

Struvite precipitation for nutrient recovery from clarified shrimp pond sludge supernatant under brackish conditions

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Abstract. Coastal intensive shrimp ponds generate sludge-derived supernatant containing reactive nitrogen and phosphorus that may contribute to eutrophication if discharged without appropriate treatment. This study evaluated struvite precipitation for nutrient recovery from clarified supernatant of white-leg shrimp pond sludge collected in Thuan An Ward, Hue City, Vietnam, under post-flood brackish conditions. The collected supernatant retained a relatively high native Mg^{2+} concentration (100.7 ± 9.2 mg/L), whereas NH_4^+-N and $PO_4^{3-}-P$ were substantially diluted after flooding; therefore, NH_4^+ and PO_4^{3-} were supplemented to restore the stoichiometric window required for crystallisation. Batch jar tests evaluated the effects of pH (8.0–9.5), Mg/N/P molar ratio (1:1:1–1.5:1:1), and reaction time (30–120 min). The optimum conditions were pH 9.0, Mg/N/P = 1:1:1, and 30 min, achieving recovery efficiencies of $61.6 \pm 1.0\%$ for NH_4^+-N and $82.1 \pm 0.3\%$ for $PO_4^{3-}-P$. XRD identified struvite as the predominant crystalline phase, while SEM and optical microscopy showed prismatic crystals consistent with struvite morphology. These findings demonstrate that, even under post-flood brackish conditions, clarified shrimp sludge supernatant can serve as a magnesium-rich matrix for struvite-based nutrient recovery, highlighting a promising route for resource recovery in coastal aquaculture.

Keywords: struvite crystallisation, nutrient recovery, shrimp pond sludge, brackish wastewater, coastal aquaculture

1 Introduction

White-leg shrimp (*Litopenaeus vannamei*) farming is a major export-oriented aquaculture sector in Vietnam [1]. However, the intensification of shrimp culture has also increased environmental pressure, particularly the accumulation and discharge of nutrient-rich pond residues. Among these residues, clarified supernatant derived from bottom sludge is of particular concern because it can act as a mobile source of reactive nitrogen and phosphorus, thereby increasing the risk of eutrophication in receiving waters if discharged without adequate management [2, 3].

Shrimp pond sludge is generated mainly from uneaten feed, feces, microbial biomass, and

other particulate deposits that accumulate during culture. Its environmental significance lies not only in the mass of solids produced, but also in the fact that pond sediments can function as both a nutrient sink and a secondary nutrient source within the pond system. Earlier nutrient-budget work in intensive shrimp ponds demonstrated the central role of sediments in phosphorus accumulation and their potential contribution to nitrogen recycling. More recently, sludge from shrimp ponds in Hue City was reported to contain substantial organic matter and nutrient levels, with organic matter of 17.8–29.9%, total nitrogen of 13.5–32.5 g/kg, and total phosphate of 7.9–20.1 g/kg [4], underscoring its dual identity as both an environmental pollutant and a potentially valuable secondary resource [2].

Conventional sludge-management strategies in aquaculture, including aerobic stabilisation, anaerobic digestion, settling, and disposal-oriented treatments, are mainly designed to reduce waste loads rather than recover nutrients in a concentrated, reusable form [5]. This limitation is particularly relevant in pond-based aquaculture, where nutrient-enriched waste streams are often large in volume and difficult to effectively manage cost [5].

From a resource-recovery perspective, struvite precipitation is attractive because it converts dissolved ammonium and phosphate into magnesium ammonium phosphate hexahydrate ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$), a defined crystalline product with recognised agronomic value [6–9]. Struvite typically forms as a defined orthorhombic crystalline phase, often with straight-prismatic morphology, and its relatively low water solubility has made it attractive as a multi-nutrient slow-release fertiliser capable of supplying N, P, and Mg in a single recovered product [6, 10]. The process is governed primarily by pH, supersaturation, stoichiometric balance among Mg^{2+} , NH_4^+ , and PO_4^{3-} , and the presence of competing ions, making wastewater matrix effects central to process performance [6, 7, 10, 11].

Although the struvite literature is extensive, most studies have focused on municipal sidestreams, livestock effluents, digestates, or synthetic solutions rather than aquaculture-derived brackish matrices [5]. This gap is particularly relevant in coastal aquaculture because brackish matrices differ fundamentally from freshwater and municipal wastewaters in ionic composition, especially with respect to naturally occurring magnesium [8, 9]. Zhang et al. demonstrated that under marine/brackish aquaculture conditions, struvite results from magnesium already present in the system, highlighting a distinctive advantage of saline environments for crystallisation [8]. At the same

time, real coastal aquaculture systems are hydrologically unstable. In central Vietnam, post-flood dilution can sharply depress dissolved NH_4^+ -N and PO_4^{3-} -P even when the water's brackish character and part of its Mg^{2+} background are retained. This creates a scientifically important and practically relevant scenario: a real brackish matrix that remains favourable for magnesium availability, yet becomes temporarily unfavourable for crystallisation because of post-flood nutrient dilution.

Accordingly, this study evaluated the feasibility of struvite precipitation for nutrient recovery from clarified supernatant of white-leg shrimp pond sludge collected under post-flood brackish conditions in Hue City, Vietnam. Because flood-driven dilution substantially reduced native NH_4^+ -N and PO_4^{3-} -P concentrations, these ions were supplemented to restore the target Mg/N/P stoichiometric ratios while preserving the original brackish matrix and naturally occurring Mg^{2+} background. The effects of pH, molar ratio, and reaction time on nutrient recovery were systematically investigated, and the recovered precipitate was further characterised by using XRD and SEM to clarify its predominant crystalline phase and morphology.

2 Materials and methods

2.1 Sample collection and preservation

Samples were collected from the sludge-drainage stream of a white-leg shrimp pond located in Thuan An Ward, Hue City, Vietnam (formerly Phu Hai Commune, Phu Vang District). The sampling point was the terminal settling-drain channel ($16^\circ 52'00''$ N, $108^\circ 09'00''$ E), which receives pond-bottom wastewater discharged through the siphon system and was therefore selected as the integrated outlet stream most relevant to the struvite precipitation experiments. Sampling was conducted at this location from November 15 to

December 15, 2025, during three independent sampling events. Immediately before each event, the outlet flow was gently mixed to minimise short-term local heterogeneity at the sampling point.

Samples were collected in clean 1.5 L PET bottles, kept at 4–6 °C, and transported to the laboratory the same day for analysis and batch experiments. Sample preservation followed TCVN 5996:1995. Field parameters, namely temperature, pH, dissolved oxygen (DO), turbidity, and salinity, were measured *in situ* by using a Horiba U5000 multiparameter meter (Japan).

Before the struvite precipitation experiments, the collected samples were allowed to settle for 30 min and then passed through two sieves with mesh sizes of 2.0 mm and 0.5 mm to remove coarse debris. The clarified supernatant obtained after settling and screening was used as the reaction matrix for the subsequent precipitation experiments.

2.2 Experimental design for struvite precipitation

Struvite precipitation experiments were performed with clarified supernatant derived from shrimp pond sludge collected under post-flood brackish conditions. Because native $\text{NH}_4^+\text{-N}$ and $\text{PO}_4^{3-}\text{-P}$ concentrations were substantially diluted after flooding, NH_4Cl and KH_2PO_4 were added to restore the target stoichiometric conditions for crystallisation, whereas native Mg^{2+} in the brackish supernatant was retained and not externally supplemented. Before each experiment, the collected sample was allowed to settle, and the clarified upper layer was separated and further filtered to remove residual suspended solids with a Whatman GF/F filter (0.45 μm , UK).

Batch precipitation experiments were conducted in 1 L glass beakers by using a four-position jar-test system (JLT4, Velp Scientifica,

Italy) to evaluate the effects of pH (8.0–9.5), the Mg/N/P molar ratio (1:1:1–1.5:1:1), and reaction time (30–120 min) (Fig. 1). During the pH experiments, the Mg/N/P molar ratio was fixed at 1:1:1, the stirring speed at 50 rpm, and the reaction time at 30 min. During the molar-ratio experiments, pH was fixed at the optimum value obtained from the first set, whereas stirring speed and reaction time were maintained at 50 rpm and 30 min, respectively. During the reaction-time experiments, both pH and the Mg/N/P molar ratio were fixed at the optimum values identified in the preceding tests. All experiments were conducted in triplicate.

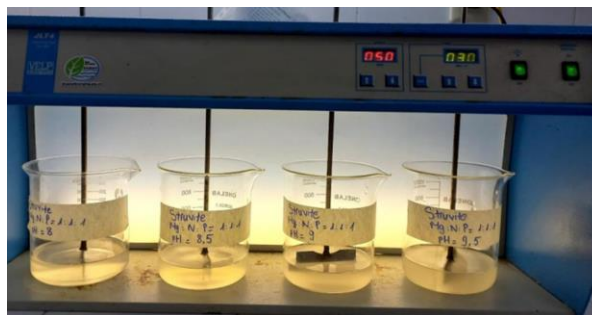


Fig. 1. Struvite precipitation experiment setup

For each run, 200 mL of clarified supernatant was mixed with stock NH_4Cl (1.0 M) and KH_2PO_4 (0.5 M) solutions to establish the target molar ratio while preserving the native Mg^{2+} background of the sample. The mixture was rapidly stirred at 150 rpm for 1 min; after that, the pH was adjusted to the desired value by using a 0.1 N NaOH solution (Merck) and monitored with a HANNA HI8424 pH electrode. The mixture was then stirred at 50 rpm for the designated reaction time to allow crystal growth, followed by 30 min of quiescent settling.

At the end of each run, the supernatant was analysed for $\text{NH}_4^+\text{-N}$ and $\text{PO}_4^{3-}\text{-P}$, and the recovered precipitate was dried at 40 °C for 48 h and weighed as dry precipitate mass. Crystal morphology was initially examined by using an Olympus CX33 optical microscope (Japan), and

representative precipitate samples were further characterised by using XRD and SEM.

2.3 Characterisation of the recovered precipitate

The recovered precipitate was characterised by using X-ray diffraction (XRD) with a RINT2000/PC diffractometer (Rigaku, Japan) to identify its predominant crystalline phase. Its morphology and surface features were further examined by using scanning electron microscopy (SEM) with a Hitachi S-4800 microscope (Japan).

2.4 Analytical methods

The main analytical parameters used to evaluate the precipitation experiments were $\text{NH}_4^+\text{-N}$, $\text{PO}_4^{3-}\text{-P}$, Ca^{2+} , and Mg^{2+} concentrations and total hardness. All analyses were conducted in accordance with the Standard Methods for the Examination of Water and Wastewater [12]. $\text{NH}_4^+\text{-N}$ was determined by using Method 4500- $\text{NH}_3\text{ F}$, whereas $\text{PO}_4^{3-}\text{-P}$ was determined by using the ascorbic acid method (Method 4500- P E) via spectrophotometric measurement with a UV-1800 UV-Vis spectrophotometer (Japan). Total hardness was determined via EDTA titration (Method 2340 C), and Ca^{2+} was determined with the murexide titrimetric method (Method 3500- Ca B). Mg^{2+} concentration was calculated from the difference between total hardness (expressed as $\text{mg CaCO}_3/\text{L}$) and the CaCO_3 -equivalent concentration of Ca^{2+} , and the resulting value was then converted to Mg^{2+} concentration (mg/L).

2.5 Data processing

Experimental data were processed by using Microsoft Excel, and all results are reported as mean $\pm$ standard deviation of triplicate experiments. Nutrient recovery efficiency (%) was calculated according to Equation (1):

$$\text{Recovery efficiency (\%)} = \frac{(C_0 - C)}{C_0} \times 100 \quad (1)$$

where C_0 and C are the initial and final concentrations (mg/L) of $\text{NH}_4^+\text{-N}$ or $\text{PO}_4^{3-}\text{-P}$, respectively.

The dry precipitate mass obtained in each batch was additionally normalised to the initial sample volume to allow comparison among experimental conditions.

3 Results and discussion

3.1 Characteristics of clarified shrimp pond sludge supernatant

After coarse debris had been removed with 2.0 mm and 0.5 mm sieves, the clarified sludge supernatant appeared light green on visual inspection, consistent with the presence of residual dissolved organic matter and microalgal material typically observed in shrimp pond effluents toward the end of the culture cycle. The main physicochemical characteristics of the clarified supernatant collected under post-flood brackish conditions and used for the struvite precipitation experiments are summarised in Table 1.

The clarified supernatant exhibited a slightly alkaline pH and low salinity, which was consistent with post-flood brackish conditions. A relatively high Mg^{2+} concentration was retained in the matrix, whereas $\text{PO}_4^{3-}\text{-P}$ remained very low. $\text{NH}_4^+\text{-N}$ was present at a moderate level; however, together with phosphate, it was still insufficient to establish the stoichiometric balance required for efficient struvite crystallisation without supplementation. These characteristics justify the experimental strategy adopted in this study, namely retaining the native Mg^{2+} background while supplementing NH_4^+ and PO_4^{3-} to restore the target crystallisation window.

Table 1. Physicochemical characteristics of clarified supernatant derived from white-leg shrimp pond sludge used in struvite precipitation experiments

Parameter	Unit	Range	Mean ± SD (<i>n</i> = 3)
pH	–	8.3–8.9	8.6 ± 0.3
Salinity	ppt	2.8–2.9	2.83 ± 0.06
Dissolved oxygen	mg/L	5.9–6.7	6.3 ± 0.4
Total hardness	mg CaCO ₃ /L	570–600	585 ± 15.0
Ca ²⁺	mg/L	56–60	58 ± 2.0
Mg ²⁺	mg/L	91.9–110.3	100.7 ± 9.2
NH ₄ ⁺ -N	mg/L	1.80–4.70	3.43 ± 1.48
PO ₄ ³⁻ -P	mg/L	0.08–0.25	0.18 ± 0.09

The clarified supernatant exhibited a slightly alkaline pH and low salinity, which was consistent with post-flood brackish conditions. A relatively high Mg²⁺ concentration was retained in the matrix, whereas PO₄³⁻-P remained very low. NH₄⁺-N was present at a moderate level; however, together with phosphate, it was still insufficient to establish the stoichiometric balance required for efficient struvite crystallisation without supplementation. These characteristics justify the experimental strategy adopted in this study, namely retaining the native Mg²⁺ background while supplementing NH₄⁺ and PO₄³⁻ to restore the target crystallisation window.

3.2 Factors affecting N and P recovery during struvite precipitation

Effect of pH

pH is one of the most influential operational parameters governing struvite precipitation because it affects phosphate speciation, the ammonium-ammonia equilibrium, supersaturation, and precipitate solubility. Under insufficiently

alkaline conditions, supersaturation may remain extremely low for efficient crystal nucleation and growth [7]. By contrast, excessively high pH may promote competing magnesium-containing precipitates, thereby reducing the selectivity of struvite formation [13].

The effect of pH (8.0, 8.5, 9.0, and 9.5) was evaluated under fixed conditions of Mg/N/P at 1:1:1, 50 rpm, and 30 min. As shown in Fig. 2 and Table 2, both NH₄⁺-N and PO₄³⁻-P recovery increased markedly as pH increased from 8.0 to 9.0. At pH 8.0, recovery efficiencies were only 37.5 ± 0.3% for NH₄⁺-N and 40.4 ± 0.3% for PO₄³⁻-P, indicating limited precipitation under relatively low supersaturation. Increasing pH to 9.0 substantially improved nutrient recovery, with NH₄⁺-N and PO₄³⁻-P recovery reaching 61.6 ± 1.0% and 82.1 ± 0.3%, respectively. Under the same conditions, the normalised dry precipitate yield reached its maximum value (0.546 ± 0.022 g/L), indicating that pH 9.0 provided the most favourable crystallisation performance among the tested levels.

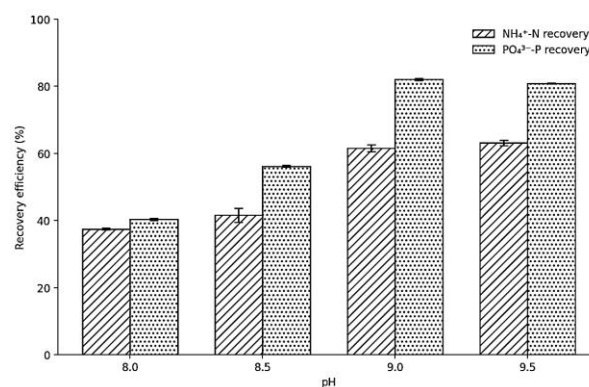


Fig. 2. Recovery efficiencies of NH₄⁺-N and PO₄³⁻-P at different pH levels during struvite precipitation. Values are presented as mean ± SD (*n* = 3)

At pH 9.5, the NH₄⁺-N recovery increased slightly further to 63.2 ± 0.8%, whereas the PO₄³⁻-P recovery decreased slightly to 80.9 ± 0.2%, accompanied by a lower precipitate yield (0.518 ± 0.001 g/L). This pattern suggests that although higher alkalinity may still support ammonium

removal, it does not improve overall struvite recovery and may instead favour competing precipitation pathways. A similar pH range (8.5–9.0) was commonly reported as favourable for struvite crystallisation in nutrient-rich wastewaters [7, 14].

Overall, pH 9.0 was considered the most suitable condition for struvite precipitation in the clarified shrimp pond sludge supernatant because it provided the best balance among the phosphorus recovery, the ammonium recovery, and the precipitate yield, while avoiding the less favourable behaviour observed at higher alkalinity.

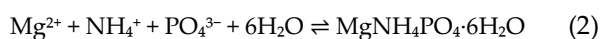
Table 2. Effect of pH on $\text{NH}_4^+\text{-N}$ recovery, $\text{PO}_4^{3-}\text{-P}$ recovery, and normalised dry precipitate yield during struvite precipitation

pH	$\text{NH}_4^+\text{-N}$ recovery (%)	$\text{PO}_4^{3-}\text{-P}$ recovery (%)	Normalised dry precipitate yield (g/L)
8.0	37.5 ± 0.3	40.4 ± 0.3	0.148 ± 0.001
8.5	41.6 ± 2.1	56.2 ± 0.3	0.335 ± 0.005
9.0	61.6 ± 1.0	82.1 ± 0.3	0.546 ± 0.022
9.5	63.2 ± 0.8	80.9 ± 0.2	0.518 ± 0.001

Note: Values are presented as mean $\pm$ SD ($n = 3$).

Effect of Mg/N/P molar ratio

The molar ratio of Mg^{2+} , NH_4^+ , and PO_4^{3-} directly determines the stoichiometric balance required for struvite crystallisation. The ideal precipitation reaction is



As shown in Eq. (2), a 1:1:1 molar ratio favours struvite formation, whereas deviations from stoichiometric balance may reduce precipitation efficiency or promote competing pathways [6]. In real wastewater systems, however, the effective optimum still depends on matrix composition, ion competition, and crystallisation kinetics.

Under brackish aquaculture conditions, Mg^{2+} is often naturally abundant because of its marine origin [8, 9]. In the present study, the post-flood clarified supernatant retained a relatively high native Mg^{2+} background, whereas $\text{NH}_4^+\text{-N}$ and $\text{PO}_4^{3-}\text{-P}$ were diluted to unusually low levels. Therefore, the molar-ratio experiment did not involve actual Mg supplementation; instead, native Mg^{2+} was retained while NH_4^+ and PO_4^{3-} were adjusted to create three target conditions: 1:1:1, 1.2:1:1, and 1.5:1:1, corresponding to increasing levels of relative Mg excess. All other conditions were fixed at pH 9.0, 50 rpm, and 30 min.

As shown in Fig. 3 and Table 3, the best overall performance was obtained at Mg/N/P of 1:1:1, with recovery efficiencies of $61.6 \pm 1.0\%$ for $\text{NH}_4^+\text{-N}$ and $82.1 \pm 0.3\%$ for $\text{PO}_4^{3-}\text{-P}$, with the highest normalised dry precipitate yield (0.546 ± 0.022 g/L). When the nominal Mg/N/P ratio increased to 1.2:1:1 and 1.5:1:1, both nutrient recovery and precipitate yield decreased markedly. At 1.2:1:1, $\text{NH}_4^+\text{-N}$ and $\text{PO}_4^{3-}\text{-P}$ recovery dropped to $51.8 \pm 3.7\%$ and $47.8 \pm 0.1\%$, respectively, with a yield of 0.449 ± 0.001 g/L. At 1.5:1:1, $\text{NH}_4^+\text{-N}$ recovery decreased further to $38.2 \pm 1.9\%$, whereas $\text{PO}_4^{3-}\text{-P}$ recovery remained low at $49.6 \pm 4.6\%$, with a similar precipitate yield (0.452 ± 0.001 g/L).

These results indicate that, in the present brackish matrix, relative excess of Mg^{2+} did not improve crystallisation performance. Because the native Mg^{2+} concentration was retained while NH_4^+ and PO_4^{3-} were adjusted, shifting the nominal Mg/N/P ratio to 1.2:1:1 or 1.5:1:1 effectively reduced the availability of NH_4^+ and PO_4^{3-} relative to Mg^{2+} and moved the system away from the 1:1:1 stoichiometry required for struvite formation. This imbalance likely lowered the ion activity product of Mg^{2+} , NH_4^+ , and PO_4^{3-} relative to the precipitation threshold, thereby decreasing supersaturation, nutrient recovery, and precipitate

yield. In addition, magnesium-rich alkaline systems may favour competing magnesium-bearing precipitates, which can reduce the selectivity of struvite formation [8].

The practical implication is that the advantage of brackish aquaculture matrices lies not in the presence of excess Mg^{2+} alone, but in the possibility of using native Mg^{2+} as an intrinsic reactant while optimising the complementary NH_4^+ and PO_4^{3-} inputs. Accordingly, $Mg/N/P = 1:1:1$ was identified as the most suitable ratio under the present experimental conditions because it provided the best balance among NH_4^+ -N recovery, PO_4^{3-} -P recovery, and precipitate yield, while minimising the unfavourable behaviour observed under relative Mg excess.

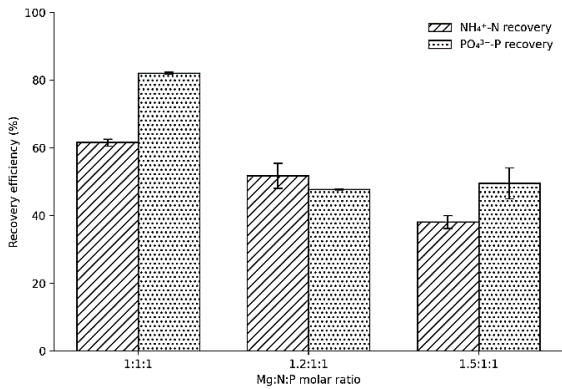


Fig. 3. Recovery efficiencies of NH_4^+ -N and PO_4^{3-} -P at different Mg/N/P molar ratios during struvite precipitation. Values are presented as mean ± SD ($n = 3$)

Table 3. Effect of Mg/N/P molar ratio on NH_4^+ -N recovery, PO_4^{3-} -P recovery, and normalised dry precipitate yield during struvite precipitation

Mg/N/P molar ratio	NH_4^+ -N recovery (%)	PO_4^{3-} -P recovery (%)	Normalised dry precipitate yield (g/L)
1:1:1	61.6 ± 1.0	82.1 ± 0.3	0.546 ± 0.022
1.2:1:1	51.8 ± 3.7	47.8 ± 0.1	0.449 ± 0.001
1.5:1:1	38.2 ± 1.9	49.6 ± 4.6	0.452 ± 0.001

Note: Values are presented as mean ± SD ($n = 3$).

Effect of reaction time

Reaction time is an important kinetic parameter in struvite crystallisation because it affects nucleation, crystal growth, and the dynamic balance between precipitation and possible redissolution or competing processes in the reaction system. In nutrient-containing wastewater, struvite formation may occur rapidly during the early stage when pH and ionic stoichiometry are favourable [7, 14]. However, extending the reaction time does not necessarily improve nutrient recovery, as prolonged mixing and ageing may affect precipitate stability, crystal aggregation, and separation behaviour [7].

The effect of reaction time (30, 60, 90, and 120 min) was evaluated under fixed conditions of $Mg/N/P = 1:1:1$, pH 9.0, and 50 rpm. As shown in Fig. 4 and Table 4, the best overall performance was observed at 30 min, when the NH_4^+ -N and PO_4^{3-} -P recoveries reached $61.6 \pm 1.0\%$ and $82.1 \pm 0.3\%$, respectively, with the highest normalised dry precipitate yield (0.546 ± 0.022 g/L). These results indicate that precipitation proceeded rapidly under the selected reaction conditions, and that a substantial fraction of soluble nutrients was removed from the liquid phase within the first 30 min. The difference between the NH_4^+ -N and PO_4^{3-} -P recoveries at this condition should be interpreted in terms of liquid-phase concentration decreases, rather than as direct evidence of strictly one-to-one stoichiometric incorporation into pure struvite.

When the reaction time was extended to 60 and 90 min, the NH_4^+ -N recovery changed only slightly, reaching $61.2 \pm 3.6\%$ and $65.1 \pm 2.5\%$, respectively. In contrast, the PO_4^{3-} -P recovery decreased progressively to $75.8 \pm 1.0\%$ at 60 min and $70.8 \pm 0.6\%$ at 90 min. At 120 min, the NH_4^+ -N recovery remained within a similar range ($63.4 \pm 2.9\%$), whereas the PO_4^{3-} -P recovery declined further to $60.1 \pm 0.3\%$. Over the same periods, the normalised dry precipitate yield also decreased

from 0.546 ± 0.022 g/L at 30 min to 0.466 ± 0.001 g/L at 120 min.

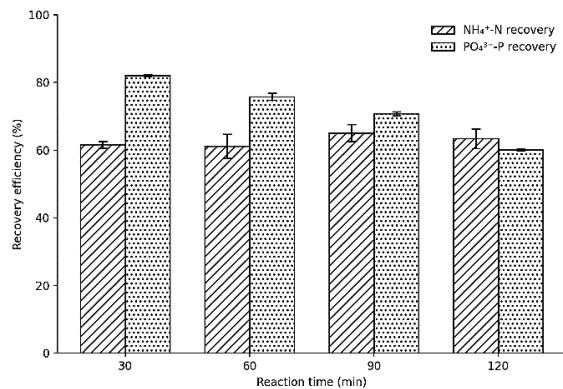


Fig. 4. Recovery efficiencies of $\text{NH}_4^+\text{-N}$ and $\text{PO}_4^{3-}\text{-P}$ at different reaction times during struvite precipitation. Values are presented as mean $\pm$ SD ($n = 3$)

Table 4. Effect of reaction time on $\text{NH}_4^+\text{-N}$ recovery, $\text{PO}_4^{3-}\text{-P}$ recovery, and normalised dry precipitate yield during struvite precipitation

Reaction time (min)	$\text{NH}_4^+\text{-N}$ recovery (%)	$\text{PO}_4^{3-}\text{-P}$ recovery (%)	Normalised dry precipitate yield (g/L)
30	61.6 ± 1.0	82.1 ± 0.3	0.546 ± 0.022
60	61.2 ± 3.6	75.8 ± 1.0	0.521 ± 0.001
90	65.1 ± 2.5	70.8 ± 0.6	0.508 ± 0.001
120	63.4 ± 2.9	60.1 ± 0.3	0.466 ± 0.001

Note: Values are presented as mean $\pm$ SD ($n = 3$).

This pattern suggests that extending reaction time beyond 30 min failed to improve the overall recovery of struvite-forming constituents. Instead, prolonged reaction might reduce effective precipitate retention through weaker aggregation, partial redissolution of less stable phases, or the formation of finer particles that were less readily separated from the supernatant. Although the $\text{NH}_4^+\text{-N}$ recovery showed a slight increase at 90 min, this gain was not accompanied by improved the phosphate recovery or the precipitate yield. Therefore, from both the process-performance and operational perspective, 30 min was considered the most suitable reaction time because it provided the best balance among the $\text{NH}_4^+\text{-N}$ recovery, the

$\text{PO}_4^{3-}\text{-P}$ recovery, and the precipitate yield, while also favouring a shorter, more practical treatment cycle.

3.3 Characteristics of the recovered struvite-rich precipitate

Preliminary morphology of the recovered precipitate

The precipitate selected for characterisation was obtained under the optimum conditions identified in this study (pH 9.0, $\text{Mg/N/P} = 1:1:1$, stirring speed 50 rpm, and reaction time 30 min), which is consistent with conditions commonly reported as favourable for struvite crystallisation in wastewater systems [6, 7]. Visual inspection showed that the recovered precipitate was pale-white, fine-grained, and readily separable from the liquid phase. Such characteristics are commonly associated with struvite-rich precipitation under mildly alkaline conditions and favourable ionic stoichiometry [7, 14].

Preliminary optical microscopy showed that the recovered crystals were predominantly elongated prismatic particles, consistent with the morphology commonly reported for struvite. After drying at 40 °C for 48 h, the product remained physically stable and suitable for subsequent characterisation. Representative images of the precipitate in suspension after drying and under optical microscopy are presented in Fig. 5.

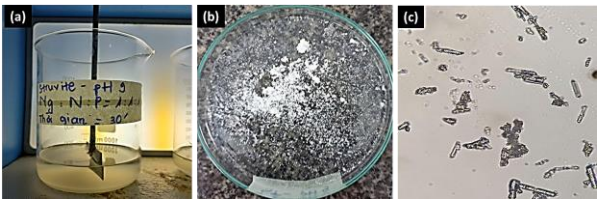


Fig. 5. Images of the recovered precipitate obtained at pH 9.0, $\text{Mg/N/P} = 1:1:1$, 50 rpm, and 30 min: (a) precipitate formed in suspension, (b) dried precipitate, and (c) optical micrograph of the crystals (10 $\times$ magnification)

Characterisation of the recovered precipitate by using XRD and SEM

The recovered precipitate obtained at pH 9.0, Mg/N/P = 1:1:1, and 30 min was selected for XRD and SEM analysis because these conditions yielded the best overall recovery performance. The XRD pattern showed several sharp and well-resolved reflections, indicating the formation of a predominantly crystalline product (Fig. 6). Major peaks were observed at approximately 15.8, 20.9, 21.5, 27.1, 30.7, 32.0, and 33.3° (2 θ), with the strongest reflection at 20.9°. These peaks matched well with the characteristic reflections of struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$; ICDD PDF No. 01-077-2303), indicating that struvite was the predominant crystalline phase in the recovered precipitate. Although several weaker reflections were also present in the higher-angle region ($2\theta = 44\text{--}53^\circ$), no dominant foreign reflections suggesting a major secondary crystalline phase were observed. The slightly elevated background at low angles may indicate the presence of a minor amorphous fraction or residual matrix-derived impurities. Overall, the XRD results strongly support the formation of a struvite-rich precipitate.

The SEM analysis further showed that the recovered precipitate consisted mainly of micrometre-scale crystals aggregated into compact clusters (Fig. 7). Most particles exhibited prismatic to short-tabular morphologies, with elongated shapes and relatively distinct edges. Their surfaces exhibited rough and heterogeneous, with fine particles adhering to the crystal surface. This morphology suggests that crystal growth may have occurred with secondary nucleation, surface overgrowth, or attachment of co-precipitated particles from the real brackish matrix. Compared with struvite crystals formed in pure synthetic systems, the crystals observed here were less regular and more strongly aggregated, which is reasonable, given the presence of dissolved salts and residual impurities in the clarified shrimp

sludge supernatant. Nevertheless, their overall morphology remained consistent with that of struvite.

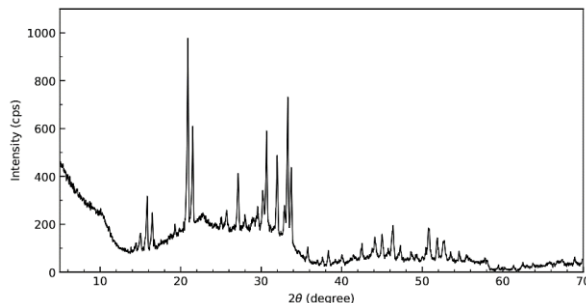


Fig. 6. X-ray diffraction pattern of the recovered precipitate obtained under the selected optimum condition

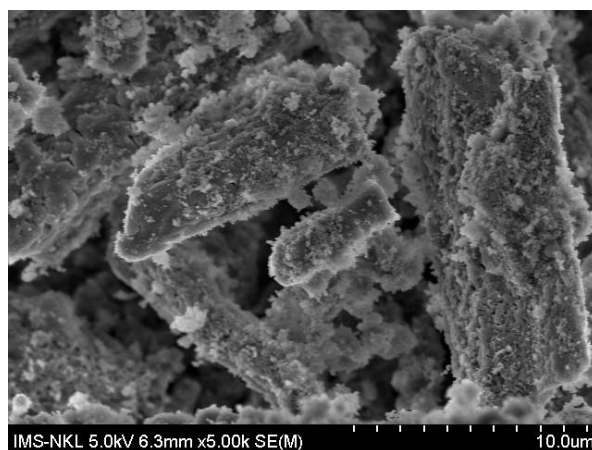


Fig. 7. SEM micrograph of the recovered precipitate obtained under the selected optimum condition

Taken together, the XRD and SEM results provide complementary evidence that the recovered product was not only morphologically consistent with struvite but also structurally dominated by the struvite phase. Based on the available data, we can, therefore, conclude that struvite was the predominant crystalline phase in the recovered precipitate under the selected optimum conditions.

4 Conclusions

This study demonstrated the feasibility of struvite precipitation for nutrient recovery from clarified supernatant of white-leg shrimp pond sludge

under post-flood brackish conditions. The investigated supernatant retained a relatively high native Mg^{2+} concentration (100.7 ± 9.2 mg/L), whereas $\text{NH}_4^+\text{-N}$ and $\text{PO}_4^{3-}\text{-P}$ were diluted and therefore required stoichiometric adjustment prior to crystallisation. Under the tested conditions, the best overall performance was achieved at pH 9.0, $\text{Mg/N/P} = 1:1:1$, and 30 min, yielding recovery efficiencies of $61.6 \pm 1.0\%$ for $\text{NH}_4^+\text{-N}$ and $82.1 \pm 0.3\%$ for $\text{PO}_4^{3-}\text{-P}$, with the highest normalised dry precipitate yield (0.546 ± 0.022 g/L). The recovered product exhibited prismatic morphology under optical microscopy and SEM, while XRD confirmed that struvite was the predominant crystalline phase. Collectively, these findings show that clarified brackish shrimp sludge supernatant can function as a magnesium-rich matrix for struvite-based nutrient recovery.

The present findings should be interpreted within the scope of the investigated wastewater matrix. Because the samples were collected under post-flood conditions, their nutrient composition may not fully represent the normal seasonal characteristics of shrimp pond supernatant. Moreover, although XRD and SEM confirmed that struvite was the predominant phase, additional analyses are still required to quantify minor secondary phases, verify product purity, and assess agronomic suitability and safety. Future studies should therefore validate the process using seasonally representative shrimp wastewater, broaden the dataset across hydrological conditions, and evaluate pilot-scale performance and operating costs under field conditions.

Conflict of interest

The authors declare no conflicts of interest related to the publication of this article.

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References

1. Vietnam Association of Seafood Exporters and Producers (VASEP). Vietnam shrimp industry report 2021–2025: overview and outlook to 2030 [Internet]. 2026 [cited 2026 Apr 2]. Available from: <https://vasep.com.vn/ban-tin-bao-cao/bao-cao-san-pham-thuy-san/bao-cao-nganh-hang-tom-2021-2025-du-bao-den-nam-2030-26614.html>
2. Funge-Smith SJ, Briggs MRP. Nutrient budgets in intensive shrimp ponds: implications for sustainability. *Aquaculture*. 1998;164:117-33.
3. Pongthanapanich T, Nguyen KAT, Jolly CM. Risk management practices of small intensive shrimp farmers in the Mekong Delta of Viet Nam. Rome: Food and Agriculture Organization of the United Nations; 2019. (FAO Fisheries and Aquaculture Circular No. 1194).
4. Lich NQ, Vuong LD, Son TM, Linh VQ. Physicochemical and biological characteristics of shrimp pond sludge in the Thua Thien Hue Province, Vietnam. *Journal of Experimental Biology and Agricultural Sciences*. 2022;10(5):1024-32.
5. Tabrett S, Ramsay I, Paterson BD, Burford MA. A review of the benefits and limitations of waste nutrient treatment in aquaculture pond facilities. *Reviews in Aquaculture*. 2024;16(4):1766-86.
6. Doyle JD, Parsons SA. Struvite formation, control and recovery. *Water Research*. 2002;36(16):3925-40.
7. Le Corre KS, Valsami-Jones E, Hobbs P, Parsons SA. Phosphorus recovery from wastewater by struvite crystallization: a review. *Critical Reviews in Environmental Science and Technology*. 2009;39(6):433-77
8. Zhang X, Hu J, Spanjers H, van Lier JB. Struvite crystallization under a marine/brackish aquaculture condition. *Bioresource Technology*. 2016;219:37-44.
9. Ong JH, Huang S, Hu X, Xu R. Struvite precipitation for low-level ammonium removal in mariculture wastewater: feasibility study. *Bioresource Technology*. 2025;424:132270.

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10. Ohlinger KN, Young TM, Schroeder ED. Predicting struvite formation in digestion. *Water Research*. 1998;32(12):3607-14.
 11. Hao XD, Wang CC, Lan L, van Loosdrecht MCM. Struvite formation, analytical methods and effects of pH and Ca^{2+} . *Water Science and Technology*. 2008;58(8):1687-92.
 12. American Public Health Association, American Water Works Association, Water Environment Federation. Standard methods for the examination of water and wastewater. 23rd ed. Washington (DC): American Public Health Association; 2017.
 13. Hussain M, Ahmad T, Lu J, Zhang Y, Uddin S. Production of slow release crystal fertilizer from wastewaters through struvite crystallization: a review. *Journal of Cleaner Production*. 2020;262:121200.
 14. Yetilmezsoy K, Sapci-Zengin Z. Recovery of ammonium nitrogen from the effluent of UASB treating poultry manure wastewater by MAP precipitation as a slow release fertilizer. *Journal of Hazardous Materials*. 2009;166(1):327-35.