Article

Removal of Fluoride from Phosphogypsum Leaching Solution with Phosphate Tailing Based Layered Double Hydroxides: Kinetics and Equilibrium Isotherms

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Abstract: In this work, ternary and quaternary layered double oxides (PTB-LDO3 and PTB-LDO4) based on phosphate tailings were synthesized by the coprecipitation method. The as-prepared samples were characterized and applied to remove fluorine ions from a phosphogypsum leaching solution. The results indicated that both the precursor of PTB-LDO3 and PTB-LDO4 showed a layered structure with characteristic diffraction peaks of hydrotalcite. Compared with PTB-LDO4, PTB-LDO3 exhibited better adsorption performance at pH 5–6 and a dosage of 0.04 mg L$^{-1}$. The adsorption kinetics results revealed that the adsorption of fluorine by PTB-LDO3 and PTB-LDO4 reached the adsorption equilibrium in about 3 h, and followed the pseudo-second-order model. The adsorption data could be fitted better with the Langmuir isotherm with the maximum adsorption amounts of 26.03 mg g$^{-1}$ and 15.66 mg g$^{-1}$ for PTB-LDO3 and PTB-LDO4, respectively. The adsorption of fluorine by PTB-LDO3 and PTB-LDO4 were both spontaneous and exothermic, and exhibited excellent reusability and stability. This study provides a possibility for the combined treatment of phosphorus chemical solid waste (phosphorus tailings) and phosphorus chemical wastewater (phosphogypsum leaching liquid).

Keywords: phosphate tailings; layered double oxides; adsorption; phosphogypsum leaching solution

1. Introduction

Phosphate tailings (PTs) and phosphogypsum are important by-products of phosphate rock mining and phosphorus chemical industry, respectively. In China, the annual output of phosphogypsum and phosphorus tailings is as high as 80 billion tons, but the utilization rate is less than 30% [1]. In particular, there are still a large number of phosphogypsum and phosphorus tailings that are directly stored in the open air. This not only occupies a large amount of land resources, but also causes phosphorus, fluorine and other pollutants to enter the soil with the leachate, seriously polluting the surrounding ecological environment [2]. The fluorine concentration in the groundwater near the phosphogypsum dump site was 4.13–32.38 mg L$^{-1}$, which has exceeded the Quality Standard for Ground
Water [3]. Severe fluorosis can lead to abnormal teeth, even endanger bone health and renal function in infants and young children [4–6]. Therefore, there is a need to difluoride the phosphogypsum leaching solution.

In recent years, numerous technologies have been developed to treat fluoride ions in aqueous solutions, including electrocoagulation [7], reverse osmosis membrane [8], ion exchange [9], adsorption [10] and others. Among these methods, adsorption materials based on solid waste have attracted extensively attention because of their mature development, low cost, simple operation, environment-friendliness, and high efficiency [11]. A large number of adsorbents with various substrates have been developed, such as acidic alumina [12], rare earth metal oxides [13] and activated carbon [14], etc. However, the drawbacks of low specific surface area and high cost for traditional adsorbent materials have limited their application in practical water treatment. Therefore, it is urgent to develop efficient materials for the removal of fluoride.

Layered double hydroxides (LDHs) are layered minerals similar to brucite, composed of divalent and trivalent cations and interlayer exchangeable anions. Divalent ions in the LDHs network can be replaced by trivalent ions with similar radii, resulting in the accumulation of positive charges on the laminates [15]. These extra positive charges need to be counteracted by the interlayer anions, which facilitate the intercalation of anions and water molecules [16]. The general formula representing LDHs is \[ \text{LDHs} = [M_{x}^{2+}M_{y}^{3+}(\text{OH})_{2}(x+y)]^{n-} \cdot mH_{2}O \] (\( M_{x}^{2+} \), divalent metal ions; \( M_{y}^{3+} \), trivalent metal ions; \( A^{n-} \), exchangeable anion) [17]. Due to the excessive positive charges on the layers, LDHs can attract anions in water through electrostatic adsorption and further exchange with interlayer anions. In particular, the layered double oxide (LDO) obtained after calcination of LDHs can adsorb anions in the solution into the interlayer, thereby restoring the original layered hydroxide structure of LDHs. This property is called the “memory effect” of LDHs [18]. Based on this property of LDHs, a series of hydrotalcite-like compounds had been developed to remove fluorine from wastewater. Lv et al. found that the adsorption capacity of Mg-Al-CO$_3$ layered double hydroxide calcined at 500 °C for F$^-$ can reach 16 mg g$^{-1}$ [19]. Zhao et al. and Zhang et al. studied the mesoporous Co-Al LDO and Li-Al LDO, synthesized by the microemulsion method, showed good adsorption effect on fluoride ions in water [20,21]. Cai et al. found that the doping of the rare metal element La could significantly improve the adsorption performance of Li-Al-LDH for fluoride ions [22]. Most of the phosphate rock in our country is of medium and low grade, and the flotation process needs to be used to enrich the phosphate rock before utilization. During the flotation process, a large amount of PTs will be produced, which are rich in calcium, magnesium, aluminum, iron and other metal elements. Therefore, PTs can be used as an ideal raw material for the preparation of LDHs or LDO, which can effectively reduce the cost of hydrotalcite and realize the recycling of solid waste.

In this work, ternary and quaternary layered double oxides (PTB-LDO3 and PTB-LDO4) based on phosphate tailings were synthesized and applied for the removal of fluoride from the phosphogypsum leaching solution. Batch adsorption experiments were systematically carried out to optimize the dosage, solution pH, and adsorption kinetics, isotherms and thermodynamics were investigated to understand the adsorption mechanisms. This green and novel adsorption material using solid waste as raw material is expected to realize the reduction and resource utilization of phosphorus tailings, and effectively realize the removal of fluorine in phosphogypsum leaching solution.

2. Experimental Plan

2.1. Materials

PTs and phosphogypsum were collected from a phosphate mine enterprise in Hubei Province, China. Sodium citrate dihydrate (Na$_3$C$_6$H$_5$O$_7$·2H$_2$O) and sodium fluoride (NaF) were analytical grade and purchased from Aladdin. Magnesium chloride hexahydrate (MgCl$_2$·6H$_2$O), aluminum chloride hexahydrate (AlCl$_3$·6H$_2$O), iron chloride hexahydrate (FeCl$_3$·6H$_2$O), used for adjusting the metal ion molar ratio and synthesizing hydrotalcite, were
analysis grade and purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) Simulated wastewater for gradient concentration was made by dissolving appropriate sodium fluoride in phosphogypsum leaching solution.

2.2. Synthesis of PTB-LDO3 and PTB-LDO4

In this work, PTs-based LDHs were synthesized via the reported coprecipitation method [23]. 100 g of PTs were added to 200 mL of hydrochloric acid (w/w, 35%) and reacted at 60 °C for 30 min, filtered to obtain a mixed salt solution containing calcium, magnesium, aluminum, iron and other impurities. Subsequently, ammonia (w/w, 23%) was added to the mixed salt solution to adjust the pH value of the solution to 6, and was then filtered to get a purified salt solution. An appropriate amount of MgCl$_2$·6H$_2$O, AlCl$_3$·6H$_2$O and FeCl$_3$·6H$_2$O was added to the above salt solution; the molar ratio of Ca$^{2+}$-Mg$^{2+}$ and Al$^{3+}$-Fe$^{3+}$ was adjusted to 1, and the molar ratio of divalent-trivalent to 3. The solution was then adjusted to pH 11 by dropping 0.1 mol/L and 0.01 mol/L NaOH sodium, and stirred energetically at 60 °C for 0.5 h. The above mixture was aged at 90 °C for 24 h, centrifuged, washed until the filtrate was neutral, then vacuum-dried at 60 °C to obtain PTB-LDH3 and PTB-LDH4. The resulting materials were placed in a tubular furnace and calcinated at 400 °C for 4 h to obtain PTB-LDO3 and PTB-LDO4.

2.3. Characterization

A scanning electron microscope (SEM) (ZEISS Gemini SEM 300 from Carl Zeiss AG, Oberkochen, Germany) was used to analyze the micro-surface morphology of samples. The X-ray diffraction pattern (XRD, Rigaku Miniflex, Tokyo, Japan) was determined in 2θ from 5 to 90°. The BET specific surface area and pore diameter were determined through the Brunauer-Emmett-Teller (BET) method using the Micrometrics 2020HD88 apparatus (From Micrometrics Instrument Co., Norcross, GA, USA) to carry out N$_2$ adsorption-desorption experiments on the product at 77 K. Simultaneously, the Barret-Joyner-Halenda (BJH) method was used to calculate the pore size distribution. A Fourier transform infrared spectroscopy (FTIR, Vertex 70, Bruker, Optic, Inc., Billerica, MA, USA) was used to understand the surface functional groups and interlayer anions of the samples.

2.4. Adsorption Ability Assessment of PTB-LDO3 and PTB-LDO4

In this work, the effects of the dosage of hydrotalcite and the initial pH of simulated wastewater on the adsorption performance of hydrotalcite were investigated. In addition, adsorption kinetics, thermodynamics and isotherm experiments of the absorbents were carried out to understand the adsorption mechanism.

PTB-LDOs with different dosage (0.2, 0.4, 0.6, 0.8, 1.0, 1.2 g·L$^{-1}$) were mixed with 50 mL NaF solution at different concentrations. The pH was adjusted by 0.1 mol L$^{-1}$ HCl or 0.1 mol L$^{-1}$ NaOH solutions and carried out in the range of 4.0 to 11.0. Then the simulated wastewater with adsorbent was placed in a PET centrifuge tube of 50 mL and carried out in a shaker at a desired temperature (298, 308, and 318 K) and oscillated at the speed of 150 RPM until the adsorption equilibrium was reached. The removal rates (R: %) and adsorption capacity ($q_t$: mg g$^{-1}$) of PTB-LDOs were calculated by the following Formulas (1) and (2):

\[
q_e = \frac{(C_0 - C_e) \times V}{m} \quad (1)
\]

\[
R = \frac{C_0 - C_e}{C_0} \times 100\% \quad (2)
\]

where $C_0$ and $C_e$ (mg/L) are the initial and equilibrium concentrations of F$^-$ in solution, respectively. m (mg) is the weight of adsorbent and V (L) is the volume of the solution.

In this work, the concentration of F$^-$ was determined using fluoride ion selective electrodes (FISE, PF 2-01 from INESA Scientific Instrument Co., Ltd., Shanghai, China) with a solid-state mono-crystalline membrane [24].
3. Results and Discussion

3.1. Characterization

3.1.1. SEM Analysis

SEM provided a visual basis for supervising the nature of hydrotalcite products. Representative SEM images of as-prepared samples were showed in Figure 1, in which PTB-LDH3, PTB-LDH4, PTB-LDO3, and PTB-LDO4 were corresponded to Figure 1a–d, respectively. It was obvious that PTB-LDH3 and PTB-LDH4 had multi-layer scale shapes, which was in accordance with its lamellar structure. After calcination, layered double hydroxides were transformed to mixed metal oxides, causing the lamellar structure to collapse. Figure 1a–d shows that the scale shapes disappeared and combined together into a whole.

![SEM images](image-url)

**Figure 1.** SEM image of (a) PTB-LDH3, (b) PTB-LDH4, (c) PTB-LDO3 and (d) PTB-LDO4.

3.1.2. BET Analysis

In order to show the microstructure of hydrotalcite prepared in this study, PTB-LDHs and PTB-LDOs were characterized by N\textsubscript{2} adsorption and desorption and the results were listed in the Table 1. It can be seen from Figure 2a that the isotherms on the diagram have obvious hysteresis loops, which accord with the characteristics of IV adsorption isotherms [25], and also indicate that the hydrotalcite synthesized in this experiment belongs to mesoporous adsorption materials [26]. Moreover, the hysteresis isotherm showed in Figure 2a had no obvious saturated adsorption platform, and the variation range of the hysteresis loop was not sharp, which indicated that the pore size of the hydrotalcite prepared in this study is not regular [25]. It could be seen from Table 1 that PTB-LDH3 had a larger specific surface area and pore volume than PTB-LDH4. Moreover, the specific surface area and pore volume of PTB-LDOs calcined by two kinds of hydrotalcite are larger than the original PTB-LDHs. These not only showed that the adsorption effect of PTB-LDH3 was better than that of PTB-LDH4, but also that the adsorption performance of roasted PTB-LDOs was better than that of PTB-LDHs, which was consistent with the results of subsequent adsorption experiments. In the process of calcination, the crystal structure of PTB-LDH3 and PTB-LDH4 was destroyed, so that the original interlayer structure and the anions were lost. Therefore, more porous structures were formed in the original position, thus the number of holes in PTB-LDOs was larger than that in PTB-LDHs, and its adsorption property had also been enhanced. According to the nitrogen adsorption and desorption experiment, the total
pore volume and pore size of PTB-LDH3, PTB-LDO3, PTB-LDH4, PTB-LDO4 were 0.342, 0.615, 0.041, 0.347 cm$^3$ g$^{-1}$ and 19.10, 6.61, 14.17, 19.15 nm, respectively. These belong to the size range of mesoporous, and indicate that the treated object fluorine can enter the interlayer of the above four kinds of hydrotalcite products.

Table 1. Specific surface area, and pore volume parameters of PTB-LDH3, PTB-LDH4, PTB-LDO3 and PTB-LDO4.

<table>
<thead>
<tr>
<th>Materials</th>
<th>$S_{BET}$ $^b$/m$^2$ g$^{-1}$</th>
<th>$S_{SPA}$ $^b$/m$^2$ g$^{-1}$</th>
<th>$V_{SPA}$ $^c$/cm$^3$ g$^{-1}$</th>
<th>$D_p$ $^d$/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTB-LDH3</td>
<td>71.6387</td>
<td>70.4108</td>
<td>0.3421</td>
<td>19.1017</td>
</tr>
<tr>
<td>PTB-LDO3</td>
<td>372.3441</td>
<td>363.9801</td>
<td>0.6145</td>
<td>6.6017</td>
</tr>
<tr>
<td>PTB-LDH4</td>
<td>11.4616</td>
<td>11.0509</td>
<td>0.0406</td>
<td>14.1789</td>
</tr>
<tr>
<td>PTB-LDO4</td>
<td>72.4138</td>
<td>70.6970</td>
<td>0.3468</td>
<td>19.1575</td>
</tr>
</tbody>
</table>

Determined by N$_2$ adsorption using the Brunauer-Emmett-Teller (BET) method (a), Single point surface area (b), Single point adsorption total pore volume (c), Adsorption average pore width (4V/A by BET) (d).

Figure 2. N$_2$ adsorption-desorption isotherms of PTB-LDH3, PTB-LDH4, PTB-LDO3, and PTB-LDO4 at 77 K by (a) BET method and (b) pore size distribution by BJH adsorption and (c) desorption.

3.1.3. FTIR Analysis

FTIR can help us to obtain the information of functional groups in the product by measuring the absorption of the characteristic spectrum in the infrared region by some characteristic functional groups. As depicted in Figure 3, the absorption peak at ~3400 cm$^{-1}$ should be caused by the hydroxyl group inserted between the layers. Compared with the absorption peak of free O-H at ~3600 cm$^{-1}$, this peak obviously shifts to a low wavenumber, indicating that hydroxyl fully fits into the interlayer structure of hydrotalcite; in addition, hydrogen bonding occurred with interlayer NO$_3^-$, CO$_3^{2-}$ and layer bounded OH$^-$ [27]. Moreover, it is shown in Figure 3 that there is an absorption peak at ~1600 cm$^{-1}$ that may be related to OH$^-$. According to the structure and composition of LDHs, it was speculated that this absorption peak may be caused by the O-H groups in interlayer H$_2$O molecules, and that this conjecture was consistent with the absorption peak of crystalline H$_2$O between
1670–1600 cm$^{-1}$. By comparison, it can be found that the absorption peak at 1350 cm$^{-1}$ in PTB-LDHs was greatly weakened in PTB-LDOs after calcination, considering that this absorption peak was caused by the vibration of CO$_3^{2-}$ and NO$_3^-$ anions intercalated between layers [28]. After calcination, the interlayer anions of hydrotalcite disappeared, resulting in the insertion site of fluoride ions. As for the absorption peaks at shorter wavelengths under 1000 cm$^{-1}$, according to the standard spectrum, it should be the vibration absorption produced by metal oxides/hydroxides in hydrotalcite [29]. From the above explanation, ternary/quaternary layered double hydroxides might be successfully synthesized in this experiment, and the interlayer insertion anions can be determined to be CO$_3^{2-}$, OH$^-$ and NO$_3^-$.

![Figure 3. FTIR spectrums of (a) PTB-LDH3, (b) PTB-LDH4, (c) PTB-LDO3 and (d) PTB-LDO4.](image)

3.1.4. XRD Analysis

The X-ray diffraction patterns of PTB-LDH3, PTB-LDH4, PTB-LDO3 and PTB-LDO4 were shown in Figure 4. It can be seen from Figure 4a,c that the clearly exposing planes of crystals were (003), (006), and (009) except for the obvious diffraction peaks of the LDHs’ phase, implying the successful formation of PTB-LDHs with typical layered double hydroxide structure [30]. After calcination, the characteristic peak of hydrotalcite disappears (Figure 4b,d), indicating that the layered structure has collapsed. At the same time, a strong metal oxide peak appeared (such as the peak at 43.16 and 63.48) indicating that PTB-LDH has been transformed into PTB-LDO.

![Figure 4. XRD patterns of (a) PTB-LDH3, (b) PTB-LDH4, (c) PTB-LDO3, and (d) PTB-LDO4.](image)
3.2. Explanation of Absorption Experiment

3.2.1. Effect of pH

pH is one of the most important factors affecting the adsorption process. As shown in Figure 5, pH showed similar effects on the adsorption properties of PTB-LDO3 and PTB-LDO4. The changing trend of equilibrium adsorption capacity of both PTB-LDO3 and PTB-LDO4 was increasing sharply in the low pH range and then decreased slowly in the high pH range with the increase in pH value. On the whole, the absorption capability at lower pH level was better than that in higher pH. It was inferred that some of the PTB-LDOs would be dissolved by abundant H\(^+\) in the acid environment; its layered double structure was destroyed at the same time and lost its function of absorption [31]. This inference was confirmed by the detected metal elements in aqueous after adsorption under the condition of low initial pH. When the initial pH value was in the neutral range, there was no large amount of hydrogen ions in the solution to dissolve the LDOs. At the same time, there were no other anions in the aqueous environment which would compete with fluoride ions. Besides, in the weak acid condition, the surface of the adsorbent could accumulate some positive charge, which had the ability to enhance the positive charge of the adsorbent surface and could attract fluoride ions easier when pH value ranged from 5 to 6. When the initial pH value came to the alkaline range, the ions gathered on the surface of the adsorbent turned to anions, which had a rejection effect on fluoride ions. Another reason was that sodium ions in sodium fluoride solution were attracted by the negative charge on the surface, occupied part of the adsorption sites, and caused the decrease in adsorption capacity. Furthermore, fluoride and hydroxide ions have similar radius and the same charge, so they have similar adsorption capacity for adsorbents. Therefore, a large number of hydroxide ions in alkaline environment compete with fluorine ions, resulting in a decrease in the equilibrium adsorption amount.

It can be seen from Figure 5 that, compared with PTB-LDO3, the equilibrium adsorption amount of PTB-LDO4 decreased less under all initial pH conditions. Similar to the single active alumina adsorbent, the adsorption mode of PTB-LDO on aluminum is to attract fluorine ions in water to the surface through the electrostatic effect of surface charge, and then complete the intercalation adsorption [32]. Accordingly, the unsaturated adsorption sites of iron in PTB-LDOs firstly attract water molecules and hydroxyl ions, and then form active hydroxyl groups. Then, the fluorine ions in water are exchanged with active hydroxyl groups to realize adsorption [33]. This was mainly caused by the difference between PTB-LDO3 and PTB-LDO4. Moreover, the affinity of aluminum to fluoride is stronger than that of iron. In acidic environments, aluminum can coordinate with
fluoride ions to form aluminum fluoride or aluminum fluoride, which helps to improve adsorption capacity.

3.2.2. Effects of Dosage

It can be seen from Figure 6 that the adsorption equilibrium amounts reduced with the increasing of LDOs dosages. However, the equilibrium removal rates of $F^-$ increased gradually at the same time. These indicated that the adsorption process was a surface adsorption progress. When the dosage was at a low level, the LDO could thoroughly disperse and most of the absorption sites would be greatly used, so the adsorption equilibrium amount was at the high level. The equilibrium removal rate was at a low level due to the limited substrate concentration. As the dosage increased, the total absorption sites increased so that the equilibrium removal rate gradually went on. Moreover, the number of effective absorption sites will be less than that in theory because the probability of collision and aggregation of LDOs is much larger, resulting in a significant decrease in the adsorption equilibrium.

![Figure 6](image_url)

**Figure 6.** Effect of (a) PTB-LDO3 and (b) PTB-LDO4 dosages on the adsorption of $F^-$ (solution: 10 mg L$^{-1}$, pH 5.5, 6 h).

3.3. Adsorption Kinetics

The study on the kinetics of fluorine absorption by PTB-LDOs can help us to understand the adsorption mechanism and its adsorption mode (Figure 7). Because the composition and structure of the two kinds of PTB-LDOs are similar, and the pollutants they aim at are the same, we can see that the modes of PTB-LDO3 and PTB-LDO4 in the process of fluoride adsorption are basically the same. In the first 20 min, the adsorption rates of the two kinds of PTB-LDOs exhibited similar results, and both adsorbed rapidly. After 20 min, the adsorption rate of PTB-LDO4 decreased earlier than that of PTB-LDO3. From then, the instantaneous adsorption rate of PTB-LDO4 was less than that of PTB-LDO3. According to the analysis of the different adsorption mechanisms of aluminum and iron, it can be speculated that the active hydroxyl exchange adsorption process of the iron part of the PTB-LDO4 began to play a part in adsorption at 20 min. Moreover, based on the results of BET analysis, the larger specific surface area is another reason why PTB-LDO3 can maintain high-speed absorption for a longer time. After 30 min, the adsorption rates of both PTB-LDOs decreased gradually, and finally both of them reached the adsorption equilibrium at around 150 min. In order to clarify the adsorption mechanism of PTB-LDO3 and PTB-LDO4 prepared in this work, and to understand the controlling factors in the adsorption process, we used pseudo-first-order kinetics and pseudo-second-order kinetics to fit two adsorption capacity-time curves to judge the characteristics of adsorption behav-
ior [34,35]. The models of first-order and second-order dynamics conform to the following two equations.

\[ q_t = q_e \left(1 - e^{-k_1 t}\right) \]  

\[ q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \]

In the above two formulas, \(q_t\) and \(q_e\) (mg g\(^{-1}\)) are the instantaneous adsorption capacity at time \((t, \text{min})\) and equilibrium adsorption capacity of LDO for \(F^-\), respectively. Meanwhile \(k_1\) and \(k_2\) are the constants of pseudo-first-order kinetics and pseudo-second-order kinetics, severally.

The intra-particle diffusion model can also be used to describe the adsorption process [36], and its formula is:

\[ q_t = K_p t^{-0.5} + C \]  

where \(K_p\) is the intra-particle diffusion rate constant, and \(C\) is the intercept constant of adsorption constant.

The model fittings were shown in Figure 7a,b, and the corresponding kinetic parameters for the adsorption of fluoride ions by PTB-LDO3 and PTB-LDO4 were listed in Table S1 in Support Information (SI). It was found that the pseudo-first-order kinetic model exhibited a higher correlation coefficient \((R^2)\) for both PTB-LDO3 and PTB-LDO4. Moreover, \(q_e\) calculated by pseudo-first-order for both PTB-LDO3 and PTB-LDO4 were all very close to the experimental data, which indicated that fluoride ions’ adsorption reaction with PTB-LDO3 and PTB-LDO4 could be properly described by the pseudo-first-order kinetic model. In the meantime, the values of \(C\) in the intra-particle diffusion formula were both not zero, which indicated that there were other factors together with intra-particle diffusion to control the adsorption reaction rate [37].

![Figure 7](image.png)

**Figure 7.** Effect of adsorption time on adsorption capacity and kinetic model fitting of \(F^-\) for PTB-LDO3 and PTB-LDO4 (solution: 10 mg L\(^{-1}\), pH = 5.5, 0.40 g L\(^{-1}\) dosages).

### 3.4. Adsorption Isotherm

The adsorption isotherm is helpful to understand the adsorption model, thermodynamic properties and maximum adsorption capacity of the adsorbent. The Langmuir and Freundlich isothermal adsorption models were used to fit the curves and the results were shown in Figure 8. The Langmuir and Freundlich isothermal adsorption models can be
expressed by the following formula and the results of the parameters of two models were listed in Table S2 [38,39].

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

(6)

\[
\ln q_e = \frac{1}{n}\ln C_e + \ln K_f
\]  

(7)

where \(C_e (\text{mg L}^{-1})\) was \(\text{F}^-\) concentration in solution when adsorbent reaches adsorption equilibrium, \(q_e\) and \(q_m (\text{mg g}^{-1})\) was equilibrium and maximum adsorption capacity respectively. \(b\) was Langmuir constant, \(n\) and \(K_f\) are Friedrich constants.

As shown in Figure 8 and Table S2, on the basis of the correlation coefficient (\(R^2\)), the Langmuir model can better describe the isothermal adsorption process of fluorine ion (\(\text{F}^-\)) in adsorbed water by PTB-LDO3 and PTB-LDO4. This showed that the adsorption of \(\text{F}^-\) by PTB-LDO3 and PTB-LDO4 was similar to the process of adsorption on the monolayer uniform surface. Meanwhile, according to the Langmuir model, the maximum adsorption capacities of PTB-LDO3 and PTB-LDO4 were 26.03 mg· g\(^{-1}\) and 15.67 mg· g\(^{-1}\), respectively.

The value of \(E\) based on the D-R model can provide correlative information about the adsorption mechanism, especially the type of adsorption of fluoride ions on PTB-LDO3 and PTB-LDO4 can be determined [40,41]: (1) \(E < 8 \text{ kJ mol}^{-1}\), physical adsorption prevails; (2) \(8 \text{ kJ mol}^{-1} < E < 16 \text{ kJ mol}^{-1}\), ion exchange adsorption dominates; (3) \(E > 16 \text{ kJ mol}^{-1}\); the interaction may be chemical adsorption.

It can be seen from Table S2 that the adsorption energy under all conditions was below 8 kJ/mol, which indicated that the removal of fluoride ions by PTB-LDO3 and PTB-LDO4 might depend on physical interaction.

Figure 8. Adsorption isotherms for \(\text{F}^-\) and parameters fitted by Langmuir, Freundlich, D-R, Temkin models of (a,c) PTB-LDO3 and (b,d) PTB-LDO4 (solutions: 2, 5, 8, 10, 15, 20 mg L\(^{-1}\), pH = 5.5, 0.40 g L\(^{-1}\) dosages, 3 h).

In addition to the traditional Langmuir and Freundlich adsorption model, D-R and Temkin models had been more and more widely used in thermodynamic analysis in recent years. Especially based on the \(E\) value of the D-R model, the information about the adsorption mechanism could be obtained. For example, the equations for the two adsorption patterns are as follows [40,41].

\[
\ln q_e = \ln q_m - k_D\varepsilon^2
\]  

(8)
where the meaning of $q_e$ (mg g$^{-1}$), $q_m$ (mg g$^{-1}$) and $C_e$ (mg L$^{-1}$) was the same as that in (6) and (7), $k_D$ (mol$^2$ J$^{-2}$) was a constant related to adsorption energy, $A_T$ was an equilibrium binding constant and $b_T$ was the Temkin constant related to the heat of adsorption. $\varepsilon$ was the Polanyi potential ($\varepsilon = RT \ln \left(1 + \frac{1}{C_e}\right)$), which was an important parameter to D-R model. The average adsorption energy $E$ (kJ mol$^{-1}$) was related to $k_D$, and its expression was below [40,41], and all the above parameter values are shown in Table S2.

$$
E = \frac{1}{\sqrt{2k_D}}
$$

As shown in Figure 8 and Table S2, on the basis of the correlation coefficient ($R^2$), the Langmuir model can better describe the isothermal adsorption process of fluoride ion ($F^-$) in adsorbed water by PTB-LDO3 and PTB-LDO4. This showed that the adsorption of $F^-$ by PTB-LDO3 and PTB-LDO4 was similar to the process of adsorption on the monolayer uniform surface. Meanwhile, according to the Langmuir model, the maximum adsorption capacities of PTB-LDO3 and PTB-LDO4 were 26.03 mg g$^{-1}$ and 15.67 mg g$^{-1}$, respectively.

The value of $E$ based on the D-R model can provide correlative information about the adsorption mechanism, especially the type of adsorption of fluoride ions on PTB-LDO3 and PTB-LDO4 can be determined [42]: (1) $E < 8$ kJ mol$^{-1}$, physical adsorption prevails; (2) $8$ kJ mol$^{-1} < E < 16$ kJ mol$^{-1}$, ion exchange adsorption dominates; (3) $E > 16$ kJ mol$^{-1}$; the interaction may be chemical adsorption. It can be seen from Table S2 that the adsorption energy under all conditions was below 8 kJ/mol, which indicated that the removal of fluoride ions by PTB-LDO3 and PTB-LDO4 might depend on physical interaction.

### 3.5. Adsorption Thermodynamics

The thermodynamics of PTB-LDO3 and PTB-LDO4 adsorption process can be used to evaluate the spontaneity of adsorption reaction. The entropy change ($\Delta S$), enthalpy change ($\Delta H$) and Gibbs free energy change ($\Delta G$) in the adsorption process can reflect the evaluation of $F^-$ adsorption capacity of PTB-LDO3 and PTB-LDO4, which can be calculated by the following formula [43]:

$$
\ln b = \frac{\Delta S}{R} - \frac{\Delta H}{RT}
$$

$$
\Delta G = \Delta H - T\Delta S
$$

where $b$ was the Langmuir constant calculated in the previous section. The values of $\Delta H$, $\Delta S$, $\Delta G$ and correlation coefficients ($R^2$) were listed in the Table 2.

<table>
<thead>
<tr>
<th>T(K)/Absorbent</th>
<th>$\Delta S$ (J mol$^{-1}$ K$^{-1}$)</th>
<th>$\Delta H$ (kJ mol$^{-1}$)</th>
<th>$\Delta G$ (kJ mol$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>298/PTB-LDO3</td>
<td>36.12</td>
<td>-1.686</td>
<td>-12.45</td>
<td>0.9367</td>
</tr>
<tr>
<td>308/PTB-LDO3</td>
<td></td>
<td>-12.81</td>
<td></td>
<td></td>
</tr>
<tr>
<td>318/PTB-LDO3</td>
<td></td>
<td>-13.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>298/PTB-LDO4</td>
<td>21.65</td>
<td>-6.322</td>
<td>-12.77</td>
<td>0.9492</td>
</tr>
<tr>
<td>308/PTB-LDO4</td>
<td></td>
<td>-12.99</td>
<td></td>
<td></td>
</tr>
<tr>
<td>318/PTB-LDO4</td>
<td></td>
<td>-13.21</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The $\Delta H$ of $F^-$ adsorption process calculated by PTB-LDO3, PTB-LDO4 were $-1.686$ and $-6.322$ KJ mol$^{-1}$ respectively, indicating that the adsorption process was an exothermic reaction. At the same time, the results of $\Delta S$ were 36.12 and 21.65 J·K$^{-1}$·mol$^{-1}$ respectively, and their non-negativity reflected the irreversible increase in system disorder in the process of adsorption, indicating that PTB-LDO3 and PTB-LDO4 had good adsorption effect on $F^-$. The negative value of $\Delta G$ (calculated at 298K, 308K and 318K for PTB-LDO3 and PTB-LDO4
to be $-12.45$, $-12.81$, $-13.17$ and $-12.77$, $-12.99$, $-13.21$ KJ·mol$^{-1}$ respectively) indicated the spontaneous nature of the adsorption of F$^-$ by PTB-LDO3 and PTB-LDO4.

### 3.6. Comparison with Other Literature

PTB-LDO3 and PTB-LDO4 prepared in this study were also compared with other adsorbents previously reported and listed in Table 3. It can be seen that PTB-LDO3 and PTB-LDO4 had a large specific surface area and good adsorption capacity for F$^-$, especially the adsorption capacity of PTB-LDO3 reached 26.89 mg g$^{-1}$. As a result, PTB-LDO3 and PTB-LDO4 prepared by cheap phosphate tailings towards F$^-$ removal could achieve similar or better results, and greatly reduce the cost, because the proportion of metal elements in hydrotalcite in this study was similar to that in the leaching solution of phosphate tailings. Therefore, the phosphate PTB-LDO3 and PTB-LDO4 prepared in this paper has great potential in water pollution treatment.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>$q_{\text{max}}$ (mg g$^{-1}$)</th>
<th>pH</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgAlFe-HTlc500</td>
<td>25.4</td>
<td>6</td>
<td>[44]</td>
</tr>
<tr>
<td>Iron-tin mixed oxide</td>
<td>10.47</td>
<td>6.4</td>
<td>[45]</td>
</tr>
<tr>
<td>KMnO4-modified carbon</td>
<td>15.9</td>
<td>2</td>
<td>[46]</td>
</tr>
<tr>
<td>Iron-aluminum mixed oxide</td>
<td>17.73</td>
<td>6.9</td>
<td>[47]</td>
</tr>
<tr>
<td>Nd-modified chitosan</td>
<td>22.38</td>
<td>7</td>
<td>[48]</td>
</tr>
<tr>
<td>CSLDH-75</td>
<td>12.12</td>
<td>5-8</td>
<td>[49]</td>
</tr>
<tr>
<td>PTB-LDO3</td>
<td>26.03</td>
<td>5-6</td>
<td>Present study</td>
</tr>
<tr>
<td>PTB-LDO4</td>
<td>15.66</td>
<td>5-6</td>
<td>Present study</td>
</tr>
</tbody>
</table>

### 4. Conclusions

In this work, ternary and quaternary hydrotalcite based on PTs had been successfully synthesized by the coprecipitation method. The results indicated that both the precursor of PTB-LDO3 and PTB-LDO4 showed the layered structure, and characteristic diffraction peaks of hydrotalcite. In addition, PTB-LDO3 had a larger specific surface area than PTB-LDO4 and showed better adsorption performance on the removal of F$^-$. Compared with PTB-LDO4, PTB-LDO3 exhibited better adsorption performance when the pH value ranged from 5 to 6, and dosages decided at 0.04 mg L$^{-1}$. The adsorption kinetics results revealed that the adsorption of fluorine by PTB-LDO3 and PTB-LDO4 reached the adsorption equilibrium in about 3 h, and followed the pseudo-second-order model. The adsorption data could be fitted better with the Langmuir isotherm with the maximum adsorption amounts of 26.03 mg g$^{-1}$ and 15.66 mg g$^{-1}$ for PTB-LDO3 and PTB-LDO4, respectively. The adsorption of fluorine by PTB-LDO3 and PTB-LDO4 were both spontaneous and exothermic, and exhibited excellent reusability and stability. This study provides a possibility for the combined treatment of phosphorus chemical solid waste (phosphorus tailings) and phosphorus chemical wastewater (phosphogypsum leaching liquid).

### Supplementary Materials

The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/min12070858, Table S1: Fitting parameters by pseudo-first-order, pseudo-second-order models and intra-particle diffusion model for the Adsorption equilibrium time of PTB-LDO3 and PTB-LDO4; Table S2: Parameters fitted by Langmuir, Freundlich, D-R and Temkin models for F$^-$ by PTB-LDO3 and PTB-LDO4.

### Author Contributions

Writing—original draft, Y.L.; Methodology, H.Z. (Han Zhang) and D.X.; Writing—review & editing, H.W.; Software, L.X. and Z.Z.; Methodology & Formal analysis, Q.C. and H.Z. (Hong Zhou); Conceptualization, J.Y.; Funding acquisition, Z.P. and D.W. All authors have read and agreed to the published version of the manuscript.
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**Data Availability Statement:** The data presented in this study are available on request from the corresponding author.

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**Conflicts of Interest:** The authors declare no competing financial interest.

**References**


