Ammonium nitrogen removal from slurry-type swine wastewater by pretreatment using struvite crystallization for nitrogen control of anaerobic digestion


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Abstract  Precipitation of ammonium together with phosphate and magnesium is a possible alternative for lowering the nitrogen content of wastewater. In this study we examine the removal of ammonium nitrogen and phosphorus from slurry-type swine wastewater containing high concentrations of nutrients by the addition of phosphoric acid along with either calcium oxide or magnesium oxide, which leads to the crystallization of insoluble salts such as hydroxyapatite and struvite. The struvite crystallization method showed a high capacity for the removal of nitrogen when magnesium oxide and phosphoric acid were used as the magnesium and phosphate sources, respectively. When it was applied to swine wastewater containing a high concentration of nitrogen, the injection molar ratio of Mg\(^{2+}\):NH\(_4\)^+:PO\(_4\)^{3–} that gave maximum ammonium nitrogen removal was 3.0:1.0:1.5.

Keywords  Crystallization; magnesium ammonium phosphate; struvite; swine wastewater

Introduction

Swine wastewater includes high concentrations of organic matter and ammonium nitrogen, and hence it is difficult to treat directly using biological treatment processes. In particular, biological-nutrient removal processes are affected by a low C/N ratio, and anaerobic processes are affected by the inhibition of ammonium nitrogen in the startup period. Therefore, it is necessary to introduce a pretreatment process for the reduction of ammonium nitrogen before the biological processes begin.

Air stripping, ion exchange, and breakpoint chlorination are widely used for the removal of ammonium nitrogen, and struvite (MgNH\(_4\)PO\(_4\)·6H\(_2\)O) crystallization methods are used for the combined removal of ammonium nitrogen and phosphorus. Struvite precipitation occurs when the combined concentrations of magnesium (Mg\(^{2+}\)), ammonium (NH\(_4\)^+), and phosphate (PO\(_4\)^{3–}) exceed the struvite solubility limit. The availability of the three components is controlled by the system pH and the total dissolved concentrations of magnesium, ammonium, and phosphorus species. Because speciation of the components is pH dependent, the solubility of struvite also varies with pH: struvite solubility decreases as pH increases within the pH range expected in wastewater treatment (6.0–8.0) (Ohlinger et al., 1998).

Many studies have shown that crystallization of magnesium ammonium phosphates or calcium ammonium phosphate (CaNH\(_4\)PO\(_4\)) using magnesium and calcium as the precipitant (Momberg and Oellermann, 1992; Schulze-Rettmer, 1991; Stefanowicz et al., 1992) results in a high removal efficiency of nutrients. Moreover, using struvite is economical because the struvite crystals can be recycled by way of final oxidation in the form Mg\(_3\)(PO\(_4\))\(_2\) (Stefanowicz et al., 1992), and it has been suggested that struvite exhibits excellent fertilizer qualities under specific conditions when compared with standard fertilizers (Ghosh et al., 1996).
This present study utilized crystallization methods involving struvite or calcium ammonium phosphate (CaNH₄PO₄) to control the inhibition by ammonium nitrogen during anaerobic digestion of slurry-type swine wastewater, in order to determine the factors influencing these crystallization reactions with a view to using them in field applications.

**Materials and methods**

This research can be divided into two major parts. First, batch experiments were conducted in which calcium oxide (CaO), magnesium oxide (MgO) and phosphoric acid (H₃PO₄) were injected into synthetic wastewater (a stock solution of 0.07 M NH₄Cl). The CaO, MgO and H₃PO₄ were the sources of calcium, magnesium and orthophosphate (ortho-P) for the formation of crystalline CaNH₄PO₄ and MgNH₄PO₄·6H₂O.

The pH can be changed by adding base, commonly in the form of CaOH, NaOH, or MgOH₂. NaOH has been suggested as the more effective chemical in pH adjustment (Fujimoto et al., 1991). In this study, the pH was controlled by using a NaOH solution to examine the removal characteristics of NH₄⁺–N and phosphate at various pH values. The experiments were performed with the injection molar ratios of Ca²⁺/NH₄⁺–N, Mg²⁺/NH₄⁺–N, and ortho-P/NH₄⁺–N in the ranges 1.0–3.5, 0.7–4.9, and 0.6–1.7, respectively.

Based on the first experimental results, a batch experiment was performed with slurry-type swine wastewater. MgO was used as a coagulant and H₃PO₄ was used as the source of ortho-P. The experiments were performed with the injection molar ratios of ortho-P/NH₄⁺–N, Mg²⁺/NH₄⁺–N, and Mg²⁺/ortho-P in the ranges 0.8–2.6, 0.8–5.2, and 0.3–6.0, respectively. Moreover, we estimated the optimal injection molar ratio and rate.

At the end of each experiment, the solid phase was collected by filtration through membrane filters. The filtered precipitate was dried at 40 °C in an oven for 48 h. The drying temperature was selected to prevent the struvite crystals from losing their water of crystallization, which occurs at 60 °C (Ando et al., 1968). Dried precipitate was examined and identified as struvite using X-ray diffraction (XRD; D/Max 2000, Rigaku, Japan). The crystal structure was examined using scanning electron microscopy (SEM; JSM-6300, JEOL, Japan).

The characteristics of the slurry-type swine wastewater are summarized in Table 1. The concentrations of total solids (TS) and ammonium nitrogen (NH₄⁺–N) were 4,850–25,000 mg/L and 1,855–4,500 mg/L, respectively. The slurry-type swine wastewater used in the experiment was diluted with water at a raw wastewater-to-water ratio of 1:2. H₃PO₄ was artificially injected, because the amount of ortho-P is less than the amount of ammonium nitrogen in swine wastewater. All samples were measured using Standard Methods (APHA, 1995).

**Results and discussion**

**Experiments with stock ammonium solution**

*The removal of nitrogen and phosphate using CaO.* We intended to remove the ammonium nitrogen and phosphate by using the CaNH₄PO₄ crystallization method. CaO was used as a

<table>
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<th>Parameter</th>
<th>Value</th>
<th>Parameter</th>
<th>Value</th>
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<td>pH</td>
<td>7.0–8.5</td>
<td>Soluble COD</td>
<td>4,300–9,600</td>
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<td>Total solids</td>
<td>4,850–25,000</td>
<td>NH₄⁺–N</td>
<td>1,855–4,500</td>
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<td>Total Kjeldahl nitrogen</td>
<td>2,320–4,950</td>
<td>PO₄³⁻–P</td>
<td>45–80</td>
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<tr>
<td>Total COD</td>
<td>6,000–12,500</td>
<td>Alkalinity (as CaCO₃)</td>
<td>6,150–9,780</td>
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</table>

*Table 1* Physicochemical characteristics of slurry-type swine wastewater (unit: mg/L, except pH)
coagulant and H₃PO₄ was used as the source of phosphate. The residual NH₄⁺–N concentration and removal efficiency are shown as a function of the molar ratio of Ca²⁺/NH₄⁺–N in Table 2. The NH₄⁺–N removal efficiency was low, in the range 3.6–45.1%. This was attributable to side reactions – such as hydroxyapatite (Ca₅OH(PO₄)₃), dicalcium phosphate (CaHPO₄), and octocalcium phosphate (Ca₄H(PO₄)₃) – that occurred prior to the struvite crystallization.

The removal of nitrogen and phosphate using MgO. In cases where MgO and H₃PO₄ were used, the mechanism of struvite crystallization involves the following equations:

\[
\text{MgO + H}_3\text{PO}_4 \rightarrow \text{MgHPO}_4 + \text{H}_2\text{O} \\
3\text{MgO} + 2 \text{H}_3\text{PO}_4 \rightarrow \text{Mg}_3(\text{PO}_4)_2 + 3\text{H}_2\text{O} \\
3\text{MgO} + 2\text{NH}_4\text{Cl} + 2 \text{H}_3\text{PO}_4 \rightarrow 2\text{MgNH}_4\text{PO}_4 + \text{MgCl}_2 + 3\text{H}_2\text{O}
\]

This experiment was undertaken to estimate the optimal molar ratio of Mg²⁺/NH₄⁺–N, and the molar ratio increased from 0.7 to 4.9. Figure 1 shows the residual NH₄⁺–N concentration and removal efficiency for different molar ratios of Mg²⁺/NH₄⁺–N. When the molar ratio of Mg²⁺/NH₄⁺–N was above 2.1, the NH₄⁺–N removal efficiency was 54.0–99.1%. The NH₄⁺–N removal efficiency was high when wastewater contained high concentrations of ammonium nitrogen. The dosage of phosphate and magnesium was increased to above the stoichiometric amount. The results were consistent with those of Schulze-Rettmer (1991), who reported that side reactions such as magnesium hydroxide (Mg(OH)₂), magnesium hydroxyphosphates or magnesium hydrogen phosphate were faster than struvite crystallization.

**Table 2** Residual concentration and removal efficiency of NH₄⁺–N for different ortho-P/NH₄⁺–N and Ca²⁺/NH₄⁺–N molar ratios (synthetic wastewater).

<table>
<thead>
<tr>
<th>Item</th>
<th>Ortho-P/NH₄⁺–N molar ratio</th>
<th>Conc. (mg/L)</th>
<th>Removal (%)</th>
<th>Conc. (mg/L)</th>
<th>Removal (%)</th>
<th>Conc. (mg/L)</th>
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<td>0.60</td>
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<td>996.3</td>
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<td>Ca²⁺/NH₄⁺–N molar ratio</td>
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<td>45.1</td>
<td>866.0</td>
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<td>910.4</td>
<td>9.0</td>
<td>958.4</td>
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<td></td>
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<td>598.7</td>
<td>40.1</td>
<td>842.3</td>
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<td>3.5</td>
<td>551.1</td>
<td>44.9</td>
<td>789.6</td>
<td>31.0</td>
<td>837.4</td>
<td>16.3</td>
<td>876.6</td>
<td>12.4</td>
</tr>
</tbody>
</table>

**Figure 1** The residual NH₄⁺–N concentration and removal efficiency for different Mg²⁺/NH₄⁺–N molar ratios (synthetic wastewater).
Figure 2 shows the residual concentration and removal efficiency of NH$_4$$^+$–N for different molar ratios of ortho-P/NH$_4$$^+$–N. For this, we fixed the injection molar ratio of Mg$^2+$/NH$_4$$^+$–N, at 2.8. In accordance with Figure 2, the NH$_4$$^+$–N removal efficiency gradually increased to 99% as the molar ratio of ortho-P/NH$_4$$^+$–N increased to 1.5. Above this value the NH$_4$$^+$–N removal rate decreased, because the struvite crystallization was adversely affected by the pH.

Figure 3 shows the residual concentration and removal efficiency of NH$_4$$^+$–N for different dosages of Mg$^2+$. For this, we fixed the molar ratio of Mg$^2+$/ortho-P at 2.0. The NH$_4$$^+$–N removal efficiency increased from 20.1% to 99.2% as the dosage of Mg$^2+$ increased from 2.3 to 9.9 g/L. However, the NH$_4$$^+$–N removal efficiency gradually decreased above dosages of 9.9 g/L.

From these results, we suggest that for the removal of high concentrations of NH$_4$$^+$–N and phosphate the optimal molar ratios of ortho-P/NH$_4$$^+$–N, Mg$^2+$/NH$_4$$^+$–N, and Mg$^2+$/ortho-P are 1.4, 2.8, and 2.0, respectively.

We performed experiments to estimate the effect of pH on the struvite crystallization reaction. The range of pH values tested was 8–11. Figure 4 shows the residual concentration and removal efficiency of NH$_4$$^+$–N for different Mg$^2+$ dosages and pH values. The NH$_4$$^+$–N removal rates were: pH 11 < pH 8 < pH 9. This result is consistent with that of Schulze-Rettmer (1991), who reported that the minimum struvite solubility occurred for pH values in the range 9.0–9.5. Generally, struvite solubility decreases with increasing pH. However, as the pH value rises above 9 the solubility of struvite begins to increase, since the ammonium ion concentration decreases and the phosphate ion concentration increases.

Figure 5 shows the NH$_4$$^+$–N removal rate and variation in pH with the molar ratio
of Mg\(^{2+}\)/ortho-P. The NH\(_4^+\)–N removal efficiency was about 60% and about 70% for pH >8 and pH >10, respectively. Therefore, a pH of 8–10 is optimal for the struvite pretreatment.

Figure 6 shows the residual NH\(_4^+\)–N concentration as a function of the reaction time. On the basis of the results described above, the molar ratios of ortho-P/ NH\(_4^+\)–N, Mg\(^{2+}\)/ortho-P, and Mg\(^{2+}\)/ NH\(_4^+\)–N in this reaction were fixed at 1.4, 2.0, and 2.8, respectively. Figure 7 shows the plot of the residual NH\(_4^+\)–N concentration versus time for a Mg\(^{2+}\)/ortho-P molar ratio of 2.0. The reaction time required for >90% NH\(_4^+\)–N removal was approximately 43 minutes, with about 30 minutes being required for 80% ammonium removal. The correlation coefficient (R\(^2\)) was 0.950 and the reaction time constant was 0.0533 min\(^{-1}\). The high value of the correlation coefficient indicates that the struvite crystallization was a first-order reaction.

Experiments with slurry-type swine wastewater

The experiments using the synthetic wastewater demonstrated that the struvite crystallization was efficient at removing high concentrations of NH\(_4^+\)–N. Therefore, the same experiment was carried out using slurry-type swine wastewater.

Figure 8 shows the residual NH\(_4^+\)–N concentration and removal efficiency for different molar ratios of Mg\(^{2+}\)/NH\(_4^+\)–N. When the molar ratio of ortho-P/ NH\(_4^+\)–N was 0.86, the residual NH\(_4^+\)–N concentration decreased with increases in the molar ratio of Mg\(^{2+}\)/NH\(_4^+\)–N. For Mg\(^{2+}\)/NH\(_4^+\)–N molar ratio above 2.6, the NH\(_4^+\)–N removal efficiency was relatively constant in the range 76.2–80.9%. For injection molar ratios of ortho-P/NH\(_4^+\)–N of 1.29, 1.79, and 2.16, the removal efficiency was over 95% for Mg\(^{2+}\)/NH\(_4^+\)–N molar ratios of 4.3, 2.6, and 3.5.
Based on this result, we fixed the Mg\(^{2+}\)/NH\(_4\)\(^+\)–N molar ratio at 3.0. Figure 9 shows the residual NH\(_4\)\(^+\)–N and phosphate concentration for different ortho-P/ NH\(_4\)\(^+\)–N molar ratios. The removal efficiency was highest when the ortho-P/ NH\(_4\)\(^+\)–N injection molar ratio was 1.5.

Figure 10 shows the residual NH\(_4\)\(^+\)–N concentration and the removal efficiency for different dosages of Mg\(^{2+}\). As the amount of Mg\(^{2+}\) increased, the residual NH\(_4\)\(^+\)–N concentration decreased, with the nitrogen removal efficiency being over 98% for Mg\(^{2+}\) concentrations higher than 20 g/L.

Figure 11 shows the variation in alkalinity for different Mg\(^{2+}\) dosages. The alkalinity decreased as the amount of Mg\(^{2+}\) increased because the precipitants, such as the magnesium hydroxide, consumed alkaline species. Figure 12 shows the residual NH\(_4\)\(^+\)–N concentration and volume of the sludge as a function of pH. The NH\(_4\)\(^+\)–N removal rate was highest when the pH was 9, and the volume of the sludge was in the range 28.0–38.5\% (v/v). The optimal molar ratios of Mg\(^{2+}\)/NH\(_4\)\(^+\)–N, Mg\(^{2+}\)/ortho-P, and ortho-P/NH\(_4\)\(^+\)–N were found to be 3.0, 2.0, and 1.5, respectively. The precipitants dissolved slowly, and hence more detailed experimental research is required before the precipitants can be utilized efficiently as a fertilizer.

**Analysis of sedimentation**

The sediments formed in the batch experiment were analyzed with XRD and SEM. The measurement scope for XRD was 10\(^{\circ}\)–60\(^{\circ}\); peaks were detected at 15.82\(^{\circ}\), 16.46\(^{\circ}\), 20.83\(^{\circ}\), 21.48\(^{\circ}\), 31.95\(^{\circ}\), 33.26\(^{\circ}\), 42.92\(^{\circ}\), 43.11\(^{\circ}\), 46.25\(^{\circ}\), 50.63\(^{\circ}\), and 50.91\(^{\circ}\), as shown in Figure 13. The comparison with and analysis of JCPDS data including XRD indicated that the sediment was struvite. Figure 14 shows scanning electron micrographs of sediment materials;
this micrograph reveal that the precipitant had a flat shape which was different from that of shapeless particles. From the XRD and SEM analyses, it is assumed that the nitrogen and phosphate removal were mainly due to struvite crystallization.

Conclusions

The results of the present experiments on the pretreatment of slurry-type swine wastewater containing high concentrations of organic matter and ammonium nitrogen using struvite crystallization can be summarized as follows:

1. Of the two treatment regimes (i.e., injection of CaO and H₃PO₄ versus MgO and H₃PO₄) tested on synthetic wastewater containing a high concentration of ammonium nitrogen, the magnesium ammonium phosphate (struvite) method was very efficient.

2. When forming struvite crystals in a stock ammonium solution, the optimum molar ratio of Mg²⁺: NH₄⁺:PO₄³⁻ was 2.8:1:1.4. The removal efficiency at this molar ratio was 99.2%.

3. When the struvite crystallization method was applied to slurry-type swine wastewater, the injection molar ratio of Mg²⁺: NH₄⁺:PO₄³⁻ that gave maximum ammonium nitrogen removal and struvite crystal formation was 3.0:1:1.5. The residual content of ammonium nitrogen can be varied to suit the desired residual content and the subsequent purification process by altering the magnesium and phosphate dosages.

4. The removal efficiency of the struvite precipitation method was highest in weak alkali solutions (pH 8–10).

References


