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Removal competition mechanism of orthophosphate and pyrophosphate by CaFe-Cl-LDHs

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ABSTRACT

Large amount of phosphorous is the main factor for eutrophication. Removal of orthophosphate and pyrophosphate with CaFe-Cl-LDHs was explored in the paper. And the aim of this paper was to investigate the different mechanisms of orthophosphate and pyrophosphate removal by CaFe-Cl-LDHs. The results displayed that the removal process was precipitation-dissolution between Ca^{2+} and orthophosphate or pyrophosphate, which was fitted with the pseudo-second-order equation well; when Ca^{2+} was not enough, pyrophosphate had a competitive advantage over orthophosphate; as the concentration of pyrophosphate increased, precipitate was formed by Ca^{2+} and $P_2O_7^{4-}$. The simultaneous removal of orthophosphate and pyrophosphate on CaFe-Cl-LDHs was also evaluated to provide information for the treatment of domestic and industrial wastewaters.

Keywords: CaFe-Cl-LDHs; Orthophosphate; Pyrophosphate; Simultaneous removal

1. Introduction

Nowadays, excessive supply of phosphorous discharged into water acts as a major reason of eutrophication [1,2], which has become a worldwide phenomenon [3–5]. It is very urgent to reduce the negative effects of phosphorous.

Various techniques are used to remove phosphorous from water, including physical, chemical, and biological treatments. Physical process (such as electro dialysis) has some disadvantages due to their high costs and producing some pollution [6]. Many biological methods often need strict conditions and highly skilled operation techniques [7–14]. In recent years, adsorption has always been used as a major method to remove phosphorous. Adsorption technique has an advantage over other processes due to its characteristics of high efficiency and low cost. Many kinds of adsorbent have been used in the removal process, such as iron oxide/hydroxide, mesoporous alumina,

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RMGA, and activated carbon. [15–21]. Nature zeolite was used by Lin et al. to remove orthophosphate from high-strength wastewaters [22]. Another natural and abundant material, *Posidonia oceanica* (L.) fibers, was compared with other materials by Wahab et al. and the maximum adsorption capacity (Q_m) was calculated to be 7.45 mg/g [23]. However, when the adsorption is saturated, their absorption ability will decline, and the reuse is difficult.

In order to improve the properties of adsorbent, layered double hydroxides (LDHs) have been examined as the adsorbent. Since LDH has a unique interlayer anionic exchange ability, which improves the removal of anions [24]. And the study for the removal process using LDHs has made a certain progress [25–30]. Based on this benefit of LDH in phosphate removal [31–35], the efficient removal of phosphorous over LDH is expected.

However, previous reports always focused on a single system. For example, Ca^{2+} played an important role for the removal of phosphate when zeolite was used as adsorbent [16]; limestone and granular activated carbon were used for the removal of orthophosphate from domestic wastewater [18]. They rarely explored the relationship between orthophosphate and pyrophosphate in removal process.

In this work, CaFe-Cl-LDHs were used for the simultaneous removal of orthophosphate and pyrophosphate. The main focus is to evaluate the adsorption of CaFe-Cl-LDHs for orthophosphate, pyrophosphate, and the relationship between them. The key process parameters were reaction time, initial concentration, and the ratio of orthophosphate and pyrophosphate. In view of the different removal performances in this study, the release of Ca, P, and PP in reaction, adsorption isotherm and the adsorption kinetics were also investigated.

2. Experimental

2.1. Materials and chemicals

In the experiment, all the chemicals were of analytical grade and were used without further purification. Sodium phosphate (Na_3PO_4), sodium pyrophosphate ($Na_4P_2O_7$), calcium chloride ($CaCl_2$), ferric chloride ($FeCl_3$), sodium hydroxide (NaOH), and nitric acid (HNO_3) were obtained from Sinopharm Chemical Reagent Co., Ltd. Solutions of sodium hydroxide (NaOH) and nitric acid (HNO_3) were prepared by dissolving appropriate amount of sodium hydroxide (NaOH) and nitric acid (HNO_3) in deionized water, respectively.

2.2. Preparation of CaFe-Cl-LDHs

CaFe-Cl-LDHs were synthesized under N_2 atmosphere by the way of coprecipitation method. About 5.55 g (50 mmol) of $CaCl_2$ and 4.06 g (25 mmol) of $FeCl_3$ were dissolved into 50 ml of deionized water (Solution A). And the solution of sodium hydroxide (NaOH) was prepared by dissolving 6.4 g (160 mmol) of NaOH into 100 ml of deionized water (Solution B). Solution A was added into solution B to form a precipitate by stirring under N_2 circumstance for 60 min, and then the solution was stirred at room temperature with N_2 atmosphere for 24 h. The sample was suction filtered and washed for 2–3 times. After the synthesis, CaFe-Cl-LDHs were dried in vacuum at 105℃ and filtered (0.15 mm). Then the sample was stored in dry container for experiment.

2.3. Batch studies

The effect of initial concentration was examined by a series of concentration of orthophosphate and pyrophosphate in the removal process. Removal of orthophosphate and pyrophosphate by CaFe-Cl-LDHs was performed for various reaction times. One gram of CaFe-Cl-LDHs was added into 1,000 ml of phosphate-mixed solution (1.268 mmol TP/g LDH; 3.068 mmol TP/g LDH; 4.400 mmol TP/g LDH; 5.921 mmol TP/g LDH; 7.787 mmol TP/g LDH; P: PP = 1:1), respectively. The reaction time was 1, 5, 10, 20, 30 min, and 1, 1.5, 2, 4, 6, 8, 12, 24, 36, and 48 h. HNO_3 and NaOH were used to adjust the pH as 11. Then the solutions were filtered (0.45 μm). The pH of filtrates and the concentrations of orthophosphate and pyrophosphate were tested.

When CaFe-Cl-LDHs were used to remove phosphate, the removal process of PP involved the dissolution of LDH, precipitation of $Ca_2P_2O_7{\cdot}2H_2O$, and surface capture of PP. The major PP removal route was precipitated as $Ca_2P_2O_7{\cdot}2H_2O$ [24]. In order to further clarify the removal process under different concentrations of orthophosphate and pyrophosphate, different ratios of orthophosphate and pyrophosphate were investigated in this study. When the ratio of orthophosphate and pyrophosphate was 1:1, 1g of CaFe-Cl-LDHs was mixed with 1,000 ml of phosphate solution, maintaining the total phosphorus concentration range from 2.58 to 8.39 mmol TP/g LDH. While the ratio of orthophosphate and pyrophosphate was changed, the test was divided into five parts. In these five parts, the concentration of P was constant value, and the PP was added to the solution as follows: (a) 0.6452 mmol P/g LDH orthophosphate mixed with

0.1613–2.5806 mmol PP/g LDH; (b) 1.290 mmol P/g LDH orthophosphate mixed with 0.3226–3.2259 mmol PP/g LDH; (c) 1.936 mmol P/g LDH orthophosphate mixed with 0.6451–4.516 mmol PP/g LDH; (d) 2.581 mmol P/g LDH orthophosphate mixed with 0.6451–5.806 mmol PP/g LDH; and (e) 3.226 mmol P/g LDH orthophosphate mixed with 1.935–7.097 mmol PP/g LDH. The pH of solution was adjusted to 11 with HNO_3 and NaOH. The solution was then filtered (0.45 μm). The pH of filtrates, the concentrations of orthophosphate and pyrophosphate as well as the concentrations of Ca^{2+}, Fe^{3+} were tested. Finally, the sample was vacuum dried under the condition of reaction temperature 70℃ and tested with X-ray diffraction (XRD).

2.4. Verification tests

In order to explore the competition of orthophosphate and pyrophosphate, verification tests were used. One gram of CaFe-Cl-LDHs was mixed with 1,000 ml of phosphate-mixed solution, and the pH of the solution was adjusted to 11.0 with HNO_3 and NaOH. There were two groups of experiments (when the ratio of orthophosphate and pyrophosphate was 1:1, the initial concentration of total phosphorus was 6.625 mmol TP/g LDH; and when the ratio of orthophosphate and pyrophosphate was 2:1, the initial concentration of total phosphorus was 2.903 mmol TP/g LDH). Each experiment was, respectively, divided into three parts: firstly, the mixed solution was sealed and oscillated for 48 h at 25℃; secondly, after sealed and oscillated the mixed solution in the oscillator for 6 h at 25℃, 1 ml of pyrophosphate (the concentration of LDH was about 1,000 mg PP/g or 25 mg PP/g LDH, respectively) was added into it for 48 h; thirdly, after sealed and oscillated the mixed solution in the oscillator for 6 h at 25℃, 1 ml of orthophosphate was added into it (about 1,000 mg P/g or 25 mg P/g LDH, respectively) for 48 h, then all samples were filtered (0.45 μm). The pH of filtrates, the concentrations of orthophosphate, Ca^{2+}, and Fe^{3+} were tested.

2.5. Characterization and measurement

XRD was used to analyze the structure of CaFe-Cl-LDHs. The analysis was performed with Rigaku D/Max-2200-X-diffraction powder diffractometer using monochromatic Cu–Kα radiation operated at 40 kV.

The concentrations of orthophosphate and pyrophosphate were determined by ICS-1100 ion chromatograph (IC). The measurements of metal ion concentration were performed using inductively coupled plasma (ICP).

To determine the concentration of free ionic calcium, PHS-3 c pH meter and PCa-1–01 ray magnetic calcium ion-selective electrode were used.

3. Results and discussion

3.1. Effect of initial concentration

Variation trend of initial concentrations is displayed in Fig. 1. With the extension of time, the equilibrium concentrations of orthophosphate (P) and pyrophosphate (PP) decreased, and the removal of orthophosphate and pyrophosphate followed the similar trend.

In Fig. 1(a) and (b), when the initial concentrations of total phosphorus were 1.268 (0.7197 P + 0.5487 PP) and 3.068 (1.553 P + 1.515 PP) mmol TP/g LDH, respectively, two curves of orthophosphate and pyrophosphate almost coincided with each other; and the reactions reached equilibrium at 1–12 h. This indicated that orthophosphate and pyrophosphate could be quickly and completely precipitated to form, respectively, hydroxyapatite ($Ca_5(PO_4)_3OH$) and $CaCO_3$; when the concentration of total phosphorus was low, and there was no competition between orthophosphate and pyrophosphate.

Fig. 1(c) shows that when the initial concentration of total phosphorus was 4.400 (2.305 P + 2.095 PP) mmol TP/g LDH, concentrations of orthophosphate and pyrophosphate decreased during the process, the removal rate of orthophosphate and pyrophosphate were 66.1 and 77.4%, respectively. But the removal of orthophosphate and pyrophosphate was obviously different after 20 min, it could be noted that the concentration of pyrophosphate was lower than orthophosphate.

When the concentrations of phosphorus were 5.921 (3.129 P + 2.792 PP) mmol TP/g LDH (Fig. 1(d)) and 7.787 (4.010 P + 3.777 PP) mmol TP/g LDH (Fig. 1(e)), the removal rate of pyrophosphate and orthophosphate were 43.1, 36.5, 56.6, and 51.0%, respectively. It was concluded that the removal amount of pyrophosphate was higher than orthophosphate in the simultaneous removal process. This is because that the ratio of Ca/P is different in $Ca_2P_2O_7{\cdot}2H_2O$ or $Ca_5(PO_4)_3OH$, more Ca^{2+} is needed to form $Ca_5(PO_4)_3OH$ under the same condition.

In conclusion, when the initial concentration of total phosphorus was low, Ca^{2+} released from CaFe-Cl-LDHs was enough. There was no competition between orthophosphate and pyrophosphate. As the concentration of total phosphorus increased, Ca^{2+} used

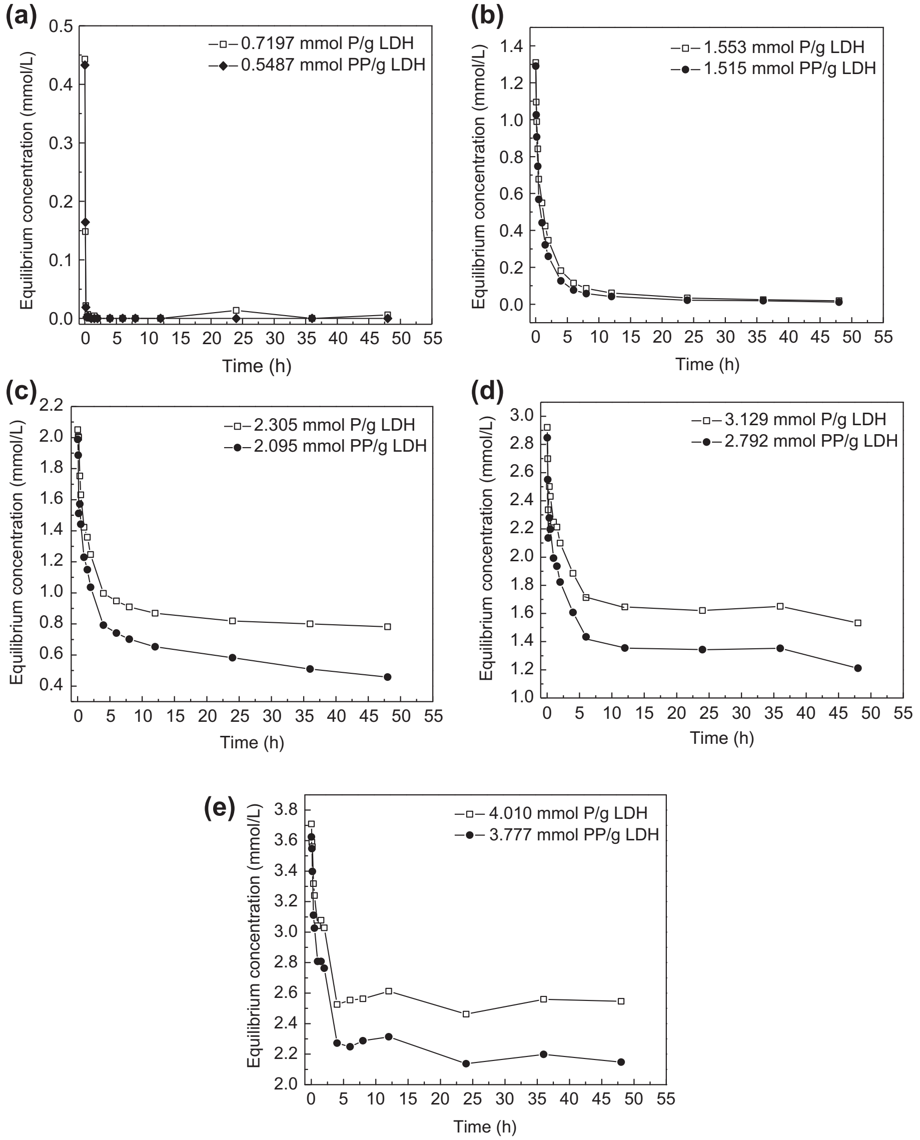

Fig. 1. The effect of initial concentration on the removal of orthophosphate and pyrophosphate simultaneously by CaFe-Cl-LDHs under different time: (a) 1.268 mmol TP/g LDH, (b) 3.068 mmol TP/g LDH, (c) 4.400 mmol TP/g LDH, (d) 5.921 mmol TP/g LDH, and (e) 7.787 mmol TP/g LDH.

by orthophosphate and pyrophosphate was not enough, the shortage of Ca^{2+} resulted in the difference of orthophosphate and pyrophosphate removal.

3.2. Effect of the ratio of orthophosphate and pyrophosphate

3.2.1. Constant initial ratio of orthophosphate and pyrophosphate

When the initial ratio of orthophosphate and pyrophosphate was kept constant at one, the removal process of orthophosphate and pyrophosphate followed the similar trend under different initial concentration of total phosphorus, which is presented in Fig. 2. The adsorption amount was nearly 1.50 mmol/g. And, there was a correlation between the removal trend of total phosphorus and orthophosphate or pyrophosphate. When the initial concentration of phosphorus was 3.75 mmol/L, the saturated adsorption amounts of phosphorus were about 3.25 mmol/g.

Free calcium (Ca), pH, and total Ca are shown in Fig. 3. After the reaction reached equilibrium, pH increased to 12.0 compared with the initial 11.0. This suggests that dissolution process of CaFe-Cl-LDHs occurs during the removal of phosphate.

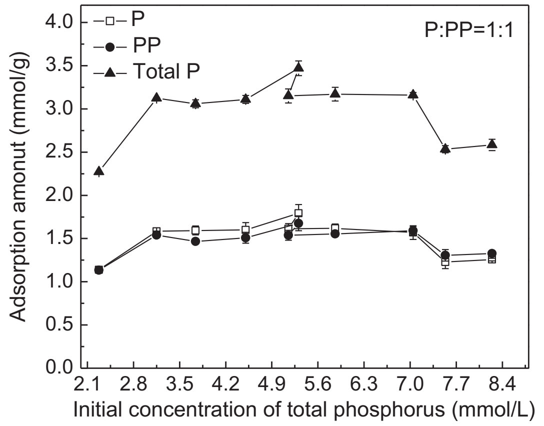

Fig. 2. The effect of initial concentrations on the removal of orthophosphate and pyrophosphate simultaneously by CaFe-Cl-LDHs.

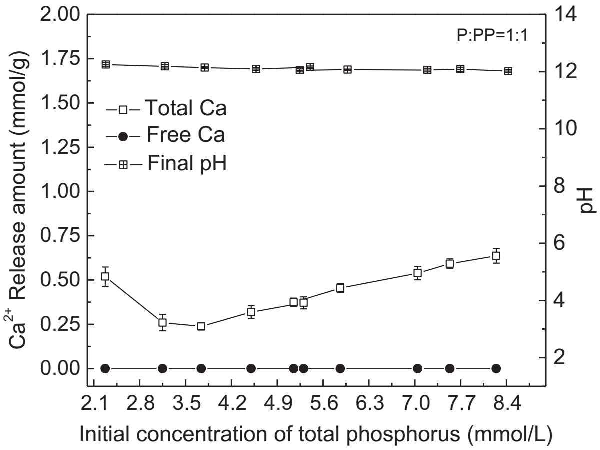

Fig. 3. The release of Ca in the removal process of coexisting system by CaFe-LDHs.

The concentration of free calcium (Ca) in the reaction was stable, which always maintained at about zero. With the increasing of initial concentration, total Ca decreased firstly, and then increased. It is because the complex (formed by Ca^{2+} and pyrophosphate) was generated at the initial concentration range of 2.58–8.39 mmol/L, and with further increase of initial concentration, the reaction product for pyrophosphate was changed from $Ca_2P_2O_7$ to Ca $(P_2O_7)^{2-}$, which altered the trend of total Ca.

3.2.2. Different initial ratios of orthophosphate and pyrophosphate

In the removal process of orthophosphate and pyrophosphate by CaFe-Cl-LDHs, the removal effect under different initial ratios of orthophosphate and pyrophosphate (P:PP) is compared in Fig. 4.

In these reactions, while the concentration of orthophosphate remained constant, the concentration of pyrophosphate increased gradually, i.e. the initial ratio of orthophosphate and pyrophosphate increased, the removal amount of pyrophosphate (PP) increased, but the effect on the removal of orthophosphate, concentration of Ca^{2+}, and pH was different.

As shown in Fig. 4(a), when the initial concentration of orthophosphate was 0.6452 mmol P/g LDH, the removal rate of orthophosphate was close to 100%. The relationship between the removal of orthophosphate and the initial concentration of pyrophosphate was linear. Orthophosphate and pyrophosphate precipitated completely when the concentration of total phosphorus was low, which indicates that orthophosphate and pyrophosphate did not compete with each other.

In Fig. 4(b), the concentration of orthophosphate and pH of this system were nearly maintained stable. While the initial concentration of pyrophosphate increased, the equilibrium concentration of Ca was changed, which decreased sharply first and then increased slowly. The concentration of Ca decreased to 0.0553 mmol/g as the initial concentration of pyrophosphate was 2.5806 mmol/g LDH, while the concentration of Ca decreased to 0.0978 mmol/g along with the initial concentration of pyrophosphate increased to 2.903 mmol/g LDH. The possible reason for this trend is the change of chemical product, which leads to the decrease of Ca concentration.

According to the data in Fig. 4(c) and (d), the trends of orthophosphate and pyrophosphate were similar to each other. When the concentration of pyrophosphate increased to 1.925 mmol/L, Ca^{2+} was precipitated by PO_4^{3-} and $P_2O_7^{4-}$ easily.

Fig. 4(c) displays that the concentration of Ca decreased firstly, and it approached zero when the concentration of pyrophosphate was 1.613 mmol/L, which was due to the formation of calcium–phosphate compound. Then, after the turning point, the concentration of Ca was continually increased and the maximum concentration was 0.7080 mmol/g, indicating that complexation could be enhanced along with the concentration of pyrophosphate increased. However, in Fig. 4(d), the concentration of Ca increased from 0.119 to 1.053 mmol/g during the whole process, because the initial concentrations of orthophosphate and pyrophosphate were very high, the complex was formed at the beginning of the reaction. When the concentration of pyrophosphate increased to 3.226 mmol P/g LDH, Ca concentration also increased, and then reached stability, the final concentration of Ca was about 1.15 mmol/L (Fig. 4(e)).

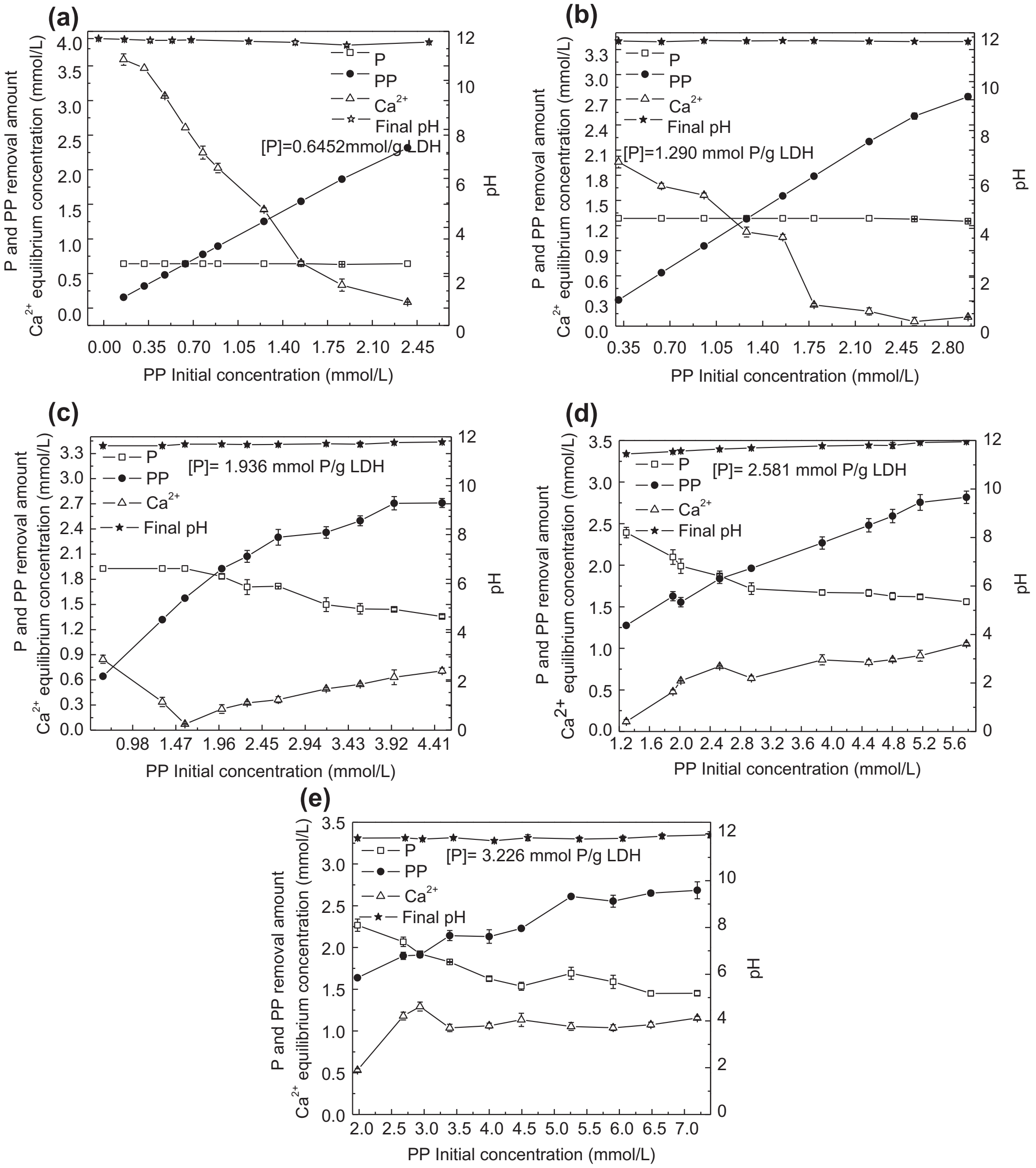

Fig. 4. The effect of the ratio of orthophosphate and pyrophosphate in the removal process: (a) [P] = 0.6452 mmol P/g LDH, (b) [P] = 1.290 mmol P/g LDH, (c) [P] = 1.936 mmol P/g LDH, (d) [P] = 2.581 mmol P/g LDH, and (e) [P] = 3.226 mmol P/g LDH.

3.3. The release of Ca, P, and PP in the reaction

In order to explain the competitive relationship of this reaction, the release of Ca, orthophosphate, and pyrophosphate are shown in Fig. 5.

The Ca^{2+} ions in the system would affect the removal of orthophosphate and pyrophosphate [22]. In the removal reaction, the release for Ca was near to zero, which is represented in Fig. 5(a), (b), and (c). Ca and phosphate were precipitated. It is noticeable that the concentration of Ca continually increased along with the increase in the concentration of pyrophosphate (Fig. 5(d) and (e)), which confirms the existence of the complexation. Orthophosphate and pyrophosphate did not compete with each other when the calcium ion in the solution was enough. And when the concentration of Ca decreased, the competitiveness of pyrophosphate was better than orthophosphate.

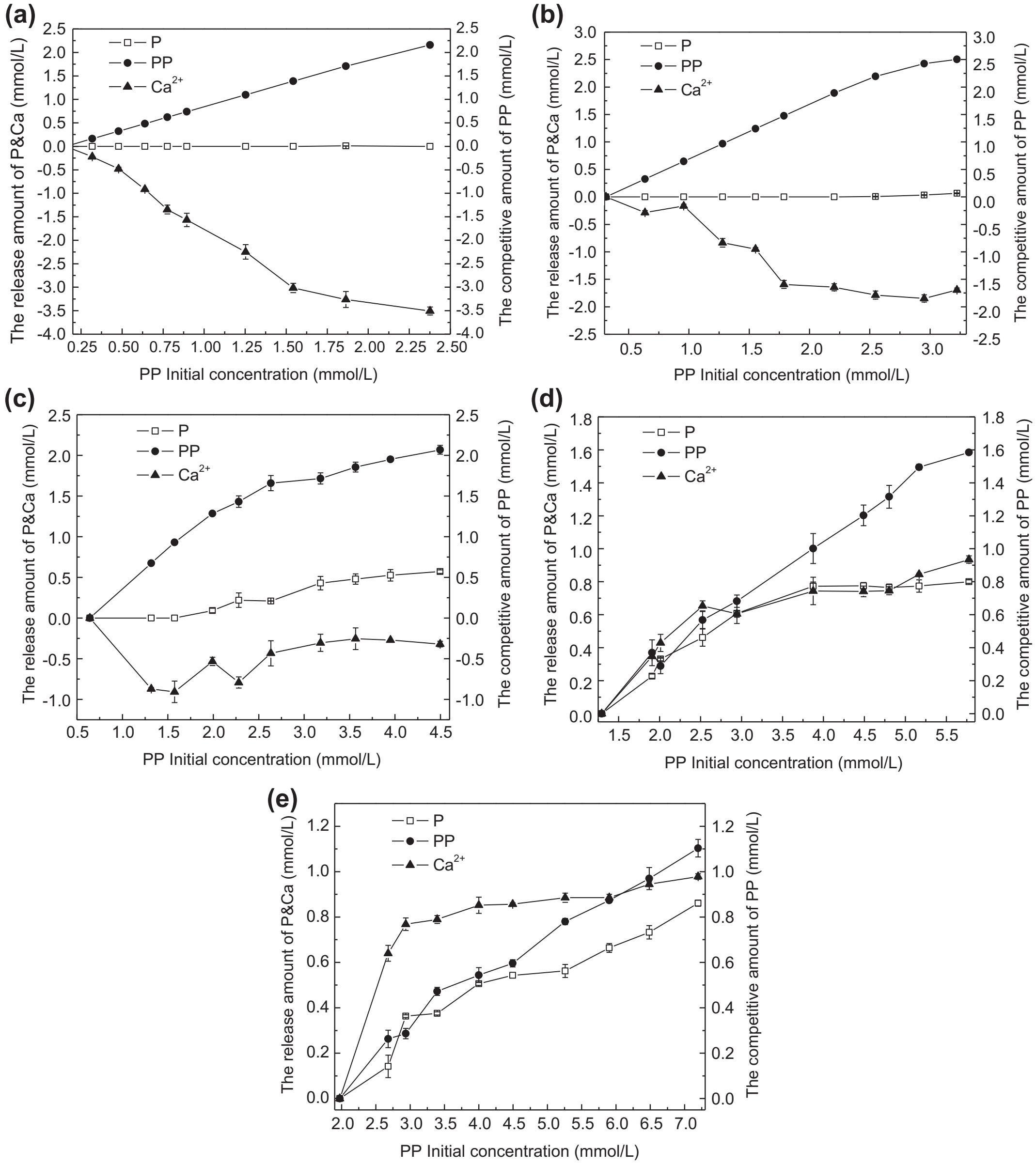

Fig. 5. The release of PO_4^{3-} and $P_2O_7^{4-}$ and Ca: (a) [P] = 0.6452 mmol P/g LDH, (b) [P] = 1.290 mmol P/g LDH, (c) [P] = 1.936 mmol P/g LDH, (d) [P] = 2.581 mmol P/g LDH, and (e) [P] = 3.226 mmol P/g LDH.

3.4. Adsorption kinetic

Fig. 6 displays the removal of orthophosphate and pyrophosphate (P:PP = 1:1) by CaFe-Cl-LDHs along with the reaction time. It could be seen that adsorption amount of P (Fig. 6(a)) and pyrophosphate (Fig. 6(b)) increased with the extension of time until equilibrium was reached. The final adsorption amounts of P and PP were similar when the concentration of TP ranged from 3.068 to 7.787 mmol TP/g LDH. However, at 1.268 mmol TP/g LDH, the time was shorter to reach equilibrium; the final adsorption amounts of P and PP were about 22.31 and 17.71 mmol/g, respectively.

Kinetic data of orthophosphate and pyrophosphate by CaFe-Cl-LDHs was analyzed in terms of pseudo-first-order, pseudo-second-order sorption equations, and Elovich equation.

According to the correlation coefficient (R^2) values (Tables 1 and 2), the results were better fitted with pseudo-second-order equation. And the correlation coefficient (R^2) values of Elovich equation were all above 0.9 after the concentration increased to

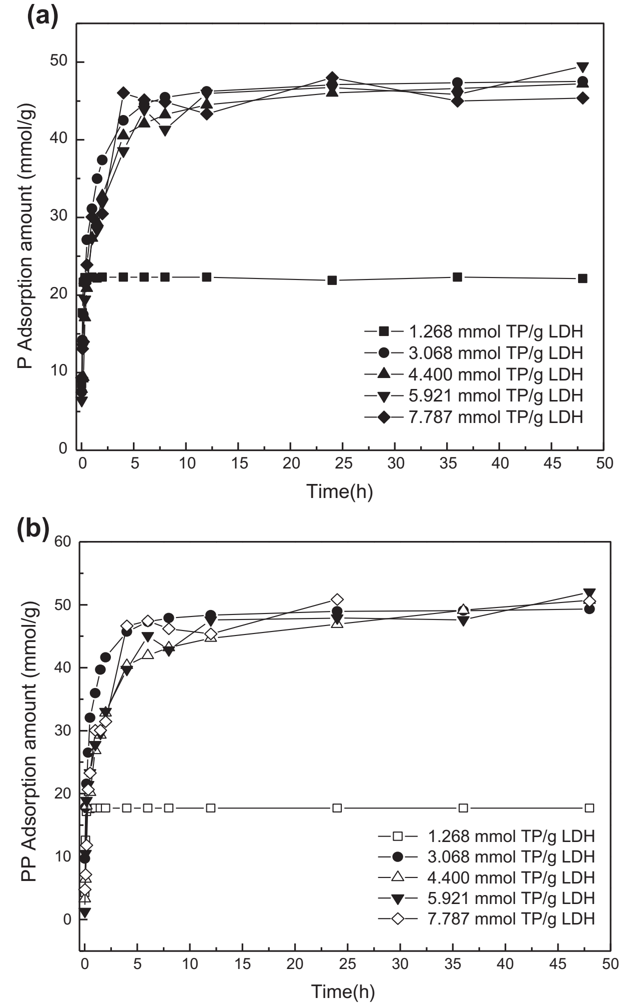

Fig. 6. The effect of reaction time on the removal of orthophosphate (a) and pyrophosphate (b) from the mixed system on CaFe-Cl-LDHs.

0.3226 mmol TP/0.1 g LDH, implying that in this process, homogeneous reaction turned into heterogeneous reaction with the increased initial concentration of phosphorus; the removal process of orthophosphate and pyrophosphate by CaFe-Cl-LDHs was similar with each other; the difference was that the removal amount of pyrophosphate was larger than orthophosphate.

3.5. Verification tests

In order to confirm the competition of orthophosphate and pyrophosphate, verification tests were conducted. In these tests, small volume of orthophosphate or pyrophosphate was added into the system (the concentrations of three groups were 6.625 mmol TP/g LDH). As long as the ratio of orthophosphate and pyrophosphate was 1:1, the adsorption effect did not change obviously. On the other hand, release of Ca was evidently increased when pyrophosphate was added; while the release of Ca was only slightly decreased with the addition of orthophosphate (Fig. 7).

It was concluded that the precipitation products formed by Ca and orthophosphate or pyrophosphate were stable. And the precipitation would not change when the concentration of orthophosphate or pyrophosphate increased. In this process, the release of Ca (from 0.536 to 0.982 mmol/g) increased obviously, which confirms the complexation of Ca and pyrophosphate ions.

In Fig. 8, the ratio of orthophosphate and pyrophosphate was 2:1. Due to that the initial concentration of the total phosphorus was low, when orthophosphate or pyrophosphate was added, the removal of total

Table 1
The adsorption kinetic parameters of orthophosphate of the mixed system on CaFe-Cl-LDHs

		Concentration (mmol TP/0.1 g LDH)				
Equation		0.1613	0.3226	0.4839	0.6452	0.8065
Pseudo-first-order equation	K_1 (1/h)	15.94	2.84	0.88	1.16	0.99
	q_{e1} (mmol/g)	0.57	1.48	1.46	1.45	1.51
	R^2	0.9963	0.8665	0.9018	0.8535	0.9130
Pseudo-second-order equation	K_2 (g/mmol h)	29.27	4.42	1.40	1.87	1.53
	q_{e2} (mmol/g)	0.59	1.56	1.55	1.54	1.62
	R^2	0.9415	0.9558	0.9574	0.9385	0.9615
Elovich equation	A	2.72×10^6	100.17	10.80	12.64	8.81
	B	1.06	5.41	6.49	6.48	7.03
	R^2	0.4308	0.9321	0.9723	0.9764	0.9355

Table 2
The adsorption kinetic parameters of pyrophosphate on CaFe-Cl-LDHs

		Concentration (mmol TP/0.1 g LDH)				
Equation		0.1613	0.3226	0.4839	0.6452	0.8065
Pseudo-first-order equation	K_1 (1/h)	23.48	1.84	0.99	0.98	1.28
	q_{e1} (mmol/g)	0.71	1.42	1.41	1.42	1.41
	R^2	0.9768	0.8805	0.9369	0.8507	0.8251
Pseudo-second-order equation	K_2 (g/mmol h)	44.13	2.87	1.49	1.49	1.58
	q_{e2} (mmol/g)	0.73	1.50	1.50	1.51	1.48
	R^2	0.9625	0.9608	0.9713	0.9292	0.9051
Elovich equation	A	2.90×10^8	38.71	13.32	21.36	31.73
	B	1.04	5.78	6.16	5.85	5.62
	R^2	0.4078	0.9517	0.9372	0.9654	0.9014

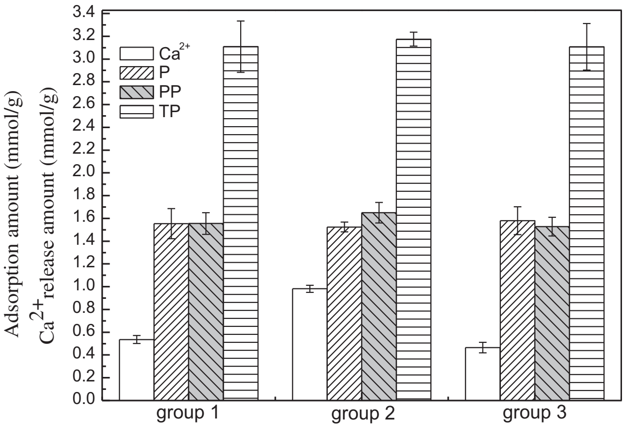

Fig. 7. The effect of orthophosphate or pyrophosphate on the simultaneous removal process by CaFe-LDHs. (P: PP = 1).

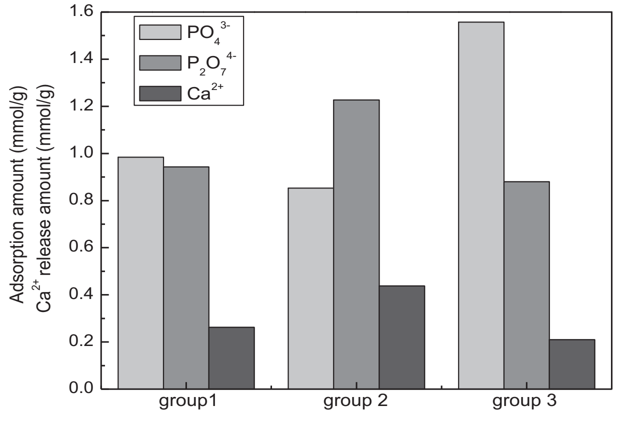

Fig. 8. The effect of orthophosphate or pyrophosphate on the simultaneous removal process by CaFe-LDHs. (P: PP = 2).

phosphate increased. Adsorption quantity of PO_4^{3-} decreased from 0.98434 to 0.8530 mmol/g when $P_2O_7^{4-}$ was added, implying that there was a competitive relationship between PO_4^{3-} and $P_2O_7^{4-}$ for Ca, and the adsorption amount of $P_2O_7^{4-}$ continually increased until reaching the saturated adsorption (1.2273 mmol/g). The adsorption amount of PO_4^{3-} increased until saturation was reached (1.5571 mmol/g) when PO_4^{3-} was added, while the adsorption amount of $P_2O_7^{4-}$ increased slightly.

It was observed that the release of Ca was obviously increased along with the addition of $P_2O_7^{4-}$. The equations for the reaction of the removal process are as follows:

$$10Ca^{2+} + 6PO_4^{3-} \longrightarrow Ca_{10}\,(PO_4)_6(OH)_2 \tag{1}$$

$$Ca^{2+} + P_2O_7^{4-} \longrightarrow Ca_2P_2O_7 \tag{2}$$

When the amount of $P_2O_7^{4-}$ was large, it could be described by the following formula.

$$Ca^{2+} + P_2O_7^{4-} \longrightarrow Ca\,(P_20_7)^{2-} \tag{3}$$

The process mentioned in Eq. (3) led to the decrease of Ca^{2+} concentration. And then, the decrease of Ca^{2+} concentration made the Eqs. (1) and (2) turn to the opposite direction. In that way, the removal amount of orthophosphate was slightly decreased when $P_2O_7^{4-}$ was added into these systems. At the same time, the release of Ca increased, due to the fact that the production of $P_2O_7^{4-}$ and ($Ca\,(P_2O_7)^{2-}$) was soluble.

4. Conclusions

The removal competition mechanism of orthophosphate and pyrophosphate on CaFe-Cl-LDHs was investigated. The main process was precipitation–dissolution between Ca^{2+} and orthophosphate or pyrophosphate. At a low concentration of total phosphorus, there was no competition between orthophosphate and pyrophosphate; when the concentration of total phosphate increased, the removal amount of pyrophosphate was larger than orthophosphate. This phenomenon showed that the removal rate of pyrophosphate by CaFe-Cl-LDHs was faster. However, when the concentration of Ca^{2+} was not enough, pyrophosphate had a competitive advantage over orthophosphate. Additionally, as the concentration of pyrophosphate increased until the total phosphorus was about 4.5 mmol/g, the released amount of Ca^{2+} increased, which is due to the complexing action between Ca^{2+} and $P_2O_7^{4-}$.

Acknowledgments

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