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Engineered Struvite Precipitation: Impacts of Component-Ion Molar Ratios and pH

Jun Wang1; Joel G. Burken, M.ASCE2; Xiaoqi (Jackie) Zhang3; and Rao Surampalli, M.ASCE4

Abstract: Struvite precipitation has the potential for removing and recovering phosphorus from agricultural wastewater streams, such as concentrated animal feeding operations wastewater. However, impacts of anticipated component-ion molar ratios and potentially interfering ions are unknown as are the compounding pH relationship with respect to all potential complexes. This research experimentally investigates and mathematically models these factors. Emphasis is placed upon the composition of formed deposits and model validation with experimental data. Results show that calcium is a major interfering ion affecting the deposit composition, decreasing struvite purity. X-ray diffraction (XRD) and scanning electron microscopy + energy dispersive spectrometry were used to study the deposit structure and elemental composition. Results revealed that the precipitates formed at a pH of 8.7 have regular crystal shape, and XRD analysis confirmed that the precipitates are high-purity struvite. Higher pH (> 10) leads to the formation of amorphous precipitate and decreases the struvite purity in the deposits. To maximize struvite purity, the ratio of Ca to P should be less than 0.5 and the pH near 8.7.

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CE Database subject headings: Agricultural wastes; Water pollution; Wastewater; Nutrients; Phosphorus; pH; Calcium; Ammonia.

Introduction

Phosphorus is generally regarded as the primary nutrient responsible for eutrophication of rivers and lakes (Mombarg and Oellermann 1992). To combat increased eutrophication, the United States and numerous European countries have promulgated strict wastewater discharge standards on P levels to protect water bodies. Unregulated and nonpoint sources such as agricultural wastes still reach surface waters. Of P used in livestock feeding, an estimated 70% is directly excreted as waste (Greaves et al. 1999). While excess P is problematic, phosphorus is also a limited resource. Phosphorus is a widely used raw material in agriculture and industry, primarily as one of the main crop fertilizers but also in animal feeding and food supplements. According to an investigation by the European Chemical Industry Council in 1998, over 150 million tons of phosphorus are extracted and processed per year globally, and agriculture use as fertilizers and feed concentrates accounts for 85% (CEEP 1998).

At the current utilization rate, the phosphate mineralogy which can be utilized economically is estimated to provide the necessary P supply for as little as 50 years (Driver et al. 1999). Dual benefits can be achieved if phosphorus can be recovered and recycled from wastewater streams, as not only will nutrient enrichment of rivers be prevented, but conservation of a finite resource will be accomplished.

Phosphorus Removal Technologies

The recognized phosphorus removal technologies include chemical precipitation, biological phosphorus removal, crystallization, tertiary filtration, and ion exchange (Morse et al. 1998). Most of these processes produce wastes which need to be landfilled or incinerated, the ethos of sustainability, however, makes these options unattractive (Durrant et al. 1999). Biological P removal is mainly used for low P concentrated municipal wastewater. Elusive mechanistic understanding makes these biological methods tricky. Crystallization processes stand out because they do not only achieve high P removal, but also recover P from wastewater as useful products, including struvite, calcium phosphate, and hydroxyapatite. Chemical makeup and formation stoichiometry are shown in Table 1 and Eqs. (1)–(3). The recovery of phosphorus by crystallization has been reported to reduce sludge volume under specific conditions by up to 49% compared to chemical phosphorus removal (Woods et al. 1999).

\[
\begin{align*}
\text{Mg}^{2+} + \text{NH}_4^+ + \text{HPO}_4^{2-} + 6\text{H}_2\text{O} &\rightarrow \text{MgNH}_2\text{PO}_4 + 6\text{H}_2\text{O} + \text{H}^+ \\
3\text{PO}_4^{3-} + 5\text{Ca}^{2+} + \text{OH}^- &\rightarrow \text{Ca}_3(\text{PO}_4)_2 \text{OH} \\
2\text{PO}_4^{3-} + 3\text{Ca}^{2+} &\rightarrow \text{Ca}_3(\text{PO}_4)_2
\end{align*}
\]

Struvite and hydroxyapatite can be used in agriculture as fertilizers; struvite, however, is preferred for numerous reasons. First, nutrients are released at a slower rate compared to other fertilizers. Plants can take up the nutrients before being rapidly leached,
and less frequent application is therefore required (Munch and Barr 2001). Second, the impurities caused by heavy metals in the recovered struvite are two or three orders of magnitude lower than that of commercial phosphate fertilizers (Brett et al. 1997). Lastly, the essential nutrients P, N, and Mg are applied simultaneously with essentially no unnecessary components in the fertilizer. Struvite contains both magnesium and phosphate, which plants require in a ratio of 3:2 Mg:P (Taiz and Zeiger 1991).

The processes also have additional advantages in addition to the chemical advantages. The footprint of a struvite crystallization reactor is considerably smaller than that of biological P removal infrastructure; and the process has fewer problematic operational concerns. Struvite crystallization may have the potential to cheaply remove P and ammonium-nitrogen from wastewater relative to biological P removal and standard nitrification-denitrification techniques or caustic stripping (Webb et al. 1995). The struvite crystallization process has been favorably applied to the treatment of wastewater and is also an interfering ion to struvite formation (Munch and Oellermann 1992). The reaction of PO₄ with Ca can form a number of related products depending on reaction conditions (Momberg et al. 1992). Struvite formation is affected by the interaction of calcium and magnesium, depending on their relative concentrations struvite formation can be inhibited as calcium phosphate precipitates form (Mombarg and Oellermann 1992). The reaction of PO₄ with Ca can form a number of related products depending on reaction conditions (Greaves et al. 1999). By modifying the chemical composition of wastewater, increasing Mg/Ca ratios, efficient struvite formation can be achieved (Battistoni et al. 2000). Recent work has also shown that physical parameters can be optimized to improve struvite precipitation efficiency. Seeding materials and optimal mixing conditions were shown to achieve maximum removal in less than 30 min, with pure struvite crystals resulting (Wang et al. 2005). For several different calcium phosphates, the saturation level of phosphate for a given calcium concentration depends strongly on the pH (Stumm and Morgan 1970). Numerous researchers have investigated the optimum pH values and concluded that the precipitation of hydroxyapatite occurs at pH values above 9.5, whereas effective struvite precipitation occurs at pH at 8.0 and above. Under different ratios of Mg/Ca, struvite or hydroxyapatite could be formed within the pH range of 8–10 (Battistoni et al. 2000). The optimum pH for struvite published by a number of researchers displays a range of values, from 8.0 to 10.7 (Stumm and Morgan 1970; Booram et al. 1975; Momberg and Oellermann 1992; Buchanan et al. 1994; Ohlinger et al. 1998; Booker et al. 1999).

The component-ion molar ratios also have great impact on the composition of the precipitate. Previous research revealed that a stoichiometric excess of ammonium (30–80 ppm) will help drive the reaction to form relatively pure struvite (Stratful et al. 2001), while excess magnesium decreases struvite purity (Demeestre et al. 2001). Recent research predicts phosphate removal is optimal when the molar ratio of magnesium to total phosphorus is 1.6 (Burns et al. 2001). In a similar research, a magnesium to phosphorus ratio of 1.3 was ideal environment for struvite formation (Munch and Barr 2001).

Struvite solubility product is a critical parameter in chemical equilibrium calculation and process modeling. Depending on the complexes formed in a solution and the chemical speciation determined, a range of solubility product constants have been published (Buchanan et al. 1994). A widely used pKsp value is 12.6 (Taylor et al. 1963; Stumm and Morgan 1970; Burns and Finlayson 1982; Loewenthal et al. 1994; Aage et al. 1991; Ohlinger et al. 1998). Other research accounting for activity have found pKsp values near 13.2 (Burns and Finlayson 1982; Ohlinger et al. 1998).

### Table 1. Characteristics of Phosphorus-Containing Crystallization Process Products

<table>
<thead>
<tr>
<th>Deposit</th>
<th>Molecular formula</th>
<th>Molecular weight (g/mol)</th>
<th>Phosphorus content (% mass)</th>
<th>Nitrogen content (% mass)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Struvite</td>
<td>MgNH₄PO₄·6H₂O</td>
<td>245.41</td>
<td>12.6</td>
<td>5.7</td>
</tr>
<tr>
<td>Calcium phosphate</td>
<td>Ca₅(PO₄)₂</td>
<td>310.18</td>
<td>19.9</td>
<td>N/A</td>
</tr>
<tr>
<td>Hydroxyapatite</td>
<td>Ca₅(PO₄)₂·OH</td>
<td>502.31</td>
<td>18.5</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Note: N/A = not available.

### Factors in Struvite Crystallization Process
To produce pure struvite deposit, many factors need to be carefully controlled. Factors include component-ion ratios, potential interfering ions, and pH values. Calcium is a common cation in wastewater and is also an interfering ion to struvite formation. Struvite formation is affected by the interaction of calcium and magnesium, depending on their relative concentrations struvite formation can be inhibited as calcium phosphate precipitates form (Mombarg and Oellermann 1992). The reaction of PO₄ with Ca can form a number of related products depending on reaction conditions (Greaves et al. 1999). By modifying the chemical composition of wastewater, increasing Mg/Ca ratios, efficient struvite formation can be achieved (Battistoni et al. 2000). Recent work has also shown that physical parameters can be optimized to improve struvite precipitation efficiency. Seeding materials and optimal mixing conditions were shown to achieve maximum removal in less than 30 min, with pure struvite crystals resulting (Wang et al. 2005). For several different calcium phosphates, the saturation level of phosphate for a given calcium concentration depends strongly on the pH (Stumm and Morgan 1970). Numerous researchers have investigated the optimum pH values and concluded that the precipitation of hydroxyapatite occurs at pH values above 9.5, whereas effective struvite precipitation occurs at pH at 8.0 and above. Under different ratios of Mg/Ca, struvite or hydroxyapatite could be formed within the pH range of 8–10 (Battistoni et al. 2000). The optimum pH for struvite published by a number of researchers displays a range of values, from 8.0 to 10.7 (Stumm and Morgan 1970; Booram et al. 1975; Momberg and Oellermann 1992; Buchanan et al. 1994; Ohlinger et al. 1998; Booker et al. 1999).

### Confined Animal Feeding Operations Wastewater
Confined animal feeding operations (CAFO) wastewater contributes P to surface water bodies. Although anaerobic lagoons have been widely applied to treat CAFO wastewater in the United States, the reactive P concentration in the effluent, however, can be extremely high. Over 200 mg/L P was measured in wastewaters tested in this study. Lagoon effluent is usually applied as irrigation water increasing the possibility that excessive P is flushed into surface waters during wet seasons (Greaves et al. 1999). Therefore effective removal of P from CAFO wastewater has direct and substantial value to surface water quality. Although researchers have studied the application of struvite crystallization on animal wastewater (Webb and Ho 1992; Wrigley et al. 1992; Webb et al. 1995), understanding and modeling of the impact

### Table 2. Initial Concentrations and Molar Ratios of Four Major Ions in Synthetic Wastewater Solutions

<table>
<thead>
<tr>
<th>Solution</th>
<th>Concentration (ppm)</th>
<th>Molar ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mg²⁺</td>
<td>Ca²⁺</td>
</tr>
<tr>
<td>1</td>
<td>96</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>96</td>
<td>80</td>
</tr>
<tr>
<td>3</td>
<td>96</td>
<td>160</td>
</tr>
<tr>
<td>4</td>
<td>48</td>
<td>40</td>
</tr>
<tr>
<td>5</td>
<td>24</td>
<td>40</td>
</tr>
</tbody>
</table>
of pH, component-ion molar ratios, and interfering ions on CAFO wastewater is still lacking. This study provides a better understanding of these aspects.

Materials and Methods

Solution Preparation

Chemical compositions of the effluents from two anaerobic lagoons treating piggery wastes in central Missouri were investigated. According to the measured value ranges, five synthetic wastewater solutions were then formulated to mimic typical magnesium, calcium, ammonium, and phosphate concentrations that could be expected in the effluent of anaerobic lagoons. Four samples were prepared for each solution, each sample was adjusted to a different pH for reaction. The solutions were prepared with magnesium sulfate heptahydrate (MgSO₄·7H₂O), dehydrate calcium chloride (CaCl₂), ammonium chloride (NH₄Cl), and ammonium phosphate monobasic [(NH₄)H₂PO₄]. To eliminate the effect of adding chemicals to solution ionic strength, 14.0 g of sodium perchlorate (NaClO₄) was added to each 1 L solution to increase the background ionic strength to 0.1 M. All chemicals were ACS grade (Fisher Scientific). The prepared samples were mixed with stir bars at room temperature for 24 h before being used in the experiment. The initial concentrations and molar ratios of four ions are listed in Table 2.

Precipitate Formation and Dissolution

The prepared solutions were transferred into five 1 L Erlenmeyer flasks. Each solution was adjusted to the designated pH with 1.0 N and 0.1 N NaOH solution (ACS grade, Fisher Scientific). An Orion 230A plus digital pH meter was used to monitor solution pH values. The solutions were mixed continuously for 12 h on a magnetic stir plate. After 12 h of reaction, the solutions were filtered with 0.45-μm membrane filter paper (Millipore Corp.). The solids were dried in a desiccator under room temperature for 24 h, then weighed and stored in capped 5-mL glass vials. Each dried precipitate sample was weighed with an analytical balance, dissolved with 5 mL of 1.0 N HNO₃ (ACS, Fisher Scientific), and transferred into a 0.5 L volumetric flask. The volumetric flask was filled up to 500 mL with deionized water. The solutions were mixed with stir bars for 1 h, and analyzed for Mg, Ca, PO₄, and NH₄-N concentrations with the analytical methods described below.

Analytic Methods

Magnesium and calcium concentrations in solutions were measured by Atomic Absorption Spectrometric Methods 3500-Mg B and 3500-Ca B, respectively (Clesceri et al. 1989). Ammonium concentration was measured by HACH HR, Test'N Tube Method (HACH method 10031), phosphate level was assessed by the HACH amino acid method (HACH Method 8178). The crystalline phases in the precipitates were analyzed with x-ray diffraction (XRD) in the Material Research Center at the University of Missouri-Rolla. Both crystalline and amorphous phases in the precipitate samples were analyzed with scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS) in the Electron Microscopy Laboratory at the University of Missouri-Rolla to determine the elemental composition.

Table 2. Parameters Used in MINEQL Modeling

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6–12</td>
</tr>
<tr>
<td>pK₉ of struvite</td>
<td>12.6</td>
</tr>
<tr>
<td>Ionic strength (M)</td>
<td>0.1</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>25</td>
</tr>
</tbody>
</table>

Fig. 1. Component-ion concentration in effluent of Solution 1 (Mg:Ca:PO₄:NH₄=2:0.5:1:20, points represent experimental results, lines represent model predictions)

Fig. 2. Component-ion concentration in effluent of Solution 2 (Mg:Ca:PO₄:NH₄=2:1:1:20, points represent experimental results, lines represent model predictions)

Fig. 3. Component-ion concentration in effluent of Solution 5 (Mg:Ca:PO₄:NH₄=0.5:0.5:1:20, points represent experimental results, lines represent model predictions)
Fig. 4. Molar ratios of NH₄, Ca, and Mg normalized to PO₄ (i.e., PO₄=1.0) in deposits formed at various initial component-ion molar concentrations

Modeling Software

MINEQL+ version 4.5, an equilibrium speciation model developed by Environmental Research Software, was used to model the struvite precipitation process in this study. Compared with other applications for the similar purpose, MINEQL+ has a significant advantage, which is allowing users to create a personal thermodynamic database. Struvite is not included in the supplied internal database. In this study, a custom thermodynamic database was created for struvite by providing equilibrium constants, enthalpy values, and stoichiometric coefficients to the database (Table 3). With the custom database included, the program calculates equilibrium concentrations of ion species based on the input of component-ion concentrations, using the pKₐs, pH, temperature, and ionic strength as shown in Table 3. MINEQL+ does not include kinetic aspects, and comparison of model output and experiments should consider that some precipitates do form more rapidly and experimental period is important.

Results and Discussion

Optimum pH

Struvite precipitation has been noted to occur over a wide pH range (7-11) but with varying precipitation potential. In addition, other undesired by-products may be formed, such as brucite [Mg(OH)₂], hydroxyapatite [Ca₁₀(PO₄)₆OH], and calcium phosphates Ca₃H₂PO₄·3H₂O and CaHPO₄·2H₂O that are often not differentiated from struvite. Therefore determination of the optimum pH enables the formation of the maximum amount and highest purity of struvite, not just targeting P removal. Model results show that the optimum pH is near 8.7, as the struvite precipitation potential reaches maximum while precipitation of undesired by-products is minimized. Combining the typical pH range for struvite precipitation and model prediction,

Fig. 5. NH₄/PO₄ molar ratios in the deposits formed with various initial component-ion concentrations
Fig. 6. X-ray diffraction spectra of deposit samples formed at pH=8.7 (top) and 10.5 (bottom) overlaid with struvite standard. Deposits formed in Solution 2, initial molar ion ratio: Mg/Cu/P=2/1/1.
four operational pH values, 7.8, 8.7, 9.2, and 10.5, were adopted to experimentally evaluate the purity of the deposits formed under different conditions.

**Effluent Composition Analysis**

Comparison of equilibrium ionic concentrations from experimental results and model prediction for Solutions 1, 2, and 5 (Table 2) are shown in Figs. 1–3. *MINEQL* predictions tracked experimental results. P concentration dropped from 190 mg/L to below 5 mg/L at pH=10.5 for Solutions 1 and 2; while for the Solution 5, P concentration in the effluent was 48.7 mg/L at pH=10.5 with removal efficiency of 74%. For the first two solutions, the sum of Ca and Mg molar concentrations is much higher than that of P, 2.5:1 and 3:1, respectively. While in the last solution, the ratio is only 1:1, suggesting that the ratio 1:1 is adequately high to induce maximum P precipitation from solution, but to attain high P removal, the Ca and Mg molar concentration must be in stoichiometric excess than that of P. The different Ca/Mg ratios in the first two solutions did not significantly affect P removal, however, modeling revealed that ratios impact which precipitates form. According to the *MINEQL* results, Ca$_4$H$_2$(PO$_4$)$_3$·3H$_2$O and CaHPO$_4$·2H$_2$O will precipitate preferentially rather than struvite. If the Ca/P ratio is high, P will be removed as calcium precipitates and struvite formation will be inhibited.

pH is a critical parameter in the process. For all the solutions, improved P removal was achieved as pH increased from 7.8 to 10.5, see Figs. 1–3, even though struvite purity is altered. Model results show P removal efficiency will decline as pH increases above 11 due to two reasons. First, at higher pH, Mg(OH)$_2$ is formed preferentially with a lower solubility, $pK_{sp}=10.7$. P-containing precipitates that may have been formed can be dissolved due to the low Mg$^{2+}$ concentration. This trend is more apparent when (Ca+Mg)/P is low because of the deficiency of cations in the solution phase (Fig. 3). Second, higher pH will deprotonate NH$_3^+$, a component-ion of struvite, and NH$_3$ volatilization will deplete the aqueous NH$_3$/NH$_4^+$ [Eq. (4)]. The appropriate selection of operational pH is important in achieving high P removal efficiency. However, the optimum pH value is wastewater composition dependent: different wastewater streams have different optimum pH values primarily as a function of Ca:Mg:P:NH$_4^+$ ratios. The composition of CAFO wastewater varies greatly; therefore model analysis aids to determine the optimum value for each case.

\[
\text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_3 + \text{H}_2\text{O}, \quad pK_A = 9.26 \tag{4}
\]

**Deposit Composition Analysis**

The elemental analysis depicted in Fig. 4 revealed that calcium concentration has substantial impact on the composition of deposits. Struvite is the only precipitate that has NH$_4^+$ in it under the experimental setting, therefore, when precipitates are dissolved and analyzed NH$_4^+$ molar concentration is roughly equal to the struvite molar concentration in the initial deposit. When the molar ratio of Ca, Mg, and PO$_4^{3-}$ was 0.5:2:1, the deposits formed at a pH of 7.8, 8.7, and 9.2 had nearly 1 to 1 ratios for NH$_4^+$ and P, and the calcium concentrations were below detection, see Fig. 4. These results suggest that these three samples were struvite with high purity. When pH was at 10.5, the ratio of NH$_4^+$ to P dropped significantly to 0.22, and the concentration of calcium rose concurrently.

The formation of calcium phosphate precipitates was demonstrated. With an increased calcium ratio in the synthetic wastewater, NH$_4^+$ ratios dropped while calcium ratios rose in deposits. When the ratio of Ca, Mg, and NH$_4^+$ was 2:2:1 (Solution 3), calcium precipitate was formed at a pH as low as 7.8. When the pH was increased to 10.5, NH$_4^+$ concentration is essentially zero suggesting deposits were void of struvite. The results indicate that when molar concentrations of Mg and NH$_4$ are not limiting for struvite formation, Ca concentration is the major factor that affects the composition of deposits. When the Ca/P ratio is less than 0.5, relatively pure struvite can be produced if the pH is less than 9.2. When the Mg/P ratio is less than 1, both Mg and Ca concentrations impact the deposit composition. Even if Ca/P is low (0.5), a calcium containing deposit is formed at a pH of 8.7 when Mg/P is 0.5. A pH of 8.7 is close to published optimum operational pH values. This suggests that Mg is a critical parameter and should be monitored to optimize struvite precipitation.

The ratios of NH$_4$/PO$_4$ in the deposits were plotted for various solutions, Fig. 5, as struvite purity can be roughly estimated by the NH$_4$/PO$_4$ ratio. A clear trend can be observed: struvite purity decreased when the calcium concentrations increased. When Ca:Mg was 0.5:2, the maximum struvite purity was 85%, while this ratio dropped to 61% when Ca:Mg was 1:2, and only 38% when Ca:Mg was 2:2. For all solutions, the optimum removal was obtained when the pH was between 8 and 9, showing that the pH of near 8.7 is optimal for high purity struvite precipitation. In real applications, high purity struvite is preferred to increase the market value without the need for subsequent purification process and operation cost.

The collected precipitates were analyzed with XRD to confirm the composition formed under different conditions. Those formed under pH=8.7 match struvite standard spectra as shown in Fig. 6. Struvite is the only crystalline phase in the deposit, indicating high purity struvite with no apparent amorphous phase. For the samples formed at pH=10.5, a broad hump centered at approximately 30° is apparent, which is due to amorphous materials in the sample. Existence of both struvite crystals and amorphous calcium precipitates is clear. The experimental results are consistent with model prediction. Samples formed at various conditions were further analyzed with SEM and EDS. The SEM images shown in Fig. 7(a) reveal that the deposits formed have typical struvite trapezoidal shape. EDS analysis also matches the standard struvite pattern, see Fig. 8. Optical and elemental analyses further confirm that the deposits formed under this condition are nearly pure struvite. The solids formed at pH=10.5 are amorphous when observed via SEM as shown in Fig. 7(b). No visible crystals were observed under SEM analysis. EDS also detected
A high concentration of calcium, which is consistent with the elemental analysis results and model predictions.

**Engineering Implications**

Collection and transport of CAFO wastewater to centralized treatment plants is not economical or feasible. The combination of anaerobic treatment and struvite crystallization processes may provide an economical and feasible solution to prevent excessive P discharge. In anaerobic treatment, most organic P and Poly-P degrade to reactive P, and most organic N is biologically converted to ammonium. The subsequent crystallization reactor can take advantage of these component ions and produce struvite. Struvite precipitation is better understood with respect to component-ion ratios, optimal pH, and competing ions for typical CAFO wastewater compositions. From this new understanding, potential applications can be considered. CAFO wastewater varies significantly in composition, calcium and each component-ion concentrations should be measured to determine whether the wastewater is suitable for the struvite crystallization process directly or additional processes are needed. Mg should also be closely monitored. If the Mg/P ratio is less than 1, Mg should be added to increase Mg concentration in the solution. If the Ca/P ratio is higher than 0.5, precipitates formed will not be pure struvite, but P will still be removed.

Processes to treat CAFO wastewater can be proposed. First wastewater is treated with anaerobic biological processes to decrease BOD and solids. Through anaerobic biological degradation, organic nitrogen and phosphate will be converted to NH₄⁺ and reactive P, including H₂PO₄⁻, HPO₄²⁻, and PO₄³⁻, increasing the struvite component-ion concentrations. The anaerobic process thereby creates an environment promoting struvite precipitation. Component-ion ratios were good for struvite formation in two lagoons in central Missouri, see Table 4. If the suspended solids concentration in the lagoon effluent is too high, additional solid removal processes can prevent excessive solids entering the crystallization reactor and decreasing precipitated struvite purity. However, traditional coagulants alum, ferrous salts, or lime should not be used because they will react with reactive P in the solution and could precipitate as aluminum phosphate (AlPO₄), ferrous phosphate (FePO₄), and hydroxyapatite [Ca₁₀(PO₄)₆(OH)₂]. Hydraulic solids removal, dissolved air flotation, or polymer addition are acceptable solids removal technologies. In the struvite crystallization reactor, magnesium chloride can be added if required to adjust the Mg/P ratio, and sodium hydroxide can be added to control the pH inside the reactor to promote struvite precipitation. Aeration of the effluent water from an anaerobic process has been shown to raise the pH to above 8 by striping CO₂. Alternatively, magnesium hydroxide could be added to concurrently raise pH and increase magnesium. Treated effluent is discharged from the top of the reactor; settled struvite is collected at the bottom of the reactor.

**Conclusions**

This research investigated the potential of struvite crystallization as a method to remove and recover reactive phosphorus from CAFO wastewater, while concurrently removing ammonium and magnesium. Specific conclusions can be drawn from the research completed. Calcium is the major competing ion in struvite formation, and struvite purity can be greatly decreased when the Ca/Mg ratio is higher than 1. Identification of Ca as an interference is particularly important as Ca is a common ion in process water. MINEQL+ 4.5 was also used to predict optimum pH and P removal efficiency in the struvite precipitation process with reasonable parameter settings added to the commercial package. When considering competitive precipitation with calcium phosphates, the optimal pH of 8.7 was lower than what had been previously published when not considering competitive precipitation or struvite purity. The higher pH values lead to pre-

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**Table 4. Parameters Measured in Two Anaerobic Swine Lagoons in Central Missouri**

<table>
<thead>
<tr>
<th>Component</th>
<th>Lagoon A</th>
<th>Lagoon B</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.9–7.3</td>
<td>6.7–7.6</td>
</tr>
<tr>
<td>SCOD (mg/L)</td>
<td>600–1,500</td>
<td>130–800</td>
</tr>
<tr>
<td>Mg (mg/L)</td>
<td>30.0–64.0</td>
<td>30.0–43.5</td>
</tr>
<tr>
<td>Ca (mg/L)</td>
<td>100.5–110.7</td>
<td>105.4–120.9</td>
</tr>
<tr>
<td>NH₄ (mg/L)</td>
<td>295.4–630.7</td>
<td>172.0–480.0</td>
</tr>
<tr>
<td>PO₄³⁻ (mg/L)</td>
<td>64.6–181.7</td>
<td>125.8–240.3</td>
</tr>
<tr>
<td>T-N (mg/L)</td>
<td>637.5–867.0</td>
<td>588.2–676.1</td>
</tr>
<tr>
<td>T-P (mg/L)</td>
<td>110.2–311.4</td>
<td>175.5–351.7</td>
</tr>
<tr>
<td>TS (mg/L)</td>
<td>1,800–4,000</td>
<td>1,500–2,000</td>
</tr>
</tbody>
</table>
precipitates other than struvite, reducing the value of the produced precipitate. Previously only P removal and precipitation was targeted, disregarding the specific precipitate formed. Finally, if P removal is the targeted goal and not struvite purity, magnesium and calcium should be in stoichiometric excess to phosphate to attain highest phosphate removal. This research suggests with a design targeted for each specific CAFO wastewater (swine, dairy, beef, etc.), struvite precipitation could be an effective and promising nutrient removal technology.

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