Open Access Library Journal
2026, Volume 13, e14994
ISSN Online: 2333-9721
ISSN Print: 2333-9705

Different Calcium Sources Used in HAP Reactions for Phosphorus Removal from Wastewater

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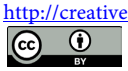
How to cite this paper: Feng, Z.Z. (2026) Different Calcium Sources Used in HAP Reactions for Phosphorus Removal from Wastewater. *Open Access Library Journal*, **13**: e14994.
https://doi.org/10.4236/oalib.1114994

Received: February 5, 2026
Accepted: March 3, 2026
Published: March 6, 2026



Abstract

The hydroxyapatite crystallization method (HAP) was employed as a phosphorus recovery technology to investigate the effects of different calcium sources on phosphorus removal and recovery from phosphorus-containing wastewater. The results indicate that when $CaCl_2$ was used as the sole calcium source, NaOH was required to be added during the reaction to maintain an alkaline environment, resulting in a PO_4^{3-}-P removal efficiency exceeding 80%. When CaO was used as the sole calcium source, PO_4^{3-}-P removal exceeded 70%; however, the supernatant pH increased to above 11 after the reaction. When $CaCl_2$ and CaO were combined as the calcium source, a $CaCl_2$/CaO mass ratio of 2.6 resulted in a PO_4^{3-}-P removal efficiency of approximately 80%, while the supernatant pH remained at 7.8 after the reaction. The proposed mixed $CaCl_2$/CaO calcium source provides new insights into the HAP crystallization process and supports the integration of HAP crystallization with biological phosphorus removal technologies, thereby enabling the simultaneous recovery and reuse of phosphorus resources.

Subject Areas

Environmental Chemistry

Keywords

Hydroxyapatite Crystallization Method (HAP), $CaCl_2$, CaO, Phosphorus Removal

1. Introduction

Phosphorus is a vital non-renewable resource that plays a crucial role in agricul-

ture and industry. However, the world currently faces a widespread phosphorus crisis. Despite global phosphate rock reserves exceeding 30 billion tons, economically viable high-purity phosphate resources are extremely limited, with estimates suggesting these reserves may only meet demand for less than 50 years. Studies indicate that at current consumption rates, global phosphate reserves could be depleted within 100 to 400 years, leading to its classification as a critical mineral [1] [2].

Consequently, phosphorus enters water bodies through anthropogenic activities such as wastewater discharge and the excessive application of fertilizers and pesticides. Excessive phosphorus emissions cause eutrophication, a key factor in water quality deterioration and algal blooms [3]. In response, various treatment technologies, including biological methods, chemical precipitation, adsorption, and ion exchange, have been developed. Chemical precipitation is particularly effective for high-phosphorus wastewater streams (e.g., from livestock farming or sludge digestion) and also generates phosphate by-products, thereby enabling the recovery and regeneration of phosphorus resources [4].

Among chemical precipitation methods, recovery in the form of hydroxyapatite (HAP) or magnesium ammonium phosphate (MAP) via crystallization is prominent. While MAP crystallization offers high efficiency and stability, it faces challenges such as higher costs and specific nitrogen requirements [5]. In contrast, the HAP process has emerged as a primary route for phosphorus recovery due to its lower cost and operational simplicity.

HAP crystallization is a kinetic process involving nucleation and growth, influenced by factors such as pH, supersaturation, and temperature [5]. Calcium chloride ($CaCl_2$) is commonly used as the calcium source, with NaOH typically added to maintain the alkaline pH necessary for efficient PO_4^{3-}-P removal and crystallization [6]. However, in practical applications, the use of high-concentration NaOH is limited by its corrosivity and the operational complexity associated with its continuous addition. To streamline the process, calcium oxide (CaO), a common alkaline substance, can be considered as an alternative [7]. Upon hydration, CaO provides both calcium ions and alkalinity, satisfying the key requirements for HAP formation. This property of CaO effectively eliminates the need for separate NaOH addition. Furthermore, studies have shown that calcination of precursors can yield highly crystalline and dispersed HAP nanoparticles [8]. A significant drawback of using CaO alone, however, is the persistently high alkalinity (pH > 11) of the post-reaction supernatant, which complicates subsequent discharge or reuse. Considering the respective advantages and disadvantages of $CaCl_2$ and CaO, this study proposes a novel approach combining both calcium sources.

The objectives of this study are: 1) to investigate the factors influencing HAP formation using $CaCl_2$ alone; 2) to investigate the factors influencing HAP formation using CaO alone; 3) to investigate the factors influencing HAP formation when CaO and $CaCl_2$ are combined, with the aim of eliminating the need for ex-

ternal alkali addition and reducing the final solution pH.

2. Materials and Methods

2.1. Experimental Setup

Using a magnetic stirring apparatus to investigate the performance of CaO alkalinity, as shown in Figure 1. The beaker has a volume of 1 L, equipped with an internal rotor to ensure thorough reaction. A pH meter is employed to monitor pH changes in the solution during dissolution.

Batch experiments for HAP phosphorus recovery using a six-stage coagulation mixer (ZR4-6) were conducted. The schematic diagram of the apparatus is shown in Figure 2. Reaction conditions under various parameters were investigated, and the pH of the solution during dissolution was monitored using a pH meter. In these six-link coagulation mixer, each container is placed openly, and the agitator blades are vertical flat plates.

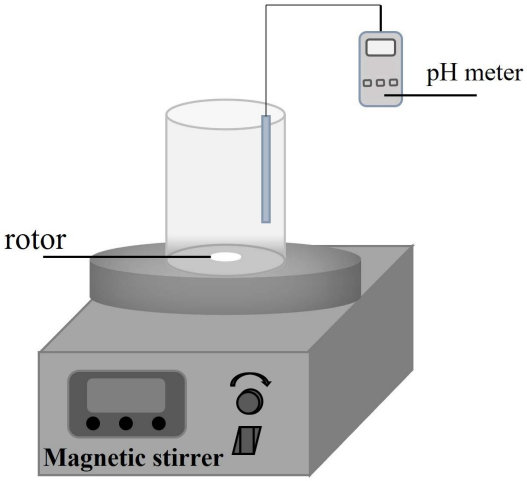


Figure 1. Magnetic stirrer.

Figure 2. Six-stage coagulation mixing unit.

2.2. Experimental Materials

In this experiment, simulated wastewater was used, PO_4^{3-}-P is provided solely by KH_2PO_4, without any Mg^{2+}, NH^{4+}, or carbonate, with a PO_4^{3-}-P concentration

ranging from 50 to 200 mg/L. OH^- was supplied by a 2 mol/L NaOH solution. Additionally, the $CaCl_2$ and CaO used in the experiment were both analytical grade, with a purity exceeding 98%.

2.3. Experimental Design

The experimental temperature was maintained at 25˚C± 1˚C, and samples were taken immediately upon reaching the preset reaction time. The duration of sedimentation was calculated from the time stirring stopped, and the supernatant was collected 3 ± 1 cm below the liquid surface after static settling.

2.3.1. Experiments with $CaCl_2$ as the Sole Calcium Source

When $CaCl_2$ was used as the calcium source, PO_4^{3-}-P removal was investigated under the following conditions: 1) At a fixed Ca/P molar ratio of 1.6, solutions with initial PO_4^{3-}-P concentrations of 50, 100, 150, and 200 mg/L were prepared. The initial pH was adjusted to 9.5, and no alkali was added during the 15-minute stirring period, followed by precipitation. 2) With an initial PO_4^{3-}-P concentration of 90 mg/L, Ca/P molar ratios were varied (1.6, 1.8, 2.0, 2.2, 2.4, 2.6). After 15 min of stirring and 1 h of precipitation, PO_4^{3-}-P removal and Ca^{2+} utilization rates were determined. 3) At Ca/P = 1.6 and initial PO_4^{3-}-P about 90 mg/L, experiments were conducted with and without the addition of 5 wt% calcite seed crystals. The pH was maintained near 9.5 by titrating with a 2 mol/L NaOH solution during the 15 min reaction. 4) Conditions were similar to 3), but the pH was maintained between 7 and 8.

2.3.2. Experiments with CaO as the Sole Calcium Source

1) Alkalinity contribution: Varying masses of CaO (0.01 - 0.05 g) were added to 200 mL deionized water under stirring, and the stabilized pH was recorded. 2) At Ca/P = 1.6 and initial PO_4^{3-}-P concentrations of 50 and 100 mg/L, reactions proceeded for 15 min followed by 1 h precipitation. 3) Six 500 mL samples of a saturated CaO solution (1.29 g/L) were prepared. KH_2PO_4 was added to achieve Ca/P ratios from 1.6 to 2.6. After 15 min stirring and 1 h precipitation, PO_4^{3-}-P removal and final pH were measured.

2.3.3. Experiments with a Blended $CaCl_2$/CaO Calcium Source

1) At a $CaCl_2$/CaO mass ratio of 1:1 and initial PO_4^{3-}-P of 100 mg/L, residual PO_4^{3-}-P and pH were monitored over time. 2) The mass ratio was varied (1.0, 2.6, 3.4), and residual PO_4^{3-}-P and pH were measured after 15 min stirring and 1 h settling. 3) At an optimal mass ratio of 2.6, the effect of stirring speed (200, 250, 300, 350 rpm) on PO_4^{3-}-P removal was examined (initial PO_4^{3-}-P = 90 mg/L).

2.4. Analytical Methods

To ensure data reliability, three measurements were taken for each water sample, and the average value was calculated. Prior to analysis, all aqueous samples were

filtered through a 0.45 μm polyethersulfone (PES) membrane. Orthophosphate (PO_4^{3-}-P) concentration was determined using standard methods [9]. pH was measured using a portable meter (Hach HQ40d, USA). The actual pH does not differ from the preset pH by more than 0.5.

2.5. Calculation

Phosphorus removal efficiency (%)

$$\text{Phosphorus removal efficiency}(\%) = \frac{C_0 - C_1}{C_0} \times 100\% \quad (1)$$

C_0 is the initial concentration of PO_4^{3-}-P in the solution (mg/L), and C_1 is the concentration of PO_4^{3-}-P after the reaction (mg/L).

Ca^{2+} removal efficiency (%)

$$Ca^{2+} \text{ removal efficiency}(\%) = \frac{C_{0'} - C_{1'}}{C_{0'}} \times 100\% \quad (2)$$

$C_{0'}$ is the initial concentration of Ca^{2+} in the solution (mg/L), and $C_{1'}$ is the concentration of Ca^{2+} after the reaction (mg/L).

Ca/P Molar Ratio: Moles of Ca (molar mass 40) per mole of P (molar mass 31).

3. Results and Discussion

3.1. Factors Affecting the Use of $CaCl_2$ in HAP Recovery Methods

3.1.1. Initial P concentration Value

Calcium was supplied as $CaCl_2$, and the initial pH was adjusted to 9.5. No NaOH was added to control the pH during the reaction. As shown in **Figure 3**, the

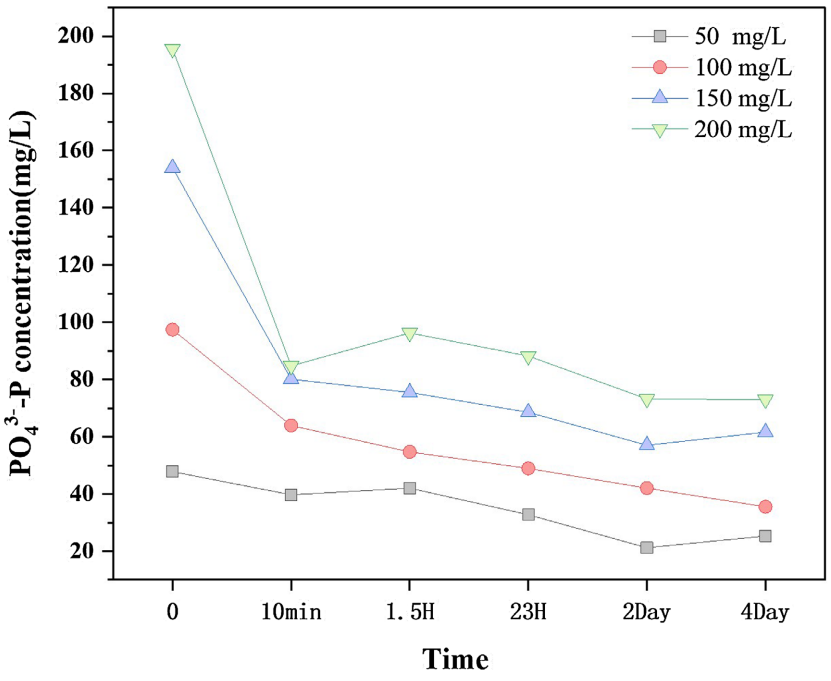


Figure 3. Reaction of $CaCl_2$ with different concentrations of PO_4^{3-}-P .

PO_4^{3-}-P concentration decreased significantly after 10 minutes of stirring at all concentrations tested. A higher initial PO_4^{3-}-P concentration resulted in a more rapid decrease in PO_4^{3-}-P concentration. For example, with an initial PO_4^{3-}-P concentration of 50 mg/L, the removal rate after 10 minutes was only 22.53%. In contrast, at an initial concentration of 200 mg/L, the removal rate reached 57.68% within the same time period. This trend is consistent with the principle that higher initial reactant concentrations favor the forward progression of the reaction [10]. The reaction rate is directly proportional to the reactant concentration. Consequently, elevated phosphate concentrations increase the activity of PO_4^{3-}-P in solution, thereby driving the reaction toward hydroxyapatite (HAP) formation. After stirring was ceased, the PO_4^{3-}-P concentration decreased slowly and exhibited fluctuations. This behavior can be attributed to intermediate phase transitions during HAP formation. Amorphous calcium phosphate (ACP) forms rapidly initially and then gradually converts to more stable phases, such as octacalcium phosphate (OCP) or dibasic calcium phosphate (DCPD), over prolonged reaction time [11]. Simultaneously, the adsorption of ions onto the surfaces of the formed HAP crystals contributed to fluctuations in the residual PO_4^{3-}-P concentration. In summary, for the HAP crystallization process, a higher initial PO_4^{3-}-P concentration yielded a higher removal rate within the same reaction period. Furthermore, even without the addition of NaOH for pH control during the reaction, PO_4^{3-}-P removal rates of 50% - 60% were achievable.

3.1.2. Ca/P Molar Ratio

The effect of varying the Ca/P molar ratio on the reaction is presented in **Figure 4**. In these experiments, the initial PO_4^{3-}-P concentration was fixed at 90 mg/L, and no NaOH was added for pH adjustment. When the Ca/P molar ratio was increased from 1.6 to 2.6, the effluent PO_4^{3-}-P concentration decreased from 60.80 mg/L to 45.81 mg/L, corresponding to an increase in the PO_4^{3-}-P removal rate from 34.71% to 48.45%. This improvement is attributed to the increased Ca^{2+} concentration, which enhances solution supersaturation. This, in turn, strengthens the crystallization kinetics and shifts the equilibrium toward the formation of hydroxyapatite (HAP). Consequently, at a fixed initial PO_4^{3-}-P concentration, a greater proportion of PO_4^{3-}-P ions are incorporated into HAP, leading to a lower final PO_4^{3-}-P concentration [12]. Simultaneously, in the early stages of the reaction during the formation of precursors like amorphous calcium phosphate (ACP), Ca^{2+} neutralizes surface charges. This reduction in electrostatic repulsion between particles accelerates nucleation, enhances PO_4^{3-}-P binding, and thereby improves the overall reaction efficiency.

Furthermore, as the Ca/P molar ratio was raised, the calculated Ca^{2+} removal rate exhibited a decreasing trend, declining from 33.26% to 27.34%. Although a higher Ca^{2+} input promotes HAP formation and nucleation, an excessively high Ca^{2+} concentration at a fixed PO_4^{3-}-P level significantly exceeds the stoichiometric requirement for HAP. This leads to incomplete utilization of Ca^{2+} and its

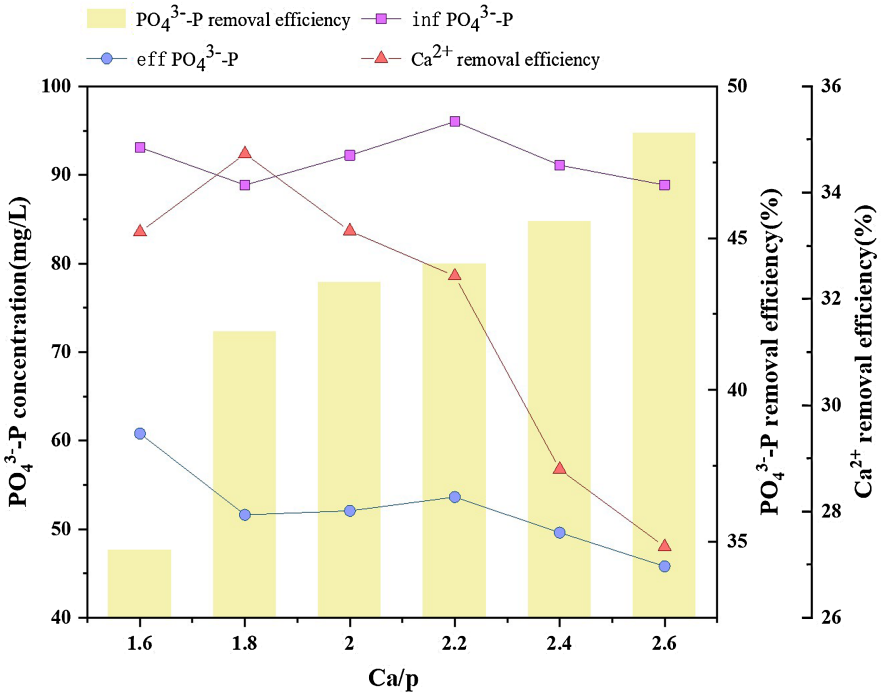


Figure 4. Reaction behavior of $CaCl_2$ and PO_4^{3-}-P at different Ca/P molar ratios.

residual accumulation, resulting in the precipitation of side products such as $Ca(OH)_2$ and $CaCO_3$ [13]. Consequently, the Ca^{2+} removal rate shows an inverse relationship with its dosage. Therefore, to ensure high Ca^{2+} utilization—*i.e.*, a low residual Ca^{2+} concentration after the reaction—a Ca/P molar ratio of 1.6 was selected for subsequent experiments.

3.1.3. pH and Seed Crystal Addition

The reaction was conducted at a Ca/P molar ratio of 1.6 without seed crystals. A 2 mol/L NaOH solution was continuously added dropwise during the initial 15 minutes to maintain the pH at approximately 9.5. As shown in **Figure 5** for an initial PO_4^{3-}-P concentration of 94.13 mg/L, the concentration decreased to 14.16 mg/L after 5 minutes. After 15 minutes, the concentration was 16.28 mg/L, and after 1 hour, it reached 14.82 mg/L. Under these pH-maintained conditions, the PO_4^{3-}-P removal rate reached 84%, which is significantly higher than the rate observed without NaOH replenishment.

The formation of HAP is significantly influenced by the system pH, as the overall reaction consumes alkali. Previous studies indicate that the crystallization efficiency of HAP is optimal within a pH range of 9.0 - 10.0 [4]. The system pH decisively governs the speciation of phosphate (PO_4^{3-}-P) in aqueous solution. As alkalinity increases, the molar fraction of phosphate species favorable for HAP crystallization increases. This promotes the forward reaction and accelerates the crystallization process. Therefore, the timely supplementation of alkali during the reaction enhances phosphate utilization and removal [14].

In a parallel experiment, 5 wt% calcite was added as a seed crystal prior to the

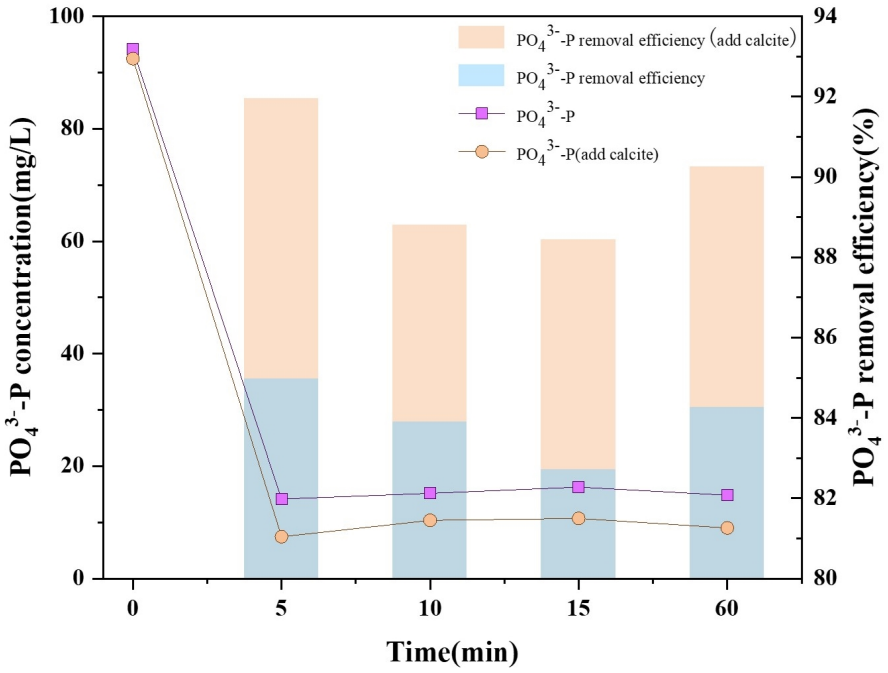


Figure 5. Reaction of PO_4^{3-}-P under pH and seed addition conditions.

reaction. This resulted in a decrease in the PO_4^{3-}-P concentration to 7.45 mg/L after 5 minutes. The removal rate reached 90.25% within 1 hour, representing a significant increase compared to the control group without seed crystals. The addition of seed crystals promotes heterogeneous nucleation. Compared to homogeneous nucleation, heterogeneous nucleation on the provided surfaces lowers the activation energy barrier. This enables the reaction to proceed without requiring high supersaturation, thereby shortening the induction period and accelerating the overall reaction rate. Furthermore, the atomic arrangement on the calcite surface closely resembles that of HAP crystals, which enhances the efficiency of phosphorus fixation [15] [16].

3.1.4. Low Alkalinity Provides

To further investigate the influence of alkalinity on HAP formation and to ensure that the supernatant after precipitation would have low alkalinity suitable for direct discharge, the solution pH was maintained between 7 and 8 throughout the reaction. The removal efficiency after a 30-minute reaction period is shown in Figure 6. Initially, the pH was 9.5. Upon the addition of $CaCl_2$, the pH decreased to 7.45 within 2 minutes, while the PO_4^{3-}-P concentration dropped to 48.94 mg/L. Subsequently, NaOH was added dropwise to stabilize the pH within the target range of 7 - 8. As the reaction progressed, the PO_4^{3-}-P concentration decreased, whereas the removal rate increased. After 30 minutes, the PO_4^{3-}-P concentration had decreased to 18.96 mg/L, and the removal rate had increased to 79.58%. Maintaining a near-neutral pH throughout the reaction process thus enabled a high PO_4^{3-}-P removal rate. This outcome supports the potential for subsequent supernatant reuse or direct discharge.

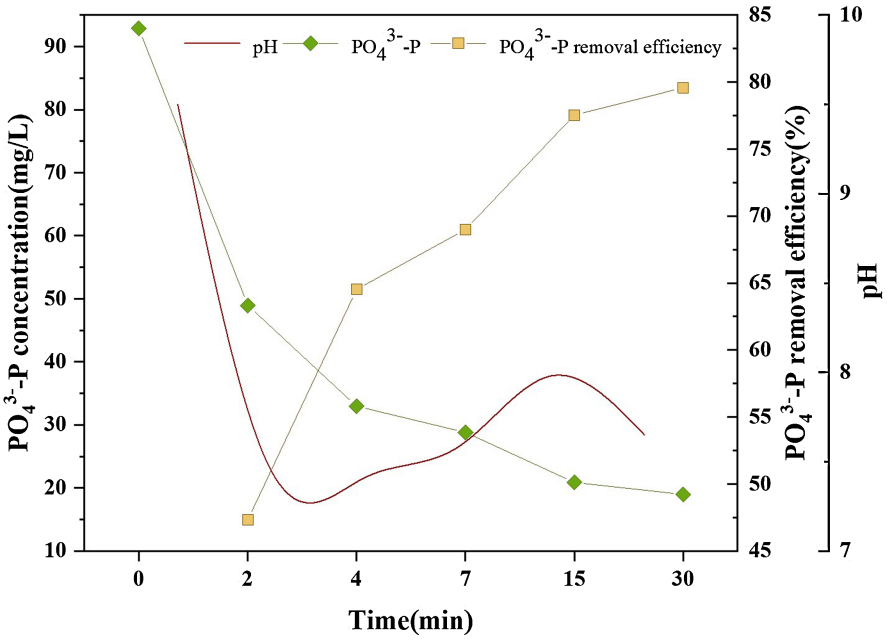


Figure 6. Removal of PO_4^{3-}-P during low pH reactions.

3.2. Factors Affecting the Use of CaO in HAP Recovery Methods

3.2.1. CaO Contributes to Alkalinity

Calcium oxide (CaO) reacts with water to form sparingly soluble calcium hydroxide ($Ca(OH)_2$), thereby increasing the solution alkalinity. Figure 7 illustrates the pH changes in a 200 mL deionized water solution upon the addition of varying masses of CaO. The initial pH of the deionized water ranged from 7.52 to 7.98.

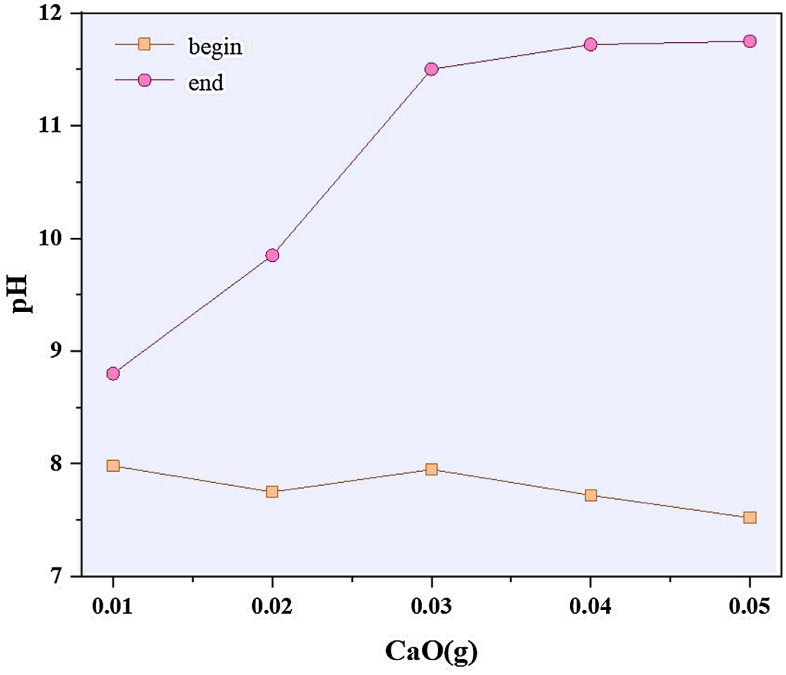


Figure 7. CaO solution pH.

When the mass of added CaO was increased from 0.01 to 0.05 g, the solution pH rose from 8.8 to 11.75 after stabilization, indicating a highly alkaline environment. The rate of pH increase diminished as the mass of added CaO increased. This can be attributed to the dispersion efficiency of CaO particles during mixing. Additionally, carbon dioxide from the air was absorbed by the highly alkaline solution through the open container during the dissolution of CaO to $Ca(OH)_2$. This consumption of OH^- ions caused the measured pH to fall below the theoretical value. In summary, within conventional treatment systems, CaO serves as an effective source of alkalinity, creating a highly alkaline environment that meets the requirements for HAP formation.

3.2.2. Initial P Concentration Value

CaO was utilized as the reactant for HAP formation to supply Ca^{2+} ions and maintain an alkaline environment upon dissolution. The removal efficiency for different initial PO_4^{3-}-P concentrations after 15 min of reaction and 1 h of precipitation is shown in Figure 8. In the absence of calcite seed crystals, the PO_4^{3-}-P concentration decreased markedly after 15 min. For an initial concentration of 53.56 mg/L, it dropped to 13.14 mg/L, while for an initial concentration of 104.37 mg/L, it declined to 27.00 mg/L. Following a 1-hour precipitation period, the PO_4^{3-}-P concentration remained relatively unchanged, with a removal rate consistently around 76.84%. As CaO reacts with water and binds phosphate, the system approaches equilibrium, whereby the residual ion concentrations are governed by their solubility products. Upon completion of the reaction, the concentrations of PO_4^{3-}-P , OH^-, and Ca^{2+} stabilize at a fixed stoichiometric ratio. Therefore, given sufficient alkalinity, the PO_4^{3-}-P removal rate converges to a consistent value after 1 hour of precipitation.

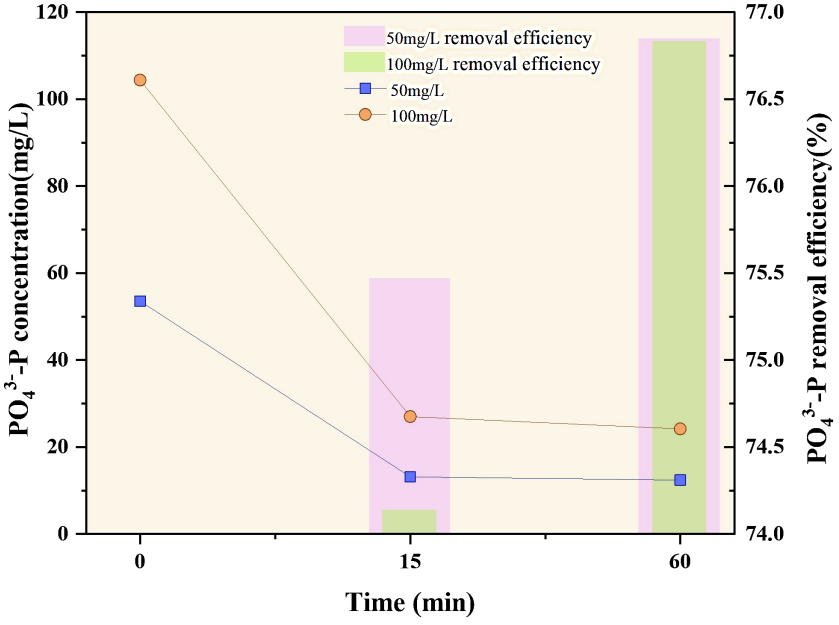


Figure 8. Reaction of CaO with different concentrations of PO_4^{3-}-P .

3.2.3. Ca/P Molar Ratio

A freshly prepared saturated CaO solution (1.29 g/L) was used. Different Ca/P molar ratios were established by adding varying masses of potassium dihydrogen phosphate (KH_2PO_4). The corresponding reaction outcomes are presented in **Figure 9**. As the Ca/P molar ratio was decreased from 2.6 to 1.6, the mass of P added increased from 138 to 225.4 g, whereas the residual mass of P rose from 0.3 to 62.95 g. Consequently, the P removal rate decreased from 99.77% to 72.07%. Correspondingly, the final solution pH after 1 h of precipitation dropped from 12.44 to 11.91 as the Ca/P molar ratio was lowered.

Under conditions of CaO saturation, the OH^- concentration remains constant, sustaining a highly alkaline environment. Higher pH values promote greater supersaturation during nucleation, which accelerates crystal growth [17]. An increase in the amount of P reactant leads to greater participation of phosphate in HAP formation. This consumes more OH^- in the early stage of the reaction, causing a more pronounced decrease in the solution pH. As the reaction proceeds, the available Ca^{2+} becomes limiting. Consequently, fewer Ca^{2+} ions combine with the remaining phosphate, thereby reducing its removal rate.

Compared with $CaCl_2$, which supplies Ca^{2+} but requires NaOH addition to maintain alkalinity, CaO inherently sustains an alkaline environment through its dissolution while achieving comparable removal rates. However, the supernatant pH after 1 h of precipitation consistently exceeded 11.5, indicating a persistently highly alkaline state that is unsuitable for subsequent processing. First, a high pH promotes the formation of unstable intermediate phases such as amorphous calcium phosphate (ACP), which are prone to redissolution. Furthermore, the high alkalinity of the supernatant precludes its direct discharge, necessitating a neutralization step prior to any further processing or disposal.

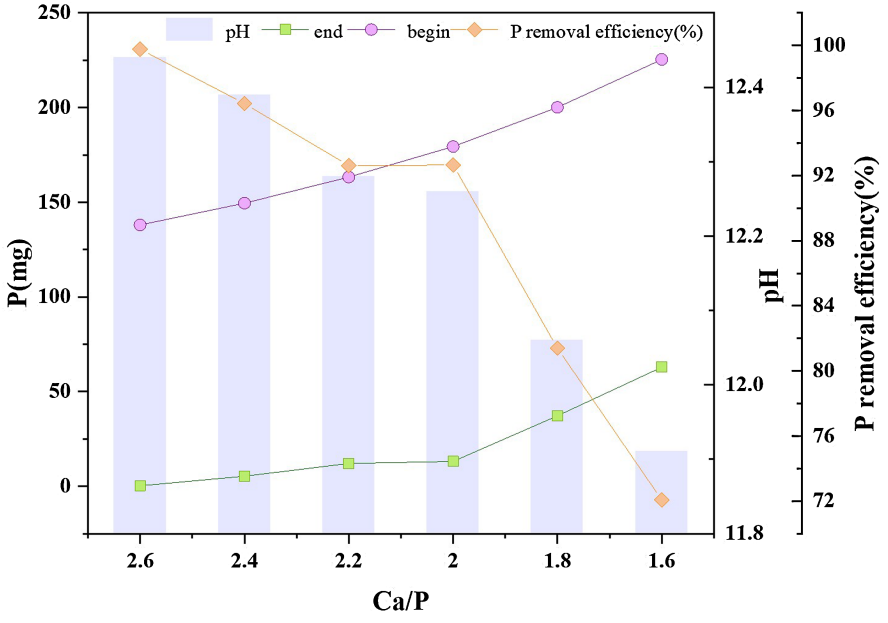


Figure 9. Reaction behavior of CaO with PO_4^{3-}-P at different Ca/P molar ratios.

3.3. $CaCl_2$ Combined with CaO for Phosphorus Recovery

3.3.1. Equal Amounts of $CaCl_2$ and CaO are Used for HAP Formation

The temporal variations in residual PO_4^{3-} concentration and pH under continuous stirring, at a $CaCl_2$-to-CaO mass ratio of 1:1, are shown in Figure 10. As the reaction progressed, both parameters gradually stabilized. The initial pH was 10.85 with a PO_4^{3-}-P concentration of 98.55 mg/L. After 3 min, the pH decreased to 8.98 and the concentration to 15.27 mg/L. After 5.5 h, the pH had further decreased to 7.76 and the concentration to 12.70 mg/L. Throughout the reaction, the PO_4^{3-}-P removal rate ranged from 82.23% to 87.53%, indicating a high and stable removal efficiency.

The use of a 1:1 mass ratio of $CaCl_2$ to CaO proved to be a feasible strategy for HAP formation. This approach addresses two key limitations: it eliminates the need for continuous alkali supplementation (as required when using $CaCl_2$ alone) and avoids the persistently high pH associated with reactions using only CaO. After 16 min, the pH reached 8.77. Achieving a pH below 8 required an impractically long time. Therefore, the mass ratio of $CaCl_2$ to CaO was adjusted in subsequent experiments to further investigate the reaction dynamics.

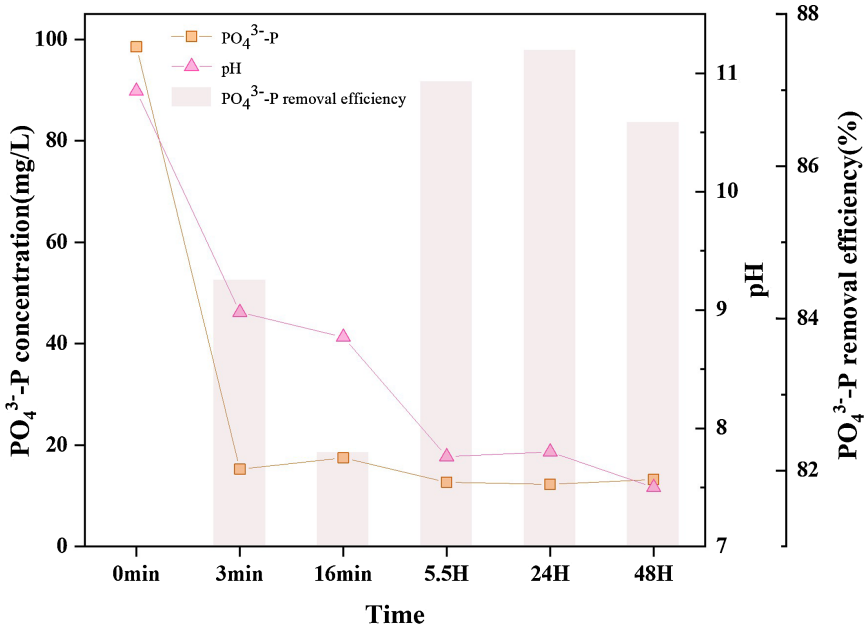


Figure 10. Reaction of equal amounts of $CaCl_2$/CaO with PO_4^{3-}-P .

3.3.2. $CaCl_2$ Combined with CaO for Phosphorus Recovery

The effects of varying the mass ratios of $CaCl_2$ to CaO on the reaction are summarized in Figure 11. As the mass ratio of $CaCl_2$/CaO increased, the proportion of CaO correspondingly decreased. When the mass ratio was increased from 1.0 to 3.4, the initial pH decreased from 10.4 to 9.5. Following 15 min of stirring and a subsequent 1 h precipitation period, the pH further decreased from 8.24 to 7.8. The reduced proportion of CaO decreased the availability of OH^- ions, thereby lowering the initial pH. Nevertheless, sufficient OH^- was supplied to sustain the

HAP formation reaction.

At the fixed Ca/P molar ratio of 1.6, $CaCl_2$ served as the Ca^{2+} source. Simultaneously, it inhibited the dissolution of $Ca(OH)_2$ through the common-ion effect and promoted the forward OH^--consuming reaction, both of which favored HAP formation. Consequently, after 1 h of precipitation, the PO_4^{3-}-P concentration decreased from 23.14 to 17.80 mg/L, resulting in a corresponding increase in the phosphate removal rate.

Under the condition of a Ca/P molar ratio of 1.6, when the mass ratio of $CaCl_2$/CaO is 2.6, CaO provides both the calcium source and alkalinity. After reacting for 15 minutes and precipitating for 1 hour, the pH of the reaction solution decreased from an initial 9.8 to 7.8, and the removal rate of PO_4^{3-}-P was 79.36%, which is similar to the result when NaOH is used to provide alkalinity (3.1.4). When NaOH provides alkalinity, after reacting for 30 minutes, the solution pH decreased from 9.5 to 7.65, and the PO_4^{3-}-P removal rate was 79.58%. The pH drop is basically the same in both cases, indicating that under the reaction conditions with a $CaCl_2$/CaO mass ratio of 2.6, the alkalinity required for the HAP reaction can be met. Compared with using NaOH to provide alkalinity, the reaction process is easy.

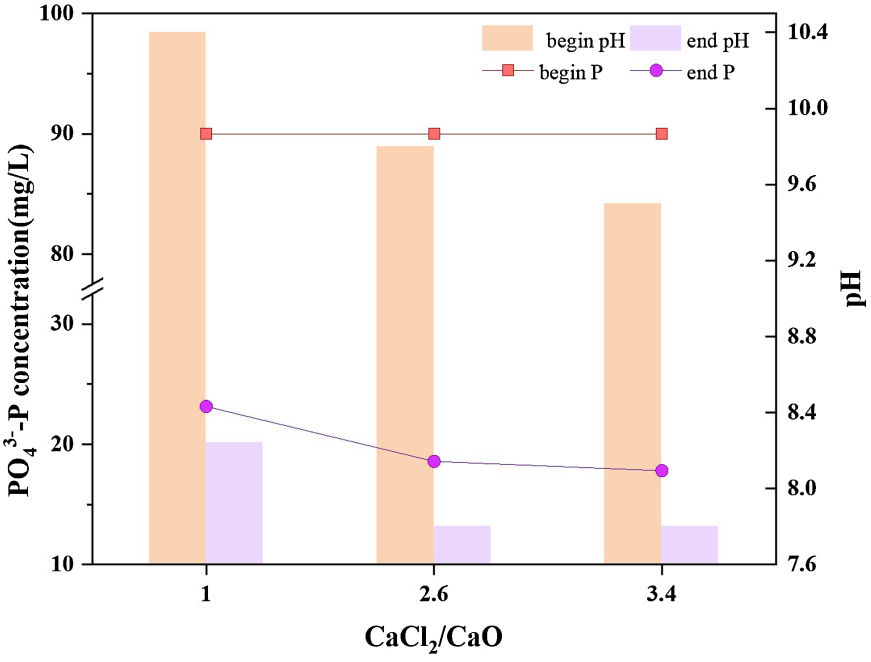


Figure 11. Reaction of different amounts of $CaCl_2$/CaO with PO_4^{3-}-P .

3.3.3. Speed Influence

The PO_4^{3-}-P removal efficiency at a $CaCl_2$-to-CaO mass ratio of 2.6 is shown in Figure 12. Experiments were conducted at stirring speeds of 200, 250, 300, and 350 rpm with an initial PO_4^{3-}-P concentration of 90 mg/L, followed by 15 min of stirring and 1 h of settling. At 200 rpm, the PO_4^{3-}-P removal rate was 79.37%, increasing to 81.59% at 350 rpm. However, at intermediate speeds of 250 and 300

rpm, the removal rate decreased to approximately 77.7%.

At lower stirring speeds, the precipitates formed were larger and settled more rapidly. As the stirring speed increased, the enhanced shear forces mechanically disrupted the initially formed precipitates, breaking them into finer particles. This resulted in a higher residual PO_4^{3-}-P concentration after settling, corresponding to the observed decrease in removal rate at intermediate speeds. At even higher stirring speeds, a secondary nucleation process was readily induced. The intensified turbulence promoted collisions between particles and microcrystals, facilitating their aggregation and growth. This led to a reduction in the residual PO_4^{3-}-P concentration [18], explaining the recovery of the removal rate at 350 rpm.

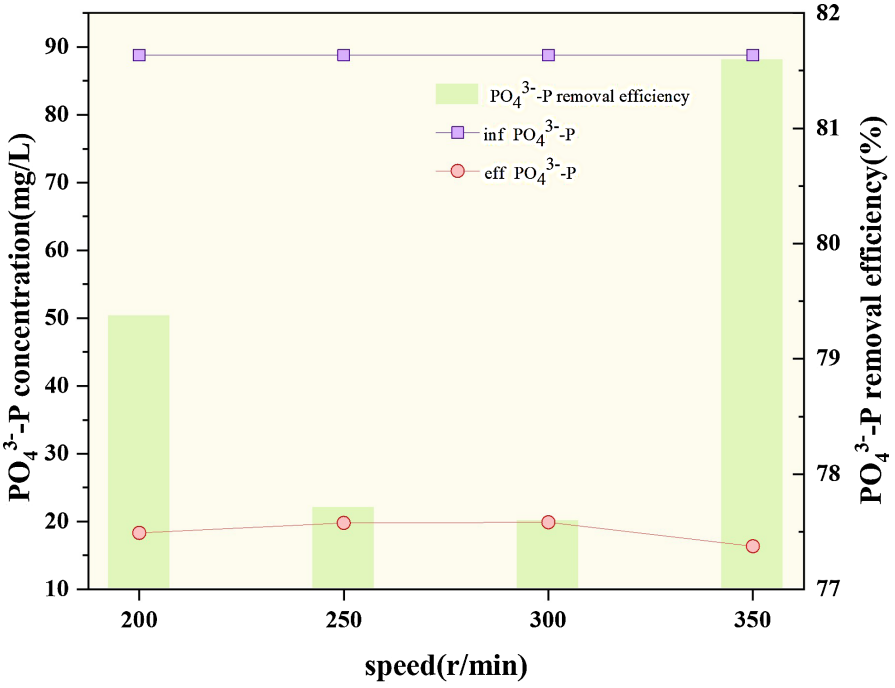


Figure 12. Reaction behavior of PO_4^{3-}-P at different rotational speeds.

4. Conclusions

This study systematically investigated the influence of different calcium sources on the hydroxyapatite (HAP) formation process and established an effective method utilizing a combined CaO and $CaCl_2$ calcium source. The following conclusions were drawn:

1) When $CaCl_2$ was used as the sole calcium source without pH control (no NaOH addition), the phosphate (PO_4^{3-}-P) removal rate was positively correlated with its initial concentration and the Ca/P molar ratio, but remained limited to 50% - 60%. In contrast, when the pH was maintained by NaOH addition, the removal rate reached approximately 80%.

2) CaO dissolution in water provides inherent alkalinity. The solution pH increased with CaO dosage until saturation was achieved. When used as the sole calcium source, phosphate removal rates are comparable at initial phosphate con-

centrations of 50 - 100 mg/L. In a saturated CaO solution, the phosphate removal efficiency varied from 72% to 99.77% across a Ca/P molar ratio range of 1.6 to 2.6, although the resultant supernatant pH remained above 11.

3) A combined $CaCl_2$/CaO system proved effective for HAP formation. At an optimal $CaCl_2$/CaO mass ratio of 2.6 and a stirring speed of 200 rpm, the post-precipitation supernatant pH was reduced to 7.8, while achieving a phosphate removal rate of 79%.

Conflicts of Interest

The author declares no conflicts of interest.

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