



Chemical phosphorus removal optimization from coating wastewater using iron–calcium salt

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ABSTRACT

Phosphorus is a commonly used compound in coatings; thus, wastewater from coating plants usually contains large amounts of phosphate. Given its unidirectionality in the ecological cycle, phosphorus must be removed from coating wastewater and recycled. Herein, phosphorus was removed and recovered from industrial coating wastewater through chemical precipitation. The effects and mechanisms of this removal and recovery using the iron salt, calcium salt, and iron–calcium salt methods were analyzed. When the proportion of iron in iron–calcium salt exceeded 0.51, the average phosphorus removal rate was more than 62.44% of the average removal rate when the iron salt or calcium salt was used alone. A synergistic phenomenon was demonstrated with the iron–calcium salt method; the phosphorus removal rate reached 96.13% when the molar ratio of iron–calcium salt to phosphorus was 1.50. The precipitation flocs produced using the iron–calcium salt integrated the advantages of the iron and calcium salt methods; they had a large particle size and were easily crystallized. This study demonstrates a valuable method for the removal and recovery of phosphorus from industrial coating wastewater.

Keywords: Coating wastewater; Iron–calcium compound salt; Phosphorus removal; Antagonistic synergistic phenomenon

1. Introduction

Painting operation is a main source of environmental issues in vehicle manufacturing industry and it linked more than 60% of environmental impacts in this industry [1,2]. The global vehicle production has exceeded 70 million vehicles annually in the last decade. In 2021 alone, 80.1 million motor vehicles were manufactured worldwide [3]. Phosphating is an important coating process in

which a solution containing phosphoric acid or phosphate is used to form an insoluble phosphate film on the surface of the substrate metal. This film protects the substrate metal from corrosion. After phosphating, the phosphating solution and residue attached to the metal surface are removed by washing with water. Consequently, a large amount of phosphorus-containing wastewater is released [4].

Phosphorus is an essential element in the synthesis of protein molecules and the growth and reproduction of organisms [2]. Phosphorus is unidirectional, follows

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a typical sedimentary cycle, lacks a gaseous phase, and impedes transfer in the environment [3,4]. Given its widespread global use and unidirectional circulation, phosphorus threatens to deplete phosphate rock within the next 50–100 y [5,6]. Phosphorus is involved through certain sparingly soluble compounds in alkaline environments, and dissolution occurs in acidic environments [7]. At present, there are no synthetic substitutes can instead of this element. Currently, synthetic substitutes to this element are unavailable. However, excessive amounts of phosphorus discharge into the surface water of rivers and lakes can cause ecological problems such as eutrophication and the degradation of natural waters [8,9]. The presence of phosphorus in the water sediment can affect the quality of drinking water and the ecosystem of rivers and lakes.

Therefore, it is imperative that phosphorus is removed from coating wastewater and recycled before it enters the sedimentary cycle. Traditional methods of phosphorus removal include the biological method, and chemical method [10,11]. Although both methods can effectively remove organic matter from wastewater, the biological method has a lower phosphorus removal rate than the chemical method [12,13]. In addition, the water quality and volume of industrial wastewater often fluctuate greatly, affecting biological phosphorus removal. Therefore, phosphorus is usually removed from coating wastewater through chemical precipitation to meet the increasingly stringent emission standards [14–16]. Iron salt and calcium salt are usually used for phosphorus removal because of their low cost and high removal efficiency [17,18]. However, iron salt will hydrolyzed in water to make effluent acidic, ferrous salt method requires highly amount of dosage and the phosphorus removal rate is relative high only during the pH of 7–8 [19,20], while calcium salts need a high pH of about 10 [21]. To improve the phosphorus removal performance of metal salts, researchers have combined different metal salts or adsorbing materials. Qiu et al. [19] achieved more than 99% phosphorus removal efficiency with iron–calcium compound salt. Ji et al. [22] used hydrogen peroxide coordination-calcium salt precipitation to for deep phosphorus removal and phosphorus concentration in solution is lower than 10 ppm after phosphorus removal ratio of 99%. Xu et al. [23] combined iron salt with magnetic oxide and obtained a phosphate adsorption percentage of 97.97%. To the best of our knowledge, calcium and iron salts are common and inexpensive coagulants, and iron–calcium salts have yet to be used to remove phosphorus from coating wastewater.

Therefore, this study evaluated and compared the phosphorus removal rates obtained using the iron salt, calcium salt, and iron–calcium salt methods. It also elucidated the mechanisms of the removal methods and analyzed the phosphorus removal rates, turbidity and pH changes, X-ray diffraction (XRD) spectra, and floccule (floc) particle size.

2. Experimental

2.1. Materials

The wastewater samples were collected from the coating factory named Tianjin Shangyi Metal Products Co.,

Ltd., China. The samples were neutralized; most metal ions were removed by adding sodium hydroxide. The pH of the wastewater was 7.0 ± 0.15 and the total phosphorus concentration was 130 ± 17 mg/L. Sodium hydroxide (NaOH, AR) with a concentration of 50% (w/w) was used to adjust pH. The calcium and iron salts used were calcium hydroxide ($\text{Ca}(\text{OH})_2$, AR) and ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, AR), respectively.

2.2. Experimental process

Sodium hydroxide was used to adjust the optimal pH for the reaction process. Note that the pH value of the initial coating wastewater was adjusted, but the pH was not adjusted during the reaction process. Then, 500 mL of coating wastewater was placed into a 1,000 mL glass reactor and then in a six-unit electric mixer (JJ-4a, Youlian, China). The wastewater in the glass reactor was homogenized via stirring. After adding the precipitant, the mixture was mixed rapidly (300 rpm) for 1 min and then gently mixed (40 rpm) for 20 min. The particle size of the mixture was immediately determined at the end of the mixing time. The supernatant was used to determine the concentrations of residual phosphorus, calcium, and iron ions. The precipitates were centrifuged at 8,000 rpm for 10 min and then freeze dried. After they were dried completely, the precipitates were ground with a mortar until the particle size was less than 0.3 mm. Finally, the specific components of the precipitates were analyzed.

2.3. Analytic methods

The standard methods for the examination of water and wastewater were employed. The pH of the coating wastewater was monitored using a portable pH meter (DDB-303A, Leici, China). The floc size was detected with a laser particle size counter (Versacount, IBR, USA). XRD spectrum analysis was completed using an X-ray diffractometer (MiniFlex600, Rigaku, Japan).

3. Results and discussion

3.1. Effect of adding iron salt and calcium salt separately on phosphorus removal

The effect of iron and calcium salts on the rate of phosphorus removal from coating wastewater was investigated by changing the amounts of FeCl_3 and $\text{Ca}(\text{OH})_2$. In this experiment, the removal rate of phosphorus was investigated at the following molar ratios: 0, 0.25, 0.50, 0.75, 1.00, 1.25, 1.50, 1.75, 2.00, 2.25, 2.50, and 2.75. The changes in the total phosphorus removal rate with varying Fe/P and Ca/P molar ratios are shown in Fig. 1.

As shown in Fig. 1, the total phosphorus removal rate in the supernatant of coating wastewater increased rapidly when the Fe/P and Ca/P molar ratios were increased from 0 to 1.50. When the molar ratio was 1.50, the removal rates of total phosphorus with iron and calcium salts were 94.94% and 90.78%, respectively. As the Fe/P molar ratio increased, the total phosphorus removal rate decreased. When the Fe/P molar ratio was 2.75, the total phosphorus

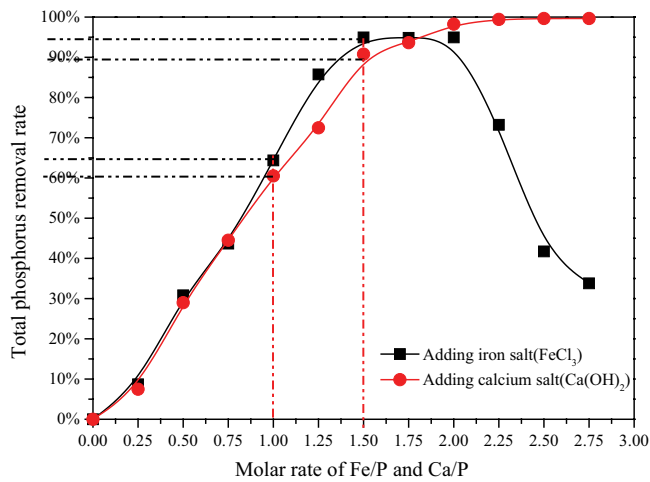


Fig. 1. Change in total phosphorus removal rate with increasing Fe/P and Ca/P molar ratios.

removal rate was 33.80%. However, when the Ca/P molar ratio was increased from 1.50, the total phosphorus removal rate increased slowly and then stabilized. When the Ca/P molar ratio was 2.75, the total phosphorus removal rate was 99.65%. This study shows that the removal rates of phosphorus per mole of iron and calcium salts were 64.37% and 60.51%, respectively.

When iron salt was added to the coating wastewater for phosphorus removal, it mainly existed as ionic Fe^{3+} and as hydroxyl complexes of Fe. Therefore, phosphorus can be removed in two ways when using iron salt.

3.1.1. Ionic Fe^{3+}

The concentrations of the weak acid and base of an easily hydrolyzed substance in coating wastewater, such as phosphorus, varied under different pH conditions. At pH 7, PO_4^{3-} was the main component in coating wastewater, and ionic Fe^{3+} mainly reacted with the dissolved PO_4^{3-} to form

the precipitate FePO_4 [16]. This played an important role in iron salt dephosphorization.

3.1.2. Hydroxyl complexes

The other parts of iron salt were hydrolyzed, yielding different hydroxyl complexes. Iron salt in a polymerized form or coagulant state can totally or partially neutralize the charge in wastewater, allowing the colloidal particles to aggregate into large flocs [24]. The colloidal PO_4^{3-} in the wastewater precipitated through adsorption bridging and floc sweeping. The removal effect of this process was relatively low. Thus, this reaction played an auxiliary role in iron salt phosphorus removal [25]. The acidity of the coating wastewater also increased with the increase in FeCl_3 concentration. This result can be ascribed to the fact that the hydrogen ion generated by the primary hydrolysis of Fe^{3+} reduced the pH of coating wastewater. Then, this increase in acidity inhibited the hydrolysis of Fe^{3+} according to the chemical principle. As shown in Fig. 2a, when the Fe/P molar ratio was increased to 1.50, the pH of the coating wastewater decreased to approximately 2.0. When the pH decreased from 7 to 2, the concentration of PO_4^{3-} gradually decreased, and H_2PO_4^- became the main component. This phenomenon caused part of the phosphate precipitation to redissolved in water, which consequently increased the concentration of the total phosphorus. Hence, the supernatant appeared yellow and turbid because of the excessive addition of iron salt. The change in turbidity with varying molar ratio is demonstrated in Fig. 2b. The turbidity of wastewater increased as the Fe/P molar ratio continued to increase after 1.50. Results showed that the optimal Fe/P molar ratio was 1.50:1 for total phosphorus removal from coating wastewater using iron salt.

When Ca(OH)_2 was added to the coating wastewater and the mechanism was analyzed, the phosphorus removal rate depended on the relative ion concentration and pH of the wastewater. $\text{Ca}_3(\text{OH})(\text{PO}_4)_3$ is the main product of the dephosphorization reaction initiated by adding Ca(OH)_2 . Fig. 3 shows the solubility and supersaturation curves of

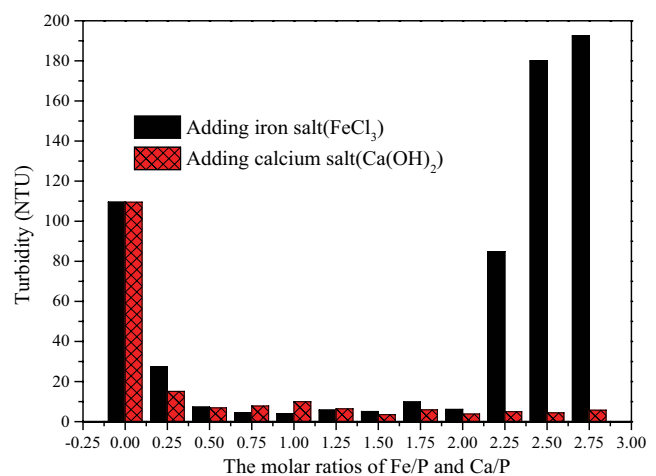
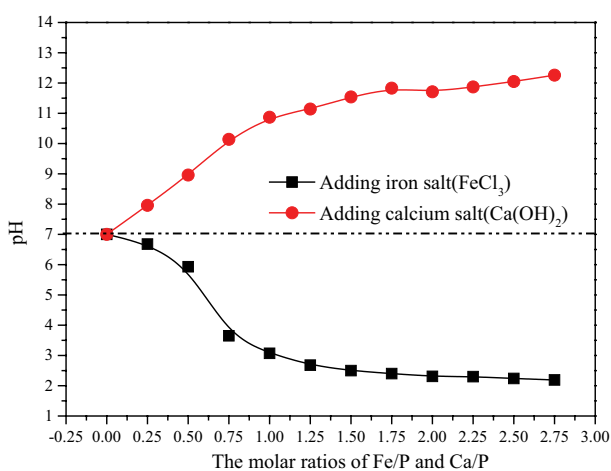


Fig. 2. Effects of different Fe/P and Ca/P molar ratios on coating wastewater treatment: (a) pH change with molar ratio and (b) turbidity change with molar ratio.

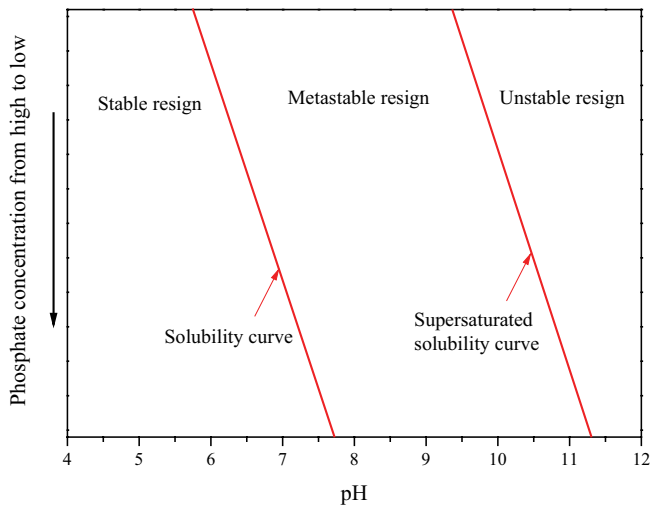


Fig. 3. Solubility and supersaturation curves of $\text{Ca}_5(\text{OH})\cdot(\text{PO}_4)_3$.

$\text{Ca}_5(\text{OH})\cdot(\text{PO}_4)_3$, which can be divided into stable, metastable, and unstable regions. The initial pH of the coating wastewater was 7. Under this condition, no precipitation occurred; the Ca^{2+} , OH^- , and PO_4^{3-} ions in the wastewater remained in the ionic state and the concentrations of Ca^{2+} and OH^- were low. The Ca^{2+} concentration and the pH also increased with increasing Ca/P molar ratio (Fig. 2). In the metastable region, some precipitation formed in the wastewater because the concentrations of the three ions increased with increasing Ca/P molar ratio. Consequently, the ion product was greater than the solubility product, and the main reaction was completed. Ca^{2+} reacted with PO_4^{3-} to form the insoluble precipitates $\text{Ca}_3(\text{PO}_4)_2$ and $\text{Ca}_5(\text{OH})\cdot(\text{PO}_4)_3$, which removed phosphorus from the wastewater.

When iron or calcium salt was used for phosphorus removal and the Fe/P or Ca/P molar ratio was 1.50, the total phosphorus removal rates of iron and calcium salts were 94.94% and 90.78%, respectively. The iron salt method is effective in removing phosphorus from coating wastewater; however, it has some limitations, such as the low pH of the treated effluent, the high cost of iron salt, and the difficulty in dosage control. The use of calcium salts for phosphorus removal is economical and effective but can lead to unacceptably high effluent pH (≥ 10). After determining the properties of iron salt and calcium salt precipitants on phosphorus removal from wastewater, the effect and mechanism of iron–calcium salts were investigated.

3.2. Effect of iron–calcium salt on phosphorus removal

3.2.1. Phosphorus removal rate per unit mole of iron–calcium salt

The results of this experiment can be defined as antagonistic or synergistic. The phenomenon was considered synergistic if the phosphorus removal rate per mole obtained using the iron–calcium salt as a precipitant was higher than the sum of the phosphorus removal rates obtained using the iron or calcium salt alone. The phenomenon was considered antagonistic if the sum of the phosphorus removal rates per mole obtained using the iron or calcium salt alone

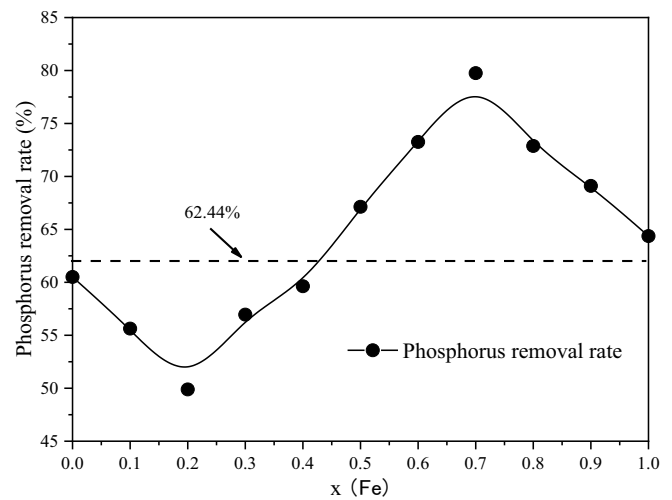


Fig. 4. Change in phosphorus removal rate with $x(\text{Fe})$.

as a precipitant was less than the phosphorus removal rate obtained using the iron–calcium salt [26].

The molar ratio (A/P) of iron–calcium salt (A) to phosphorus (P) was controlled at 1 to investigate the effect of iron–calcium salts on the phosphorus removal rate from coating wastewater. Batch experiments with different dosages of FeCl_3 and $\text{Ca}(\text{OH})_2$ were conducted to investigate the proportion of iron salt ($x(\text{Fe})$) in the iron–calcium salt. The $x(\text{Fe})$ results were 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1.0. As previously mentioned in chapter 3.1, the removal rates of phosphorus per mole of iron and calcium salts in the experiment were 64.37% and 60.51%, respectively. Therefore, the average value of 62.44% was the determining value of synergistic or antagonistic reactions.

The phosphorus removal rate and pH change with $x(\text{Fe})$ are shown in Figs. 4 and 5. As shown in Fig. 4, the phosphorus removal rate decreased when $x(\text{Fe})$ ranged from 0 to 0.2 and reached the lowest value of 49.88% when $x(\text{Fe}) = 0.2$. The phosphorus removal rate continued to increase when $x(\text{Fe})$ increased from 0.2 to 0.7 and reached its maximum value of 79.75% when $x(\text{Fe}) = 0.7$. As $x(\text{Fe})$ continued to increase from 0.7, the removal rate of phosphorus showed a downward trend. When $x(\text{Fe})$ was less than 0.43, the removal rate of phosphorus using the iron–calcium salt was lower than 62.44%, indicating an antagonistic phenomenon. When $x(\text{Fe})$ was greater than 0.43, the removal rate of phosphorus using the iron–calcium salt was higher than 62.44%, indicating a synergistic phenomenon. As shown in Fig. 5, the pH decreased with increasing $x(\text{Fe})$. When $x(\text{Fe})$ was less than 0.51, the pH of the coating wastewater was consistently greater than 7. When $x(\text{Fe})$ was greater than 0.5, the pH of the coating wastewater decreased to approximately 3. The pH of the inlet water of biotreated structures should be within the range of 6.5–9.5 while $x(\text{Fe})$ should be within the range of 0.1–0.5 to meet the influent requirements of subsequent biological treatment.

When $x(\text{Fe})$ was greater than 0.43, the removal effect of phosphorus on coating wastewater was better when iron–calcium salt was used than when iron or calcium salt alone was used. When $x(\text{Fe}) = 0.7$, the phosphorus removal in coating wastewater reached its peak. When $x(\text{Fe})$ was in

the range of 0.1–0.5, the pH of the treated coating wastewater was 6.5–9.5. The results of this study suggest that the iron–calcium salt is the most efficient for phosphorus removal from coating wastewater, and 0.51 is the optimal $x(\text{Fe})$ to reach a pH of 6.5 and the highest phosphorus removal rate of 67.5%.

3.2.2. Effect of phosphorus removal with different A/P molar ratios

After the optimum $x(\text{Fe})$ was determined to be 0.51, the effect of different A/P molar ratios (0, 0.25, 0.50, 0.75, 1.00, 1.25, 1.50, 1.75, 2.00, 2.25, 2.50, and 2.75) on phosphorus removal was investigated.

The changes in phosphorus removal rates with different A/P molar ratios follow the DoseResp equation ($y = -52,736.04 + 52,835.51/(1 + 10^{166 \times (-0.89 - x)})$), with a correlation coefficient of $R_{\text{adj}}^2 = 0.99$ (Fig. 6). When the molar ratio of A/P increased from 1 to 1.50, the removal rate of phosphorus increased rapidly from 67.13% to 96.13%. This trend

continued until the phosphorus removal rate stabilized at approximately 99.65%.

The pH of the effluent with different A/P molar ratios was in the range of 6.5–7.0 and showed minimal change (Fig. 7). This result meets the allowable range of inlet water (6.5–9.5) as per the Code for Design of Outdoor Wastewater Engineering (GB 50014-2006). The turbidity of the effluent was in the range of 3–6 NTU and demonstrated minimal change, indicating that turbidity was effectively and stably removed when the A/P molar ratio was in the range of 1–2.75. As reported in Section 3.1, the use of iron or calcium salt alone affected the pH and turbidity of the treated wastewater; however, the use of iron–calcium salt exerted no significant change. Therefore, the iron–calcium salt method is the most effective for the chemical removal of phosphorus from coating wastewater.

The removal rate of phosphorus in coating wastewater was better when the iron–calcium salt was used than when the iron or calcium salt alone was used. When the A/P molar ratio was 1.50, the phosphorus removal rate of coating

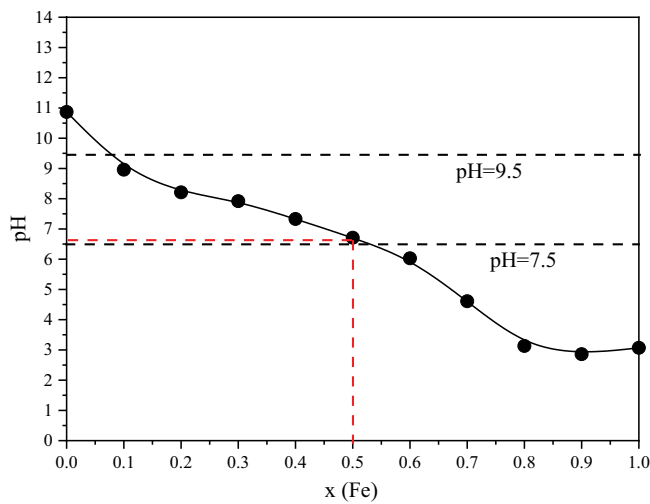


Fig. 5. Change in pH with $x(\text{Fe})$.

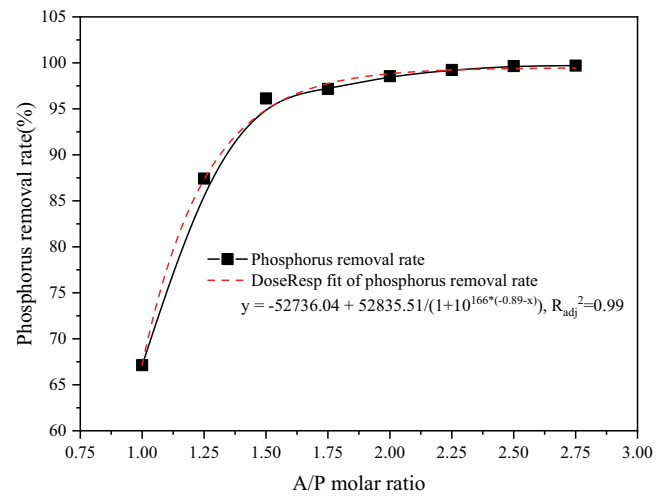


Fig. 6. Change in phosphorus removal rate with A/P molar ratio.

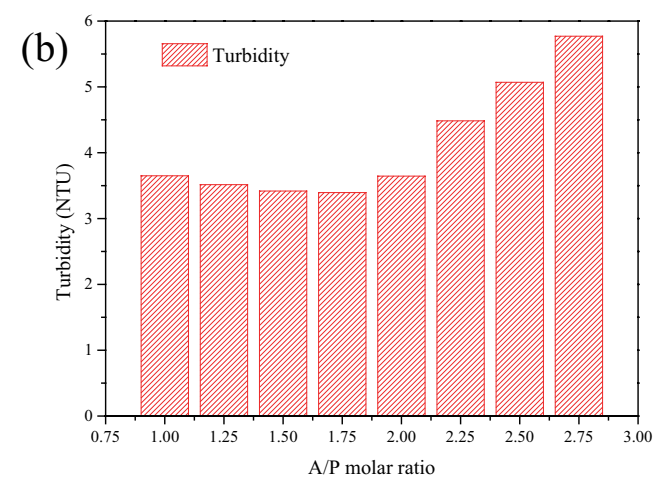
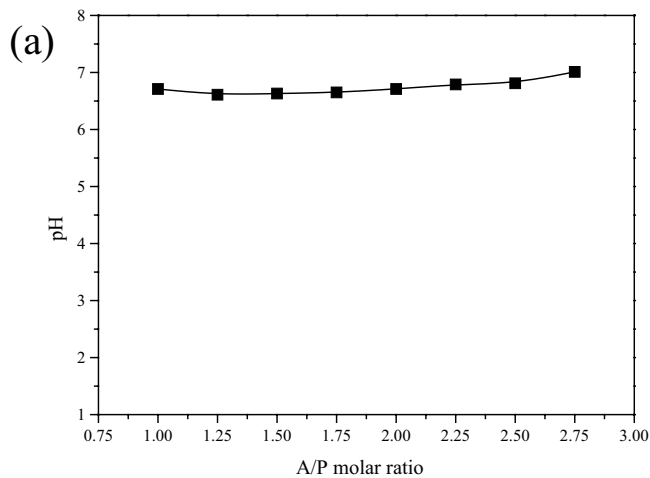


Fig. 7. Effects of different A/P molar ratios on pH and turbidity: (a) pH change with molar ratio and (b) turbidity change with molar ratio.

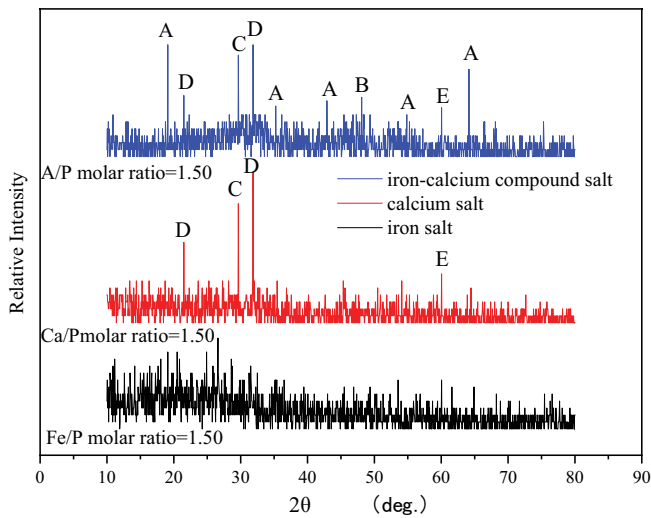


Fig. 8. XRD spectra of three floc samples: (A: $\text{Fe}(\text{OH})_3$; B: FePO_4 ; C: $\text{Ca}_3(\text{PO}_4)_2$; D: $\text{Ca}_5(\text{OH})(\text{PO}_4)_3$; E: $\text{Zn}_3(\text{PO}_4)_2$).

wastewater reached 96.13%, which was higher than that when the iron or calcium salt was used alone (94.94% and 90.78%, respectively), and the pH and turbidity were stable at 6.5–7.0 and 3.0–6.0, respectively. Based on the removal rate of phosphorus and the pH of the treated wastewater, the optimal A/P molar ratio of the iron–calcium salt was 1.50.

3.3. Analysis of precipitation products from chemical phosphorus removal

Three samples were selected for analysis. The samples were the precipitation flocs produced by iron salt, calcium salt, and iron–calcium compound salt at the molar ratio of 1.50. The floc sedimentation products were analyzed by XRD, floc particle sizes were detected by a laser particle size analyzer, and floc morphologies were observed by high-power microscope analysis.

The XRD spectra of the precipitation flocs from different phosphorus removal methods are shown in Fig. 8. The diffraction peaks of the precipitates produced after dephosphorization with iron salt were weak, indicating that their structures were not crystalline and were difficult to be recovered. Conversely, the diffraction peaks of the precipitation flocs generated by calcium salt were clear, indicating crystal formation, which was conducive to phosphorus removal and recovery [27]. $\text{Ca}_5(\text{OH})(\text{PO}_4)_3$ and some $\text{Ca}_3(\text{PO}_4)_2$ precipitates were produced when the Ca/P molar ratio was 1.50. The diffraction peaks of the precipitates produced using the iron–calcium salt was integrated with the diffraction peaks of iron and calcium salt dephosphorization. The precipitates produced using this method included $\text{Fe}(\text{OH})_3$, FePO_4 , $\text{Ca}_3(\text{PO}_4)_2$, and $\text{Ca}_5(\text{OH})(\text{PO}_4)_3$.

Fig. 9 shows the changes in floc size distribution from the three phosphorus removal methods. The diameter of the particles obtained by 50% volume fraction was $D(0.5)$, which is the average size of the precipitate volume [28].

Fig. 9 shows that for the iron salt method, the particle size $D(0.5) = 53.75 \mu\text{m}$ when the Fe/P molar ratio was 1.50. For the calcium salt method, the particle size $D(0.5) = 24.1$

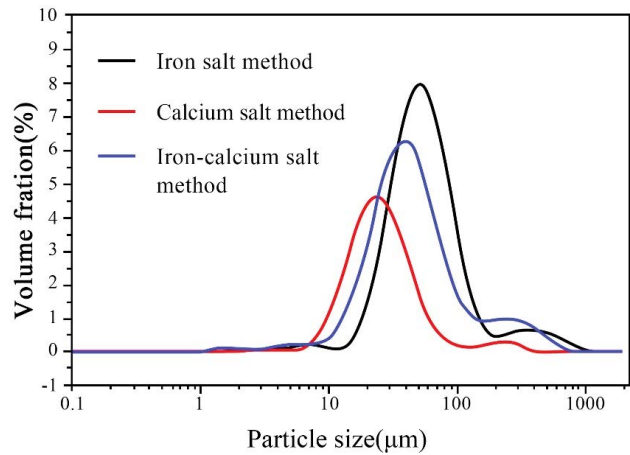
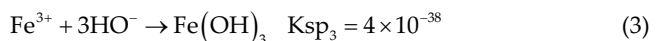
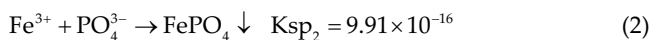
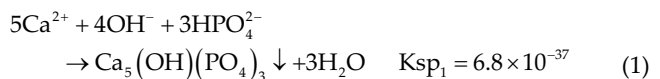


Fig. 9. Floc size distribution with different phosphorus removal methods.

μm when the Ca/P molar ratio was 1.50. Finally, for the iron–calcium salt method, the particle size $D(0.5) = 39.90 \mu\text{m}$ when the A/P molar ratio was 1.50. This is in the range of the particle sizes from the iron and calcium methods. It means that the precipitated flocs produced using the iron–calcium salt demonstrate the advantages of iron and calcium salts in phosphorus removal.

Using the iron–calcium salt is a better phosphorus removal method than using the iron or calcium salt alone. This result may be ascribed to the effect of phosphorus from coating wastewater on the flocs formed from the addition of iron and calcium salts. The main reactions between phosphorus and iron or calcium salts are shown in Eqs. (1)–(3) [29,30]. The solubility product floc precipitate has been listed in each reaction equation.



As shown in the above reaction equations, $K_{\text{sp}3} < K_{\text{sp}1} < K_{\text{sp}2}$. Therefore, when the iron–calcium salt was used to treat the coating wastewater and PO_4^{3-} and OH^- existed simultaneously, Ca^{2+} ions were more likely to react with PO_4^{3-} to form $(\text{Ca})_5(\text{OH})(\text{PO}_4)_3$ and Fe^{3+} ions were more likely to react with OH^- to form $\text{Fe}(\text{OH})_3$. The precipitation floc particle size produced using the calcium salt method was small and did not easily settle in the coating wastewater. The removal of phosphorus using iron salt produced a relatively large floc that accelerated the settling rate of insoluble phosphate precipitation in the coating wastewater. The precipitation produced using the iron–calcium salt integrated the advantages of using the iron and calcium salts alone, which improved the

efficiency of phosphorus removal and accelerated the sedimentation rate in the coating wastewater.

4. Conclusion

The phosphorus removal rates obtained using the iron and calcium salt methods were 94.94% and 90.78%, respectively, when the Fe/P and Ca/P molar ratios were set to 1.50. Iron salt decreases the pH of the treated effluent and has high cost, along with difficulty in dosage control. Calcium salt results in an unacceptable effluent pH exceeding 10.

When $x(\text{Fe})$ was less than 0.43, the phosphorus removal rate with the iron–calcium salt method was less than 62.44% of the average value obtained with the iron and calcium salt methods alone. This result indicates that the iron–calcium salt method demonstrated an antagonistic effect on phosphorus removal from coating wastewater. When $x(\text{Fe})$ was greater than 0.43, the iron–calcium salt method exhibited a synergistic effect.

When the A/P molar ratio was 1.50, the removal rate of phosphorus was higher when iron–calcium salt was used than when iron or calcium salt alone was used. The phosphorus removal rate reached 96.13%. Additionally, there is little change in the pH and turbidity of coating wastewater after treatment at different A/P molar ratios, which stay in the range of 6.5–7.0 and 3.0–6.0, respectively.

The iron–calcium salt method integrated the advantages of the iron and calcium salt methods to improve the phosphorus removal rate and accelerate the sedimentation rate of the precipitates in coating wastewater.

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