STRUVITE PRECIPITATION POTENTIAL
FOR NUTRIENT RECOVERY FROM
ANAEROBICALLY TREATED WASTES

Ann Miles*, Timothy G. Ellis**

*HDR Engineering, Inc., 8404 Indian Hills Drive, Omaha, NE 68114
**Dept. of Civil and Construction Eng., Iowa State University, Ames, IA 50011-3232

ABSTRACT

Geochemical equilibrium speciation modeling was used to determine optimum conditions for precipitation of magnesium ammonium phosphate, or struvite, for the recovery of nutrients from anaerobically digested wastes. Despite a wide range of pH values with the potential to precipitate struvite, the optimum pH was determined to be 9.0. Bench experiments conducted on effluent from an anaerobic sequencing batch reactor (ASBR) treating swine wastes achieved a maximum of 88% ammonia removal at a pH of 9.5 with added magnesium and phosphate to achieve an ammonium: magnesium: phosphate molar ratio of 1:1.25:1. Struvite precipitation was performed on a continuous basis in a pilot-scale ASBR treating swine wastes. Through the addition of supplemental magnesium and phosphate, the ammonia concentration was reduced from 1500 mg/L as nitrogen to less than 10 mg/L. The supernatant from the struvite precipitation clarifier was recycled to the feed of the ASBR without adverse impact, simulating on-farm effluent reuse as flush water.

KEYWORDS

anaerobic digestion, anaerobic sequencing batch reactor, MINTEQA2, speciation modeling, struvite

INTRODUCTION

Anaerobic digestion is often the preferred treatment for many high strength wastes, such as industrial wastes, agricultural byproducts, and wastewater treatment plant sludges, because it results in high conversions of potentially oxygen demanding and odorous organics to biogas. Depending on the wastestream, it also produces a liquid/biosolids mixture which is high in nitrogen and phosphorus, valuable fertilizer ingredients. Recovery of these nutrients from the treated wastes is a potential source of revenue, partially offsetting the costs of treatment. Struvite precipitation may be the best way to achieve these objectives.

Struvite, or magnesium ammonium phosphate hexahydrate, is a mineral that often precipitates from wastewater during anaerobic digestion when ammonium, phosphate, and magnesium ions are released. This precipitate has been implicated in the scaling of heat exchangers and piping, deposits in seafood canning, and the formation of kidney stones (Abdelrazig et al., 1988; Mohajit et al., 1989). Due to the high concentrations of dissolved orthophosphates and/or ammonia and magnesium ions encountered, there is strong potential for forming the precipitate in the biological treatment of hog wastes (Maqueda et al., 1994; Webb and Ho, 1992 and Wrigley et al., 1992), poultry wastes (Manninen, et al., 1989), wine distillery effluents (Lowenthal et al., 1994), and biosolids from biological phosphorus removal processes (Fujimoto et al., 1991). Typically, struvite formation is detrimental
since it clogs pipes, reduces efficiency in heat exchangers, and restricts flow in surface aerators (Mohajit \textit{et al.}, 1989). The objectives for the research reported herein were to predict conditions for optimum struvite precipitation potential using an equilibrium speciation model, perform batch tests to verify model predictions, and evaluate struvite precipitation and recovery in a pilot-scale treatment system.

\textbf{METHODS AND MATERIALS}

\textbf{Equilibrium Speciation Modeling} MINTEQA2, version 3.11, (EPA, 1991) is a geochemical equilibrium speciation model developed by the U.S. Environmental Protection Agency. The model is capable of computing equilibria among the dissolved, adsorbed, solid, and gas phases of dilute aqueous solutions in the laboratory or in natural systems. MINTEQA2 is the successor to MINTEQ, a model developed at Battelle Pacific Northwest Laboratory. MINTEQ was developed by combining the fundamental mathematical structure of MINEQL with the well-developed thermodynamic database of the US Geological Survey’s WATEQ3 model (EPA, 1991). MINTEQA2 is complemented by PRODEFA2, an interactive program which creates the needed input files and utilizes the Newton-Raphson approximation method to solve simultaneous nonlinear equations (EPA, 1991). The model allows full speciation of the struvite system to compute the concentration of each species. MINTEQA2 speciation for struvite includes $\text{H}_2\text{PO}_4^-$, $\text{H}_3\text{PO}_4$, $\text{OH}^-$, $\text{NH}_3$ (aq), $\text{MgOH}^+$, $\text{MgPO}_4^-$, $\text{MgH}_2\text{PO}_4^+$, $\text{MgHPO}_4$ (aq), $\text{HPO}_4^{2-}$, $\text{Mg}^{2+}$, $\text{PO}_4^{3-}$, $\text{NH}_4^+$. Applicable mass-balance, acid-base, and complex formation equilibria equations for struvite chemistry were published by Buchanan (1994).

MINTEQA2 modeling was used in conjunction with laboratory studies to predict the potential for struvite precipitation as a function of pH and magnesium, ammonium, and phosphate molar ratio. Each model prediction was run at a temperature of 25 degrees Celsius and a negligible ionic strength. If the ionic strength is fixed, it becomes independent of the solution chemistry (EPA, 1991). This implies that there are inert ions present in large enough concentration so that their impact on ionic strength is important. However, since these ions are non-reactive, they do not need to be included as actual components to be input into the model. Therefore, only the total concentration of magnesium, phosphate, and ammonia were input into the model. A separate set of runs was completed that included all of the other major ions found in an anaerobic digester effluent (including calcium, sodium, nitrate, nitrite, and chloride). No major difference was seen in the results as compared to the limited input. The runs were performed over a series of pH values to determine how the concentration of each constituent changes with pH.

\textbf{Bench-scale studies.} Predictions from MINTEQA2 modeling were confirmed with bench-scale studies using a high ammonia (1000-3500 mg/L as N) concentration effluent from an anaerobic sequencing batch reactor (ASBR) treating swine wastes. Additionally, experiments were conducted to optimize mixing time, flocculation, and settling characteristics for maximum removal of ammonia and precipitation of struvite. Details of these experiments have been published previously (Williams and Ellis, 1998).

\textbf{Pilot-scale studies.} Studies were performed using an 84-L pilot-scale ASBR treating swine wastes. Operational and performance characteristics of the ASBR have been published elsewhere (Troyer, \textit{et al.}, 1997). Struvite precipitation was carried out in a separate clarifier. Approximately 2.8 L of anaerobic digester effluent was pumped into a 4 L clarifier each day during the ASBR decant cycle. After 2.8 L of digester effluent had been pumped into the clarifier, supplemental magnesium and phosphate were added to the clarifier using dedicated chemical feed pumps. Stoichiometrically, there was excess ammonia in the effluent so that supplemental magnesium and phosphate had to be added to optimize struvite precipitation and ammonia removal. During the first month of operation, the supplemental chemicals included magnesium hydroxide (50% slurry) and 0-46-0 phosphate fertilizer (50% solution) and/or potassium phosphate (50% solution). These chemicals were selected based on economic considerations and ease of addition. The mixtures were stored in 1-gallon (3.785 L) jars and were mixed continuously to avoid solids settling prior to addition to the clarifier. However, as time progressed, it became evident that both the 50% Mg(OH)$_2$ slurry and the fertilizer solution were being deposited in tubing, causing plugging problems. Consequently, the magnesium and phosphate ions needed for struvite precipitation were not reaching the clarifier in a soluble state, resulting in lower than expected ammonia removals. Therefore,
After one month of operation the chemicals were changed to magnesium oxide (1 M) and potassium phosphate monobasic (1 M) solutions to achieve the desired stoichiometric ratio and pH. These mixtures were stored in 1-gallon (3.785 L) jars and were mixed continuously prior to addition to the clarifier.

After addition of the chemicals, the contents of the clarifier were mixed at approximately 150 rpm for 5 minutes. After this time, the contents were allowed to settle in the clarifier for 20 minutes. The supernatant was then pumped from the clarifier to a holding tank, followed by the pumping out of precipitated solids from the bottom of the clarifier. The supernatant was tested for ammonia concentration and pH. During the first month of operation, the supernatant was discarded. After approximately one month of operation, the supernatant was returned to the raw feed at a ratio of approximately 1:1. The solids were collected in a carboy for further analysis. All pumps used were controlled by ChronTrol timers and all mixers were Eastern Model 5VB-C. Mg²⁺, NH₄⁺, and HPO₄²⁻ were analyzed by ion chromatography (Dionex), after filtration through 0.45 µm pore-size filters and dilution.

**RESULTS AND DISCUSSION**

**Modeling Results.** MINTEQA2 was used to calculate the equilibrium concentration of selected ions in solution. The ion activity product (IAP) was then calculated by multiplying the equilibrium concentration of each ion of interest. If the IAP is greater than 7.08 X 10⁻¹⁴, the K_{sp} of struvite, then the solution is said to be supersaturated with respect to struvite ions, and struvite precipitation is possible.

As the pH increased, the concentrations of Mg²⁺ and NH₄⁺ decreased. However, the concentration of PO₄³⁻ increased due to the greater availability of orthophosphate at higher pH values (Buchanan, 1994). Figure 1 shows how the log(Mg²⁺), log(NH₄⁺), and log(PO₄³⁻) concentrations changed with varied pH and molar ratio. As pH increased, magnesium and ammonium ion concentration decreased, while phosphate ion concentration increased. This resulted in an optimum pH for struvite precipitation of approximately 9.0.

Figure 2 shows the calculated IAP as a function of the ammonium: magnesium: phosphate molar ratio and pH. The pK_{sp} of struvite is 13.15, and Figure 2 indicates that struvite precipitation is possible over the range of pH values from 4 to 14. However, other complexes, such as newberyite and bobierrite, will also be forming and will consume ions involved in struvite formation. The MINTEQA2 model does not include struvite in its thermodynamic database, and therefore the only way to determine equilibrium conditions is to manually calculate the IAP for struvite at each pH value, as was done in this study.

Results for the different molar ratios were very similar, albeit the molar ratio of constituents was different. It appears from Figure 2 that the maximum concentration of struvite ions occurred at approximately pH 9 for samples with the molar ratios where magnesium and phosphate were in excess. These results are consistent with laboratory data that showed a greater degree of ammonium removal through precipitation as struvite when magnesium and phosphate were supplied in excess of the stoichiometric requirement.

**Bench-scale studies.** Based on the results of the MINTEQA2 modeling, bench-scale batch experiments to verify conditions for struvite precipitation. Optimum conditions for struvite precipitation were determined, including mixing and settling times, pH, molar ratio, and most effective supplemental chemicals to use in order to alter the pH and molar ratio. Figure 3 shows the high degree of ammonia removal for ASBR effluent with a molar ratio for NH₃:Mg:PO₄-P of 1:1.25:1 and an optimum pH of 9.5. These results agree with the modeling result for an optimum pH in the range of 9.0-9.5.

**Pilot-scale study.** A pilot-scale reactor that had been operated in the laboratory for a period of several years for the treatment of swine manure from a local farm (Troyer et al., 1997) was modified to incorporate struvite precipitation for the recovery of nutrients. Several operational problems were encountered in the conversion included plugging of tubing and solids accumulation in the bottom of the clarifier due to pumping problems. Plugging of tubing was caused by high solids in the chemicals and low flow rates through the tubing. Magnesium
hydroxide, when added as a 50% slurry, and phosphate fertilizer when added as a 50% solution, both experienced this problem. As a consequence, insufficient volumes of these chemicals were added to the clarifier at various times throughout the study. Unfortunately, because the chemicals were automatically injected into the clarifier, it was often difficult to determine if proper amounts had been added. It can be assumed that when ammonia removals are less than expected removals (80-90%), one or both of the chemicals had been deficient. Table 2 shows conditions and results for the first 30 days of operation. All molar ratios listed assume that magnesium and phosphate concentrations in the wastewater itself contribute insignificant amounts to the total molar concentration. Molar ratios listed are theoretical ratios; however, because of plugging problems mentioned above, these values may not be actual ratios.

As shown, the final phosphate concentration for Day 4 through Day 15 was zero. In addition, ammonia removals were low (29-72%). These data indicate that phosphate was not being pumped into the clarifier due to operational problems. Phosphate was limiting the reaction, although the molar ratios indicated that struvite formation should have been occurring.

Figure 1. Magnesium, ammonium, and phosphate concentrations calculated by MINTEQA2 at each pH as a function of the ammonium: magnesium: phosphate molar ratio. The molar ratio is indicated beside the symbols to the right of the plot.
Figure 2. Ion activity product calculated by MINTEQA2 at each pH as a function of the ammonium: magnesium: phosphate molar ratio. The molar ratio is indicated beside the symbols to the right of the plot.

Figure 3. Ammonia removal over pH range for $\text{NH}_3$:$\text{Mg}$:$\text{PO}_4$-P of 1:1.25:1. Initial $\text{NH}_3$ concentration was approximately 3500 mg/L.
Table 2. Ammonia removal through precipitation as struvite in a clarifier following a lab-scale ASBR treating swine wastes. The effluent was not recycled to the ASBR in this experiment. Plugging problems caused insufficient supplemental chemicals to be added to the reactor through Day 16 and that molar ratios for Days 1 through 15 are the target values.

<table>
<thead>
<tr>
<th>Day</th>
<th>Initial Conc. (mg/L)</th>
<th>Final Conc. (mg/L)</th>
<th>Molar Ratio</th>
<th>Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Mg</td>
<td>PO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>NH&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td></td>
<td>(mg/L)</td>
<td></td>
<td>(mg/L)</td>
<td></td>
</tr>
<tr>
<td>Day 1</td>
<td>1089</td>
<td>18</td>
<td>0</td>
<td>642</td>
</tr>
<tr>
<td>Day 3</td>
<td>1115</td>
<td>21</td>
<td>178</td>
<td>687</td>
</tr>
<tr>
<td>Day 4</td>
<td>1097</td>
<td>23</td>
<td>173</td>
<td>780</td>
</tr>
<tr>
<td>Day 6</td>
<td>1025</td>
<td>23</td>
<td>0</td>
<td>732</td>
</tr>
<tr>
<td>Day 7</td>
<td>1127</td>
<td>21</td>
<td>264</td>
<td>620</td>
</tr>
<tr>
<td>Day 9</td>
<td>1030</td>
<td>13</td>
<td>54</td>
<td>532</td>
</tr>
<tr>
<td>Day 10</td>
<td>1106</td>
<td>25</td>
<td>155</td>
<td>358</td>
</tr>
<tr>
<td>Day 12</td>
<td>1061</td>
<td>18</td>
<td>78</td>
<td>445</td>
</tr>
<tr>
<td>Day 13</td>
<td>1062</td>
<td>25</td>
<td>169</td>
<td>474</td>
</tr>
<tr>
<td>Day 15</td>
<td>994</td>
<td>15</td>
<td>0</td>
<td>743</td>
</tr>
<tr>
<td>Day 16</td>
<td>886</td>
<td>-</td>
<td>-</td>
<td>594</td>
</tr>
<tr>
<td>Day 18</td>
<td>852</td>
<td>59</td>
<td>477</td>
<td>581</td>
</tr>
<tr>
<td>Day 20</td>
<td>895</td>
<td>94</td>
<td>527</td>
<td>418</td>
</tr>
<tr>
<td>Day 22</td>
<td>912</td>
<td>164</td>
<td>602</td>
<td>257</td>
</tr>
<tr>
<td>Day 23</td>
<td>907</td>
<td>114</td>
<td>701</td>
<td>336</td>
</tr>
<tr>
<td>Day 24</td>
<td>878</td>
<td>93</td>
<td>603</td>
<td>208</td>
</tr>
<tr>
<td>Day 25</td>
<td>809</td>
<td>-</td>
<td>-</td>
<td>474</td>
</tr>
<tr>
<td>Day 26</td>
<td>924</td>
<td>234</td>
<td>739</td>
<td>110</td>
</tr>
<tr>
<td>Day 27</td>
<td>909</td>
<td>67</td>
<td>480</td>
<td>92</td>
</tr>
<tr>
<td>Day 28</td>
<td>792</td>
<td>78</td>
<td>542</td>
<td>98</td>
</tr>
<tr>
<td>Day 29</td>
<td>751</td>
<td>150</td>
<td>645</td>
<td>16</td>
</tr>
<tr>
<td>Day 30</td>
<td>706</td>
<td>-</td>
<td>58</td>
<td>-</td>
</tr>
</tbody>
</table>

At Day 16, tubing was replaced so plugging would not become a problem. From Day 16 to Day 24, both magnesium and phosphate volumes added to the reactor were slowly increased. Ammonia removals increased from 33% at a molar ratio of NH<sub>3</sub>:Mg:PO<sub>4</sub> of 1:1.2:2.4 to 76% at 1:4.7:6.7. Expected removals at these molar ratios were higher than observed removals. pH values for these days ranged from 6.5 to 7.3. It is believed that although magnesium and phosphate were supplied in excess, the fertilizer depressed the pH to values below the optimum range (pH 8-10), therefore preventing optimum struvite formation.

Days 25 to 30 provided the best results in terms of ammonia removal. The amount of fertilizer added each day was decreased, while the amount of potassium phosphate was increased. This allowed continued addition of excess phosphate, without the large decrease in pH due to the fertilizer. Ammonia removal of 98% was recorded on Day 29 with a molar ratio of NH<sub>3</sub>:Mg:PO<sub>4</sub> of 1:6.9:2.8 and a final pH of 7.5. Solids samples from Day 28, Day 29, and Day 30 were analyzed by X-ray diffraction and were determined to be struvite.

After it was determined that operational conditions in the reactor were conducive to struvite precipitation and operational conditions in the anaerobic sequencing batch reactor were stable, the supernatant was recycled to the raw feed bucket at approximately one part feed to one part supernatant. In the past, raw feed was diluted with tap water at the same ratio. Conditions were modified slightly so that chemicals could be added to the struvite reactor as 1 M MgO and 1 M KH<sub>2</sub>PO<sub>4</sub> and the solutions were less likely to cause plugging problems. It was determined that both magnesium and phosphate should be added in excess based on an ammonia concentration to the struvite reactor of 1700 mg/L. The molar ratio of NH<sub>3</sub>:Mg:PO<sub>4</sub> used, based on this concentration, was approximately 1:2:1.5. Performance was tracked on the anaerobic sequencing batch reactor to determine if the supernatant was causing any adverse effects on the quality of the effluent. Table 3 shows results of 6 weeks of recycle operation.
Influent ammonia concentration to the ASBR gradually decreased over time. This was probably not due to the supernatant being used as dilution water because the raw feed had typically been diluted with tap water. The influent feed to the ASBR was more than likely varied over time as the sample aged. Typically, the raw feed was picked up from the hog lot once every few weeks, with excess being stored at 4°C.

As shown in Table 3, effluent concentrations of ammonia from the struvite reactor were almost always less than 10 mg/L. This indicates that over 99% of the ammonia was removed from the raw feed after struvite precipitation. The influent ammonia concentration to the struvite reactor never reached the theoretical value of 1700 mg/L. This means that magnesium and phosphate were more than likely over-supplied. Although this leads to ammonia being the limiting factor, costs of chemical addition may be too great for this to be feasible in a full-scale treatment plant.

Recycle of supernatant water to the raw feed did not cause adverse conditions within the ASBR. Some minor operational problems with the ASBR during the experiment led to unstable conditions within the reactor. Chemical oxygen demand (COD), volatile fatty acids (VFAs), and pH were monitored during the time period considered. However, results were inconclusive. Operational problems included a leak in the anaerobic reactor, pumping problems which caused an overflow in the clarifier, and automatic controller problems which led to shortened, and in some cases lengthened, solids retention times within the reactor. However, none of the instability problems within the reactor are believed to be caused by the low ammonia concentration in the dilution water.

Table 3. Ammonia Concentrations in ASBR.

<table>
<thead>
<tr>
<th>Day</th>
<th>Feed</th>
<th>ASBR Effluent</th>
<th>Clarifier Effluent</th>
</tr>
</thead>
<tbody>
<tr>
<td>31</td>
<td>1567</td>
<td>1761</td>
<td>4</td>
</tr>
<tr>
<td>33</td>
<td>1550</td>
<td>1682</td>
<td>7</td>
</tr>
<tr>
<td>35</td>
<td>1439</td>
<td>1516</td>
<td>6</td>
</tr>
<tr>
<td>36</td>
<td>1308</td>
<td>1524</td>
<td>10</td>
</tr>
<tr>
<td>39</td>
<td>1320</td>
<td>1526</td>
<td>11</td>
</tr>
<tr>
<td>40</td>
<td>1350</td>
<td>1463</td>
<td>12</td>
</tr>
<tr>
<td>41</td>
<td>1296</td>
<td>1404</td>
<td>5</td>
</tr>
<tr>
<td>44</td>
<td>1277</td>
<td>1398</td>
<td>6</td>
</tr>
<tr>
<td>45</td>
<td>1304</td>
<td>1281</td>
<td>6</td>
</tr>
<tr>
<td>47</td>
<td>1163</td>
<td>1203</td>
<td>4</td>
</tr>
<tr>
<td>51</td>
<td>1179</td>
<td>1250</td>
<td>6</td>
</tr>
<tr>
<td>56</td>
<td>942</td>
<td>926</td>
<td>2</td>
</tr>
<tr>
<td>57</td>
<td>968</td>
<td>978</td>
<td>3</td>
</tr>
<tr>
<td>60</td>
<td>836</td>
<td>852</td>
<td>4</td>
</tr>
<tr>
<td>67</td>
<td>687</td>
<td>684</td>
<td>3</td>
</tr>
<tr>
<td>68</td>
<td>769</td>
<td>652</td>
<td>3</td>
</tr>
<tr>
<td>72</td>
<td>764</td>
<td>592</td>
<td>4</td>
</tr>
</tbody>
</table>

**CONCLUSIONS**

Computer modeling of the swine waste was performed using MINTEQA2. This model allowed laboratory conditions to be duplicated, in a sense, without the added expense of chemicals. MINTEQA2 was able to compute the concentration of each species applicable to struvite precipitation at various pH values and molar ratios. Optimal pH for struvite precipitation was verified with bench-scale batch tests as 9.0 - 9.5 resulting in over 88% ammonia removal.
The performance of a pilot-scale reactor system was outstanding in terms of percent ammonia removal. Ammonia concentration was reduced from 1500 mg/L to less than 10 mg/L by supplying magnesium oxide and potassium phosphate to an effluent waste stream of an operating ASBR. The struvite crystals were settled out of the effluent, where they could be used as fertilizer. The supernatant was successfully recycled to the head of the ASBR and added as dilution water to the raw feed at approximately one part feed to one part supernatant. Despite operational problems that may occur in the struvite reactor if pumps and/or tubing are not designed to carry high solids, struvite precipitation may prove to be an ideal way to reduce the ammonia load and recover nutrients from anaerobically treated wastes.

REFERENCES


