

# Struvite precipitation in anaerobic swine lagoon liquid: effect of pH and Mg:P ratio and determination of rate constant

Nathan O. Nelson \*, Robert L. Mikkelsen, Dean L. Hesterberg

*Department of Soil Science, North Carolina State University, Box 7619, Raleigh, NC 27695-7619, USA*

Received 13 April 2002; received in revised form 24 February 2003; accepted 25 February 2003

## Abstract

Because of increased concern about surface water eutrophication from nutrient-enriched agricultural runoff, many swine producers are encouraged to decrease application rates of waste-based P. Precipitation and subsequent removal of magnesium ammonium phosphate ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ), commonly known as struvite, is a promising mechanism for N and P removal from anaerobic swine lagoon effluent. The objectives of this research were to (i) quantify the effects of adjusting pH and Mg:P ratio on struvite precipitation and (ii) determine the rate constant pH effect for struvite precipitation in anaerobic swine lagoon liquid. Concentrations of  $\text{PO}_4\text{-P}$  in liquid from two anaerobic swine lagoons were determined after 24 h of equilibration for a pH range of 7.5–9.5 and Mg:P ratios between 1:1 and 1.6:1. Struvite formation reduced the  $\text{PO}_4\text{-P}$  concentration in the effluents to as low as  $2 \text{ mg l}^{-1}$ . Minimum concentrations of  $\text{PO}_4\text{-P}$  occurred between pH 8.9 and 9.25 at all Mg:P ratios. Struvite precipitation decreased  $\text{PO}_4\text{-P}$  concentrations by 85% within 20 min at pH 9.0 for an initial Mg:P ratio of 1.2:1. The rate of  $\text{PO}_4\text{-P}$  decrease was described by a first-order kinetic model, with rate constants of 3.7, 7.9, and  $12.3 \text{ h}^{-1}$  at pH 8.4, 8.7 and 9.0 respectively. Our results indicate that induced struvite formation is a technically feasible method to remove N and P from swine lagoon liquid and it may allow swine producers to recover nutrients for off-farm sale.

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**Keywords:** Magnesium–ammonium–phosphate; Struvite; Solubility curve; Animal waste treatment; Crystal growth; Phosphorus; Precipitation kinetics

## 1. Introduction

A common method of swine waste management is to store and treat it in an anaerobic lagoon and land-apply the excess liquid to meet the N requirements of the growing crop. Because the average available N:P ratio of swine lagoon liquid is between 2:1 and 4:1 and the N:P ratio of common receiver crops ranges from 4:1 to 9:1, manure applications designed to meet crop N requirements can over apply P by 2–3 times (Barker et al., 1994; Mikkelsen, 1997). The over application of P to crop fields increases the risk of P loss to nearby surface waters and the associated risk of eutrophication (Sharpley et al., 1996; Daniel et al., 1994). In order to comply with new nutrient management standards many swine producers may have to reduce their P application rates, which would require increased land and additional N fertilizer.

Therefore, an alternative to reducing waste application rates is to decrease the P concentration of the waste through precipitation of insoluble phosphate minerals.

A promising method of P removal from anaerobic swine lagoon liquid is through the precipitation of magnesium ammonium phosphate hexahydrate ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ), commonly known as struvite. Struvite constituent ions,  $\text{Mg}^{2+}$ ,  $\text{NH}_4^+$ , and orthophosphate ( $\text{PO}_4\text{-P}$ ), are among the predominant ions present in anaerobic swine lagoon effluent, thereby minimizing the need to add chemicals (Battistoni et al., 1997). Average total  $\text{NH}_4^+$  and  $\text{Mg}^{2+}$  concentrations in anaerobic swine lagoons are 9.6 and 0.5 times the stoichiometric demand for complete  $\text{PO}_4\text{-P}$  precipitation as struvite (Barker et al., 1994). Although the addition of Mg can enhance struvite precipitation (Beal et al., 1999), it is not required because most lagoons are already supersaturated with respect to this mineral (Webb and Ho, 1992; Barker, 1996). Struvite precipitation could benefit swine operations because struvite is a valuable slow-release fertilizer (Bridger et al., 1962), thereby creating a valuable use for

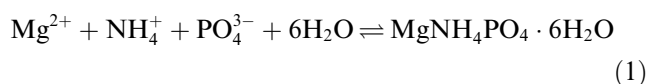
\* Corresponding author. Tel.: +1-919-513-3032; fax: +1-919-515-2167.

E-mail address: [nonelson@unity.ncsu.edu](mailto:nonelson@unity.ncsu.edu) (N.O. Nelson).

the recovered precipitate and removing the nutrients off-farm. Furthermore, controlled precipitation and recovery of struvite could also decrease maintenance costs of recycle flush wastewater systems by eliminating undesirable struvite precipitation in pipes and pumps.

Pilot- and full-scale waste treatment systems that use struvite precipitation to remove P from industrial wastewater (Unitika Ltd., 1994), municipal wastewater (Liberti et al., 1986; Ohlinger et al., 2000), and anaerobically digested calf manure (Schuiling and Andrade, 1999) are reported to be in operation. Additional research to quantify the effects of pH and Mg:P ratios on struvite formation in anaerobic swine lagoon liquid will help in applying struvite precipitation as a method of P removal.

Struvite is formed as  $\text{Mg}^{2+}$ ,  $\text{NH}_4^+$ , and  $\text{PO}_4^{3-}$  react in 1:1:1 molar ratios (Eq. (1)) with a formation constant ( $K^0$ ) of  $1.41 \times 10^{13}$  (Buchanan et al., 1994). The equilibrium ion-activity product ( $\text{IAP}_{\text{eq}}$ ) for struvite is  $7.08 \times 10^{-14}$  (Eq. (2)). Therefore, in a given solution, struvite will be favored to precipitate if the product of  $\text{Mg}^{2+}$ ,  $\text{NH}_4^+$ , and  $\text{PO}_4^{3-}$  activities ( $\text{IAP}$ ) exceeds the  $\text{IAP}_{\text{eq}}$ . Although  $\text{H}^+$  concentration does not directly enter the  $\text{IAP}$  equation, struvite precipitation is highly pH dependent because the activities of both  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  are pH dependent. As pH increases from 7 to 9, the percent of total ammoniacal N present as  $\text{NH}_4^+$  decreases from 99% to 64% (Stumm and Morgan, 1970). In the same range of pH change, the fraction of total  $\text{PO}_4\text{-P}$  present as the  $\text{PO}_4^{3-}$  anion increases 250 fold (Stumm and Morgan, 1970). Because of the overwhelming increase in the proportion of total  $\text{PO}_4\text{-P}$  present as  $\text{PO}_4^{3-}$  within the pH range of 7–9, the pH effect on  $\text{PO}_4^{3-}$  activity has a greater influence on struvite precipitation than does the pH effect on  $\text{NH}_4^+$  activity.



$$\text{IAP}_{\text{eq}} = (\text{Mg}^{2+})(\text{NH}_4^+)(\text{PO}_4^{3-}) = 7.08 \times 10^{-14} \quad (2)$$

Published values for the pH of minimum struvite solubility range from 9 to 10.7. Buchanan et al. (1994) used an aquatic chemistry equilibrium model (M1NTEQA2; EPA, 1991) to model struvite formation and found that with concentrations typical of anaerobic lagoons, struvite precipitation could be expected between the pH values of 7 and 11, with minimum solubility at pH 9. Using different equilibrium constants and additional Mg- $\text{PO}_4$  species, Ohlinger et al. (1998) modeled struvite precipitation in wastewater and found minimum solubility between pH 10.3 and 10.7, depending on ionic strength. Shin and Lee (1997) observed continued decrease in  $\text{PO}_4\text{-P}$  and  $\text{NH}_4^+$  concentrations due to struvite precipitation as pH was increased to 10.5.

Magnesium additions to wastewater have also been used to enhance struvite precipitation. Beal et al. (1999)

precipitated struvite from swine waste by increasing the molar Mg:P ratio from 0.25:1 to 0.65:1 and 1.1:1 with MgO additions, which simultaneously increased the pH to >8. They found that  $\text{PO}_4\text{-P}$  removal increased with increasing Mg, however, further increasing the pH of the Mg adjusted waste did not increase  $\text{PO}_4\text{-P}$  removal. Maekawa et al. (1995) also adjusted the Mg:P ratios of swine wastewater from 2:3 to 3:2 and increased the pH, with maximum  $\text{PO}_4\text{-P}$  removal occurring at a Mg:P ratio of 3:2.

Published information about struvite precipitation kinetics is limited to only a few studies. Gunn (1976) developed expressions for struvite induction time in homogeneously nucleating solutions. It was concluded that once nucleation had occurred, crystal growth rate exceeds the nucleation rate because of greater activation energy required for nucleation of non-associated ions as compared to the activation energy for deposition of ions on a crystal surface (Gunn, 1976).

Ohlinger et al. (1999) studied struvite formation kinetics in pure solutions and in wastewater. Nucleation was found to be the controlling process for struvite formation during the induction period in both pure solutions and in wastewater. It was also demonstrated that nucleation was primarily affected by the degree of supersaturation, and therefore was a reaction-controlled process. Contrary to the nucleation process, the crystal growth rate was transport-controlled. Furthermore, the preferential accumulation of struvite around areas of high mixing energy (i.e. pumps and pipes) in wastewater treatment systems was found to be primarily affected by growth kinetics rather than nucleation kinetics (Ohlinger et al., 1999). Extrapolations from these findings imply that a high degree of supersaturation would maximize the nucleation rate and thorough mixing would maximize crystal growth. These results were later applied to a benchtop scale fluidized bed reactor (Ohlinger et al., 2000). By assuming first-order reaction kinetics with respect to orthophosphate ( $\text{PO}_4\text{-P}$ ) concentration, a rate constant of  $4.2 \text{ h}^{-1}$  was calculated at pH 8.3. Because waste composition will affect ion activities, it is necessary to measure the rate constant for struvite formation in anaerobic swine lagoon liquid.

The twofold objective of this research was to (i) quantify the effect of adjusting both pH and Mg:P ratio on struvite precipitation and resultant P concentration in anaerobic swine lagoon liquid and (ii) determine the rate constant for struvite precipitation in anaerobic swine lagoon liquid at different pH values.

## 2. Methods

Anaerobic swine lagoon liquid was collected from two active farms in North Carolina (designated LW, and RM). The RM lagoon was sampled in August 1999

and the LW lagoon was sampled twice, once in July of 1999 (LW1) and again in August of 2000 (LW2). After collection, the effluent was stored at 4 °C for 24 h in a 30-l glass carboy, allowing any solids that were disturbed in the collection process to settle. Following the 24-h settling period, effluent was siphoned off the top of the container, transferred into 2.5-l glass containers, and stored at 4 °C until use. Initial pH and concentrations of  $\text{Mg}^{2+}$ ,  $\text{NH}_4^+$ , and  $\text{PO}_4\text{-P}$  present in the lagoon liquid are displayed in Table 1.

Struvite solubility in anaerobic swine lagoon effluent was determined through a series of laboratory batch experiments. The Mg:P ratio was initially adjusted by adding the appropriate quantity of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  to 2 l of effluent and mixing for 10 min to dissolve. Subsamples of Mg-adjusted effluent were added to each of eight beakers (250 ml per beaker). The effluent pH in each beaker was adjusted with 1.0 M NaOH, creating a pH range of 7.5–9.5 and 7.75–9.5 for the LW1 and RM effluents respectively. The beakers were covered with parafilm to reduce  $\text{NH}_3$  volatilization. After a 24-h quiescent equilibration period at 25 °C, a 20-ml aliquot of effluent was pipetted from each beaker at 2 cm below the surface for  $\text{PO}_4\text{-P}$  and  $\text{Mg}^{2+}$  analysis. Because pH was not controlled during the equilibration period, the final pH was measured following removal of the 20-ml aliquot. Solubility curves were developed using the final pH. Precipitate from the eight beakers was combined to obtain an adequate sample mass and saved for subsequent chemical and mineralogical analyses. This process was repeated using Mg:P ratios of 1:1, 1.2:1, 1.4:1, and 1.6:1 for the LW1 effluent and 1.1:1, 1.2:1, 1.4:1, and 1.6:1 for the RM effluent.

Ortho-phosphate analysis of the equilibrated effluent was performed using a colorimetric procedure (Murphy and Riley, 1962). Magnesium concentrations in the equilibrated effluent were measured with a Perkin-Elmer Model 3100 atomic absorption spectrometer. The samples were not individually analyzed for  $\text{NH}_4^+$  because it was present in great excess (Table 1). Precipitate recovered from the solubility experiments was dissolved in 0.01 M HCl and analyzed for  $\text{Mg}^{2+}$  and total P with Inductively Coupled Plasma spectrometry. The C and N content of the precipitate was determined by combus-

tion with a Perkin-Elmer PE 2400 CHN elemental analyzer. Random powder mounts of collected precipitate were prepared and analyzed with a Rigaku D/MAX-B X-ray diffractometer using unresolved  $\text{CuK}_\alpha$  radiation at 1.5419 Å with a graphite crystal monochromator and a Ni  $\beta$  filter. Statistical analysis of the pH and  $\text{PO}_4\text{-P}$  data was performed with the PROC MIXED procedure (SAS Institute, 1998).

Struvite formation kinetics were measured using a continuously stirred batch reactor method (Amacher, 1991). An Erlenmeyer flask outfitted with a rubber stopper, pH electrode, thermometer, magnetic stirrer, and sampling syringe was used for the reactor. The reactor was filled with 1100 ml LW2 lagoon liquid and brought to room temperature (22–24 °C). An 8-ml sample of reactor liquid was removed just prior to beginning the reaction (time 0) to determine initial  $\text{Mg}^{2+}$ ,  $\text{NH}_4^+$ , and  $\text{PO}_4\text{-P}$  concentrations. Immediately after the time 0 sample was removed, 10 ml of 1 M NaOH was added to the reactor, bringing the pH to 9.0. The reactor solution was sampled (8 ml) at 1-min intervals for the first 20 min, at 5-min intervals between 20 and 60 min, and at 10-min intervals between 60 and 120 min. After each sample was removed from the reactor, it was immediately forced through a glass fiber pre-filter (Millipore® AP20) and a 0.45- $\mu\text{m}$  mixed cellulose ester membrane filter (Millipore® HAWP) that were attached in series to the end of the sampling syringe. To stop the reaction, 20  $\mu\text{l}$  of 6 M HCl was immediately added to the filtrate. The sampling and filtering process took a maximum of 15 s. The entire procedure was repeated twice with fresh lagoon liquid, where only 7 and 4 ml of 1 M NaOH were added to the reactor, which raised the pH to 8.7 and 8.4 respectively. The filtered sample aliquots were analyzed for  $\text{Mg}^{2+}$ ,  $\text{NH}_4^+$ , and  $\text{PO}_4\text{-P}$ . Ammonium and  $\text{PO}_4\text{-P}$  concentrations were measured colorimetrically using a Lachat QuickChem 8000 auto analyzer instrument (Lachat Instruments, 1995). Magnesium concentrations were measured with a Perkin-Elmer Model 3100 atomic adsorption spectrometer.

The kinetic rate constant was determined by fitting a first-order kinetic model to the data. The modified expression for a first-order reaction relates the disappearance of a reactant ( $-\text{d}C/\text{d}t$ ) to the rate constant ( $k$ ) and

Table 1

Concentrations of selected constituents of anaerobic swine lagoon liquid used for the development of struvite supersaturation curves

| Effluent | Mg <sup>a</sup><br>(mg l <sup>-1</sup> ) | NH <sub>4</sub> -N <sup>b</sup><br>(mg l <sup>-1</sup> ) | PO <sub>4</sub> -P<br>(mg l <sup>-1</sup> ) | K <sup>c</sup><br>(mg l <sup>-1</sup> ) | Ca<br>(mg l <sup>-1</sup> ) | S<br>(mg l <sup>-1</sup> ) | Na<br>(mg l <sup>-1</sup> ) | Fe<br>(mg l <sup>-1</sup> ) | pH   | Molar<br>Mg:P ratio |
|----------|--|--|---|---|-----------------------------|----------------------------|-----------------------------|-----------------------------|------|---------------------|
| RM       | 48.4                                     | 533  | 55.4  | 664                                     | 152                         | 45.2                       | 4.4                         | 2.8                         | 7.84 | 1.1:1               |
| LW1      | 50.5                                     | 272  | 63.8  | 350                                     | 145                         | 33.5                       | 217                         | 3.7                         | 7.53 | 1.0:1               |
| LW2      | 46.7                                     | 142  | 50.5  |   |                             |                            |                             |                             | 7.5  | 1.2:1               |

<sup>a</sup> The Mg and  $\text{PO}_4\text{-P}$  concentrations were determined using the methods listed in the text.

<sup>b</sup> The  $\text{NH}_4\text{-N}$  concentration for RM and LW1 was estimated as 80% of the total N concentration, where total N was determined by combustion of a filtered effluent sample in a CSN analyzer.

<sup>c</sup> The K, Ca, S, Na, and Fe concentrations of digested and filtered samples were determined by inductively-coupled plasma spectrometry.

the reactant concentration at time  $t$  ( $C$ ) minus the reactant concentration at equilibrium ( $C_{eq}$ ) (Eq. (3)). Integrating Eq. (3) gives the linear form of the first-order rate equation (Eq. (4)), where  $C_0$  is the initial concentration of the reactant. Assuming first-order reaction kinetics, a plot of  $\ln(C - C_{eq})$  against time gives a straight line with slope  $-k$ .

$$-dC/dt = k(C - C_{eq}) \quad (3)$$

$$\ln(C - C_{eq}) = -kt + \ln(C_0 - C_{eq}) \quad (4)$$

### 3. Results and discussion

Phosphorus concentration in both LW and RM effluents decreased with increasing pH and Mg:P ratio (Fig. 1). Multiple regression analysis was performed to determine which experimental factors and interactions significantly effected  $PO_4$ -P concentrations. Data were fit with a full model consisting of Mg, Mg quadratic, pH, and pH quadratic, and all associated interaction terms. Fitting the full model to the data is analogous to performing individual quadratic regressions for each Mg:P ratio. A reduced model was found by systematically eliminating insignificant higher order terms (Type III  $p > 0.05$ ) until all remaining variables were significant ( $p < 0.05$ ). A full and reduced model  $F$ -test was used to confirm that the coefficients for terms appearing in the full model but left out of the reduced model were zero ( $p > 0.05$ ). The multiple regression model that best fit the data consisted of Mg and pH linear terms and a pH quadratic term. The Mg quadratic term and all Mg  $\times$  pH interactions were not significant ( $p > 0.05$ ). Lack of Mg quadratic and Mg  $\times$  pH interactions is apparent in Fig. 1a and b, where regression lines have the same slope and reach a minimum at the same pH. Therefore, adding Mg to the effluent produces the same effect regardless of pH.

A visible precipitate formed at the bottom of each beaker, with noticeably greater quantities in the beakers with increased solution pH. The collected precipitate was positively identified as struvite by X-ray diffraction analysis. No other crystalline solids were detected from the diffraction patterns. Chemical analysis of the precipitate was also consistent with struvite (Table 2). The presence of C in the struvite precipitated from the lagoon effluent was probably organic C, as indicated by a gray discoloration of these samples compared with pure (white) struvite samples.

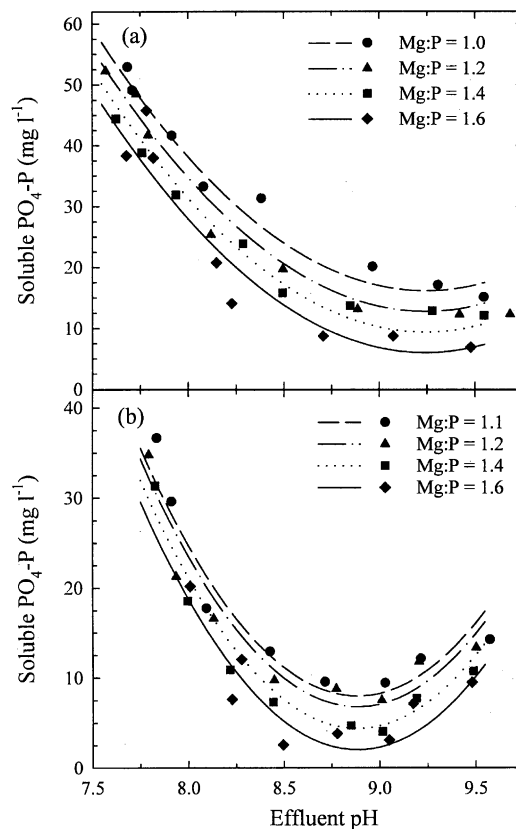


Fig. 1. Dissolved  $PO_4$ -P concentrations in anaerobic swine lagoon effluent solutions from the LW lagoon (a) and RM lagoon (b) after equilibrating for 24 h and forming struvite. Curves are predicted  $PO_4$ -P concentrations using multiple linear regression as described in the text.

Maximum  $PO_4$ -P removal (minimum struvite solubility) occurred at pH 9.25 and 8.9 for the LW1 and RM effluents respectively (Fig. 1). Orthophosphate concentration decreased by 91% in the LW1 effluent, from  $64 \text{ mg l}^{-1}$  in the untreated effluent to  $6 \text{ mg l}^{-1}$  in effluent with Mg:P ratio of 1.6:1. Orthophosphate concentration decreased by 96% in the RM effluent, from  $55 \text{ mg l}^{-1}$  in the untreated effluent to  $2 \text{ mg l}^{-1}$  in effluent with Mg:P ratio of 1.6:1. There was a slight increase in pH and decrease in  $PO_4$ -P concentration of effluent samples that did not receive NaOH or Mg addition. The increase in pH was attributed to  $CO_2$  loss from the effluent, which may have occurred from initial stirring or during the 24-h equilibrium time. An increase in  $PO_4$ -P concentration occurred at  $pH > 9$  in the RM effluent, suggesting an increase in struvite solubility at

Table 2

Chemical analysis of precipitate collected from the sediment of the anaerobic swine lagoon liquid used to create the solubility curves

| Precipitate source          | Mg ( $\text{g kg}^{-1}$ ) | N ( $\text{g kg}^{-1}$ ) | P ( $\text{g kg}^{-1}$ ) | C ( $\text{g kg}^{-1}$ ) | Mg:N:P molar ratio |
|-----------------------------|---------------------------|--------------------------|--------------------------|--------------------------|--------------------|
| LW1 effluent                | 94.9                      | 52.8                     | 121.8                    | 6.3                      | 0.99:0.96:1        |
| RM effluent                 | 86.5                      | 48.7                     | 111.2                    | 33.0                     | 0.99:0.97:1        |
| Pure struvite (theoretical) | 99.0                      | 57.1                     | 126.2                    | 0.0                      | 1:1:1              |

higher pH. Higher  $\text{NH}_4^+$  concentration initially present in the RM liquid could be the cause of increased struvite solubility at  $\text{pH} > 9$ . Orthophosphate concentration in the LW1 liquid tended to remain more constant at higher pH. The pH for minimum struvite solubility observed in these experiments agrees well with Buchanan et al. (1994) who predicted minimum struvite solubility at pH 9 in most wastewaters, as opposed to Ohlinger et al. (1998) who predicted minimum struvite solubility at pH 10.3.

The Mg:P ratio did not affect the pH of minimum struvite solubility (Fig. 1), which is also reflected in the lack of a  $\text{Mg}^{2+}$  by pH interaction ( $p > 0.05$ ). However, increasing the Mg:P ratio resulted in decreased  $\text{PO}_4\text{-P}$  concentration at any given pH ( $p < 0.001$ ). For example, increasing the Mg:P ratio further decreased the minimum  $\text{PO}_4\text{-P}$  concentration from 16 to 6  $\text{mg l}^{-1}$  in the LW1 effluent at pH 9.25. A similar decrease was also observed in the RM effluent. At each Mg:P ratio, the RM effluent had a lower  $\text{PO}_4\text{-P}$  concentration than the LW1. The lower  $\text{PO}_4\text{-P}$  concentration in RM effluent is most likely a result of its higher  $\text{NH}_4^+$  concentration (Table 1). The effect of increasing Mg:P ratio is important from a practical standpoint because  $\text{PO}_4\text{-P}$  reduction can be achieved with a smaller increase in pH. For example, in the LW1 effluent, a goal of reducing the  $\text{PO}_4\text{-P}$  concentration to 20  $\text{mg l}^{-1}$  can be achieved at pH 8.25 with a Mg:P ratio of 1.6:1, compared to pH 8.75 with a Mg:P ratio of 1:1. This could help achieve adequate  $\text{PO}_4\text{-P}$  removal with lower inputs of alkali, thereby avoiding potentially negative effects of high pH on lagoon biology or  $\text{NH}_3$  volatilization. This  $\text{Mg}^{2+}$  effect agrees with findings of Beal et al. (1999) who also observed decreased  $\text{PO}_4\text{-P}$  concentration with increased Mg:P ratio, and is consistent with thermodynamic predictions (Eq. (2)).

The curves in Fig. 1 were generated using least squares analysis, which is useful for denoting general trends and making statistical comparisons between treatments. However, these best-fit curves do not contain practical relevance to the chemical processes involved in the precipitation of struvite. A more

chemically meaningful model of struvite precipitation would involve the speciation of the lagoon liquid based on the thermodynamic constants of possible chemical species that may exist in the solution. Therefore, the chemical equilibrium model MINTEQA2 version 3.11 (EPA, 1991) was used to compare the experimental results with thermodynamically predicted saturation curves. The predominant ions present in the LW1 and RM effluents were identified from lagoon liquid analysis (Table 3) and the  $\text{Mg}^{2+}$  concentration was entered at Mg:P ratios corresponding to what was used in the experiment. Because previous research has shown that struvite precipitation is kinetically favored over hydroxyapatite (Salimi et al., 1985), hydroxyapatite was not allowed to precipitate in the model.

The equilibrium P concentrations predicted by MINTEQA2 were consistently less than what was observed, especially as pH deviated from 9. Additionally, there was a surplus of cations causing a large charge imbalance. Organic compounds in the lagoon liquid, which contain deprotonated carboxylic and phenolic groups at this pH, are most likely responsible for balancing the cation surplus. Furthermore, these organic compounds have the potential to form soluble complexes with  $\text{Mg}^{2+}$ , thereby reducing its activity and increasing the equilibrium  $\text{PO}_4\text{-P}$  concentration (Schulze-Rettmer, 1991). To simulate the effect of soluble organic compounds present in wastewater, citrate was entered as a component in the MINTEQA2 simulations. Simulations were repeated with citrate entered at concentrations equal to 0.25, 0.5, 0.75, and 1.0 times the anion deficit. Simulations that included citrate, at concentrations equal to 0.75 and 0.5 times the anion charge deficit for the LW1 and RM effluents respectively, minimized the error sum of squares and the mean residual, thereby giving the best correlation between  $\text{PO}_4\text{-P}$  concentration predicted by MINTEQA2 and the observed  $\text{PO}_4\text{-P}$  concentration (Table 4). Although entering citrate as a component greatly improved the MINTEQA2 predictions, discrepancies between measured and predicted  $\text{PO}_4\text{-P}$  concentrations are notable at  $\text{pH} > 9$ , specifically for the RM liquid (Fig. 2).

Table 3

Ion concentrations used for MINTEQA2 input. Mg was entered at molar Mg:P ratios of 1:1, 1.2:1, 1.4:1, and 1.6:1 for the LW1 liquid and 1.1:1, 1.2:1, 1.4:1, and 1.6:1 for the RM liquid. The citrate concentration is based on the quantity of citrate equal to 0.75 and 0.5 times the excess charge for LW1 and RM lagoon liquids respectively

| Effluent | $\text{NH}_4^+$ <sup>a</sup><br>(mmol l <sup>-1</sup> ) | $\text{PO}_4^{3-}$<br>(mmol l <sup>-1</sup> ) | $\text{K}^+$ <sup>b</sup><br>(mmol l <sup>-1</sup> ) | $\text{Ca}^{2+}$<br>(mmol l <sup>-1</sup> ) | $\text{SO}_4^{2-}$<br>(mmol l <sup>-1</sup> ) | $\text{Na}^+$<br>(mmol l <sup>-1</sup> ) | $\text{Cl}^-$ <sup>c</sup><br>(mmol l <sup>-1</sup> ) | $\text{CO}_3^{2-}$ <sup>d</sup><br>(mmol l <sup>-1</sup> ) | Excess +<br>charge<br>(mmol l <sup>-1</sup> ) | Citrate<br>(mmol l <sup>-1</sup> ) |
|----------|---|---|--|---|---|--|---|--|---|------------------------------------|
| LW1      | 15.68   | 2.06  | 11.65  | 3.64  | 1.04  | 9.42                                     | 9.42  | 0.184  | 30.10   | 7.53                               |
| RM       | 30.44   | 1.79  | 22.06  | 3.79  | 1.41  | 0.19                                     | 0.19  | 0.36   | 55.11   | 9.19                               |

<sup>a</sup> Estimates for  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$ , are based on the concentrations listed in Table 1.

<sup>b</sup> Estimates for  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ , and  $\text{Na}^+$  are based on the total elemental K, Ca, S, and Na concentrations listed in Table 1.

<sup>c</sup>  $\text{Cl}^-$  concentration was estimated as equal to  $\text{Na}^+$  concentration.

<sup>d</sup>  $\text{CO}_3^{2-}$  concentration was estimated with MINTEQA2 by placing the solution in equilibrium with the atmospheric partial pressure of  $\text{CO}_2$ .

Table 4

Error sums of squares (Error SS) mean residuals, and standard deviations (stdev) of the residuals for predictions of soluble P concentration made with the regression equations and with MINTEQA2 simulations. MINTEQA2 simulations were repeated including citrate as a component at 0.25 (0.25 citrate), 0.5 (0.5 citrate), 0.75 (0.75 citrate), and 1.0 (1.0 citrate) times the concentration required to balance the excess positive charge

| Model                   | LW1 effluent |               |                   | RM effluent |               |                   |
|-------------------------|--------------|---------------|-------------------|-------------|---------------|-------------------|
|                         | Error SS     | Mean residual | Stdev of residual | Error SS    | Mean residual | Stdev of residual |
| Regression equation     | 296          | −0.02         | 3.09              | 184         | −0.02         | 2.43              |
| MINTEQA2 (no citrate)   | 2332         | 246.11        | 3.76              | 1019        | 128.32        | 4.03              |
| MINTEQA2 (0.25 citrate) | 2393         | 240.48        | 4.35              | 1227        | 152.95        | 4.00              |
| MINTEQA2 (0.5 citrate)  | 799          | 107.57        | 3.75              | 550         | 37.82         | 4.04              |
| MINTEQA2 (0.75 citrate) | 569          | −32.93        | 4.16              | 859         | −57.15        | 4.94              |
| MINTEQA2 (1.0 citrate)  | 1444         | −139.20       | 5.20              | 1651        | −132.35       | 5.97              |

### 3.1. Kinetics

The concentrations of struvite constituents ( $\text{NH}_4^+$ ,  $\text{Mg}^{2+}$ ,  $\text{PO}_4\text{-P}$ ) in the LW2 lagoon liquid reached steady state 35, 45, and 60 min after the addition of NaOH at pH 9.0, 8.7 and 8.4 respectively. The available N:P ratio (mass basis) of the lagoon effluent was increased from 2:1 prior to treatment to 4:1, 8:1, and 10:1 at steady state for pH 8.4, 8.7, and 9.0 respectively. The N:P ratios

resulting from pH increase to 8.7 and 9.0 would allow the waste to be applied on a N basis without over-applying P. An attempt was made to recover the precipitate but the quantity of precipitate produced was insufficient for analysis. Therefore, the likelihood of struvite formation was confirmed by comparing the molar decrease of  $\text{PO}_4\text{-P}$  to that of  $\text{Mg}^{2+}$  and  $\text{NH}_4^+$ . There was a 20–40% (mol/mol) greater decrease in  $\text{PO}_4\text{-P}$  compared with  $\text{Mg}^{2+}$  and  $\text{NH}_4^+$  (Table 5), which could be a result of precipitation of some Ca-phosphate minerals. However, based on the concentration decrease of  $\text{Mg}^{2+}$  and  $\text{NH}_4^+$ , the majority of  $\text{PO}_4\text{-P}$  (>80% at pH 9) precipitated as struvite. The molar decrease in struvite constituents approached that of pure struvite precipitation (1:1:1 decrease in  $\text{Mg}^{2+}$ ,  $\text{NH}_4^+$ , and  $\text{PO}_4\text{-P}$ ) as pH increased. This also corresponds with increasing struvite precipitation rate constants (Table 5), thereby agreeing with Salimi et al. (1985) who postulated that  $\text{Mg}^{2+}$  ions kinetically inhibit the formation of Ca-phosphates because Mg-phosphates precipitate faster than Ca-phosphates.

Modeling the decrease in dissolved P was the research objective; therefore, the rate constant was determined with respect to  $\text{PO}_4\text{-P}$  decrease. First-order kinetics was assumed and the rate constant was determined by fitting  $\text{PO}_4\text{-P}$  concentrations using Eq. (4) (Fig. 3). The proper fit of Eq. (3) assumes minimal reverse reaction, therefore, only the data collected in the initial part of the reaction prior to reaching steady state were used to fit the model. Because of an apparent lag phase in the formation of struvite at pH 8.4 (Fig. 4), possibly due to nucleation kinetics, the first-order kinetic model was fit using data collected between 9 and 25 min. The struvite precipitation rate increased with increasing pH, as indicated by the increase in the calculated first-order rate constants (Table 5). The increased pH would increase the rate constant by increasing the nucleation rate. The increased nucleation would have given more surface area on which crystal growth could take place, thereby increasing the observed rate of crystal growth. Reasonable fits ( $r^2 \geq 0.95$ ) of the data suggest that the first-order kinetic model was sufficient (Figs. 3 and 4). To further support the assumption of first-order kinetics,

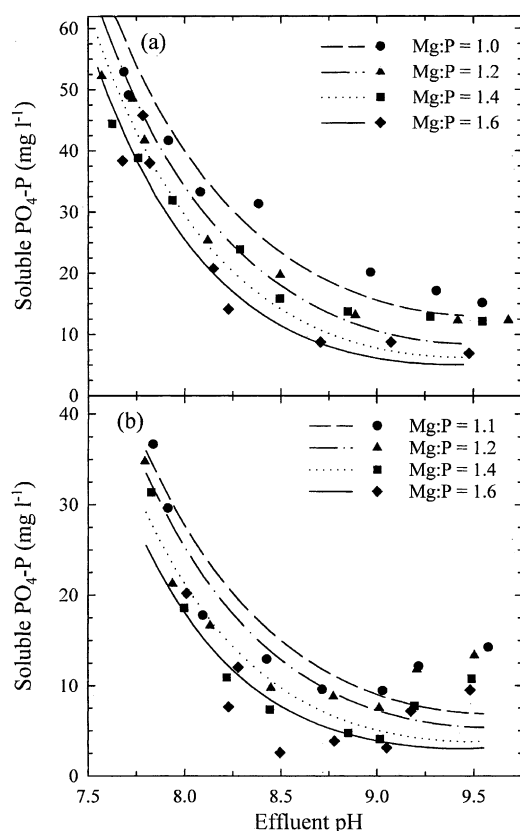


Fig. 2. Dissolved  $\text{PO}_4\text{-P}$  concentrations in anaerobic swine lagoon effluent solutions from the LW lagoon (a) and RM lagoon (b) after equilibrating for 24 h and forming struvite. Curves are predicted  $\text{PO}_4\text{-P}$  concentrations using MINTEQA2 with citrate entered at concentrations equal to 0.75 and 0.5 times the charge imbalance for the LW1 and RM effluents respectively (see text).

Table 5

Steady-state concentrations of  $\text{Mg}^{2+}$ ,  $\text{NH}_4^+$ , and  $\text{PO}_4\text{-P}$ , as affected by solution pH in anaerobic lagoon liquid used to determine struvite precipitation kinetics and corresponding parameters, 95% confidence intervals (95% CI), and error sums of squares for the first-order model (Eq. (2))

| pH  | Mg<br>( $\text{mg l}^{-1}$ ) | $\text{NH}_4\text{-N}$<br>( $\text{mg l}^{-1}$ ) | $\text{PO}_4\text{-P}$<br>( $\text{mg l}^{-1}$ ) | Ratio of molar<br>reduction $\text{Mg}:\text{NH}_4:\text{P}^a$ | $k$ ( $\text{h}^{-1}$ ) | 95% CI for $k$ | Error sum<br>of squares |
|-----|------------------------------|--|--|--|-------------------------|----------------|-------------------------|
| 8.4 | 28.9                         | 133  | 19.4   | 0.7:0.6:1  | 3.7                     | $\pm 0.59$     | 387                     |
| 8.7 | 21.4                         | 127  | 9.9  | 0.8:0.8:1  | 7.9                     | $\pm 1.3$      | 245                     |
| 9.0 | 19.1                         | 124  | 7.6  | 0.8:1:1  | 12.3                    | $\pm 2.4$      | 87                      |

<sup>a</sup> Molar reduction =  $C_{i\text{initial}} - C_{i\text{steady-state}}$ , where  $C$  is the molar concentration of component  $i$  and  $i = \text{Mg}_T, \text{NH}_{4T}, \text{PO}_4\text{-P}_T$ .

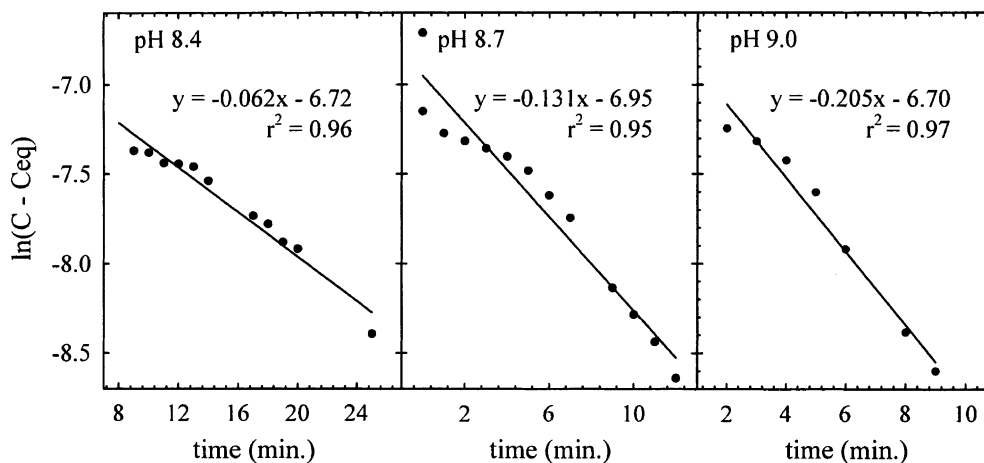


Fig. 3. Fit of  $\text{PO}_4\text{-P}$  concentration to the linear form of the first-order kinetic (Eq. (2)) model at pH 8.4, 8.7, and 9.0. ( $C$  is the molar concentration of orthophosphate at time  $t$  and  $C_{eq}$  is molar orthophosphate concentration at steady-state.)

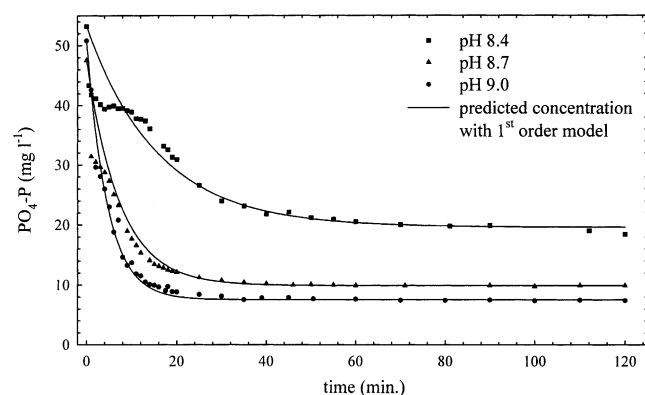


Fig. 4. Measured kinetics data with first-order model predictions for struvite precipitation from anaerobic swine lagoon liquid with pH adjusted to 8.4, 8.7, and 9.0.

the  $\text{PO}_4\text{-P}$  data were fit to a modified form of the interface-controlled crystal growth (ICCG) model (Stumm and Morgan, 1970; Phelan and Mattigod, 1987), which was used to calculate an empirical rate constant and reaction order. The reaction orders calculated by the ICCG model were not significantly different and averaged 1.03, thereby supporting the use of a first-order kinetic model to describe the decrease in dissolved  $\text{PO}_4\text{-P}$  concentration.

The first-order rate constant of  $4.2 \text{ h}^{-1}$  at pH 8.3 reported by Ohlinger et al. (2000) fits within the 95% confidence interval for the calculated rate constant at pH 8.4 in the present work (Table 5). Although the difference is not statically significant, the measured rate constant of  $3.7 \text{ h}^{-1}$  at pH 8.4 is slightly less than would be expected in comparison with results by Ohlinger et al. (2000). The lower rate constant reported in the present work is most likely a result of the induction time included in the measurement. The rate constant reported by Ohlinger et al. (2000) was determined with a fluidized bed reactor operating at steady state, therefore, it did not include the induction time.

#### 4. Conclusions

Changes in both the pH and/or  $\text{Mg}:\text{P}$  ratio promoted struvite precipitation in anaerobic swine lagoon liquid, indicating that an engineering solution could be devised to facilitate the controlled precipitation and recovery of struvite for the dual purpose of P removal from lagoon liquid and production of a slow-release fertilizer. Struvite formation reduced  $\text{PO}_4\text{-P}$  concentration of the two studied effluents by 91% and 96%, with steady-state

$\text{PO}_4\text{-P}$  concentrations of 6 and  $2\text{ mg l}^{-1}$  respectively. The pH for minimum struvite solubility was between 8.9 and 9.25 and was not effected by the Mg:P ratio. The  $\text{PO}_4\text{-P}$  reduction in the studied effluents sufficiently increased the N:P ratio of the lagoon liquid so the treated wastewater could continue to be land applied at current agronomic rates (N-based application) without accumulating P in the soil.

Steady state  $\text{PO}_4\text{-P}$  concentrations in the lagoon liquid can be modeled using the chemical speciation model MINTEQA2. The correlation between MINTEQA2 predictions and collected data was improved by including an organic acid as a component in the lagoon liquid, which simulated the effect of dissolved and particulate organic components in actual wastewater that tend to form soluble complexes with Mg and decrease it's activity.

Struvite precipitation in anaerobic swine lagoon liquid follows first-order kinetics with respect to  $\text{PO}_4\text{-P}$  concentration. The first-order nature of struvite precipitation is demonstrated by the good fit ( $r^2 \geq 0.95$ ) of the data to the first-order kinetic model and also by the mean calculated reaction order of 1.03 for the ICCG model. The first-order rate constants for struvite precipitation in anaerobic swine lagoon liquid increase as the pH rises from 8.4 to 9.0.

Struvite precipitation decreased the  $\text{PO}_4\text{-P}$  concentration in anaerobic swine lagoon liquid from an initial concentration of  $51\text{ mg l}^{-1}$  to a steady-state concentration of  $7.6\text{ mg l}^{-1}$  in approximately 30 min at pH 9.0 and a Mg:P ratio of 1.2:1. These results indicate that struvite precipitation in anaerobic swine lagoon liquid proceeds at a rate sufficient to make this a technologically feasible method of P removal. Future research could include the design and operation of lab-scale or pilot-scale reactors based on first-order kinetics with respect to  $\text{PO}_4\text{-P}$  concentration.

## References

- Amacher, M.C., 1991. Methods of obtaining and analyzing kinetic data. In: Sparks, D.L., Suarez, D.L. (Eds.) *Rates of Soil Chemical Processes*. SSSA Special Publication no. 27, SSSA, Madison WI, pp. 19–59.
- Barker, J.C., 1996. Crystalline (salt) formation in wastewater recycling systems. North Carolina Cooperative Extension Service. Publication Number: EBAE 082–81, Raleigh, NC.
- Barker, J.C., Zublena, J.P., Campbell, C.R., 1994. *Agri-waste management: Livestock manure production and characterization in North Carolina*. NC Cooperative Extension Service, North Carolina State University.
- Battistoni, P., Fava, G., Pavan, P., Musacco, A., Cecchi, F., 1997. Phosphate removal in anaerobic liquors by struvite crystallization without the addition of chemicals: Preliminary results. *Water Res.* 31, 2925–2929.
- Beal, L.J., Burns, R.T., Stalder, K.J., 1999. Effect of anaerobic digestion on struvite production for nutrient removal from swine waste prior to land application. Presented at the 1999 ASAE Annual International Meeting. Paper No. 994042. ASAE, St. Joseph, MI.
- Bridger, G.L., Salutsky, M.L., Starosta, R.W., 1962. Metal ammonium phosphates as fertilizers. *J. Agric. Food. Chem.* 10, 181–188.
- Buchanan, J.R., Mote, C.R., Robinson, R.B., 1994. Thermodynamics of struvite formation. *Trans. ASAE* 37, 617–621.
- Daniel, T.C., Sharpley, A.N., Edwards, D.R., Wedepohl, R., Lemunyon, J.L., 1994. Minimizing surface water eutrophication from agricultural by phosphorus management. *J. Soil Water Conserv.* 49, 30–38.
- EPA, 1991. A geochemical assessment model for environmental systems: Version 3.0 user manual. U.S. EPA. EPA/600/3-91/021. Washington, DC.
- Gunn, D.J., 1976. Mechanism for the formation and growth of ionic precipitates from aqueous solution. *Faraday Discuss. Chem.* 61, 133–140.
- Lachat Instruments, 1995. QuickChem 8000 continuum series automated ion analyzer, Lachat, Inc., Milwaukee.
- Liberti, L., Limoni, N., Lopez, A., Passino, R., Boari, G., 1986. The  $10\text{ m}^3\text{ h}^{-1}$  RIM-NUT demonstration plant at West Bari for removing and recovering N and P from wastewater. *Water Res.* 20, 735–739.
- Maekawa, T., Laio, C.M., Feng, X.D., 1995. Nitrogen and phosphorus removal for swine wastewater using intermittent aeration hatch reactor followed by ammonium crystallization process. *Water Res.* 29, 2643–2650.
- Mikkelsen, R.L., 1997. Agricultural and environmental issues in the management of swine waste. In: Rechcigl, J.E., MacKinnon, H.C. (Eds.), *Agricultural Uses of By-products and Wastes*. American Chemical Society, Washington, DC, pp. 110–119.
- Murphy, J., Riley, J.P., 1962. A modified single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta* 27, 31–36.
- Ohlinger, K.N., Young, T.M., Schroeder, E.D., 1998. Predicting struvite formation in digestion. *Water Res.* 32, 3607–3614.
- Ohlinger, K.N., Young, T.M., Schroeder, E.D., 1999. Kinetics effects on preferential struvite accumulation in wastewater. *J. Environ. Eng.* 125, 730–737.
- Ohlinger, K.N., Young, T.M., Schroeder, E.D., 2000. Postdigestion struvite precipitation using a fluidized bed reactor. *J. Environ. Eng.* 126, 361–368.
- Phelan, P.J., Mattigod, S.V., 1987. Kinetics of heterogeneously initiated precipitation of calcium phosphates. *Soil. Sci. Soc. Am. J.* 51, 336–341.
- Salimi, M.H., Heughebaert, J.C., Nancollas, G.H., 1985. Crystal growth of calcium phosphates in the presence of magnesium ions. *Langmuir* 1, 119–122.
- SAS Institute, 1998. *The SAS System for Windows*, version seven. Cary, NC 27513.
- Schuilting, R.D., Andrade, A., 1999. Recovery of struvite from calf manure. *Environ. Technol.* 20, 765–768.
- Schulze-Rettmer, R., 1991. The simultaneous chemical precipitation of ammonium and phosphate in the form of magnesium–ammonium–phosphate. *Water Sci. Technol.* 23, 659–667.
- Sharpley, A.N., Daniel, T.C., Sims, J.T., Pote, D.H., 1996. Determining environmentally sound soil phosphorus levels. *J. Soil Water Conserv.* 51, 160–166.
- Shin, H.S., Lee, S.M., 1997. Removal of nutrients in wastewater by using magnesium salts. *Environ. Technol.* 19, 283–290.
- Stumm, W., Morgan, J.J., 1970. *Aquatic chemistry*. Wiley-Interscience, New York, NY, p. 583.
- Unitika Ltd., 1994. Fertilizer produced from wastewater. *Jpn. Chem. Wkly.* 35, 2.
- Webb, K.M., Ho, G.E., 1992. Struvite ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ) solubility and its application to a piggery effluent problem. *Water Sci. Technol.* 26, 2229–2232.