

Article

Evaluation of Fluoride Adsorptive Removal by Metallic Phosphates

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Abstract

Currently, various techniques are efficient in eliminating high quantities of fluoride from water, while the deep treatment of a low concentration of fluoridated water is inadequate. In this work, four metallic phosphates were synthesized, including YP, ZrP, CeP, and LaP, to enhance the elimination of fluoride. The X-ray diffractometer data demonstrated that ZrP was amorphous, while CeP, LaP, and YP were highly crystalline. YP had a strong fluoride removal ability in a neutral environment, and ZrP exhibited a superior fluoride adsorption effect in acidic media. The adsorption kinetic results suggested that YP, CeP, and LaP could achieve the adsorption equilibrium within 150 min, which was faster than ZrP. YP had the largest fluoride adsorption capacity fitted by Langmuir of 31.61 mg/g at 298 K, followed by ZrP, which was greater than those of CeP and LaP. All four metallic phosphates showed high selectivity in the interference of competing anions and organics, with YP and ZrP exhibiting superior selectivity than CeP and LaP. The adsorption mechanism was ligand exchange between metallic phosphate particles and fluoride, which was validated by Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy. The adsorption rate of metallic phosphates remained essentially stable in five consecutive adsorption–desorption cycles. Overall, metallic phosphates, especially YP and ZrP, have enormous potential in enhancing fluoride removal in the treatment of fluoridated water.

Keywords: fluoride; metallic phosphates; selective adsorption; water treatment



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1. Introduction

Toxic contaminants in water are harmful not only to aquatic life but also to human health. Among them, fluoride has a twofold effect on mankind, depending on its concentration [1]. According to WHO guidelines, the maximum concentration of fluoride in drinking water is 1.5 mg/L, which is conducive to the healthy growth of teeth and bones [2]. Excessive intake of fluoride can cause fluorosis of bones and teeth, affect the normal functioning of many organs, and even induce cancer [3]. Fluoride contaminates the environment mainly due to natural and manufactured reasons. The fluoride-containing minerals, such as cryolite, fluorite, and fluorapatite, weathered and dissolved, resulting in fluoride leaching from rocks into groundwater [4]. The primary anthropogenic sources of fluoride include wastewater from the ceramic industry, metal processing, and fertilizer [5]. In recent years, modern industries, such as the photovoltaic industry, have been developing rapidly, producing a large quantity of fluoride-containing wastewater with a complex composition, which leads to increased treatment difficulties [6]. Fluorosis has been observed in

many areas [7]. Hence, minimizing fluoride concentration of water has emerged a critical issue that needs to be addressed urgently.

Many fluoride removal techniques, such as chemical precipitation, coagulation [8], membrane separation [9], and adsorption [10], have been developed. Among them, adsorption is the most promising method for deep removal of fluoride because it is efficient, environmentally friendly, economical, easy to operate, and less waste production [11]. Many adsorbents, from natural to synthetic, have been used to absorb fluoride from water, including activated carbon [12], activated alumina [13], hydroxyapatite [14], chitosan [15], and ion exchange resin [16]. Nevertheless, most of them for fluoride have limited adsorption capability and selectivity [12].

During the previous few decades, metallic (hydrogen) oxides have been used extensively to remove fluoride efficiently [17]. The metallic (hydrogen) oxides developed so far include hydrated zirconium oxide (HZO) [18], hydrated iron oxide (HFO) [19], hydrated cerium oxide (HCO) [20], hydrated titanium oxide (HTO) [21], hydrated yttrium oxide (HYO) [22], and hydrated lanthanum oxide (HLO) [23]. Among these adsorbents, (hydrogen) oxides of zirconium and some rare earth metals demonstrated superior fluoride adsorption capabilities. However, the selective adsorption capability and stability of metallic (hydrogen) oxides need to be improved. Furthermore, most metallic (hydrogen) oxides have a limited applicable pH range and are better suited for acidic water treatment, but their stability under acidic conditions faces challenges.

Compared with the corresponding metallic (hydrogen) oxides, metallic phosphates exhibit superior chemical stability. For instance, in acidic circumstances, the metal dissolution rate of CeP was only 20% of that of hydrated cerium oxide (HCO) [24], and ZrP had remarkable chemical stability in both acidic and alkaline environments [25]. Currently, works on metallic phosphates in the field of water treatment concentrate on the adsorptive removal of heavy metal cationic contaminants [26], with fewer studies on the adsorption behavior of anions, such as fluoride [25], while more potential metallic phosphate adsorbents are yet to be developed.

In this study, four metallic phosphates were synthesized, including YP, ZrP, CeP, and LaP, for enhanced fluoride removal. The structures of metallic phosphates were examined. The fluoride adsorption by metallic phosphates relating to initial pH, reaction time, temperature, coexisting anions, and organics was investigated, and the fluoride adsorption mechanism was explored. The adsorption–desorption cycle experiments were also performed to examine the reusability of the metallic phosphates. A comparative analysis of the fluoride removal effects of the metallic phosphates was conducted to further evaluate adsorption properties of metallic phosphates in different fluoridated waters.

2. Materials and Methods

2.1. Chemicals

The chemicals used in this experiment were of analytical grade and came from Aladdin Reagent Co., Ltd. (Shanghai, China). All solutions were prepared with distilled water.

2.2. Synthesis of Metallic Phosphates

Metallic phosphates were synthesized by co-precipitation of metal ions and phosphates. Take YP as an example. A mixed solution consisting of 12.5 mL of ethanol and 0.003–0.03 mol of $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ was added to 0.015 mol of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$. The most effective ratio of Y and P was 1:1, which had been optimized (Supplemental Figure S1). After being acidified to $\text{pH} = 1$ with HCl, the mixture was stirred at 25 °C for 30 min, and the precipitate was finally recovered by centrifugation. The precipitate was washed to neutrality with distilled water and then dried for 12 h at 323 K. The other metallic

phosphates, including ZrP, CeP, and LaP, were prepared according to the same protocol as YP. Figure S1 showed that when the molar ratio of metal and phosphorus exceeded 1:1, the adsorption capacity of ZrP decreased. In contrast, the adsorption capacity of CeP and LaP continued to increase until the molar ratios reached 1:3 and 1:5, respectively. Therefore, the optimal molar ratios of metal and phosphorus for ZrP, CeP, and LaP were 1:1, 1:3, and 1:5, respectively.

2.3. Adsorption and Regeneration Experiments

Fluoride removal experiments were carried out using the batch method. The fluoride adsorption capacity of metallic phosphates in 100 mL conical flasks was comparatively investigated by treating a solution with fluoride content of 5 mg/L, and the dosage of metallic phosphates was fixed at 0.2 g/L. The impact of pH, which ranged from 1 to 11, and was adjusted by HCl and NaOH, on the fluoride adsorption by metallic phosphates was examined. The selective adsorption performance of fluoride was investigated by adding different amounts of competing anions and organics in the form of NaCl, NaNO₃, Na₂SO₄, NaHCO₃, NaH₂PO₄, humic acid (HA), tannic acid (TA), l-tryptophan, sodium alginate (ALG), and sodium dodecylbenzenesulfonate (SDBS). Fluoride adsorption was conducted under stirring at 150 rpm for 24 h at 298 K until the equilibrium. Fluoride adsorption isotherm studies were conducted at three temperatures, with the initial fluoride concentration of 2–30 mg/L. In adsorption kinetic experiments, 0.1 g of adsorbent was mixed with 500 mL of fluoride solution with a concentration of 5 mg/L at 298 K. The fluoride concentration was measured at intervals until the adsorption reached equilibrium. Adsorption–desorption cycles were carried out in a single fluoride-containing solution and actual photovoltaic wastewater to examine the reusability of the adsorbents. The exhausted adsorbents were eluted in 50 mL NaOH solution for 24 h and washed to neutral for the next adsorption–desorption cycle. All experiments were performed in triplicate to guarantee the reproducibility of the data.

2.4. Analysis and Characterization

Fluoride ion-selective electrode was used to measure the concentration of fluoride ion (HQ440D, Haxi; USA), and the ionic strength of the fluoride-containing solution was stabilized by the addition of fluoride ion-strength adjusting buffer (TISAB). The crystal structures of metallic phosphates were explored by an X-ray diffractometer (XRD, X'Pert PRO MPD; Germany). The contents of metal ion and phosphorus were measured with inductively coupled plasma emission spectrometry (ICP-OES, PerkinElmer ICP 2100; USA). An automatic specific surface and porosity analyzer (BET, Micromeritics 3Flex; USA) was employed to analyze the specific surface area of metallic phosphates, and the pore distribution was determined by the Barrett–Joyner–Halenda (BJH) method. The changes in energy spectra and surface chemical groups before and after adsorption of metallic phosphates were analyzed using X-ray photoelectron spectroscopy (XPS, Thermo Kalpha; USA) and Fourier transform infrared spectroscopy (FTIR, Nicolet iS 10; USA), respectively.

3. Results and Discussion

3.1. Characterization of Adsorbents

The X-ray diffractogram (XRD) (Figure 1a) showed that ZrP was essentially amorphous with no clear diffraction peaks, while YP, CeP, and LaP had obvious diffraction peaks and were relatively highly crystalline. Compared with the crystalline structure, the amorphous structure prevents agglomeration, favoring the increase in specific surface area [27]. The metal ion and phosphorus contents of metallic phosphates are displayed in Table S1, and combined with the XRD results, it can be inferred that the major compositions of the

metallic phosphates were YPO_4 , $\text{Zr}(\text{HPO}_4)_2$, a mixture of CePO_4 and $\text{Ce}(\text{HPO}_4)_2$, and LaPO_4 , respectively. The nitrogen adsorption–desorption isotherms of metallic phosphates are displayed in Figure S2. The hysteresis loops of metallic phosphates all belonged to the H3-type hysteresis loops, which suggested that metallic phosphates were mesoporous materials [28]. The pore diameter distribution of adsorbents is present in Figure 1b. The pore diameter of metallic phosphates was mainly distributed in the mesoporous region, with a small number of micropores also existing. The specific surface area of YP, ZrP, CeP, and LaP was 102.90, 70.21, 51.84, and 40.66 m^2/g , respectively (Table S1). The larger specific surface area provided more active sites, which were favorable for improving the adsorption capacity [29].

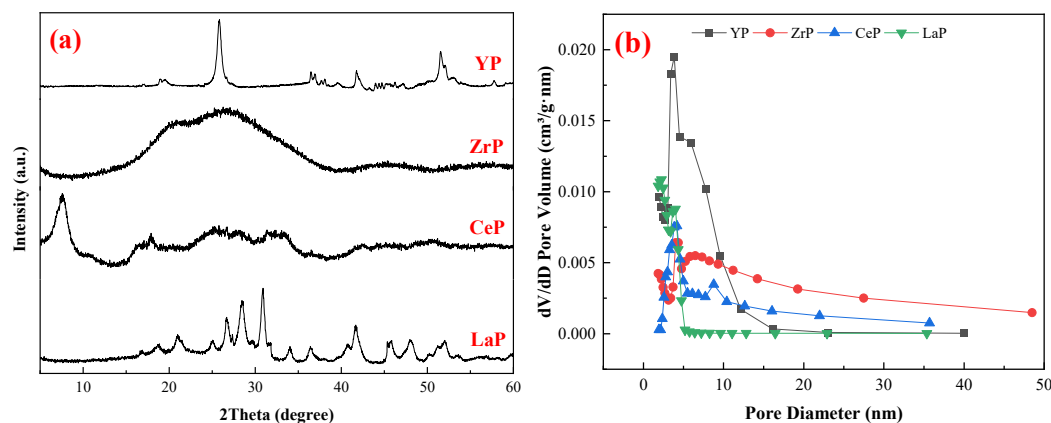


Figure 1. (a) XRD image of adsorbents. (b) Pore diameter distribution image of adsorbents.

3.2. Effect of pH on Fluoride Adsorption

The variation in the fluoride adsorption capacity of metallic phosphates with pH is depicted in Figure 2a. ZrP, CeP, and LaP had the maximum fluoride removal efficiency at a pH of 2. The fluoride adsorption ability of ZrP drastically declined with increasing pH. In contrast, the fluoride removal effect of YP was relatively stable over the pH range of 3 to 9. All four adsorbents had almost no fluoride removal capacity at a pH of 11. This was possibly connected to the form of fluoride present at different pH conditions and the surface charge of the adsorbents [30]. Fluoride in the solution mainly existed as HF in strong acidic media, which was unfavorable for adsorption by adsorbents. As shown in Figure S3, the isoelectric points of four metallic phosphates were examined, which were approximately at a pH of 0.9, and therefore the surface of metallic phosphates was electronegative over the pH range of 1 to 11, causing fluoride to be electrostatically repulsed, and it can be inferred fluoride was adsorbed mainly by specific inner-sphere complexation. As the equilibrium pH increased, a high concentration of hydroxide ions will compete adsorption sites with fluoride (Figure S4), resulting in a decrease in the adsorption capacity of fluoride [31]. Unlike the other adsorbents, YP and LaP exhibited lower fluoride adsorption capacity in strong acidic conditions, which was due to the high dissolution rate of the adsorbents (Figure 2b). Notably, ZrP still exhibited a substantial fluoride adsorption capacity when fluoride was predominantly in the form of HF, suggesting that there was a robust internal coordination complexation between ZrP and HF, which may also be present for the reaction of CeP with fluoride. In conclusion, YP and ZrP have broad application prospects for treating neutral and acidic water, respectively.

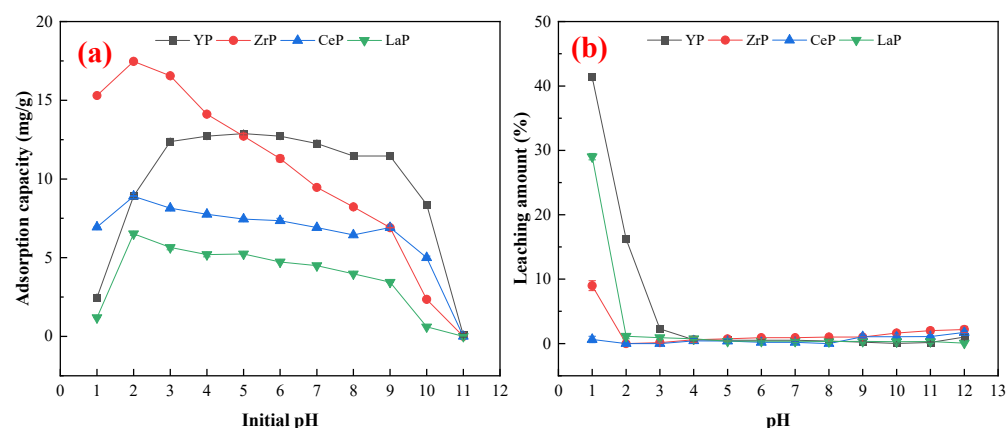


Figure 2. (a) Effect of initial pH on fluoride adsorption by adsorbents. (b) Stability of adsorbents after adsorption under different pHs. (Reaction conditions: adsorbent dosage = 0.20 g/L, initial fluoride = 5 mg/L, $T = 298$ K.)

3.3. Adsorption Kinetic Analysis

Figure 3 presents the kinetic curves of fluoride adsorption by the metallic phosphates. The four metallic phosphates went through a fast adsorption phase initially, which was ascribed to abundant active sites initially. As the exchange sites were progressively filled, the adsorption rate diminished. A reduction in the driving force of the concentration gradient caused by the difference in fluoride concentration between the aqueous solution and the adsorbent surface may also lead to a decline in fluoride adsorption rate. YP, CeP, and LaP were able to reach adsorption equilibrium within 150 min, while ZrP required 240 min, which may be associated with the crystal structure of metallic phosphates. Considering YP, CeP, and LaP were crystalline structures, fluoride was more prone to enter into the structural voids under the surface layer to participate in rapid adsorption process. ZrP was an amorphous structure, which was more disordered and preferred to adsorb slowly [32]. The pseudo-first-order and pseudo-second-order models were used to fit the kinetic curves, and the corresponding parameters are provided in Table S2. The pseudo-second-order model of four metallic phosphates was fitted to a higher degree, with larger R^2 and lower SSE, demonstrating that the adsorption process of fluoride by metallic phosphates was connected to a valence force-based chemical adsorption mechanism [33].

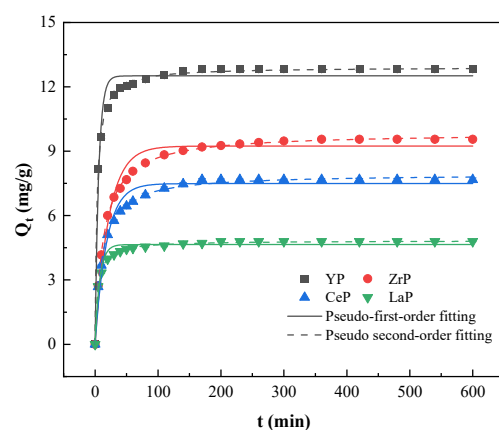


Figure 3. Adsorption kinetics of fluoride by adsorbents. (Reaction conditions: adsorbent dosage = 0.20 g/L, initial fluoride = 5 mg/L, $\text{pH} = 6.8 \pm 0.2$, $T = 298$ K.)

3.4. Adsorption Isotherm and Thermodynamic Analysis

The adsorption isotherms of fluoride by metallic phosphates at three different temperatures (283, 298, and 313 K) are displayed in Figure S5. The fluoride adsorption capacity

of the adsorbents developed steadily, and the upward trend decelerated as the rise in the equilibrium concentration, which was owing to the fact that the adsorbents contained abundant active sites in their early stage, which had not yet reached saturation. As the equilibrium concentration rose, these active sites were gradually consumed to saturation, which caused the adsorption capacity to gradually decrease in the rate of growth, slowing the upward trend. Furthermore, as the temperature went up, the fluoride removal ability of LaP rose, while that of the other metallic phosphates decreased gradually. The adsorption isotherms were fitted with Langmuir and Freundlich models, and the corresponding parameters are shown in Table S3. The Langmuir model was fitted better, highlighting that the fluoride adsorption of the adsorbents was dominated by monolayer adsorption on a homogeneous surface and may involve a chemisorption mechanism, which was in agreement with the above conclusion [34]. The $0 < RL < 1$ of the adsorbents indicated an effective interaction between the adsorbents and fluoride [35]. The maximum adsorption amounts of YP, ZrP, CeP, and LaP fitted by the Langmuir model could reach 31.61, 18.94, 15.09, and 11.84 mg/g at 298 K, respectively, which demonstrated the great adsorption potential of metallic phosphates. The high fluoride adsorption may be owing to the fact that ZrP was amorphous, and the inhomogeneity of this structure was reflected in the inhomogeneous interatomic forces, which led to a higher degree of coordination defects [36]. Another possible reason was attributed to the strongest complexation between Zr and fluoride (Table S4). CeP and LaP were crystalline and had a highly organized structure characterized by a periodic arrangement of atoms as well as equal interatomic forces, which contributed to a diminished degree of coordination defects and consequently absorbed a restricted quantity of fluoride [36]. Additionally, CeP has a low metal ion content and limited Ce-O bonds involved in adsorption (Table S1), while the minimal adsorption of LaP may originate from the weakest complexation of La and fluoride (Table S4). Interestingly, YP possessed the higher crystallinity and the largest amount of fluoride adsorption, which may be due to the fact that YP had the greatest specific surface area and the highest concentration of metal ion, which indicated that more Y-OH bonds were engaged in the adsorption of fluoride. The fitting maximum adsorption amounts of metallic phosphates were significantly higher than those of the majority of the previously reported monometal-based adsorbents (Table S5).

The thermodynamic analysis was conducted based on the results of the adsorption isotherms (Table S6). It was assumed that the temperature was constant over the studied range, and the effect of ΔH with temperature was neglected. ΔG of the adsorbents at three different temperatures was less than 0, indicating that the adsorption was a spontaneous process. $\Delta H < 0$ demonstrated that the adsorption process was exothermic. In contrast to the other adsorbents, the adsorption process of LaP was endothermic. $\Delta S > 0$ suggested the entropy increase in the whole system, and the solid/liquid interface in the fluoride adsorption process of randomness increased, revealing that the adsorption process was stable [3].

3.5. Effect of Co-Existing Anions on Fluoride Adsorption

The actual water is relatively complicated and generally contains certain inorganic anions that may interfere with the adsorption of fluoride. The equilibrium adsorption capacity of fluoride in the presence of coexisting anions is shown in Figure 4, and the adsorption of fluoride by YP, CeP, and LaP exhibited a similar trend. The negligible interference of Cl^- and NO_3^- with the removal of fluoride by YP, CeP, and LaP may be owing to the fact that Cl^- and NO_3^- were outer-sphere complexation with no specific on metallic phosphates and therefore unable to compete with fluoride [37]. SO_4^{2-} had a stronger inhibitory effect on the defluorination ability of YP, CeP, and LaP than Cl^- and NO_3^- . This was because that SO_4^{2-} can be adsorbed specifically, and therefore it competed

with fluoride more markedly than Cl^- and NO_3^- but weaker than H_2PO_4^- [19]. It was hypothesized that the relatively large spatial site resistance of H_2PO_4^- may hinder the adsorption sites [38]. On the other hand, phosphate was reported to be strongly adsorbed on high-valent metallic phosphates by inner-sphere complexation [19]. The significant inhibitory effect of HCO_3^- on the adsorption of fluoride by YP, CeP, and LaP was related to a certain alkaline buffering effect [39].

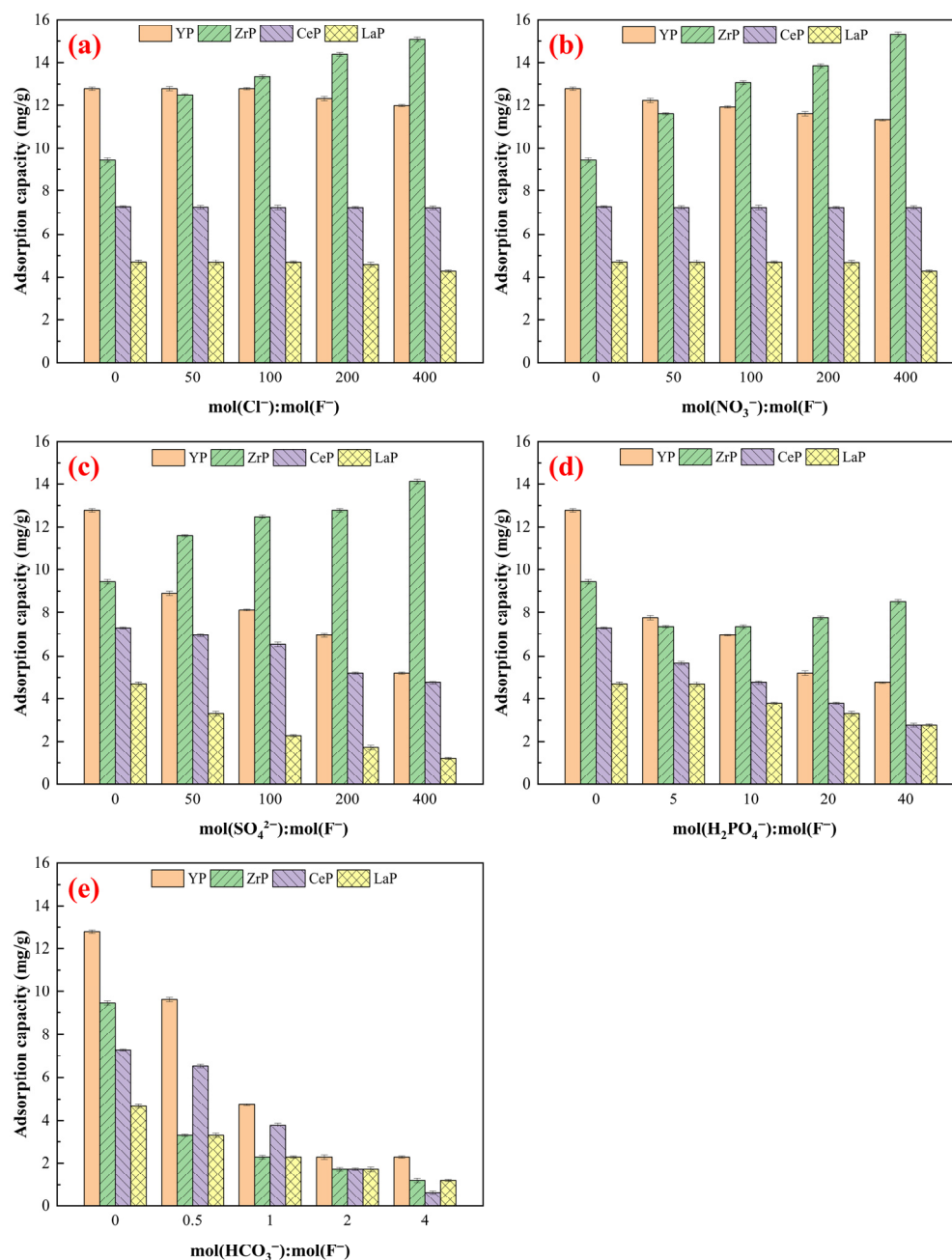


Figure 4. Effect of coexisting anions on fluoride adsorption by adsorbents: (a) Cl^- ; (b) NO_3^- ; (c) SO_4^{2-} ; (d) H_2PO_4^- ; (e) HCO_3^- . (Reaction conditions: adsorbent dosage = 0.20 g/L, initial fluoride = 5 mg/L, pH = 6.8 ± 0.2 , T = 298 K).

Different from the other metallic phosphates, ZrP exhibited a progressive adsorption enhancement rather than suppression, as the concentration of Cl^- , NO_3^- , or SO_4^{2-} increased. The improved fluoride removal can be explained by the double electric layer [40]. It may be attributed to the fact that with the addition of coexisting anions, Na^+ was inevitably introduced, which initially attached to ZrP by electrostatic attraction, weakening

the electrostatic repulsion between fluoride, which increased fluoride adsorption of ZrP. The enhanced adsorption unique to ZrP may be explained by the fact that Zr possessed the smallest atomic radius and the strongest fluoride complexing ability (Table S1), which allowed ZrP to adsorb more fluoride using Na^+ as an intermediary. Another possible reason was that the density of adsorbed fluoride by a unit of Zr was greater compared to other metallic phosphates, which resulted in stronger electrostatic repulsion, and therefore the electrical neutralization by Na^+ was more noticeable, which caused ZrP to exhibit significantly enhanced fluoride adsorption [40]. Furthermore, this possibility also applied to H_2PO_4^- ; at low H_2PO_4^- and fluoride molar ratios, competition for adsorption sites by H_2PO_4^- was dominant, which caused ZrP to exhibit less fluoride adsorption. The electroneutralization of Na^+ strengthened with the rise in the molar ratios, which promoted the fluoride adsorption to increase gradually. Similarly to other metallic phosphates, HCO_3^- exerted a significant disincentive effect on the defluorination of ZrP.

YP and ZrP all maintained high selectivity under the interference of Cl^- , NO_3^- , and SO_4^{2-} , and the selectivity of ZrP even exceeded that of YP under high molar ratios of coexisting anions and fluoride, but the fluoride removal capacities of YP and ZrP were inhibited by H_2PO_4^- and HCO_3^- . The interference degree of five anions on the adsorption of fluoride by CeP and LaP was similar. From a comprehensive point of view, YP and ZrP continuously maintain comparatively high adsorption capacities in the presence of coexisting anions, demonstrating their considerable adsorption selectivity.

3.6. Effect of Co-Existing Organics on Fluoride Adsorption

Actual water also contains various organic chemicals, which can complex with metals, affecting the fluoride adsorption by metallic phosphates. The adsorption capacities of the four adsorbents under the influence of various coexisting organics are displayed in Figure 5. The inhibition of fluoride adsorption by metallic phosphates by high concentrations of organics was not as significant as that of inorganic anions, indicating the excellent resistance to organic interference of metallic phosphates. It was noteworthy that HA and ALG had interference on the defluorination ability of metallic phosphates, especially YP, which may be due to the fact that the surface of HA and ALG was hydrophilic and contained many negative charges, which can compete adsorption sites with fluoride [41]. Another possible explanation was that the abundant carboxyl and hydroxyl groups in HA or ALG can specifically complex with metallic phosphates [42]. In addition, TA, L-tryptophan, and SDBS had no distinct effect on the fluoride removal capabilities of four metallic phosphates.

From the comparison of various metallic phosphates, YP possessed strong adsorption selectivity, especially in the presence of TA, L-tryptophan, and SDBS. ZrP, CeP, and LaP were also less affected by organic interference. In summary, four metallic phosphates perform exceptional adsorption selectivity in the presence of organic contaminants.

3.7. Fluoride Adsorption Mechanism

To determine the fluoride adsorption mechanism on metallic phosphates, YP was selected to test with FTIR and XPS.

The FTIR spectrograms before and after fluoride adsorption by YP are shown in Figure 6a. The distinctive absorption peak at 1717 cm^{-1} corresponded to the bending vibration peak of Y-OH [43]. The notable decrease in intensity and blue shift in the Y-OH absorption peak after adsorption (1710 cm^{-1}) were given to the substitution of hydroxyl groups on YP by adsorbed fluoride [44]. The stretching vibration of Y-O was primarily responsible for the absorption peak at 528 cm^{-1} [45]. After adsorption, the absorption peak had a slight blue shift (521 cm^{-1}), suggesting the potential production of Y-F complexes.

The substantial spectral band shifts and reduced peak intensities demonstrated the possible strong affinity between yttrium and fluoride [22].

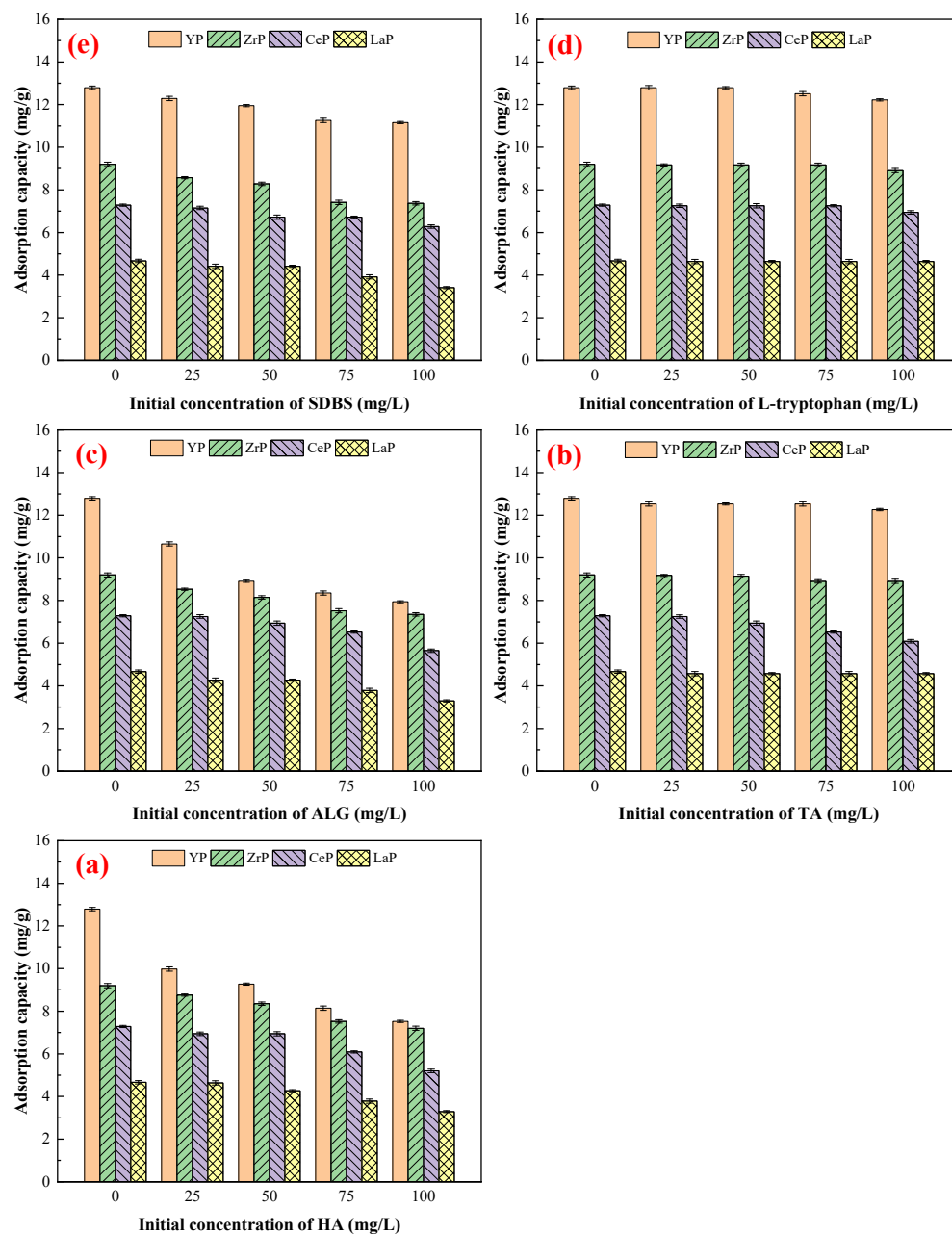


Figure 5. The effect of coexisting organics on fluoride adsorption by adsorbents: (a) HA; (b) TA; (c) ALG; (d) L-tryptophan; (e) SDBS. (Reaction conditions: adsorbent dosage = 0.20 g/L, initial fluoride = 5 mg/L, pH = 6.8 ± 0.2, T = 298 K.)

The total XPS spectrum of YP are displayed in Figure 6b. After adsorption, a new characteristic peak emerged at 684.68 eV, indicating that fluoride was adsorbed on YP. The representative Y3d signal of the pristine YP sample showed two bimodal satellite peaks (Figure 6c) situated at 157.78 eV (Y3d5/2) and 159.93 eV (Y3d3/2), respectively. After adsorption, two bimodal satellite peaks shifted to 158.00 eV and 160.15 eV, respectively, which confirmed the formation of new Y-F complexes and further demonstrated the strong affinity of fluoride adsorption. This strong interaction may be attributed to the inner-sphere complexation, and recent research has reported comparable findings [46]. Additionally, O1s spectroscopy was used to analyze the changes in hydroxyl concentration before and after

fluoride adsorption. The percentage of hydroxyl was also computed, and the results can be seen in Figure 6d. The hydroxyl of the original YP occupied 64.35%, which decreased to 63.00% after adsorption, suggesting that the surface hydroxyl group (-OH) of YP was replaced by fluoride through ligand exchange (Figure 7), which was in agreement with the results of FTIR analysis and similar to the results of previous studies [47].

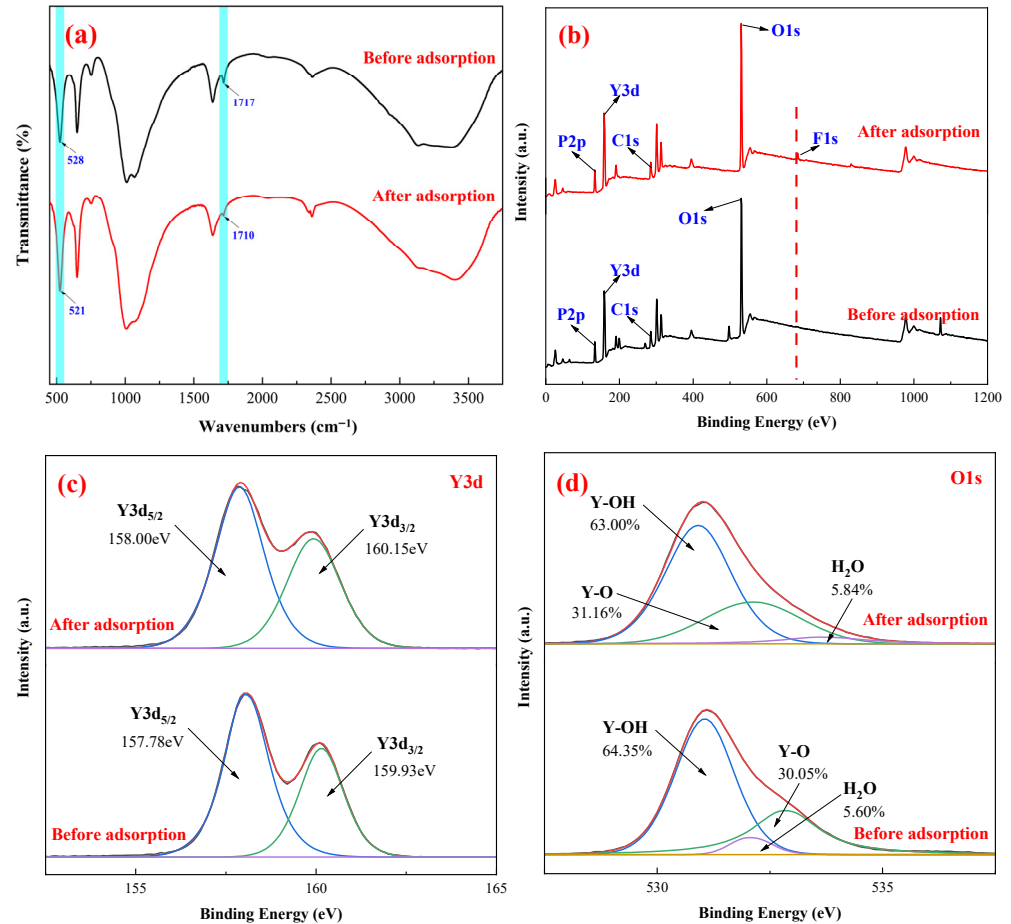


Figure 6. (a) FTIR image. (b) Wide scan spectrum. (c) Y3d_{5/2} and Y3d_{3/2} spectrum. (d) O1s spectrum of YP before and after fluoride adsorption.

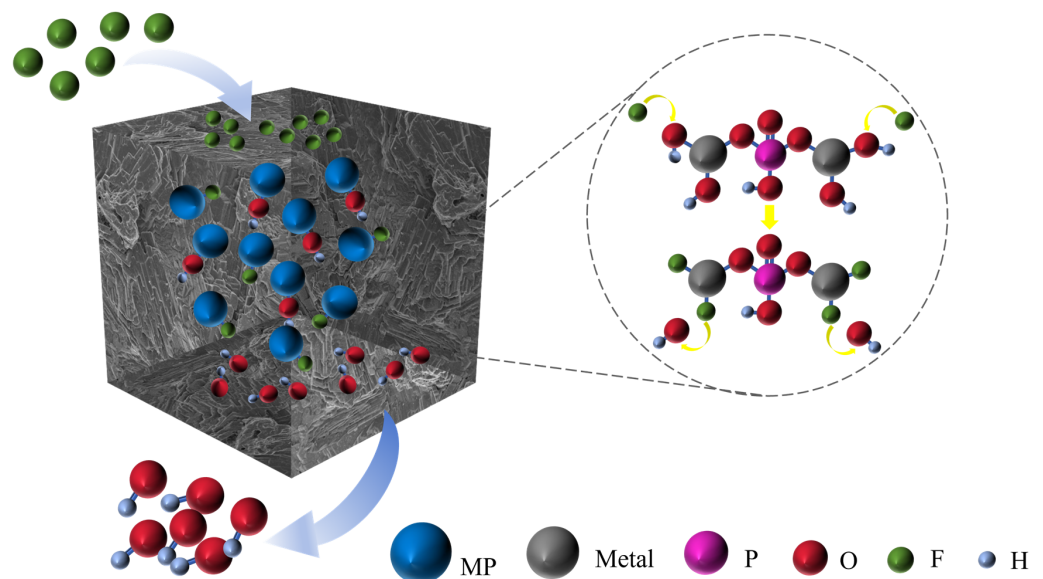


Figure 7. Schematic diagram of adsorption mechanism of fluoride on metallic phosphates.

3.8. Adsorption–Desorption Cycles

The adsorption–desorption cycles help to examine the potential of adsorbents for practical application in fluoridated water treatment. The pH effect had shown that the four metallic phosphates almost completely lost adsorption capacity for fluoride in alkaline circumstances, which indicated that NaOH solution was possibly a suitable desorbent. As shown in Figure S6, the desorption efficiency rose with the increase in NaOH concentration. The desorption rate of the adsorbents tended to be stabilized when the NaOH concentration was not less than 0.5 mol/L. Consequently, the subsequent adsorption–desorption cycles of metallic phosphates were carried out using a 0.5 mol/L NaOH solution. As illustrated in Figure 8a, the desorption rate of metallic phosphates remained essentially stable during five consecutive adsorption–desorption cycles. Metallic phosphates exhibited stable fluoride adsorption in five adsorption–desorption cycles (Figure 8b). Compared to the formulated single fluoride-containing solution, the adsorption–desorption performance of the adsorbents in actual photovoltaic wastewater showed a slight decrease, but it can still maintain a high adsorption rate (Figure S7 and Table S7). Undeniably, metallic phosphates possess outstanding reusability and stability for treating fluorinated water.

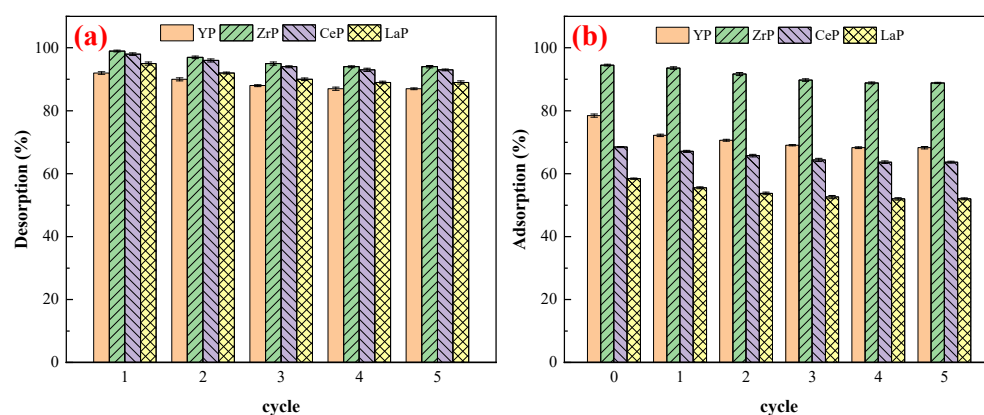


Figure 8. (a) Desorption and (b) adsorption capacity of fluoride by adsorbents in five static adsorption–desorption cycle experiments. (Reaction conditions: adsorbent dosage = 1.0 g/L, initial fluoride = 5 mg/L, pH = 6.8 ± 0.2, T = 298 K.)

Considering the excellent adsorption performance of YP and ZrP, we conducted a preliminary assessment of their synthesis process to further evaluate their scalability in industrial water treatment. The required raw materials are all commercially available products, and the estimated treatment costs for each liter of photovoltaic wastewater using YP and ZrP are approximately 4.41 RMB and 3.63 RMB, which confirms its economic feasibility [48]. Taken together, these factors suggest that YP and ZrP are promising candidates for practical industrial-scale water treatment applications.

4. Conclusions

Metallic phosphates possess enormous potential for fluoride adsorption. YP was suitable to remove fluoride from neutral water, while ZrP was ideal for the adsorption of fluoride from acidic media. The adsorption kinetics of metallic phosphates were better described by the pseudo-second-order model, and YP, CeP, and LaP reached adsorption equilibrium in 150 min, while ZrP required 240 min. The adsorption fitted by Langmuir of amorphous ZrP was higher than crystalline CeP and LaP but lower than crystalline YP. Decreasing temperature favored the adsorption of fluoride by YP, ZrP, and CeP, but disfavored the fluoride adsorption by LaP. The four metallic phosphates exhibited outstanding selectivity under the impact of coexisting anions and organics, and the defluorination selectivity of YP and ZrP was superior to that of CeP and LaP. The mechanism of adsorption was a

specific metal–ligand interaction between metallic phosphates and fluoride. The exhausted adsorbents can be regenerated via NaOH solution. Consequently, the synthesized metallic phosphate adsorbents, especially YP and ZrP, have promising application for fluoride removal from neutral and acidic waters, respectively.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/app151910454/s1>, Figure S1. The optimal molar ratio of metal and phosphorus in the synthesis of metallic phosphates; Figure S2. Nitrogen adsorption–desorption isotherms of adsorbents; Figure S3. Isoelectric points of adsorbents; Figure S4. Effect of equilibrium pH after adsorption on fluoride adsorption onto the adsorbents (Reaction conditions: $T = 298\text{ K}$, $\text{pH} = 6.8 \pm 0.2$, initial fluoride = 5 mg/L , and adsorbent dosage = 0.20 g/L); Figure S5. Adsorption isotherms of fluoride onto the adsorbents at different temperatures: (a) YP; (b) ZrP; (c) CeP; (d) LaP. (Reaction conditions: $\text{pH} = 6.8 \pm 0.2$, and adsorbent dosage = 0.20 g/L); Figure S6. Desorption capacity of fluoride onto the adsorbents in different concentrations of NaOH; Figure S7. Adsorption capacity of fluoride by adsorbents in five static adsorption–desorption cycle experiments with actual wastewater. (Reaction conditions: adsorbent dosage = 1.0 g/L , $T = 298\text{ K}$); Table S1. Primary properties of adsorbents; Table S2. Adsorption kinetic fitting parameters of adsorbents; Table S3. Adsorption isotherm fitting parameters of adsorbents; Table S4. Coordination constants of metal and fluoride; Table S5. The adsorption properties of various mono- or polymetallic-based adsorbents; Table S6. Adsorption thermodynamic fitting parameters of adsorbents; Table S7. The water quality parameters of actual photovoltaic wastewater. References [49–58] are cited in the supplementary materials.

Author Contributions: R.W.: Data curation, Writing—original draft, Formal analysis, Investigation, Visualization. Y.G.: Supervision. M.M.: Visualization. Y.S.: Conceptualization, Writing-review and editing, Funding acquisition. All authors have read and agreed to the published version of the manuscript.

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