shanghai, China. Fluoride ion electrode (Light Magnetic, PF-202) was used to measure the concentration of fluoride ions. Magnetic stirring water bath (HCJ-4E) was offered by Changzhou Enpei Instrument Manufacturing Co., Ltd., Changzhou, China. Muffle furnace (KSL-1200X) was supplied by Hefei Keying Material Technology Co., Ltd., Hefei, China.

## 2.2. Synthesis and Characterizations of La-Fe Modified Zeolite

An aliquot of 10 g of natural zeolite treated with 0.5 mol/L HCL solution was put into a reaction vessel and reacted with ferric chloride solution and lanthanum chloride solution at the liquid/liquid molar ratio of 1/2 at 60 °C for 4 h with stirring. At the same time, the pH value reached 10 after dropping ammonium hydroxide to solution. After 4 h, pour out the supernate after cooling down to room temperature. The synthetic hydroxide-containing natural zeolite was first rinsed with deionized water, and then the mixture of zeolite was dried at 105 °C for 12 h. Finally, the dried zeolites were calcined in muffle furnace at 600 °C for 2 h to harvest the La-Fe modified zeolite.

Scanning electron microscope (SEM) plus energy dispersive X-ray spectroscopy (German ZEISS Gemini SEM 300, Jena, German) was employed to exhibit the structure of natural zeolite and La-Fe zeolite. The surface chemical composition of natural zeolite and La-Fe zeolite was texted using an X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha X, Waltham, MA, USA). The functional groups on the adsorbent surface were detected by Fourier Transform infrared spectroscopy (FT-IR) (Thermo Scientific Nicolet iS20). The crystalline structure of the adsorbent was analyzed by Nanoco Empyrean X-ray diffractometer (XRD) at the scanning rate of  $2^{\circ}$ /min and  $2\theta$  range of  $10-80^{\circ}$ . The N<sub>2</sub> adsorption–desorption test was carried out using Mack ASAP 2460 at 77 K to determine the specific surface area, pore size distribution and pore volume of the adsorbent.

## 2.3. Batch Adsorption Studies

To investigate the defluorination effect of adsorbent under different conditions, batch adsorption experiments were conducted, such as the effects of contact time, external temperature, pH value, et al. The initial pH values of the fluoride ions solutions were adjusted by HCL solution or NaOH solution. In addition, 100 mg/L fluoride stock solution was prepared by dissolving 0.221 g of NaF in 1000 mL of deionized water. The known weight of the La-Fe zeolite was put into 100 mL, 10 mg/L fluorine ion solution, and adsorbed in a constant temperature magnetic stirring water bath of 200 rmp/min for a certain time to reach the adsorption equilibrium. After standing for 4 h, the supernatant was

taken and passed through  $0.45 \,\mu$ m disposable aqueous membrane. In order to maintain the ionic strength and pH value and eliminate the interference of complex ions, it is necessary to add TISABII solution to the supernatant before the measurement [18]. This is because, in the overly acidic solution, hydrogen ions will form hydrogen fluoride or difluoro-hydride ligands with fluoride ions, reducing the concentration of fluoride ions. Some ions can form complexes with fluoride ions or insoluble precipitation ions such as iron ions, aluminum ions, calcium ions, magnesium ions, etc. can interfere with the determination, and the citric acid in TISABII can mask them. In the analysis of potentiometric methods, the potential value is often linearly related to the activity of the analyzed ion, rather than the logarithm of the concentration, and the total ionic strength of the adjusted buffer solution is quite important for the accuracy of the analysis.

According to the standard curve, calculate the equilibrium concentration  $C_e$  (mg/L) of fluoride ions, and calculate the adsorption capacity  $q_e$  (mg/g) when the adsorption equilibrium is reached at the corresponding temperature. The calculation formula is (Equation (1)):

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

where  $C_0$  is the initial concentration (mg/L), *V* is the volume of the solution (L), and *m* is the dosage of zeolite (g).

### 2.4. Study on Adsorption Kinetics

At present, in order to study the kinetic mechanism of anion adsorption on solid particles, different computational models have been recommended. The adsorption form of anions can be expressed by the diffusion of anions from the solution phase to the outer surface of the adsorbent particles, adsorption on the surface of the adsorbent, complexation of anions on the surface of the adsorbent, or precipitation in the adsorbent [28].

In order to comprehend the adsorption kinetics of fluoride ions on La-Fe zeolite, this study investigated the variation of fluoride ion concentration with time at different temperatures, and selected the pseudo-first-order kinetic model (Equation (2)) [29] and the pseudo-second-order kinetic model (Equation (3)) [30] to describe the adsorption kinetics of this adsorption process:

$$q_t = q_e \left( 1 - e^{-k_1 t} \right) \tag{2}$$

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

where  $q_e$  is the adsorption capacity at equilibrium (mg/g),  $q_t$  is the adsorption capacity at t (mg/g), and  $k_1$  and  $k_2$  are the first-order adsorption rate constants and second-order adsorption rate constants.

#### 2.5. Study on Adsorption Isotherm

Adsorption isotherms are used to describe the adsorption capacity of fluoride ions at different concentrations. In this study, two adsorption isotherms were used to express the adsorption process of fluoride ions on a La-Fe modified zeolite, including Langmuir [31] isotherm (Equation (4)) and the Freundlich [32] isotherm (Equation (5)). The Freundlich model reflects the heterogeneity of the adsorbent surface, and the adsorption form belongs to multilayer adsorption, and the Langmuir adsorption isotherm model is based on mono-layer adsorption on a homogeneous surface with the same properties. The formulas are as follows:

$$q_e = \frac{q_m \cdot bC_e}{bC_e + 1} \tag{4}$$

$$q_e = K_f \cdot C_e^{\frac{1}{n}} \tag{5}$$

where  $C_e$  is the concentration of fluoride ion (mg/L),  $q_e$  is the equilibrium adsorption capacity (mg/g),  $q_m$  is the maximum adsorption capacity (mg/g), b is the constant at equilibrium

in the solution,  $K_f$  is the measure of adsorption capacity, and 1/n is the adsorption intensity of the heterogeneous system.

## 2.6. Thermodynamic Study

Adsorption thermodynamics can represent the adsorption effect after energy conversion [33]. The exploration of thermodynamics can provide a fundamental understanding of the energy change in the process of adsorption. The effects of La-Fe zeolite on the adsorption of fluoride ions at 298 K, 308 K and 318 K were studied. At the same time, the enthalpy change ( $\Delta H^0$ ), entropy change ( $\Delta S^0$ ) and Gibbs free energy ( $\Delta G^0$ ) were discussed. The use of Equations (6)–(8) assumes that the adsorption heat is constant with coverage. It can be calculated by the formulas below:

$$\Delta G^0 = -RT \ln k_d \tag{6}$$

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \tag{7}$$

$$\ln k_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{8}$$

where *R* is the ideal gas constant (8.314 J/mol·K),  $\Delta G^0$  is the Gibbs free energy variation (KJ/mol),  $\Delta H^0$  is the enthalpy change (KJ/mol),  $\Delta S^0$  is the entropy change (J/mol·K), and *T* is the thermodynamic temperature (K).

### 2.7. Dynamic Adsorption Column Experiment

Dynamic adsorption column experiments were carried out by packing 10 cm, 20 cm and 30 cm of La-Fe zeolite into three separate plexiglass columns (20 mm in diameter and 400 mm in length), which were outfitted with a water bath to maintain steady temperature. Fluoride ion solution passed through the La-Fe zeolite, and peristaltic pump (BT100-2J, China) was used to maintain constant flow rate (4 mL/min). The fluoride ion solution is taken out at regular intervals. Similar procedures were followed to investigate the effect of flow rate, including 2 mL/min, 4 mL/min and 6 mL/min.

### 3. Results and Discussion

# 3.1. Adsorbent Characterization

The microstructures of natural zeolite and La-Fe zeolite were analyzed by SEM. As shown in Figure 1a, the natural zeolite exhibits an irregular sheet-like structure. Compared with the natural zeolite, the surface of the La-Fe zeolite modified exhibits a dense flocculent structure (Figure 1b), which was covered the original structure; Figure 1c shows that La accounts for 24.94% of the total atomic amount, and Fe accounts for 10.17% of the total atomic amount. Combined with the Energy Dispersive X-ray Spectroscopy (EDS) (Figure 1c) and mapping diagram (Figure 1d–i) of the La-Fe modified zeolite, it can be known that La and Fe were successfully loaded on the natural zeolite.

The crystal structures of natural zeolite and La-Fe zeolite were analyzed by XRD. As shown in Figure 2a, the peaks around  $12.5^{\circ}$ ,  $21.15^{\circ}$ , and  $26.4^{\circ}$  were identified as Gismondine (PDF#99-0088) [34]. The main peaks near  $26.6^{\circ}$ ,  $50.1^{\circ}$ , and  $59.90^{\circ}$  belonged to (0 - 1 1), (-1 - 1 2), and (-1 - 2 1) of silicon oxide (PDF#85-0795). The main peak of an La-Fe modified zeolite was basically the same as natural zeolite. In addition, the peaks of La<sub>2</sub>O<sub>3</sub> were found at near  $30.7^{\circ}$  and 48.06, and the diffraction peaks at  $33.9^{\circ}$  and  $43.59^{\circ}$  were attributed to La<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>. However, the peaks of Fe<sub>2</sub>O<sub>3</sub> were found near  $44.1^{\circ}$ ,  $51.4^{\circ}$ , and  $75.5^{\circ}$ , which indicated that lanthanum and iron were successfully loaded on natural zeolite.



**Figure 1.** SEM images of (**a**) natural zeolite, (**b**) La-Fe zeolite, (**c**) EDS mapping of La-Fe zeolite, and (**d**–**i**) are element distribution of La, Fe, C, O, Si, and Al, respectively.



**Figure 2.** (a) XRD pattern of natural zeolite and La-Fe zeolite and (b) N<sub>2</sub> adsorption–desorption plots of natural zeolite and La-Fe zeolite, (c) FTIR spectra of natural zeolite and (d) La-Fe zeolite.

 $N_2$  adsorption–desorption analysis of natural zeolite and La-Fe zeolite were carried out, and the change of specific surface area was studied. As shown in Figure 2b, the BET surface area of natural zeolite and La-Fe modified zeolite increased slightly from 2.449 m<sup>2</sup>/g to 10.325 m<sup>2</sup>/g by simulation calculation, and the reason for the increase in a specific surface area may be due to the addition of nanoparticles. The isotherms shown in Figure 2b are type V adsorption–desorption curves and the hysteresis loop is H3, which indicates that the mesoporous structure is a slit hole formed by stacking flaky particles, which is consistent with an SEM image. The FT-IR analysis of the functional groups of natural zeolite and La-Fe zeolite was shown in Figure 2c,d, respectively. The peak in the range of  $3000-4000 \text{ cm}^{-1}$  is the -OH stretching vibration of adsorbed water [35]. A strong peak appears at 791.8 cm<sup>-1</sup> due to the stretching vibration peaks of Si-O. The peaks at 1295 cm<sup>-1</sup> and 948 cm<sup>-1</sup> are the antisymmetric stretching vibration peaks of Si-O.Si; a symmetrical stretching vibration peak of Fe-Si is at 733 cm<sup>-1</sup>, and the peak at 571 cm<sup>-1</sup> is the bending vibration peak of the Si-O bond. The infrared peak produced by the stretching vibration of La-O appears at 464.88 cm<sup>-1</sup> [36]. Compared with the natural zeolite, the infrared spectrum of modified zeolite shows a new characteristic band. The new peak near 689.8 cm<sup>-1</sup> is attributed to the metal-oxygen band [37]. In addition, because of the bending vibration of hydroxyl group of metal oxide, the corresponding peak appeared at 1166 cm<sup>-1</sup> [38], indicating that lanthanum and iron enter the framework of the zeolite silicon-oxygen tetrahedron and participate in the vibration of the framework, leading to the change of some peaks.

As shown in Figure 3a, the detailed status of natural zeolite and La-Fe zeolite was analyzed by XPS. The chemical state information of the elements above the adsorbent was given by the XPS spectrum. La-Fe zeolite not only contains the characteristic peaks of binding energy of elements such as Si 2p, Al 3p, O 1s, and C 1s, which were identical to natural zeolite, but also newly appeared La 3p and Fe 2p, which indicated that La and Fe were successfully loaded on natural zeolite. In the XPS binding energy analysis, the actual value of C 1 was 284.8 eV, and the measured value was 285.04 eV, so the binding energy was calibrated based on C 1. The XPS peaks of La  $3d_{5/2}$  and La  $3d_{3/2}$  on La-Fe zeolite were 835.8 and 851.50 eV, respectively, which represented the state of La<sub>2</sub>O<sub>3</sub> [39]. The XPS peaks of Fe  $2p_{1/2}$  and Fe  $2p_{3/2}$  were 722.69 and 710.7 eV, respectively, which represented the state of Fe<sub>3</sub>O<sub>4</sub> [40]. The peak position of O 1s at 529.56 eV represented the OH group produced by water molecules; through commutating with the OH group, the fluoride ions can adsorb on the adsorbent surface.



**Figure 3.** (a) XPS spectra of natural zeolite and La-Fe zeolite, (b) O 1s spectra of La-Fe zeolite, (c) La 3d spectra of La-Fe zeolite, (d) Fe 2p spectra of La-Fe zeolite.

# 3.2. Batch Adsorption Tests

# 3.2.1. Effect of Adsorbent Dose

The effect of the dose of absorbent was studied as shown in Figure 4a. The fluoride removal efficiency increased significantly as the adsorbent dose increased from 0.1 g to 0.5 g. The removal efficiency could reach as high as 98% at an adsorbent dose of 0.8 g. In addition, the removal efficiency increased slowly with an adsorbent dose in the range of 0.8–1.5 g, indicating that a good deal of fluoride ions was adsorbed on the surface of modified zeolite, which led to the reduction of the active sites of the adsorbent, and almost reached adsorption saturation. When further raising the adsorbent dose to 1.5 g or more, the fluoride ion removal efficiency declined slightly, suggesting that the availability of higher energy sites decreases with the occupation of a larger proportion of lower energy sites at higher doses [41], and thus the removal efficiency decline.



**Figure 4.** The effect of (**a**) adsorbent dose, (**b**) initial concentration, (**c**) competing ions, (**d**) pH, (**e**) zeta potential, (**f**) released concentration with pH.

# 3.2.2. Effect of Initial Concentration

The effects of initial concentration were shown in Figure 4b. The results demonstrated that increasing initial concentrations from 1 to 20 mg/L significantly enhances the adsorption performance. This was because there was a certain concentration difference of fluoride ions between the solid–liquid interface of La-Fe zeolite and the fluoride ions solution, resulting in a certain concentration gradient. As the concentration of fluoride ion solution increases, the driving force of the mass transfer process of liquid film on the adsorption surface also increases, which makes more fluoride ions enter the surface and pores of La-Fe modified zeolite.

### 3.2.3. Effect of Competing Ions

The existence of anions such as  $CO_3^{2-}$ ,  $HCO_3^{-}$  and  $SO_4^{2-}$  could affect the removal efficiency of fluoride ion by the adsorbent. The adsorption capacity and selectivity of La-Fe zeolite toward fluoride were examined under different ions. As shown in Figure 4c, high  $CO_3^{2-}$  and  $HCO_3^{-}$  concentrations could decrease the adsorption of fluoride. The results showed that the increase of  $CO_3^{2-}$  and  $HCO_3^{-}$  concentrations led to the increase of pH of the solution, and OH<sup>-</sup> in the solution showed a competitive effect on the adsorption of fluoride, occupying the position of fluoride ion adsorption. The slight influence of low  $SO_4^{2-}$  concentration on adsorption capacity was attributed to the selective sequence of anions according to Helfferich's electro-selectivity [42]. Within a wide concentration range,  $SO_4^{2-}$  had little effect on fluoride ion adsorption, which indicated that La-Fe zeolite had

high selectivity to fluoride ion. It is feasible to use this adsorbent to adsorb fluoride in a complex environmental system.

## 3.2.4. Effect of Initial pH

The initial pH value of the solution can regulate the surface charge of the adsorbent, which dramatically affects the adsorption capacity of adsorbent [43]. Figure 4d illustrated the removal efficiency of adsorbent for fluoride ions at different initial pH values. The results demonstrated that fluoride ion adsorption on La-Fe zeolite was maintained at above 96% at initial pH values between 5 and 7, the pH was further reduced to 1.0 or increased to 10.0, and the adsorption capacity decreased significantly. The adsorption capacity even approached to zero at pH 10. Adsorption of fluoride ions on La-Fe zeolite was through surface complexation mechanism. When the pH was decreased below 6, part of the fluoride ions were fastened because of the formation of the weak electrolyte HF between F<sup>-</sup> and H<sup>+</sup>. In addition, water will be formed by combining H<sup>+</sup> with OH<sup>-</sup> in the modified zeolite, which reduces the combination between fluoride ions. The adsorption capacity decreases significantly, and the removal efficiency drops below 20% in the alkaline pH range (pH > 8). This may be caused by the competitive adsorption of OH<sup>-</sup> and fluoride ions to the active sites on La-Fe zeolite. As the alkalinity increases, the competition becomes more and more intense.

To appreciate the change in the surface charge on the adsorbent surface, the zeta potentials of natural zeolite and La-Fe zeolite at different pH values were investigated. As shown in Figure 4e, the isoelectric point of La-Fe zeolite was 7.1, which was the pH of the solution when the surface charge of La-Fe zeolite was zero. When the pH < 7.1, the material was positively charged that can be deemed as "cation", which was beneficial to the adsorption of fluoride ion by electrostatic attraction. When the pH > 7.1, adsorbent became "anions" due to the carboxyl deprotonated and negatively charged. As a result, the electrostatic adsorption capacity of fluoride ions gradually decreases.

In order to study the stability of La-Fe zeolite in a wide pH range, the content of metal ions in the adsorbed solution at different pH values was determined. It can be seen from the Figure 4f that the content of  $La^{3+}$  in the solution is 12.76 mg/L at pH = 3.3. As the pH value continues to increase, the concentration of  $La^{3+}$  in the fluoride solution rapidly decreased to below 0.1 mg/L. However, the concentration of Fe<sup>3+</sup> in the fluoride solution was lower than 0.01 mg/L at any pH, which indicated that La-Fe zeolite has good stability in a wide pH range.

#### 3.2.5. Adsorption Kinetics

The adsorption data at different temperature were linear fitting, and the results were shown in Figure 5a,b, respectively. The fitted kinetic data were shown in Table 1. The coefficient of determination indicated that fluoride ions uptake onto La-Fe zeolite could be fitted well by the pseudo-second-model. Compared with the pseudo-first-order kinetics, the data fitted by the pseudo-second-order kinetics showed that the adsorption rate constant of the La-Fe modified zeolite was higher. The results demonstrated that the adsorption of fluoride ions by La-Fe zeolite was mainly dominated by chemical adsorption, and some fluoride ions were adsorbed by freely diffusing into the pores of zeolite.



**Figure 5.** Fitting curves of the (**a**) pseudo-first-order kinetics and (**b**) pseudo-second-order kinetics, (**c**) Langmuir isothermal adsorption mode, (**d**) Freundlich isothermal adsorption mode.

	<b>Pseudo-First-Order Kinetics</b>			Pseudo-Second-Order Kinetics		
	<i>k</i> <sub>1</sub> (/h)	<i>q<sub>e</sub></i> /(mg/g)	R <sup>2</sup>	<i>k</i> <sub>2</sub> (/h)	<i>q<sub>e</sub></i> /(mg/g)	R <sup>2</sup>
298 K	8.24	1.181	0.0575	61.96	1.187	0.5711
308 K	7.21	1.182	0.0589	40.92	1.189	0.7973
318 K	6.98	1.185	0.0593	33.14	1.194	0.7455

Table 1. Kinetic parameters of adsorption of fluoride ions by La-Fe zeolite.

# 3.2.6. Adsorption Isotherm

The adsorption isotherm curve of fluoride ion on the modified zeolite was shown in Figure 5c,d, respectively. The adsorption process was described by the Langmuir and Freundlich models, and the adsorption isotherm parameters were illustrated in Table 2. Compared with the Freundlich model, the correlation coefficient  $R^2$  of the Langmuir isotherm curve fitting is better, which can describe the adsorption process more accurately. As shown in Table 2, the 1/n values are all less than 0.5, indicating that the adsorption of fluoride ions by La-Fe modified zeolite is a favorable process. Furthermore, the adsorption of fluoride ions on the adsorbent surface is carried out in the form of single molecular layer.

Table 2. Isotherm parameters of adsorption of fluoride ions by La-Fe zeolite.

	Langmuir Model			Freundlich Model		
	$q_m (\mathrm{mg/g})$	b	$R^2$	$K_f (mg/g)$	1/n	$R^2$
298 K	1.48	1.01	0.9155	0.70	0.28	0.7476
308 K	2.06	0.58	0.9533	0.75	0.37	0.9001
318 K	2.64	0.38	0.9516	0.77	0.42	0.9469

According to the Langmuir isotherm curve fitting, the maximum adsorption capacity is not much different from the actual experiment. The adsorption capacity increased with increasing temperature and the maximum adsorption capacity was 2.64 mg/g. In order to understand the adsorption capacity of La-Fe zeolite, the maximum adsorption capacities of reported adsorbents were shown in Table 3.

Absorbents	$q_m$ (mg/g)	References
Lanthanum hydroxide modified magnetite	1.42	[44]
Fe(III)–Sn(IV) mixed oxide	10.47	[45]
Fe(III)-STI zeolite	2.31	[18]
La-ZEO-2	2.37	[20]
La-Fe zeolite	2.64	this work
KMnO <sub>4</sub> -modified carbon	15.90	[46]
Hydrous aluminum oxide-iron oxide mixture	4.18	[47]
Layered double hydroxides	16.10	[48]
Marble apatite-CM	4.23	[49]

Table 3. Comparison of the maximum adsorption capacities of various adsorbents with La-Fe zeolite.

### 3.2.7. Thermodynamics

As shown in Figure 6, the values of  $\Delta S^0$  and  $\Delta H^0$  are calculated from the slope and intercept of ln K<sub>d</sub> and 1/T on the Van't Hoff plot. Table 4 shows the thermodynamic parameters at different temperatures. The coefficient of determination ( $R^2 = 0.999$ ) shown in Figure 6 has a good linearity with the plot. The  $\Delta G^0$  of all the processes of three temperatures fluoride ions adsorption were negative, indicating that the adsorption processes were spontaneous. As the temperature gradually increases, the absolute value of  $\Delta G^0$  also increases, indicating that raising the temperature had a significant influence on the adsorption process.  $\Delta H^0 > 0$  revealed the characteristic of the adsorption process was endothermic, and  $\Delta S^0 > 0$  demonstrated that the chaos degree increases in the process of adsorption [50]. Therefore, the adsorption process of fluoride ions by La-Fe zeolite is an entropic increase reaction, which is spontaneously endothermic.



**Figure 6.** Plotting of  $\ln K_d$  versus 1/T on fluoride adsorption by La-Fe zeolite.

Table 4. Thermodynamic properties of La-Fe zeolite absorbing fluoride ions.

			$\Delta G^0$ (KJ/mol)	
$\Delta H^{2}$ (KJ/mol)	$\Delta S^{\circ}$ (KJ/mol)	298 K	308 K	318 K
12.89	0.03	-2.016	-2.546	-2.886

### 3.3. Dynamic Adsorption and Regeneration Tests

# 3.3.1. Dynamic Adsorption Test

The dynamic adsorption experiment of La-Fe zeolite with different thicknesses of La-Fe zeolite layer in three independent constant-temperature plexiglass columns was shown in Figure 7a. It can be clearly seen that the adsorption effect increases with the increase of the thickness of La-Fe zeolite layer. There were the same adsorption laws in three adsorption columns with different heights. In the early stage, La-Fe zeolite had the best adsorption performance for fluoride ions, which almost reached 100% at 360 min. It was found that, after a period of adsorption, the adsorption effect of the adsorbent for fluoride ion could still reach 85% for a long time, reaching the secondary standard that the fluoride ion content in comprehensive wastewater discharge standard was less than 1.5 mg/L. In the experiment of an independent constant temperature dynamic adsorption column with a flow rate as a variable, the same adsorption law was also reflected. It was shown in Figure 7b, as the flow rate of adsorbent was decreased from 6 mL/min to 4 mL/min, that there was an obvious increase in the adsorption time and adsorption efficiency of fluoride removal.



Figure 7. The effect of (a) filter layer height, (b) flow rate, (c) regeneration.

The results showed that, with the conditions of the same flow rate, the active sites were gradually filled because of insufficient of thickness, resulting in a gradually reduction in fluoride removal efficiency. In the condition of the same filter layer thickness, the penetration time of the La-Fe zeolite adsorption column could be prolonged with a lower flow rate, and the adsorption layer takes a long time to reach saturation. The adsorption process takes a certain time, and the low flow rate could ensure that the fluoride ions could have contact with the La-Fe zeolite for a longer time, which is convenient to fully utilizing the adsorbent and improving the utilization rate.

#### 3.3.2. Regeneration Test

The regenerability of adsorbent is a critical factor in practical applicability. For the adsorption-saturated La-Fe modified zeolite, desorption and regeneration experiments were carried out with  $Al_2(SO_4)_3$  solution with a concentration of 1%. As shown in Figure 7, the abscissa (t) and ordinate (removal efficiency) represent the removal rate of fluoride ions at different times. It can be seen from Figure 7c that, after the first cycle of regeneration, the removal efficiency of fluoride ions reached 85% after 240 min. After that, the removal efficiency of fluoride ions gradually decreased, and the removal efficiency dropped to 60.8% at 390 min. With the progress of the experiment, the adsorption capacity of the regenerated adsorption column for fluoride ions declined moderately. As for the second cycle, it can be clearly seen from Figure 7c that it was less than the first cycle, and the removal efficiency of fluoride ions was 85% at 240 min. The removal efficiency of fluoride ion was 33.47% at 390 min, which is less than half of the first cycle. As the number of regeneration cycles increases, the adsorption time was getting shorter, and the fluoride removal efficiency was also getting lower. However, after continuous regeneration and three times adsorption, more than 85% of the adsorption capacity of the La-Fe zeolite was sustained at 210 min.

Thus,  $Al_2(SO_4)_3$  solution can be used as a regenerant for adsorbing saturated La-Fe zeolite, and demonstrating that the adsorbent has good practical applicability.

#### 3.4. Adsorption Mechanism

The adsorption mechanism of fluoride ions by La-Fe zeolite was illustrated in Figure 8. In fluoride ions solution, the active sites of Fe<sup>3+</sup> and La<sup>3+</sup> on the La-Fe zeolite form into oxyhydroxides [51], and the zeolite treated by acid can be illustrated by the following reaction:

$$\text{Zeo} - \text{MeOH} + \text{H}^+ \rightleftharpoons \text{Zeo} - \text{MeOH}_2^+$$
 (9)

The adsorption reaction formulas under different pH conditions are as follows:

$$\text{Zeo} - \text{MeOH}_2^+ + \text{OH}^- \rightleftharpoons \text{Zeo} - \text{MeOH} + \text{H}_2\text{O}$$
(10)

$$\text{Zeo} - \text{MeO}^- + \text{H}^+ \rightleftharpoons \text{Zeo} - \text{MeOH}$$
 (11)

Consequently, the adsorption of anions such as  $F^-$  can be through ion exchange, and the adsorption reaction formulas are as follows:

$$\text{Zeo} - \text{MeOH} + \text{F}^- \rightleftharpoons \text{Zeo} - \text{MeF} + \text{OH}^-$$
 (12)

$$\operatorname{Zeo} - \operatorname{MeOH}_2^+ + F^- \rightleftharpoons \operatorname{Zeo} - \operatorname{MeF} + \operatorname{H}_2O$$
 (13)

At the same time, non-specific binding can also be carried out, and the reaction formula is as follows:

$$\operatorname{Zeo} - \operatorname{MeOH}_2^+ + F^- \rightleftharpoons \operatorname{Zeo} - \operatorname{MeOH}_2^+ \cdots F^-$$
 (14)

Equation (10) shows that it is beneficial to the forward reaction on positively charged zeolite particles, leading to the consumption of hydroxide ions and the decrease of the pH value of the system. In addition, Equation (11) investigates that it is beneficial to the forward reaction on the negatively charged zeolite particles. The adsorption of fluoride ion on the La-Fe modified zeolite is mainly carried out through ion exchange and complexation, as shown in Equations (12)–(14). Therefore, the zeolite system exchanged by Fe-F or La-F is the result of a complex interaction among many factors, including the initial solution pH and the reactions represented by Equations (10), (12) and (13), and the separation of La and Fe from the zeolite structure.



Figure 8. Adsorption mechanism of fluoride ions by La-Fe zeolite.

# 4. Conclusions

In this study, a fluoride ion absorbent, La-Fe zeolite, was synthesized by surface modification of Fe(III) and La(III) on natural zeolite. The batch experiments demonstrated that, under optimal conditions such as 8.0 g/L La-Fe zeolite dosage, 10 mg/L fluoride ion solution, and pH =  $6 \pm 1$ , the fluoride ion concentration can be reduced to the emission specified by the WHO Standard (1.5 mg/L) or less. The adsorption kinetics conformed to the pseudo-second-order kinetic model, and the adsorption isotherms conformed to the Langmuir model. In addition, the defluorination of La-Fe modified zeolite can be inhibited significantly by  $CO_3^{2-}$  and  $HCO_3^{-}$ . Dynamic adsorption experiments demonstrated that the adsorption time of fluoride increases with an increase in layer thickness and a decrease in flow rates; regeneration experiments showed that, after repeated regeneration, the adsorption effect can still reach more than 85% after continuous adsorption for 210 min. Fluoride adsorption on La-Fe zeolite should be a chemical adsorption process combined with controlled diffusion.

In future research, it is necessary to improve the adsorption capacity of adsorbent and also to pay attention to the environmental impact of adsorbent after adsorption saturation. Specifically, composite modification is a good measure to improve the adsorption performance of adsorbent material because it can combine the advantages of multiple modified materials. Moreover, if the adsorbed saturated material is not properly treated, it may cause serious secondary pollution to the environment. Some measures can be considered to reuse the saturated adsorbent resourcefully. For instance, the utilization of nitrogen, phosphorus and potassium by crops can be improved when the adsorption-saturated zeolite is used with fertilizers.

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