Recovery of Nitrogen and Phosphorous as Struvite From Swine Waste Biogas Digester Effluent

P. W. ANTON PERERA, ZHI-YING HAN, YING-XU CHEN, AND WEI-XIANG WU

College of Environmental and Resource Sciences, Zhejiang University, Hangzhou 310029, Zhejiang, China

Objective To investigate the feasibility of nitrogen and phosphorus recovery from swine waste biogas digester effluent and the effects of pH and NH₄⁺; Mg²⁺; PO₄³⁻ molar ratio on its precipitation. Methods Precipitation experiments with swine waste biogas digester effluent were conducted at pH 7.5, 8.0, 8.5, and 9.0 together with NH₄⁺; Mg²⁺; PO₄³⁻ molar ratios 1: 0.2; 0.08, 1: 1: 1, and 1: 1.5: 1.5. Chemical and X-ray diffraction (XRD) analysis were done to determine the composition of the precipitate. Results The highest removal and recovery of NH₄⁺ and PO₄³⁻ were achieved at pH 9.0 in each experiment. The elevation of pH to 9.0 alone could decrease the initial PO₄³⁻ concentration from 42 mg L⁻¹ to 4.7 mg L⁻¹ and 89.2% PO₄³⁻ recovery was achieved. The pH-molar ratio combination 9.0—1: 1.5: 1.5 affected 76.5% NH₄⁺ and 68.5% PO₄³⁻ recovery. The molar ratio of 1: 1: 1 together with pH elevation to 9.0 was determined to be the optimum combination for both NH₄⁺ and PO₄³⁻ removal as it recovered over 70% and 97% of the initial NH₄⁺ and PO₄³⁻, respectively. Conclusions Nitrogen and phosphorus can be recovered from biogas digester effluent as struvite.

Key words: Phosphate recovery; Ammonium nitrogen recovery; Biogas; Struvite; Swine waste

INTRODUCTION

Swine production has become a large-scale, intensive operation, which produces large volumes of waste that cannot be recycled within the system[1]. Pig excreta were rich in phosphorus as pigs typically excrete up to 70% of their P intake and nitrogen has also been present in higher quantities[2]. Different livestock waste disposal and treatment techniques are used to minimize the environmental impacts of swine waste, in which biogas production attracts more attention for its effectiveness in odor control, improved manure handling, mineralization of organic nitrogen, weed seed destruction, flies and pathogen reduction, and digested solid production, in addition to the energy benefits through biogas production[3-4]. During biogas production process, protein and other organic nitrogen compounds are degraded to form ammonia nitrogen and as a result, NH₄⁺ concentration in the bulk fluid is significantly increased. Magnesium and phosphate concentrations also increase due to cell lysis[4-5]. As the effluent contains high concentration of ammonia nitrogen and phosphate, the effluent generated from anaerobic digesters has a potential environmental risk[4-5], which can cause serious environmental problems, such as eutrophication, and dissolved oxygen depletion leading to the imbalanced aquatic ecosystem[6-8]. Despite the fact that biological nutrient removal (BNR) technologies can satisfy the discharge standard requirements[5,8], there is an ever-increasing need to supply nitrogen and phosphorous mainly to the agriculture and other sectors as well. Particularly, phosphorous is considered to be a scarce substance and it is estimated that rock phosphate deposits are sufficient only for another 100-250 years[10]. Therefore, there is a growing concern over the recovery of these nutrients from waste water ensuring their sustainable use. Crystalization of magnesium ammonium phosphate hexahydrate (MgNH₄PO₄·6H₂O, also known as struvite) has been identified as an effective way of recovering nitrogen and phosphorous from waste water. The chemical composition of struvite suggests that it is suitable for the fertilizer industry[11] and it was reported that the fertilizer effect of struvite on ryegrass is similar to that of mono-calcium phosphate[12]. If cheap processing methods are developed, struvite could be recovered from swine waste biogas digester effluent as struvite.
used in any industry where phosphate is used as a raw material[13].

The precipitation of struvite is affected by the pH, degree of saturation of the solution with component ions (magnesium, ammonium, and phosphate), temperature of the solution[14-16] and the presence of other ions, such as calcium[17]. Struvite formation has been studied with pH increment through the addition of NaOH[18-20] and air stripping[21-22], within the pH range of 7.0-11.0[23]. As a result of pH increase, the availability of phosphate ion is increased and the ammonia nitrogen content tends to decrease at pH values over 9.0[22]. The equilibrium ion-activity product (IAP_eq) for struvite is 7.08 × 10^{-14} and struvite will be precipitated when IAP of respective ions exceed IAP_eq [23]. In anaerobic digestion, NH_4^+, PO_4^{3-}, and Mg^{2+} ion concentrations in the effluent is elevated and struvite is found to be precipitated under alkaline conditions[22]. Struvite was therefore considered as a nuisance in waste water facilities, as it deposited and blocked the pipes and mechanical equipment[24-26]. Consequently, a large portion of struvite researches was directed towards removal and prevention of struvite formation rather than towards forced precipitation from solution[25,27,29]. With the recent researches focused on the sustainable use of resources, struvite precipitation has been investigated in different kinds of waste water such as swine waste[5,21,30], sludge liquor[15,31], anaerobic lagoon effluent[32], landfill leachate[18], and artificial waste water, as a method of NH_4^+ and PO_4^{3-} removal[6,14,25]. However, the potential of NH_4^+ and PO_4^{3-} recovery from biogas digester effluent through struvite precipitation has not been fully investigated. Since the pH value determines the availability of soluble NH_4^+, PO_4^{3-}, and Mg^{2+} concentrations[28] and Mg^{2+} is a limiting ion in digester effluent, studying the effect of pH and Mg^{2+}:PO_4^{3-} molar ratio amendment is useful for the optimal recovery of these nutrients.

This study was therefore carried out with the broad objective of evaluating the potential recovery of nitrogen and phosphorus from swine waste biogas digester effluent as struvite, and the effect of pH, Mg^{2+} and PO_4^{3-} molar ratio amendment on the struvite precipitation.

MATERIALS AND METHODS

Molar Ratio and pH Adjustment

The waste water used in this work was biogas digester effluent obtained from Xiasha Swine Farm, Hangzhou, Zhejiang Province, China. Supernatant was collected from the effluent discharge pond and stored at 4°C for 24 h in a refrigerator to allow the solids that were disturbed in the collection process to settle. Following the 24 h settling period, supernatant was siphoned out and stored at 4°C until further use. The water quality parameters of swine waste biogas digester effluent (SWBDE) used for the experiment are summarized in Table 1. The NH_4^+: Mg^{2+}: PO_4^{3-} molar ratio of the effluent was 1: 0.2: 0.08. Three sets of experiments were conducted to determine the struvite precipitation potential of the tested SWBDE. The first set of experiments was carried out with no NH_4^+: Mg^{2+}: PO_4^{3-} molar ratio amendment (MRNA waste water) but pH was adjusted using 1 mol/L NaOH to create a pH range of 7.5-9.0. The maximum pH value for all the experiments was set at 9.0 to prevent NH_3 emission[22-33] besides that the pH for minimum struvite solubility predicted for most waste waters was 9.0[23,32]. The second set of experiments was conducted in the same pH range supplemented with magnesium chloride hexahydrate (MgCl_2·6H_2O) and potassium di-hydrogen phosphate (KH_2PO_4) to SWBDE to meet the stoichiometric demand for complete NH_4^+ precipitation as struvite, bringing final NH_4^+: Mg^{2+}: PO_4^{3-} molar ratio to 1: 1: 1 (MRA 1 waste water). The third experiment was conducted with NH_4^+: Mg^{2+}: PO_4^{3-} ratio of 1: 1.5: 1.5 (MRA 2 waste water) at pH 9.0.

<table>
<thead>
<tr>
<th>TABLE 1</th>
<th>Concentrations of Selected Constituents and Water Quality Parameters of Swine Waste Biogas Digester Effluent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameter</td>
<td>Concentration/Value</td>
</tr>
<tr>
<td>pH</td>
<td>7.5</td>
</tr>
<tr>
<td>NH_4^+-N (mg L^{-1})</td>
<td>234</td>
</tr>
<tr>
<td>NO_3^{-}·N (mg L^{-1})</td>
<td>2.3</td>
</tr>
<tr>
<td>NO_2^{-}·N (mg L^{-1})</td>
<td>0.36</td>
</tr>
<tr>
<td>PO_4^{3-}·P (mg L^{-1})</td>
<td>42</td>
</tr>
<tr>
<td>Mg^{2+}·mg (mg L^{-1})</td>
<td>91</td>
</tr>
<tr>
<td>Ca^{2+}·mg (mg L^{-1})</td>
<td>61</td>
</tr>
<tr>
<td>COD_C·mg (mg L^{-1})</td>
<td>960</td>
</tr>
<tr>
<td>SS (g L^{-1})</td>
<td>1.7</td>
</tr>
</tbody>
</table>

All the precipitation experiments were conducted as batch reactions in 2.0 L flexi-glass bench-scale reactors with the working volume of 1.5 L at the room temperature (around 25°C). The solutions were mixed at 500 rpm with an overhead agitator during 60 min experimental period. The pH was also monitored throughout the experiment using Sartorius PB-10 pH meter (Goettingen, Germany). To investigate the changes occurring in the Mg^{2+}, NH_4^+, and PO_4^{3-} ion concentrations during the precipitation process, 10 mL aliquots of solution were drawn from the reactor at 2 cm below the surface at each 10 min intervals after adjusting the pH of the solution. These samples were then filtered through a 0.2-μm filter to
struvite crystals that may have been formed by the time of sampling. In order to ensure no further precipitation to occur in the drawn samples, 25 μL of 6 mol/L HCl was added to each sample. These samples were used for chemical analysis.

Chemical and Physical Analysis

To determine the composition of the precipitate, the solution was filtered after 1 h of the experimental period through a 0.2-μm filter. The filtered precipitate was dried at 40°C for 48 h as described by Ohlinger et al.[27]. Random powder mounts of dried precipitate were prepared and analyzed with a Rigaku D/Max-2550 PC X-ray diffractometer using unresolved CuKα̇ radiation at 1.54056 Å. X-ray diffraction (XRD) patterns observed for the precipitates were compared with struvite standard X-ray pattern (standard # 15-0762, International Centre for Diffraction data, computer database).

A portion of precipitate recovered from each experiment was dissolved in 0.1 mol/L HCl and analyzed for Mg2+, NH4+, and PO43− contents in the precipitated product as described in previous work[36]. Magnesium concentration was determined with a Thermo Elemental Solar M6 MK11 atomic absorption spectrophotometer (Thermo Electron Corporation, USA). Orthophosphate (PO43−) was measured by the ascorbic acid colorimetric method and ammonia nitrogen was measured by phenate method using a spectrometer (Unico UV-4802, China)[34]. All the analyses were made in three replicates and averages are reported.

RESULTS

Transformation of pH in Reaction Solution

The formation of struvite can be shown as in Equation 1[5,35].

\[
\text{Mg}^{2+} + \text{NH}_4^+ + \text{H}_2\text{PO}_4^- + 6\text{H}_2\text{O} \rightarrow \\
\text{MgNH}_4\text{PO}_4\cdot 6\text{H}_2\text{O} + 2\text{H}^+ 
\]

When the struvite is formed, hydrogen ions are released into the solution as illustrated in Equation 1 and consequently, the pH value of the solution decreases. Therefore, pH reduction in the reaction solution can be considered as an indicator of struvite precipitation. In the experiment conducted with MRNA waste water, the differences between the initial and the final pH after 1 h reaction were 0.09, 0.19, 0.26, and 0.36 pH units for the experiments set at pH 7.5, 8.0, 8.5, and 9.0, respectively (Fig. 1). In contrast, the variations between initial and final pH values observed in MRA 1 and MRA 2 waste water with an elevated initial pH were higher than those values observed for MRNA waste water. The experiments performed with initial pH values of 7.5, 8.0, 8.5, and 9.0 in MRA 1 waste water had 0.32, 0.54, 0.69, and 1 pH unit difference after 1 h reaction period, respectively. The pH difference observed in MRA 2 waste water at pH 9.0 was 1.3 units (Fig. 1).

In addition, a sharp decline of pH was noticed within the first 10 min of reaction followed by a moderate rate of decline during the next 5-10 min, finally reaching an equilibrium state after a gradual pH reduction. As Fig. 2 indicates, the highest pH decline within the first 10 min was recorded in the solution at pH 9.0 with 1: 1.5: 1.5 NH4+: Mg2+: PO43− molar ratio (MRA 2 waste water), followed by solutions at initial pH 9.0, 8.5, 8.0, and 7.5 with 1: 1: 1 molar ratio (MRA 1 waste water). In addition, more than 98% pH reduction was observed within the first 20 min in both MRA waste waters at pH 9.0 and other solutions also showed more than 90% pH decrease within the same period (data not shown). Nevertheless, both MRA 1 and MRA 2 waste water with an initial pH 9.0 reached the equilibrium pH state by 35 min. The time required for the MRA 1 waste water with initial pH 7.5, 8.0, and 8.5 to reach the steady state was 50, 50, and 45 min, respectively (Fig. 2).

![Fig. 1. Difference between initial and final pH in solution with MRNA (■), MRA 1 (★) and MRA 2 (▲) waste water.](image1)

![Fig. 2. Evolution of pH in struvite precipitation process in biogas digester effluent with MRA 1 (−−−) and MRA 2 (-----) waste water under pH 7.5 (■), 8.0 (●), 8.5 (▲), and 9.0 (▼).](image2)
Effect of Initial pH on Struvite Precipitation

The changes in \( \text{NH}_4^+ \), \( \text{Mg}^{2+} \), and \( \text{PO}_4^{3-} \) ion concentrations observed in MRNA waste water after the pH adjustment are shown in Fig. 3 (a-c) while those reported with MRA 1 and MRA 2 waste water are presented in Fig. 3 (d-f). In all MRNA, MRA 1, and MRA 2 waste water samples, the major portion of struvite constituents declined within the first 10 min of the reaction in solutions with a pH of 8 and above. However, the removal of \( \text{NH}_4^+ \), \( \text{Mg}^{2+} \), and \( \text{PO}_4^{3-} \) ions occurred at a slower pace in solutions with a pH of 7.5 in all the experimental settings. When the initial pH of waste water was not adjusted and left to remain at 7.5, \( \text{NH}_4^+ \), \( \text{Mg}^{2+} \), and \( \text{PO}_4^{3-} \) removal rate reached a stable state by 1 h (Fig. 3). The evolution of pH and time course changes in the concentration of struvite components during the struvite precipitation process demonstrated a similar trend (Figs. 2 and 3). The lowest removal rate of all struvite components was observed in solutions with an initial pH of 7.5 while the highest rates were observed in solutions with an initial pH of 9.0 (Table 2).

**FIG. 3.** Time course changes in \( \text{NH}_4^+ \) (a,d), \( \text{Mg}^{2+} \) (b,e) and \( \text{PO}_4^{3-} \) (c,f) concentrations with initial pH 7.5 (■), 8.0 (●), 8.5 (▲), and 9.0 (▼) in MRNA (---), MRA 1 (——), and MRA 2 (––) waste water.

Effect of Molar Ratio on Struvite Precipitation

As the theoretical \( \text{NH}_4^+ : \text{Mg}^{2+} : \text{PO}_4^{3-} \) molar ratio of struvite is 1:1:1, it can be assumed that a molar ratio closer to this value would help to recover more of each constituent ion. The amounts of \( \text{NH}_4^+ \), \( \text{Mg}^{2+} \), and \( \text{PO}_4^{3-} \) available in MRNA waste water were 16.7, 3.7, and 1.3 mmol, respectively. The limiting ions were \( \text{Mg}^{2+} \) and \( \text{PO}_4^{3-} \) and consequently, the precipitate contained only 1, 2.9, and 1.2 mmol of \( \text{NH}_4^+ \), \( \text{Mg}^{2+} \), and \( \text{PO}_4^{3-} \), respectively at pH 9.0 in MRNA waste water (Table 3). Since the highest precipitation was observed at pH 9.0 in all experiments, the amounts precipitated at pH 9.0 were plotted against the \( \text{NH}_4^+ : \text{Mg}^{2+} : \text{PO}_4^{3-} \) ratio to determine the effect of molar ratio amendment (Fig. 4). It was found that the amount of \( \text{NH}_4^+ \), \( \text{Mg}^{2+} \), and \( \text{PO}_4^{3-} \) precipitated was increased with the increasing molar ratio (Fig. 4). The highest amount of each struvite constituent was precipitated in MRA 2 waste water and the lowest was observed in MRNA wastewater (Fig. 4). The addition of \( \text{Mg}^{2+} \) and \( \text{PO}_4^{3-} \) sources to bring the molar ratio from 1: 0.2: 0.08 to 1: 1: 1 considerably increased the amount of each component precipitated at pH 9.0 to 11.8, 16.3, and 16.2 mmol of \( \text{NH}_4^+ \)-N, \( \text{Mg}^{2+} \), and \( \text{PO}_4^{3-} \)P, respectively.
TABLE 2

Struvite Constituent Removal From MRNA\(^*\), MRA 1\(^b\), and MRA 2\(^c\) Wastewater With Different Initial pH Values and N: P Ratio of the Effluent After Struvite Precipitation

<table>
<thead>
<tr>
<th>Molar Ratio</th>
<th>Initial pH</th>
<th>Removed Amount of Struvite Component (mgL(^{-1}))</th>
<th>N: P Ratio in Effluent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(\text{NH}_4^+)</td>
<td>(\text{Mg}^{2+})</td>
</tr>
<tr>
<td>1: 0.2: 0.08</td>
<td>7.5</td>
<td>1.8 (0.7)</td>
<td>17.2 (19.1)</td>
</tr>
<tr>
<td>MRNA</td>
<td>8.0</td>
<td>5.3 (2.3)</td>
<td>26.9 (29.9)</td>
</tr>
<tr>
<td>8.5</td>
<td>11.0 (4.7)</td>
<td>61.1 (67.9)</td>
<td>26.2 (62.8)</td>
</tr>
<tr>
<td>9.0</td>
<td>13.7 (5.8)</td>
<td>71.1 (79.0)</td>
<td>37.3 (89.2)</td>
</tr>
<tr>
<td>1: 1: 1</td>
<td>7.5</td>
<td>35.4 (15.1)</td>
<td>95.0 (23.4)</td>
</tr>
<tr>
<td>MRA 1</td>
<td>8.0</td>
<td>107.1 (45.7)</td>
<td>275.1 (67.8)</td>
</tr>
<tr>
<td>8.5</td>
<td>141.5 (60.5)</td>
<td>351.2 (86.5)</td>
<td>443.3 (85.6)</td>
</tr>
<tr>
<td>9.0</td>
<td>165.5 (70.5)</td>
<td>397.3 (97.9)</td>
<td>502.2 (112.9)</td>
</tr>
<tr>
<td>1: 1.5: 1.5</td>
<td>9.0</td>
<td>179.0 (76.5)</td>
<td>426.8 (90.2)</td>
</tr>
</tbody>
</table>

**Note.** \(^a\)MRNA-molar ratio non adjusted wastewater with \(\text{NH}_4^+\): \(\text{Mg}^{2+}\): \(\text{PO}_4^{3-}\) 1: 0.2: 0.08. \(^b\)MRA 1 - molar ratio adjusted wastewater with \(\text{NH}_4^+\): \(\text{Mg}^{2+}\): \(\text{PO}_4^{3-}\) 1: 1: 1. \(^c\)MRA 2 - molar ratio adjusted wastewater with \(\text{NH}_4^+\): \(\text{Mg}^{2+}\): \(\text{PO}_4^{3-}\) 1: 1.5: 1.5. \(^*\)Values in parenthesis indicate the removal of each ion expressed as the percentage of initial concentration.

TABLE 3

Struvite Constituents in the Precipitated Product Obtained from MRNA\(^*\), MRA 1\(^b\), and MRA 2\(^c\) Wastewater With Different Initial pH

<table>
<thead>
<tr>
<th>Molar Ratio</th>
<th>Initial pH</th>
<th>Struvite Constituent (mmol)</th>
<th>N: P Ratio in Precipitate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(\text{NH}_4^+)</td>
<td>(\text{Mg}^{2+})</td>
</tr>
<tr>
<td>1: 0.2: 0.08</td>
<td>7.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MRNA</td>
<td>8.0</td>
<td>0.4</td>
<td>1.1</td>
</tr>
<tr>
<td>8.5</td>
<td>0.8</td>
<td>2.5</td>
<td>0.8</td>
</tr>
<tr>
<td>9.0</td>
<td>1.0</td>
<td>2.9</td>
<td>1.2</td>
</tr>
<tr>
<td>1: 1: 1</td>
<td>7.5</td>
<td>2.5</td>
<td>3.9</td>
</tr>
<tr>
<td>MRA 1</td>
<td>8.0</td>
<td>7.6</td>
<td>11.3</td>
</tr>
<tr>
<td>8.5</td>
<td>10.1</td>
<td>14.4</td>
<td>14.3</td>
</tr>
<tr>
<td>9.0</td>
<td>11.8</td>
<td>16.3</td>
<td>16.2</td>
</tr>
<tr>
<td>1: 1.5: 1.5</td>
<td>9.0</td>
<td>12.7</td>
<td>17.5</td>
</tr>
</tbody>
</table>

**Note.** \(^a\)MRNA-molar ratio non adjusted wastewater with \(\text{NH}_4^+\): \(\text{Mg}^{2+}\): \(\text{PO}_4^{3-}\) 1: 0.2: 0.08. \(^b\)MRA 1 - molar ratio adjusted wastewater with \(\text{NH}_4^+\): \(\text{Mg}^{2+}\): \(\text{PO}_4^{3-}\) 1: 1: 1. \(^c\)MRA 2 - molar ratio adjusted wastewater with \(\text{NH}_4^+\): \(\text{Mg}^{2+}\): \(\text{PO}_4^{3-}\) 1: 1.5: 1.5.

(Table 3 and Fig. 4). Since 97.9% \(\text{Mg}^{2+}\) and 97% \(\text{PO}_4^{3-}\) ions had been removed and nearly 30% of \(\text{NH}_4^+\) was remaining in the experiment with MRA 1 wastewater experiment (Table 2), it appeared that \(\text{Mg}^{2+}\) and \(\text{PO}_4^{3-}\) were limiting ions for further precipitation of \(\text{NH}_4^+\) as struvite. However, further elevation of the molar ratio to 1: 1.5: 1.5 (16.7, 25, and 25 mmol of \(\text{NH}_4^+\), \(\text{Mg}^{2+}\), and \(\text{PO}_4^{3-}\)) gave only a little increase in the precipitation reaching a final amounts of \(\text{NH}_4^+\), \(\text{Mg}^{2+}\), and \(\text{PO}_4^{3-}\) of 12.8, 17.5, and 17.1 mmol, respectively (Table 3). Although the concentrations of \(\text{Mg}^{2+}\) and \(\text{PO}_4^{3-}\) in the reaction solution increased nearly by 8 mmol with the increase of molar ratio from 1: 1: 1 to 1: 1.5: 1.5, it triggered only about 1 mmol recovery of each struvite component (Table 3), leaving 23.5% \(\text{NH}_4^+\), 29.8% \(\text{Mg}^{2+}\), and 31.5% \(\text{PO}_4^{3-}\) in the solution at the end of precipitation (Table 2).
Effect of Struvite Precipitation on Quality of Discharge Water

The N:P ratio of the SWBDE was 5.5:1 and this ratio was increased with the recovery of struvite through the elevation of pH in the experiment with MRNA waste water (Table 2). The N: P ratios of the effluents resulting from MRNA waste water at pH 7.5 and 8.0 were 6.5:1 and 9:1, respectively (Table 2). However, the N: P ratios observed for MRNA effluents at pH 8.5 and 9.0 were 14:1 and 46.7:1, respectively. Among all the experimental combinations of pH in MRA 1 and MRA 2 waste waters, MRA 1 waste water at pH 9.0 was found to have a N: P ratio of 4.4:1 after 1 h reaction. The N: P ratio observed for the rest of the molar-pH combinations after the reaction were less than 1.5:1 (Table 2).

Composition of Precipitate at Different pH and Molar Ratios

The isolated crystalline materials after each experiment were analyzed to determine the composition of the precipitated product and the results observed are shown in Table 3. However, the amount precipitated in the MRNA waste water at pH 7.5 was not adequate to perform the precipitate analysis. Since struvite is the only possible crystal in this study that contains NH$_4^+$ as a component, all the NH$_4^+$ found in the precipitate was considered to have been derived from struvite. Since the theoretical molar ratio of Mg$^{2+}$: NH$_4^+$: PO$_4^{3-}$ in struvite is 1:1:1, it can be concluded that additional amounts of Mg$^{2+}$ and PO$_4^{3-}$ were also precipitated in each reaction except for the experiment with the MRNA effluent at pH 8.5 (Table 3). The precipitates obtained from MRA 1 waste water in which the pH was elevated to 8.0, 8.5, 9.0, and MRA 2 waste water, show a distinct relationship between Mg$^{2+}$ and PO$_4^{3-}$ having equimolar content (Table 3).

XRD Analysis of Precipitated Product

Figure 5 illustrates the X-ray diffraction patterns observed for the precipitate under each molar ratio tested at pH 9.0 and the standard X-ray pattern for struvite. Peaks of struvite were identified as the main phase in diffractometry patterns obtained for all the 3 samples shown. Similar peaks were noticed in all the other samples but not included in Fig. 5. The presence of minute peaks indicates that the precipitate contains some other components in smaller quantities, which were not identified in the current study. Based on the molar ratio analysis of the precipitate obtained in this experiment (Table 3), the XRD peaks, which did not represent the standard struvite pattern, can be described as the various forms of magnesium phosphate yet to be identified. However, the XRD and chemical analysis of the precipitate confirmed that struvite could be precipitated as the major product from swine waste biogas digester effluent.

DISCUSSION

The level of pH plays an important role in the struvite precipitation process. Stumm and Morgan$^{[33]}$ reported that when the pH increases from 7 to 9, the amount of PO$_4^{3-}$ ions increases by 250 folds while a slight reduction of NH$_4^+$ occurs in the solutions. Therefore, the increased availability of these ions in pH elevated MRNA waste water has influenced the struvite precipitation reaction and released more H$^+$ causing a pH decline in 1 h. The higher pH difference observed in the experiments with initial pH 8.0, 8.5, and 9.0 as compared to that of pH 7.5 can be attributed to the formation of more H$^+$ ions during the
struvite precipitation process\cite{16}. The greater pH decline in MRA 1 and MRA 2 waste waters as compared with the MRNA waste water at each pH level can be accounted for by two factors. First is the extra amount of $\text{Mg}^{2+}$ and $\text{PO}_4^{3-}$ ions added into the solutions that enhanced the supersaturation to precipitate more struvite. Second is the increased availability of struvite constituents with the increased pH\cite{25,28}. Both factors collectively triggered struvite precipitation and released more $\text{H}^+$ ions leading to the observed pH decline in the reaction solutions. The increased amounts of the struvite components precipitated at an elevated pH of the solution (Tables 2 and 3) further confirms this phenomenon.

Nucleation is the process that combines relevant ions to form crystal embryos, which depends on solution supersaturation. The increase in pH elevated the supersaturation state of the solution leading to nucleation and enhanced struvite precipitation\cite{28}. The precipitation of more struvite at pH 9.0 than at pH 7.5 could be attributed to the increased nucleation with increased pH\cite{25,32}. As the nucleation is a rapid process under supersaturation condition\cite{25,29}, it occurred within few minutes of pH elevation to form struvite embryos that subsequently grew into crystals. The rapid decline of $\text{NH}_4^+$, $\text{Mg}^{2+}$, and $\text{PO}_4^{3-}$ ion concentrations in the reaction solution within the first 10 min is a good indicator of struvite nucleation. Thereafter, the ion concentrations were not sufficient to prolong the precipitation in an accelerated manner and reached the equilibrium state within 60 min (Fig. 3). A similar pattern of struvite formation kinetics has also been previously reported by Nelson et al.\cite{32}. However, a considerable amount of $\text{NH}_4^+$, $\text{Mg}^{2+}$, and $\text{PO}_4^{3-}$ ions remained in the MRA 2 waste water at the initial pH of 9.0 after 1 h reaction. The low final pH (7.7) of this solution (Fig. 2) and the effective free ions available at this pH could be the limiting factors for further precipitation\cite{6}.

Molar ratio elevation of the struvite constituents enhances the supersaturation and consequently, more nucleation occurs in the solution with higher molar ratio than in the solution with lower molar ratio\cite{25}. In addition, the increased number of struvite embryos formed through nucleation created more surface area for further crystal growth, resulting in a higher amount of precipitate at the elevated molar ratios\cite{25,28}. However, the final pH of the precipitation solution (Fig. 2) restricted further precipitation of struvite components in (MRA 2) the molar elevated wastewater solution (Table 3), which is in agreement with the findings of Ali et al.\cite{6} that suggested the low availability of struvite components under low pH condition resulted from initial struvite precipitation under non-constant pH conditions\cite{6}.

The observed X-ray diffraction patterns confirmed that struvite is the major component of each precipitate. The precipitate analysis revealed that the additional amounts of $\text{Mg}^{2+}$ and $\text{PO}_4^{3-}$ were precipitated, thereby exceeding the $\text{Mg}^{2+}$:$\text{NH}_4^+$:$\text{PO}_4^{3-}$ molar ratio of 1:1:1 in each experiment. A higher $\text{Mg}^{2+}$:$\text{PO}_4^{3-}$ ratio observed in the precipitates at each pH of MRNA waste water than in MRA 1 and MRA 2 waste water (Table 3) could be attributed to the higher $\text{Mg}^{2+}$:$\text{PO}_4^{3-}$ ratio (2.8:1) available in the original waste water, which might have influenced the precipitation of magnesium phosphate in addition to struvite. Therefore, the precipitate can be better described as a mixture, comprised mainly of struvite and trace amounts of magnesium phosphate.

The N:P ratio of the effluent after struvite precipitation is an important factor to be considered for the safe and useful disposal of the effluent. It has previously been reported that livestock waste water with N:P ratio of 4:1 to 9:1 can be used for irrigation to meet the N and P demands of the receiving crops\cite{30,32}. Accordingly, the effluents resulting from the MRNA waste water at pH 7.5 and 8.0 are suitable for irrigation purposes to meet both N and P requirements of crops while that resulted from pH 8.5 and 9.0 can be used to supplement N requirements though the P content is low. The low efficiency of removing the added phosphate from the MRA 2 solution contributed to the low N:P ratios in the discharge water after 1 h experiment. These effluents may have negative environmental consequences if used in agricultural applications due to their imbalance in N:P ratio. Therefore, it can be concluded that $\text{Mg}^{2+}$:$\text{NH}_4^+$:$\text{PO}_4^{3-}$ molar ratio of 1:1:1 together with pH 9.0 is optimum for the $\text{NH}_4^+$ and $\text{PO}_4^{3-}$ recovery from the biogas digester effluent studied as it allows the recovery of 70.5% $\text{NH}_4^+$-N and 97% $\text{PO}_4^{3-}$-P. Furthermore, the effluent after precipitation has N:P ratio of 4.4:1, which is suitable for irrigating crops without causing environmental problems.

**CONCLUSIONS**

Chemical precipitation through pH elevation and $\text{Mg}^{2+}$:$\text{NH}_4^+$:$\text{PO}_4^{3-}$ molar ratio amendment can be used to recover $\text{NH}_4^+$ and $\text{PO}_4^{3-}$ as struvite from swine waste biogas digester effluent.

The $\text{Mg}^{2+}$:$\text{NH}_4^+$:$\text{PO}_4^{3-}$ molar ratio of 1:1:1 and pH 9.0 is the optimum combination for $\text{Mg}^{2+}$ and $\text{PO}_4^{3-}$ recovery through struvite precipitation as this combination not only enhances the recovery, but also the resultant effluent lies within the permissible N:P limits which is suitable for irrigation and can meet both N and P requirements of crops. A pilot scale study is recommended before field level application.

Since the $\text{NH}_4^+$ and $\text{PO}_4^{3-}$ concentrations in molar elevated solutions rapidly decline and reach a stable state within 20 min after pH adjustment, struvite precipitation from biogas digester effluent
can be developed into a large-scale commercial operation to recover \( \text{PO}_4^{3-} \) and \( \text{NH}_4^+ \).

**REFERENCES**


(Received April 20, 2007 Accepted July 23, 2007)