Struvite Precipitation for Sustainable Recovery of Nitrogen and Phosphorus from Anaerobic Digestion Effluents of Swine Manure

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Received: 16 September 2020; Accepted: 14 October 2020; Published: 16 October 2020

Abstract: In this study, we propose the application of struvite precipitation for the sustainable recovery of nitrogen (N) and phosphorus (P) from anaerobic digestion (AD) effluents derived from swine manure. The optimal conditions for four major factors that affect the recovery of N and P were derived by conducting batch experiments on AD effluents obtained from four AD facilities. The optimal conditions were a pH of 10.0, NH$_4$-N:Mg:PO$_4$-P molar ratio of 1:1.4:1, mixing intensity of 240 s$^{-1}$, and mixing duration of 2 min. Under these optimal conditions, the removal efficiencies of NH$_4$-N and PO$_4$-P were approximately 74% and 83%, respectively, whereas those of Cu and Zn were approximately 74% and 79%, respectively. Herein, a model for swine manure treatment that incorporates AD, struvite precipitation, and biological treatment processes is proposed. We applied this model to 85 public biological treatment facilities in South Korea and recovered 4722 and 51 tons/yr of NH$_4$-N and PO$_4$-P, respectively. The economic analysis of the proposed model’s performance predicts a lack of profitability due to the high cost of chemicals; however, this analysis does not consider the resulting protection of the hydrological environment. Field-scale studies should be conducted in future to prove the effectiveness of the model.

Keywords: swine manure; anaerobic digestion effluents; struvite precipitation; optimal condition; biological treatment process; application model

1. Introduction

According to the Annual Report of the Nationwide Water Pollution Source Survey published in 2017, domestic annual animal manure generation in South Korea is 50,220,000 tons/yr, of which 20,523,000 tons/yr is swine manure, representing the highest proportion of manure and accounting for approximately 41% of the total animal manure [1]. Swine manure contains high concentrations of organic matter, nitrogen (N), and phosphorus (P). Therefore, if untreated swine manure enters waterbodies, it can result in the depletion of dissolved oxygen, eutrophication, and algal blooms in the waterbodies [2,3].

Anaerobic digestion (AD) has been widely studied worldwide as an effective treatment method for swine manure [4–8] because it can recover biogas in the form of methane (CH$_4$) as an energy source, while effectively treating high concentrations of organic matter. However, AD effluents contain high concentrations of nutrients, such as ammonium nitrogen (NH$_4$-N) and orthophosphate (PO$_4$-P), and relatively high concentrations of toxic metals, such as copper (Cu) and zinc (Zn) [9–11]. Toxic metals, such as Cu and Zn, are present in high concentrations in AD effluents because they are added in the feed as micro-supplements for pig growth [12], which has been reported previously [5,9,13].

Sustainability 2020, 12, 8574; doi:10.3390/su12208574 www.mdpi.com/journal/sustainability
In South Korea, AD effluents are generally sprayed on agricultural lands or undergo post-treatment through a biological treatment process. However, spraying AD effluents containing high concentrations of N and P on agricultural lands may not be the ideal solution considering the high nutrient balance in South Korea. According to the statistics on nutrient balance reported by the Organization for Economic Cooperation and Development (OECD) in 2018, South Korea ranks first for N and second for P among OECD countries [14]. The nutrient balance serves as one of the agri-environmental indicators for the OECD. A nutrient deficit (i.e., negative value) indicates a lack of nutrients (N and P) in the soil, whereas a nutrient surplus (i.e., positive value) indicates a risk of polluting the soil, water, and air. As the agricultural season in South Korea lasts only ~ 6 months a year, it is highly likely that AD effluents sprayed on agricultural land during the non-agricultural season flow into nearby rivers and groundwater without being available for crops. When AD effluents containing high concentrations of N and toxic metals were treated by a biological treatment process, a decrease in the biological treatment efficiency, including biological nitrification and denitrification, was reported. This was due to the toxicity of free ammonia [NH$_3$(g)] and toxic metals and the low biodegradability of organic matter present in AD effluents [15–19].

As an alternative to biological treatment, high concentrations of NH$_4$-N and PO$_4$-P in AD effluents can be recovered in the form of struvite (MgNH$_4$PO$_4$·6H$_2$O) and utilized as a resource. Struvite is a crystal in which Mg$^{2+}$, NH$_4^+$, and PO$_4^{3-}$ are combined in the molar ratio or stoichiometric proportions of 1:1:1; it is also known as guanite or magnesium ammonium phosphate (MAP). Under optimal conditions, Mg$^{2+}$, NH$_4^+$, and PO$_4^{3-}$ react in a molar ratio of 1:1:1 to form struvite crystals as follows [20]:

$$\text{Mg}^{2+} + \text{NH}_4^+ + \text{PO}_4^{3-} + 6\text{H}_2\text{O} \leftrightarrow \text{MgNH}_4\text{PO}_4\cdot6\text{H}_2\text{O} \downarrow \quad (1)$$

As struvite has a higher specific gravity (1.7) than water, solid–liquid separation occurs rapidly in aqueous solutions. In addition, struvite has low solubility under alkaline conditions and relatively high solubility under acidic conditions [21]. Struvite is also effective as a high-quality fertilizer owing to its high Mg, N, and P contents and its slow-release properties [22–24]. In addition, as a significant amount of NH$_4$-N is removed with struvite precipitation, it can minimize the toxic effect of free ammonia through subsequent biological treatment, thereby enhancing biological nitrification [25,26].

Owing to these advantages, some studies based on the recovery of NH$_4$-N and PO$_4$-P in AD effluents of livestock manure with struvite precipitation have been reported. Among those, it was proven that struvite was effectively recovered from AD effluent of swine manure through X-ray diffraction (XRD) or scanning electron microscopy (SEM) analysis [23,27–29]. To date, these studies have mainly focused on the determination of key reaction parameters, including pH and stoichiometric Mg:NH$_4$-N:PO$_4$-P ratios, that affect the removal efficiency of NH$_4$-N and PO$_4$-P during struvite precipitation [23,27–36]. In rare cases, the type of magnesium source added during struvite precipitation [30]; sequence of the chemical addition of Mg (magnesium source), P (phosphate source), and alkaline reagents [32,34]; optimal reaction time [23,27,34]; and mixing intensity [27] have been studied (Table 1).
Table 1. Operating parameters affecting NH₄-N and PO₄-P crystallization in struvite precipitation of the effluent of anaerobic digestion (AD) in livestock manure.

| Livestock Manure                  | Initial Concentration (mg/L) | Sources of Mg & P                  | pH | Molar Ratio of Ions                         | Mixing Intensity (rpm) | Reaction Time (min) | Removal (%) | Reactor Types | Reference |
|-----------------------------------|------------------------------|-----------------------------------|----|-------------------------------------------|------------------------|---------------------|--------------|---------------|-----------|
| Swine manure                      | 589–607                      | MgSO₄                             | 9.5 | Mg:PO₄³⁻ = 1.5:1.0                       | 200                    | 30                  | 55           | 64           | Batch [23] |
| Swine manure                      | 2974–3907                    | MgCl₂·6H₂O                        | 8.8 | Mg:PO₄³⁻ = 1.5:1.0                       | 100                    | 60                  | 40           | 89           | Batch [27] |
| Swine manure                      | 1725–1825                    | MgCl₂·6H₂O + KH₂PO₄               | 9.0 | Mg:PO₄³⁻ = 1.5:1.0                       | n.a.                   | 10                  | 95           | 97           | CSTR [28] |
| Swine manure                      | 2511–3771                    | MgCl₂·6H₂O + sludge ash           | 10.0| Mg:NH₄⁺:PO₄³⁻ = 1.2:1:0:1.0              | 400                    | 60                  | 92           | 100          | Batch [29] |
| Dairy manure                      | 255–519                      | MgCl₂·6H₂O + Na₂HPO₄              | n.a.| Mg:NH₄⁺:PO₄³⁻ = 2.2:0:4.8               | n.a.                   | n.a.                | 95           | n.a          | Batch [30] |
| Swine manure                      | 234                          | MgCl₂·6H₂O + KH₂PO₄               | 9.0 | Mg:NH₄⁺:PO₄³⁻ = 1.0:1:0:1.0              | 500                    | 60                  | 71           | 97           | Batch [31] |
| Swine manure                      | 296                          | MgCl₂·6H₂O + KH₂PO₄               | 9.0 | Mg:NH₄⁺:PO₄³⁻ = 1.2:1:0:1.2              | 500                    | 900                 | 71           | 97           | Batch [32] |
| Poultry manure                    | 4495–4729                    | MgCl₂·6H₂O + 75% H₃PO₄            | 8.5 | Mg:NH₄⁺:PO₄³⁻ = 1.5:1:0:1.0              | 250                    | 60                  | 97           | 32           | Batch [33] |
| Cattle manure & food waste        | 1060                         | Bittern + Bone meal               | 9.0 | Mg:NH₄⁺:PO₄³⁻ = 1.3:1:0:1.3              | 300                    | 15                  | 91           | 99           | Batch [34] |
| Swine manure                      | 1660                         | MgSO₄                             | 9.0 | Mg:NH₄⁺:PO₄³⁻ = 1.3:0:0:8:8              | 250                    | n.a.                | 78           | 6            | Batch [35] |
| Cattle manure                     | 100–700                      | MgCl₂·6H₂O + 12H₂O               | 10.0| Mg:NH₄⁺:PO₄³⁻ = 1.6:1:2:1.0              | n.a.                   | n.a.                | 90           | 100          | CSTR [36] |
| Swine manure                      | 800                          | MgSO₄                             | 9.0 | n.a.                                      | n.a.                   | 1440                | n.a.         | 75           | Batch [37] |
| Cattle manure                     | 3000                         | MgCl₂                             | 9.0 | n.a.                                      | n.a.                   | n.a.                | n.a.         | 44           | CSTR [38] |

1 Bold values indicate optimal values in the studies; 2 n.a., not available; 3 CSTR, continuous stirred tank reactor.
In South Korea, there are only four public treatment facilities that treat swine manure by AD, and no facilities recover N and P by the struvite precipitation method. However, the South Korean government is implementing a policy to increase the number of AD facilities to 20 by 2022 and to install N and P recovery facilities using struvite precipitation in connection with public treatment facilities. To apply a struvite precipitation reactor to AD effluents, in accordance with the policy, optimal conditions for struvite precipitation need to be established from the viewpoint of the technology, considering the characteristics of AD effluents in South Korea, for the following two reasons. First, according to the studies reported so far, the optimal conditions for reaction parameters that affect struvite precipitation of AD effluent obtained from livestock manure, such as pH and stoichiometric Mg:NH\(_4\)-N:PO\(_4\)-P ratios, differ significantly. The variations in the removal efficiency of NH\(_4\)-N (40–97%) and PO\(_4\)-P (6–100%) under optimal conditions have also been reported to be significantly large (Table 1) [23,27–38]. Second, only a few studies have optimized the reaction time and mixing intensity in struvite precipitation of AD effluents (Table 1). Therefore, further studies that optimize these parameters are required. In addition to the technical aspects, it is also necessary to find suitable applications for the struvite precipitation method in terms of valuable resource recovery and nutrient treatment from swine manure.

Therefore, this study aims to determine the optimal conditions for the four key factors (i.e., pH, Mg:NH\(_4\)-N:PO\(_4\)-P molar ratio, mixing intensity, and mixing time) involved in struvite precipitation from AD effluents. This study also aims to suggest removal efficiencies for organic matter, N, P, and toxic metals during struvite precipitation from swine manure under optimal conditions. In addition, we propose an appropriate model for struvite precipitation application in public swine manure treatment facilities in South Korea. Based on the proposed method, the amount of N and P that can be recovered in the form of struvite crystals was estimated and the cost required during this process was analyzed to guide sustainable swine manure management.

2. Materials and Methods

2.1. Characteristics of Anaerobically Digested Swine Manure

To determine the optimal conditions for the four parameters involved in struvite precipitation, AD effluents from four AD facilities (public treatment facilities) were used. As shown in Table 2, each AD facility used a mix of swine manure and food waste to maximize the amount of methane gas recovered. For post-treatment of AD effluents, AD effluents obtained from the A1 facility were applied to agricultural farmland as liquid fertilizers, whereas those obtained from the A2, A3, and A4 facilities were treated in biological treatment facilities. For experiments, solid–liquid separated AD effluents discharged from the AD reactor of each facility were used because organic compounds affect the removal rate of NH\(_4\)-N and PO\(_4\)-P and the purity of struvite precipitates during struvite precipitation [39–42]. The AD effluents collected from the AD facilities had high concentrations of NH\(_4\)-N and relatively low concentrations of PO\(_4\)-P (Table 3). In addition, the concentrations of Cu and Zn were relatively high compared to those of other toxic metals. The A1 facility, in particular, showed higher concentrations of toxic metals than the other facilities.

| Facility | Influent Source | Mixing Ratio of Swine Manure to Food Waste | Influent Flow Rate (m\(^3\)/d) | Post-Treatment of AD Effluent |
|----------|----------------|------------------------------------------|--------------------------------|------------------------------|
| A1       | Swine manure and food waste | 8:2 | 140 | None |
| A2       | Swine manure and food waste | 6:4 | 60 | Biological treatment |
| A3       | Swine manure and food waste | 5:5 | 130 | Biological treatment |
| A4       | Swine manure and food waste | 8:2 | 100 | Biological treatment |
Table 3. Chemical compositions of anaerobic digestion (AD) effluents obtained from four facilities.

| Parameter     | Facility | Mean Value |
|---------------|----------|------------|
|               | A1       | A2         | A3         | A4         |
| pH            | 9.65     | 8.24       | 8.20       | 9.65       | 8.94 ± 0.83 |
| TOC \(^2\) (mg/L) | 1961     | 709        | 1085       | 1256       | 1253 ± 524  |
| NH\(_4\)-N (mg/L) | 1742     | 2110       | 2010       | 1990       | 1963 ± 156  |
| T-N (mg/L)    | 2505     | 2697       | 2314       | 2306       | 2455 ± 186  |
| PO\(_4\)-P (mg/L) | 36.0     | 20.9       | 1.9        | 15.8       | 18.7 ± 14.1 |
| T-P (mg/L)    | 402.5    | 74.0       | 14.8       | 62         | 138.3 ± 178.0 |
| As (mg/L)     | 0.162    | 0.171      | 0.132      | 0.236      | 0.175 ± 0.044 |
| Cd (mg/L)     | 0.021    | 0.020      | n.d.       | n.d.       | 0.021 ± 0.001 |
| Pb (mg/L)     | n.d.     | 0.132      | 0.072      | 0.078      | 0.094 ± 0.033 |
| Cu (mg/L)     | 9.714    | 1.389      | 0.146      | 0.815      | 3.016 ± 4.494 |
| Zn (mg/L)     | 43.858   | 4.772      | 0.416      | 1.679      | 12.681 ± 20.865 |
| Cr (mg/L)     | 0.251    | 0.082      | 0.024      | 0.300      | 0.164 ± 0.132 |
| Ni (mg/L)     | 0.429    | 0.078      | 0.135      | 0.403      | 0.261 ± 0.181 |

\(^1\) Standard deviation; \(^2\) total organic carbon.

2.2. Struvite Precipitation Experiments

To conduct struvite precipitation experiments from the AD effluents, magnesium chloride (MgCl\(_2\)-6H\(_2\)O) and potassium phosphate (K\(_2\)HPO\(_4\)) were dissolved in distilled water to prepare 50 g Mg/L and 50 g PO\(_4\)-P/L solutions to use as Mg and P sources, respectively. For pH adjustment, NaOH and HCl were dissolved in distilled water to prepare 3 mol/L NaOH and 3 mol/L HCl solutions, respectively.

The struvite precipitation experiments were conducted at room temperature using a jar test apparatus. The paddle mounted on the stirrer shaft of the test jar apparatus was made of stainless steel and measured 7.6 cm (width) × 2.5 cm (height). The jar was made of acrylic plastic and measured 11.5 × 11.5 × 21 cm; a 2 L sample was used in each experiment. For all experiments, pH was adjusted after the addition of Mg and P sources; the sequence of chemical addition for the struvite precipitation to achieve the optimal removal efficiency of NH\(_4\)-N and PO\(_4\)-P has been verified in previous studies \[34,43\]. The pH was kept constant during struvite precipitation. Velocity gradient (G) was used as the mixing intensity for struvite precipitation, wherein the G value was determined based on the correlation between the velocity gradient (G) and impeller speed (rpm) of the paddle, as proposed by Cornwell and Bishop \[44\]. The settling time after the struvite precipitation reaction was set to 30 min, after which some of the supernatant was aliquoted using a syringe for sample analysis.

2.3. Estimation of NH\(_4\)-N and PO\(_4\)-P Recovery as Struvite from AD Effluents

The recoverable amount of NH\(_4\)-N and PO\(_4\)-P due to the application of struvite precipitation for swine manure was estimated for the 4 AD facilities and 85 biological treatment facilities operating in South Korea. The amount of NH\(_4\)-N and PO\(_4\)-P in AD effluents from the four AD facilities was calculated using the values listed in Tables 2 and 3. When calculating the amount of NH\(_4\)-N and PO\(_4\)-P to be recovered from the 85 biological treatment facilities, an application model, where AD and struvite precipitation reactors are sequentially connected in front of the biological treatment process, was considered. The inflow rate of each of the 85 biological treatment facilities was applied as the flow rate of influent from the biological treatment process in the application model. The average AD effluent concentrations of NH\(_4\)-N and PO\(_4\)-P listed in Table 3 were used as the concentrations of NH\(_4\)-N and PO\(_4\)-P in the AD effluent in the application model. Furthermore, the average values derived under the optimal conditions for struvite precipitation were used as the removal efficiencies of NH\(_4\)-N and PO\(_4\)-P in struvite precipitation.
2.4. Analytical Procedures

Total organic carbon (TOC; standard code: ES 04311.1c), NH$_4$-N (standard code: ES 05353.3), T-N (standard code: ES 04363.4b), PO$_4$-P (standard code: ES 04360.2c), and T-P (standard code: ES 04362.2b) were measured in accordance with the Korean standard procedures [45]. Toxic metals were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES; Perkin Elmer, USA). The limits of quantification for As, Cd, Pb, Cu, Zn, Cr, and Ni were 0.05, 0.004, 0.04, 0.006, 0.002, 0.007, and 0.015 mg/L, respectively. All samples were measured immediately after sample collection.

3. Results and Discussion

3.1. Optimal Conditions for Struvite Precipitation of AD Effluents from Swine Manure

An experiment was performed to determine the optimal conditions for the four key factors that affect the recovery of NH$_4$-N and PO$_4$-P from the AD effluents by struvite precipitation, namely pH, Mg:NH$_4$-N:PO$_4$-P molar ratio, mixing intensity, and mixing time. When the final reaction pH was increased from 7 to 11, the concentrations of NH$_4$-N and PO$_4$-P in the supernatant after struvite precipitation significantly decreased with a pH of up to 10, whereas there was no significant change or a slight increase in NH$_4$-N and PO$_4$-P concentrations when the pH increased from 10 to 11 (Figure 1). Therefore, it was determined that a final pH of 10 is most effective for maximizing the recovery rates of NH$_4$-N and PO$_4$-P and will save chemical costs during struvite precipitation from AD effluents. Several studies have reported that the removal rates of NH$_4$-N and PO$_4$-P increase as the pH increases during struvite precipitation experiments on AD effluents of animal manure [23,27–29,31,34,36]. However, only the results of Gong et al. [36] and Kwon et al. [29] were consistent with those of this study in terms of the optimal pH conditions; in other studies, the optimal pH ranged from 8.5 to 9.5, which varies slightly from the results obtained in this study. Except for the A3 facility, the residual NH$_4$-N concentrations increased at a pH value of 11. This was probably due to the formation of hydroxylapatite [Ca$_{10}$(PO$_4$)$_6$(OH)$_2$] when PO$_4^{3-}$ reacts preferentially with calcium ions (Ca$^{2+}$) in AD effluents during struvite precipitation at pH 11. Several previous studies have reported that the concentration of calcium ions (Ca$^{2+}$) in AD effluents from swine manure ranges from 28 to 75 mg/L [31,32,46,47], while hydroxylapatite is known to form in the pH range of 9–10.5 [15,48,49]. In addition, it was speculated that the increase in the residual NH$_4$-N concentrations at pH 11 is due to the formation of magnesium phosphate [Mg$_3$(PO$_4$)$_2$] in the pH range of 8.5–11 [50].

Figure 1. Residual concentrations of (a) NH$_4$-N and (b) PO$_4$-P as a function of final pH during struvite precipitation of samples A1, A2, A3 and A4. The molar ratio of NH$_4$-N:Mg:PO$_4$-P was 1.0:1.0:1.0, G was 240 s$^{-1}$, and the mixing duration was 2 min.
To recover NH$_4$-N from AD effluents in the form of struvite crystals (MgNH$_4$PO$_4$·6H$_2$O), chemicals should be added to attain the stoichiometric molar ratio of Mg:NH$_4$-N:PO$_4$-P. However, actual struvite precipitation in AD effluents may require greater amounts of Mg and PO$_4$-P than the stoichiometric amounts, owing to the presence of various ionic components in the AD effluents. In this study, the P source was added based on the same molar ratio as NH$_4$-N to minimize the chemical costs; the optimal amount of Mg was mainly tested because the amount of Mg plays an important role as the limiting factor in struvite precipitation [51]. When the amount of added Mg was increased to a NH$_4$-N:Mg:PO$_4$-P molar ratio of 1:1:1–1:1:6:1, the residual NH$_4$-N concentration after struvite precipitation tended to increase, whereas the residual PO$_4$-P concentration tended to decrease (Figure 2). The increase in the residual NH$_4$-N concentration was proportionate to an increase in the amount of Mg added; this was probably due to the formation of hydroxylapatite [Ca$_{10}$(PO$_4$)$_6$(OH)$_2$] or due to magnesium phosphate [Mg$_3$(PO$_4$)$_2$] being more dominant than struvite precipitation at pH 10 [15,48–50]. These results are consistent with those reported by Kim et al. [28], in which the removal efficiency of NH$_4$-N decreased with an increasing amount of Mg. Contrary to the results obtained in this study, several studies have reported that the concentrations of residual NH$_4$-N and PO$_4$-P decreased simultaneously when the amount of added Mg increased [29,30,33,34]. This difference is believed to arise owing to the pH adjustment method during the struvite precipitation. In this study, the pH was kept constant at 10 for 2 min, during which the struvite precipitation reaction proceeded. In contrast, in the aforementioned studies, the target pH was adjusted before or after adding the Mg and P sources, but the pH was not kept constant during the reaction time; therefore, when struvite precipitation was complete, the pH decreased further than the initial pH, which can be attributed to Mg not actively participating in the reaction of hydroxylapatite [Ca$_{10}$(PO$_4$)$_6$(OH)$_2$] or magnesium phosphate [Mg$_3$(PO$_4$)$_2$]. Kwon et al. [29] reported that the initial pH had been adjusted to 9, which decreased to 6 after a reaction time of 1 h during struvite precipitation from the AD effluents of swine manure. Considering the residual NH$_4$-N and PO$_4$-P concentrations simultaneously, the optimal amount of added Mg was determined to be a NH$_4$-N:Mg:PO$_4$-P molar ratio of 1:1:4:1.

![Figure 2](image-url)

**Figure 2.** Residual concentrations of (a) NH$_4$-N and (b) PO$_4$-P as a function of Mg dosage during struvite precipitation of samples A1, A2, A3 and A4. The final pH was 10.0, G was 240 s$^{-1}$, and mixing duration was 2 min.

Table 4. N and PO$_4$-P as a function of mixing intensity during the struvite precipitation of AD effluents from swine manure, the effect was observed over the mixing intensity (G) range of 240–650 s$^{-1}$. The results show that there was minimal change in the concentration of residual NH$_4$-N and PO$_4$-P as the mixing intensity increased (Figure 3). Considering the increase in energy costs due to the increase in mixing intensity, the optimal mixing intensity was determined to be 240 s$^{-1}$. To the best
of our knowledge, Lee et al. [27] has been the only study on the optimal mixing intensity in struvite precipitation of AD effluents. They reported that there was almost no change in the removal rate of NH$_4$-N and PO$_4$-P when the mixing intensity was increased from 100 to 200 revolutions per minute (rpm), which is similar to the result obtained in this study. However, because the G value varies depending on the shape of the reactor and paddle, even with the same rpm [44], rpm cannot be considered as an accurate expression of mixing intensity, such that the mixing intensity expressed as G is more accurate and scientific, as in this study.

![Figure 3](image1.png)

**Figure 3.** Residual concentrations of (a) NH$_4$-N and (b) PO$_4$-P as a function of G during struvite precipitation of samples A1, A2, A3 and A4. The final pH was 10.0, the molar ratio of NH$_4$-N:Mg:PO$_4$-P was 1.0:1:4:1.0, and the mixing duration was 2 min.

![Figure 4](image2.png)

**Figure 4.** Residual concentrations of (a) NH$_4$-N and (b) PO$_4$-P as a function of mixing duration during struvite precipitation of samples A1, A2, A3 and A4. The final pH was 10.0, the molar ratio of NH$_4$-N:Mg:PO$_4$-P was 1.0:1.4:1.0, and G was 240 s$^{-1}$.

Previous studies based on the optimal mixing duration for struvite precipitation from AD effluents derived from livestock manure have reported optimal durations of 15–60 min [23,27,34]. In particular, no study has reported a reaction time of less than 30 min in the case of AD effluent from swine manure. Hence, it was not possible to determine the removal characteristics of NH$_4$-N and PO$_4$-P by struvite precipitation in a short reaction time. In this study, it was found that the removal efficiency of NH$_4$-N and PO$_4$-P did not increase significantly during struvite precipitation over 2 min (Figure 4). Therefore, the optimal reaction time for struvite precipitation from the AD effluents of swine manure...
was determined as 2 min. Luo et al. [23] and Siciliano and Rosa [34] also found that the removal efficiency of NH$_4$-N and PO$_4$-P did not increase after 15 min. According to their study, the removal efficiency of NH$_4$-N and PO$_4$-P increased by 5% and 4% in struvite precipitation of the AD of calf manure, respectively, when the reaction time was increased from 1 to 15 min.

### 3.2. Removal of TOC, NH$_4$-N, PO$_4$-P, and Toxic Metals from AD Effluents of Swine Manure under Optimal Conditions

Table 4 lists the removal efficiencies of TOC, NH$_4$-N, PO$_4$-P, and toxic metals (such as As, Cd, Pb, Cu, Zn, Cr, and Ni) in struvite precipitation from AD effluents of swine manure under the optimal conditions derived above. It was observed that a significant amount of TOC (Table 3) present in the AD effluents was removed (mean of ~58%) during struvite precipitation. TOC removal was probably due to a flocculation reaction of organic matter by the added Mg during struvite precipitation [25]. Considering that raw swine manure has a higher content of organic matter than AD effluents, these results suggest that it is more effective to recover N and P from AD effluents than from raw swine manure. According to previous studies, the presence of organic matter during struvite precipitation interferes with the struvite formation process and changes the shape and length of struvite crystals, thereby affecting the quality of the fertilizer [40,41,52]. Huang, et al. [42] reported that the removal efficiency of total ammonia nitrogen and PO$_4$-P decreased during struvite precipitation as the concentration of organic matter increased. Under optimal conditions, the removal efficiencies of NH$_4$-N and PO$_4$-P in struvite precipitation were analyzed as approximately 74% and 83%, respectively (Table 4). These removal efficiencies are 2% and 5% higher than the average removal efficiencies of NH$_4$-N (72%) and PO$_4$-P (78%) in struvite precipitation from AD effluents of swine manure reported in the literature [23,27–29,31,32,35,37]. This indicates that the recovery rates of N and P in struvite precipitation can be increased when operating under optimal conditions.

| Parameter | Sample Numbers (n) | Value Range | Mean Value |
|-----------|-------------------|-------------|------------|
| TOC $^1$ (mg/L) | 9 | 32.1–89.7 | 57.6 ± 22.0 $^2$ |
| NH$_4$-N | 9 | 62.2–89.6 | 73.7 ± 9.6 |
| PO$_4$-P | 9 | 68.7–89.0 | 83.0 ± 7.4 |
| As | 4 | 23.7–49.0 | 34.8 ± 12.4 |
| Cd | 4 | 0–89.6 | 22.4 ± 44.8 |
| Pb | 4 | 0–75.9 | 28.9 ± 36.0 |
| Cu | 4 | 44.1–97.2 | 74.3 ± 22.1 |
| Zn | 4 | 58.1–97.4 | 79.2 ± 16.9 |
| Cr | 4 | 13.3–100 | 65.7 ± 42.0 |
| Ni | 4 | 12.1–48.7 | 32.1 ± 17.2 |

$^1$ Total organic carbon; $^2$ standard deviation.

The concentrations of Cu and Zn were higher than those of other toxic metals in the AD effluent of the swine manure. Furthermore, they were removed with higher efficiency than other toxic metals in struvite precipitation. Chromium (Cr) showed the third highest removal efficiency after Zn and Cu (Table 4). The co-precipitation of toxic metals during struvite precipitation has also been reported previously [52–54]. According to Huang et al. [55], the removal efficiencies of Zn and Cu during struvite precipitation experiments on synthetic swine wastewater decreased rapidly as the pH increased (8.5–10.0), and there was a little change in the removal efficiencies above pH 10. Based on these results, pH 10 (i.e., the optimal pH condition derived in this study) is considered as the condition that can minimize Zn and Cu contents when recovering N and P from the AD effluents of swine manure. Interestingly, Huang et al. [55] reported the removal efficiencies of Zn and Cu at pH 10 as approximately
30% and 15%, respectively, whereas the removal efficiencies of Zn and Cu obtained in our study were approximately 79% and 74%, respectively. This suggests that higher precipitation rates of Zn and Cu should be considered when N and P are recovered from the AD effluents of swine manure.

3.3. Application Model of Struvite Precipitation for the Recovery of N and P from Swine Manure

High concentrations of organic matter resulted in a decline in N and P recovery rates and an adverse impact on the purity of struvite crystals during struvite precipitation [40–42,52]. As approximately 58% of TOC was removed during struvite precipitation from the AD effluents of swine manure in this study (Table 4), it would be more effective to apply N and P recovery from AD effluents with some organic matter removed rather than using the raw swine manure with high concentrations of organic matter. According to the literature, 50–80% of CODcr is removed during the AD of swine manure [16,37,56]. Considering this and the difficulty of biological nitrification with high concentrations of NH4-N in swine manure [25,26], the recovery of N and P from swine manure by struvite precipitation can enhance the efficiency of subsequent biological N treatment. In particular, Ryu and Lee [25] reported that N and P pretreatment of swine manure by struvite precipitation improves the nitrification efficiency of the subsequent biological treatment and increases the denitrification efficiency. Therefore, it is considered most effective to treat swine manure by AD and recover N and P from the treated AD effluents by struvite precipitation, and then perform biological treatment. A schematic of this swine manure treatment process is presented in Figure 5. When swine manure is treated by the proposed model, not only methane gas but also N and P as struvite can be recovered from the swine manure, while improving the biological treatment efficiency.

![Figure 5. Schematic of the application model for the struvite precipitation process in treating swine manure: (1) anaerobic digestion (AD) reactor; (2) solid–liquid separation of AD effluents; (3) struvite precipitation reactor; (4) struvite deposit settler; (5) biological treatment reactor; and (6) final settler.](image-url)

South Korea has four AD facilities, 85 biological treatment facilities, four composted manure treatment facilities, and two composted liquid manure treatment facilities for swine manure treatment, with biological treatment facilities clearly accounting for the greatest fraction. Swine manure contains high concentrations of organic matter, N, and P and requires a long hydraulic retention time (approximately 20–30 days) for biological treatment. Moreover, owing to nitrification inhibition caused by low temperatures in winter, there is a chronic problem of manure exceeding the effluent quality standard [25,26]. To address these issues, retrofitting facilities by incorporating AD and struvite precipitation processes into existing biological treatment facilities, as shown in Figure 5, would be
effective for sustainable swine manure treatment. From the recoverable amounts of NH$_4$-N and PO$_4$-P under the optimal conditions derived during this study (Table 4), approximately 149 and 2 tons/yr of NH$_4$-N and PO$_4$-P, respectively, could be recovered (Figure 6) by integrating the struvite precipitation process into the four AD facilities (AD + SP). Furthermore, if swine manure were treated by incorporating the AD and struvite precipitation processes into the 85 existing biological treatment (BT) facilities (AD + SP + BT), as shown in Figure 5, the amounts of NH$_4$-N and PO$_4$-P that could be recovered would be approximately 4722 and 51 tons/yr, respectively. Therefore, larger amounts of N and P could be recovered with AD + SP + BT than with the combination of the existing AD process and struvite precipitation (Figure 6).

3.4. Economic Analysis of Struvite Recovery When Treating AD Effluents of Swine Manure

Economic analysis of the recovery of NH$_4$-N and PO$_4$-P by struvite precipitation from AD effluents was conducted by analyzing the chemical costs required for struvite precipitation and the cost of commercializing the recovered struvite. The amounts of the added chemicals (MgCl$_2$·6H$_2$O, K$_2$HPO$_4$, and NaOH) were recorded during struvite precipitation. Based on these records, the amounts of industrial chemicals (46% MgCl$_2$·6H$_2$O, 85% H$_3$PO$_4$, and 98% NaOH) that would be consumed when applied at field scale were calculated for the amounts of chemicals consumed per 1 m$^3$ of AD effluents and 1 kg of recovered struvite (Figure 7).
The Korea Price Research Center, Corp. provided prices [57], which were used as the prices of chemicals for calculation purposes, as listed in Table 5. Based on the amount of chemicals and their unit prices shown in Figure 7 and Table 5, the chemical cost required to recover N and P contained in 1 m$^3$ of AD effluent was calculated as 51.63 US$/m^3$, whereas the chemical cost required to recover 1 ton of struvite was calculated as 2285.40 US$/ton. Additional costs are expected considering various factors. When these various factors are considered (e.g., chemical costs, sludge transportation and disposal, electricity, engineering, labor, capital and operating costs, and maintenance), along with the struvite sales price of 560 €/ton (661.53 US$/ton) suggested by Yetilmezsoy et al. [20], and the chemical costs derived from this study, a lack of profitability is expected for the recovery of N and P by struvite precipitation from the AD effluents of swine manure. However, struvite precipitation is an essentially irreplaceable treatment method in countries or regions where the use of solid or liquid composted manure is limited, even with a nutrient surplus. Therefore, if technological developments are made to secure high-quality fertilizer when integrating struvite precipitation with an AD process in swine manure treatment and N is reduced by struvite precipitation, enabling stable and sustainable operations of the subsequent biological treatment process will bring about additional benefits to the hydrological environment. These benefits are expected to offset the financial burden associated with the chemical costs.

Table 5. Chemical costs used in the economic analysis.

| Chemicals          | Costs in Dollars | Reference                        |
|--------------------|------------------|----------------------------------|
| 46% MgCl$_2$·6H$_2$O | 269.59 US$ per ton | Korea Price Research Center, Corp. [57] |
| 85% H$_3$PO$_4$    | 1668.07 US$ per ton |                                   |
| 98% NaOH           | 699.24 US$ per ton |                                   |
| Struvite           | 661.53 US$ per ton | Yetilmezsoy et al. [20]           |

4. Conclusions

This study aimed to propose an effective method for recovering N and P from AD effluents by struvite precipitation for sustainable swine manure treatment. The optimal conditions for four key factors (pH, NH$_4$-N:Mg:PO$_4$-P molar ratio, mixing intensity, and mixing duration) in struvite precipitation were found to be a pH of 10.0, NH$_4$-N:Mg:PO$_4$-P molar ratio of 1:1.4:1, mixing intensity of 240 s$^{-1}$, and mixing duration of 2 min. In previous studies, the mixing intensity was presented in terms of rpm of the paddles, whereas this study presents it in terms of G, which is more accurate. Furthermore, a mixing duration of 2 min, which is shorter than that reported in the literature (15 min), was found to be effective in recovering the N and P in AD effluents. The removal rates of NH$_4$-N and PO$_4$-P from the AD effluents of swine manure by struvite precipitation in nine experimental runs were approximately 74% and 83%, respectively. Furthermore, a significant amount of organic matter was removed during this process, with an average TOC removal of 58%. Therefore, it is more effective to apply struvite precipitation to AD effluents with a lower content of organic matter in swine manure treatment. Toxic metals were also found to be co-precipitated with N and P with high removal efficiency (i.e., 74% and 79% for Cu and Zn, respectively). Interestingly, when struvite precipitation was operated under optimal conditions, the recovery efficiency rates of N and P were higher than those reported in the literature. The removal rates of toxic metals (Cu and Zn) were also higher than values suggested previously, indicating that this requires consideration when using recovered struvite as a fertilizer.

Based on the results of batch experiments and to facilitate the sustainable recovery of N and P from the AD effluents of swine manure, a combined model of AD and struvite precipitation processes is proposed for existing biological treatment facilities, which are generally used for swine manure treatment in South Korea. According to the calculations in this study, applying this model to the 85 treatment facilities in South Korea could recover 4722 and 51 tons/yr of NH$_4$-N and PO$_4$-P, respectively. The results of an economic analysis, which considered the chemical costs of struvite
precipitation and profits from the commercialization of recovered struvite, show a lack of profitability. However, in countries or regions where the production and spraying of livestock manure and solid or liquid composted manure are limited, the proposed model will function as a sustainable swine manure treatment system if the additional benefits to the hydrological environment are considered. These include a reduction in the operating costs and improved treatment efficiencies due to reduced loads of N and P that flow to the biological treatment process integrated with struvite precipitation. In future, the effectiveness of the proposed model needs to be demonstrated through a field-scale study.

**Author Contributions:** Conceptualization, H.-D.R. and E.G.C.; methodology, H.-D.R. and E.G.C.; formal analysis, H.-D.R. and D.Y.L.; investigation, S.-J.K. and U.-I.B.; data curation, H.-D.R. and D.Y.L.; writing—original draft preparation, H.-D.R.; writing—review and editing, H.-D.R., E.G.C. and K.K.; supervision, E.G.C.; project administration, J.K.L. All authors have read and agreed to the published version of the manuscript.

**Funding:** This study was supported by the National Institute of Environmental Research, Republic of Korea (Project No. NIER-2019-01-01-034).

**Acknowledgments:** We are grateful to the individuals who contributed to sample collection and to all of the individuals and groups who participated in this study.

**Conflicts of Interest:** The authors declare no conflict of interest.

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