

Overcoming Challenges to Struvite Recovery from Anaerobically Digested Dairy Manure

Matthew P. Huchzermeier^{1*}, Wendong Tao²

ABSTRACT: Recovering struvite from dairy manure has consistently posed problems for researchers. This study separated solids from anaerobically digested dairy manure using a filtration system. Filtrate was rich in free magnesium (160 to 423 mg/L), ammonium (320 to 1800 mg N/L) and orthophosphate (93 to 332 mg P/L). High concentrations of free calcium (128 to 361 mg/L) and alkalinity (3309 to 6567 mg/L as CaCO₃), however, may hinder struvite precipitation. Batch precipitation tests were conducted to identify and overcome factors that interfere with struvite formation. Precipitation tests at pH 9 identified calcium and ionic strength as most probable interferences. Calcium addition did not significantly change phosphorus removal efficiency, but decreased struvite purity because of formation of calcium phosphates when Ca:P activity ratio was greater than 0.5 to 1. Batch tests demonstrated effective calcium removal from anaerobically digested dairy manure through precipitation of calcium carbonate at pH 9 to 10 while retaining magnesium and orthophosphate, lessening hindrance to struvite formation. *Water Environ. Res.*, **84**, 34 (2012).

KEYWORDS: phosphorus recovery, struvite, calcium interference, calcium removal, dairy manure.

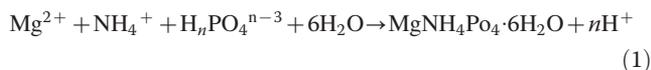
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Introduction

Dairy manure is typically managed by land application, which allows nutrients to be recycled through crop uptake. There is increasing concern that manure is being intensively applied in excess of agronomic nutrient requirements, especially at concentrated animal feeding operations (Güngör and Karthikeyan, 2008). Application rates based on crop nitrogen requirements typically result in phosphorus application rates that are more than double crop requirements (Harris et al., 2008). Excessive nutrients can then enter receiving waterbodies and degrade water quality. Excess manure either needs to be transported offsite or treated onsite. High transportation costs, seasonal application issues, odor problems, and the potential liability of environmental effects limit the feasibility of offsite transportation and discourage other farmers from using manure generated at local animal operations (Schuiling and Andrade, 1999). Similarly, collection and transport of dairy manure to centralized treatment plants is economically prohibitive (Wang et al., 2005). An alternative solution for

sustainable manure management is onsite treatment. Technologies to support use of dairy manure as feedstock in energy production and fertilizer manufacture would be valuable for producers of excess dairy manure.

Recovering phosphorus by struvite precipitation from phosphate-rich wastewaters (municipal, animal manure, industrial) has been studied. Struvite, a compound fertilizer consisting of magnesium ammonium phosphate hexahydrate, typically precipitates as stable white orthorhombic crystals according to eq. 1, where n = 0, 1, or 2 based on solution pH (Le Corre et al., 2005):



However, struvite recovery from dairy manure has posed challenges to researchers (Harris et al., 2008; Moerman et al., 2009; Schuiling and Andrade, 1999; Shen et al., 2010; Zhang et al., 2010; Zeng and Li, 2006). These challenges include high suspended solids concentration, high particulate inorganic phosphates relative to total phosphorus, high dissolved calcium (Ca²⁺) concentration, high calcium molar ratio to struvite component ions, and high ionic strength or alkalinity (Schuiling and Andrade, 1999; Shen et al., 2010; Zeng and Li, 2006; Zhang et al., 2010).

Struvite crystallization depends on factors such as component ratios, concentrations of potentially interfering ions, and wastewater pH (Bhuiyan and Mavinic, 2008; Ohlinger et al., 1998; Uludag-Demirer et al., 2005; Wang et al., 2005). Calcium is a common interfering ion to struvite formation in dairy manure (Wang et al., 2005). Precipitation of calcium phosphates has been observed in addition to or instead of struvite (Harris et al., 2008; Zeng and Li, 2006). Precipitation of hydroxyapatite has been reported at pH above 9.5 to 10 (Metcalf and Eddy, Inc., 2003; Wang et al., 2005). The presence of carbonate has been reported to inhibit calcium phosphate formation (Cao and Harris, 2008; de-Bashan and Bashan, 2004; Ferguson and McCarty, 1971). Because carbonate and phosphate both compete for calcium, high carbonate is required for preferential precipitation of calcium carbonate and to avoid nonstruvite phosphorus removal. Chemical equilibrium modeling by Shen et al. (2010) and experimentation by Cao and Harris (2008) indicated formation of MgCO₃(aq) in magnesium-rich alkaline wastewaters, potentially restricting Mg²⁺ from forming struvite. Ionic strength increases electrostatic interactions among ions in solution, reducing their activities (Ohlinger et al., 1998; Uludag-Demirer et al., 2005).

Attempts to enhance struvite recovery from dairy manure have included Mg²⁺ amendment (Uludag-Demirer et al., 2005;

¹ Department of Environmental Resources Engineering, State University of New York College of Environmental Science and Forestry, Syracuse, New York.

² Department of Environmental Resources Engineering, State University of New York College of Environmental Science and Forestry, 1 Forestry Drive, Syracuse, New York.

* e-mail: mphuchze@sy.edu.

Zeng and Li, 2006); pretreatment of dairy manure using microwave-based heating and advanced oxidation (Jin et al., 2009; Pan et al., 2006; Qureshi et al., 2008); and pretreatment by acidifying anaerobically digested manure to a pH of approximately 4 and adding a chelating agent (Shen et al., 2010; Zhang et al., 2010). Organic phosphorus and polyphosphate, commonly found in undigested dairy manure, were solubilized by microwave-based thermochemical treatment to increase struvite component ions for struvite formation. Jin et al. (2009) and Qureshi et al. (2008) found this treatment method released 4 to 30% and 65% orthophosphate, respectively. Although microwave-based thermochemical pretreatment is effective at increasing struvite component ion concentrations, it is energy-intensive and can require chemical inputs. Anaerobic digestion also has been found to enhance the ability to recover phosphorus as struvite (Wang et al., 2005). Anaerobic digestion converts organic nitrogen and phosphorus to ammonium (NH_4^+) and orthophosphate (PO_4^{3-}).

Although successful struvite recovery methods have been established for municipal wastewater and swine manure, methods for application to anaerobically digested dairy manure (ADDM) remain economically impractical or technically inefficient. The continuous production of enormous volumes of dairy manure within the United States alone warrants further research to develop struvite recovery methods for ADDM (USDA, 2009). High concentrations of struvite component ions found in ADDM, if recovered, could supply more struvite per unit wastewater volume than when recovered from municipal wastewater. Furthermore, the high Mg^{2+} content found in ADDM deems its supplementation for struvite recovery unnecessary, thereby reducing process costs.

Substantial research efforts are needed to understand how the potential interfering factors affect struvite formation from anaerobically digested dairy manure and to seek sustainable approaches to overcome the interferences. The objectives of this study were to identify interferences to struvite recovery from ADDM and to evaluate effectiveness of calcium carbonate precipitation at elevated pH values as a low-cost pretreatment to lessen hindrance of calcium to struvite recovery from ADDM.

Methods and Materials

Manure Characterization. The ADDM was collected over several months from an onsite anaerobic digester at a dairy complex located in Morrisville, New York. It was passed through a two-stage filtration system (pebble filters plus sand-pebble filters) to separate manure solids and liquid. Calcium and magnesium ions were analyzed with a Hach DR 2800 spectrophotometer (Hach Co., Loveland, Colorado) using Hach calmagite colorimetric method 8030. Ammonium was determined with a LaChat QuickChem 8500 automatic flow injection analysis system (Lachat Instruments, Loveland, Colorado) using Standard Methods 4500 H phenolate method (APHA et al., 1998). Orthophosphate was determined with the spectrophotometer using the 4500-P vanadomolybdophosphoric acid colorimetric method (APHA et al., 1998). Samples analyzed for calcium, magnesium, ammonium, and orthophosphate were vacuum-filtered through 0.45- μm cellulose nitrate membrane filters. Dilution of samples for concentrations to be in analytical ranges followed filtration to avoid water extraction of nutrients from solid phases. Alkalinity was determined using Standard

Table 1—Characteristics (mean \pm standard deviation) of anaerobically digested dairy manure filtrate.

Constituent	Concentration
Magnesium ion (Mg^{2+})	257.2 \pm 63.7 mg/L
Ammonium (NH_4^+)	434.1 \pm 120.7 mg N/L
Orthophosphate (PO_4^{3-})	209.6 \pm 83.6 mg P/L
Calcium ion (Ca^{2+})	227.5 \pm 77.4 mg/L
Total solids	13313 \pm 2855 mg/L
Total suspended solids	860 \pm 501 mg/L
Alkalinity	4938 \pm 2304 mg/L as CaCO_3
Electric conductivity	12.2 \pm 0.8 mS/cm
pH	8.1 \pm 0.2

Method 2320 B titration method (APHA et al., 1998). Total solids and total suspended solids (TSS) were determined using Standard Method 2540 (APHA et al., 1998). Glass microfiber filters with pore size 1.0 μm were chosen for TSS analysis. The pH was measured using a FG-2 Fivego portable pH meter (Mettler-Toledo, Inc., Columbus, Ohio). Electric conductivity was measured using a Hach HQ portable meter (Hach Company, Loveland, Colorado). The characteristics of ADDM filtrate are summarized in Table 1.

Identifying Hindrance to Struvite Formation. Batch experiments using ADDM filtrate, synthetic filtrate, or a mixture were conducted to evaluate the effects of real manure on struvite precipitation. This test assisted in identifying causes of hindrance to struvite recovery from ADDM filtrate and proving whether struvite formation was possible at typical struvite component ion concentrations. Synthetic filtrate was made to match struvite component ion concentrations in one of the batches of ADDM filtrate: 17.4 mM Mg^{2+} , 34.2 mM NH_4^+ , and 10.4 mM PO_4^{3-} , using analytical grade $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, NH_4Cl and KH_2PO_4 in deionized water. In each experiment, a 50-mL sample was added to a 125-mL Erlenmeyer flask and placed on a magnetic stirrer with a 5-cm Teflon-coated magnetic stir bar. Samples were gently stirred for 60 minutes at room temperature (22 °C). Solution pH was adjusted to 9.0 using 5M NaOH (Harris et al., 2008; Jin et al., 2009; Schuling and Andrade, 1999; Zeng and Li, 2006). A lid was placed over the flask opening to minimize ammonia volatilization and CO_2 exchange. At the end of the reaction period, the solution was sampled for determination of TSS, Ca^{2+} , Mg^{2+} , NH_4^+ , and PO_4^{3-} using the same methods as described for manure characterization. Recovered precipitates were dried and observed for size and morphology using a scanning electron microscope (SEM) (JEOL JSM-5800 LV SEM, Jeol Ltd., Tokyo, Japan). Elemental composition of recovered precipitates was determined by an energy-dispersive X-ray spectrometer (EDS) (EDAX, Mahwah, New Jersey). The SEM-EDS samples were prepared with vacuum carbon coating and analyzed at an accelerating voltage of 20 kV.

Effect of Calcium on Struvite Formation. Batch experiments using synthetic filtrate at various calcium concentrations were conducted to identify the effect of calcium on struvite formation. Two synthetic filtrates were made to have similar struvite component ion concentrations to real filtrate: 17.5 mM Mg^{2+} , 38.7 mM NH_4^+ , and 10.7 mM PO_4^{3-} . One synthetic filtrate contained 20.0 mM Ca^{2+} as CaCl_2 . In each experiment, 50 mL of Ca-deficient synthetic filtrate, Ca-rich synthetic filtrate, or a mixture was stirred for 60 minutes at pH of 9. At the end of

the reaction period, the solution was sampled for determination of TSS, Ca²⁺, Mg²⁺, and PO₄³⁻ using the methods as described previously. Recovered precipitates were observed and analyzed using SEM-EDS as described previously.

Calcium Removal from Anaerobically Digested Dairy Manure Filtrate. Batch precipitation tests using ADDM filtrate were conducted to examine the potential for calcium removal through chemical precipitation by evaluating the effects of varying pH and component ion molar ratios. In each test, 100 mL of ADDM filtrate was added to a 250-mL Erlenmeyer flask and MgCl₂ was supplemented as required to achieve a target Mg²⁺:PO₄³⁻ molar ratio. Samples were stirred gently for 10 minutes at room temperature (22 °C), and pH was controlled at a predetermined value between 7 and 10 using 1M HCl or 5M NaOH solution. Vessels were covered to maintain closed-vessel conditions. At the end of the reaction period, the solution was sampled to determine Ca²⁺, Mg²⁺, NH₄⁺, PO₄³⁻, TSS, and electric conductivity using the same methods as described previously. Recovered precipitates were observed and analyzed for elemental composition using SEM-EDS as described previously.

Data Analysis. Activity coefficients were calculated using the Davies modification to the Debye-Hückel equation (Davies, 1962). Ionic strength was estimated using eq. 2 for real ADDM (Güngör and Karthikeyan, 2008).

$$I = 1.6 \times 10^{-5} \times EC \quad (2)$$

Where *I* is ionic strength in molar concentration (M) and *EC* is electric conductivity in μS/cm.

Supersaturation index was calculated to evaluate the effects of ionic strength and struvite component ion concentrations on struvite precipitation according to eq. 3 (Saidou et al., 2009):

$$\Omega = \frac{\{Mg^{2+}\}\{NH_4^+\}\{PO_4^{3-}\}}{K_{sp}} \quad (3)$$

Where

Ω = supersaturation index,
 {Mg²⁺}, {NH₄⁺}, and {PO₄³⁻} = the activities of magnesium, ammonium, and phosphate ions, respectively, and
 K_{sp} = solubility product for struvite.

Many values of K_{sp} have been reported for struvite. The wide range of calculated values exists because of differences in experimental pH, temperature, and ionic strength. A K_{sp} of 3.89 × 10⁻¹⁰ (pK_{sp} = 9.41) in digestate at 20 °C was used to calculate Ω in this study (Borgerding, 1972).

The Ryzner index was calculated to evaluate the potential of CaCO₃ precipitation according to eqs. 4 and 5 (Metcalf and Eddy, Inc., 2003). A Ryzner index of less than 5.5 indicates heavy deposition of CaCO₃.

$$RI = 2pH_s - pH \quad (4)$$

$$pH_2 = -\log\left(\frac{K_{a2} \times \gamma_{Ca^{2+}} \times [Ca^{2+}] \times \gamma_{HCO_3^-} \times [HCO_3^-]}{K_{sp}}\right) \quad (5)$$

Where

RI = Ryzner index,

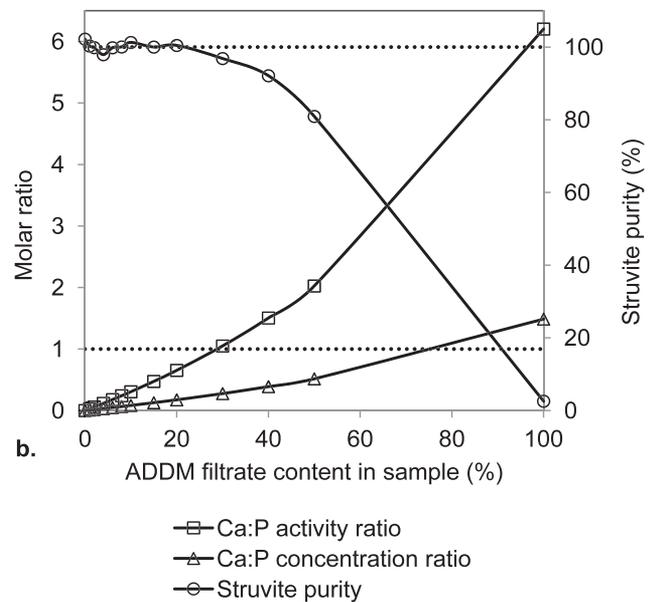
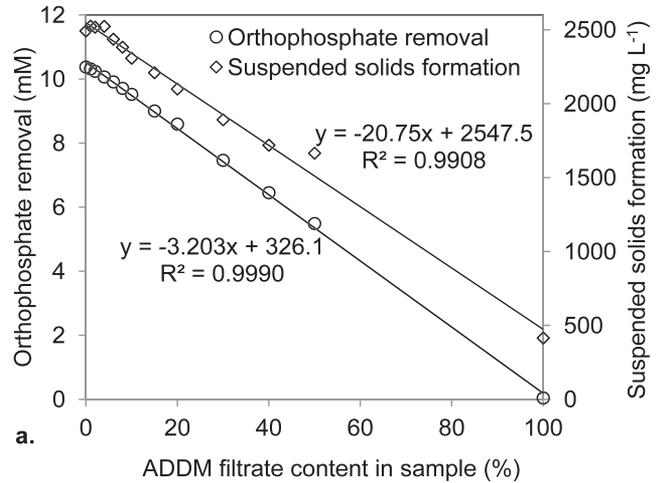


Figure 1—Effect of (a) anaerobically digested dairy manure filtrate (ADDM) on orthophosphate removal and suspended solids formation; and (b) variation of struvite purity with Ca²⁺:PO₄³⁻ in synthetic manure filtrate at pH 9.

pH_s = saturation pH for CaCO₃,
 K_{a2} = equilibrium constant for dissociation of bicarbonate (4.17 × 10⁻¹¹ at 20 °C),
 γ_i = activity coefficient for ion *i*,
 [i] = molar concentration of ion *i*, and
 K_{sp} = solubility product for calcium carbonate (5.25 × 10⁻⁹ at 20 °C) (Metcalf and Eddy, Inc., 2003).

Results and Discussion

Verifying Hindrance to Struvite Formation. Struvite precipitation at pH 9 removed 99.9% of orthophosphate from synthetic ADDM filtrate. As more real ADDM filtrate was added to the sample, orthophosphate removal was reduced. Only 0.8% of orthophosphate was removed from real ADDM filtrate. The mass of formed suspended solids decreased linearly as ADDM filtrate was increased in the sample (Figure 1a). The experiments

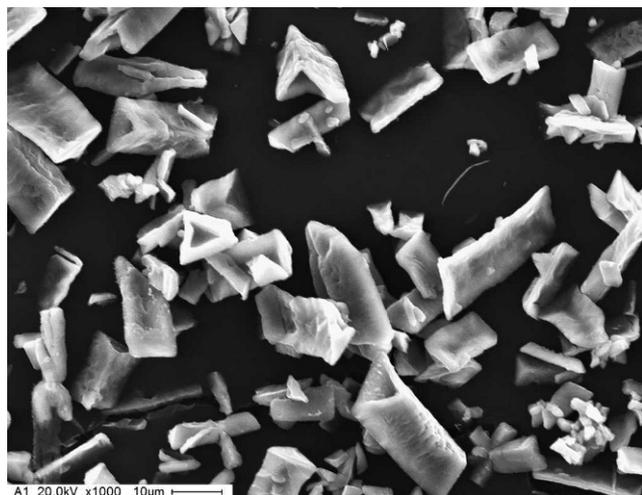


Figure 2—Scanning electron microscopic image of struvite recovered from synthetic anaerobically digested dairy manure filtrate at pH 9.

indicated a clear hindrance of real ADDM filtrate to struvite precipitation.

Precipitates recovered from synthetic ADDM filtrate (Figure 2) showed typical crystal morphology to struvite (Le Corre et al., 2005; Shen et al., 2010; Wang et al., 2005, 2010). An EDS spectrograph showed peak location and relative height consistent with pure analytical-grade struvite and confirmed recovered struvite ((Wang et al., 2005; Wang et al., 2010).

If all orthophosphate removed from solution was attributed to struvite formation, then approximately 100% of suspended solids formed were struvite particles when 20% or less real ADDM filtrate was mixed with synthetic filtrate (Figure 1b). In real ADDM filtrate, 2.6% of suspended solids formed can be attributed to struvite.

Calcium has been shown to interfere with struvite formation, inhibiting the reaction by blocking active struvite growth sites and competing for orthophosphate to form calcium phosphates (Le Corre et al., 2005; Shen et al., 2010; Zeng and Li, 2006; Zhang et al., 2010). Calcium concentration in the samples was in proportion to the percentage of real manure filtrate. It remains unclear from this or previous studies whether the hindrance to struvite formation from ADDM filtrate is caused by high ionic strength, Ca^{2+} concentration, or its molar ratio to struvite component ions, alkalinity, or a combination of these.

Because of the high ionic strength of ADDM filtrate, the activities of component ions were lower than their concentrations as analyzed, higher valence ions being affected most. Although rich in magnesium, ammonium, and orthophosphate, an ionic strength of approximately 0.196 M in ADDM filtrate lowered effective concentrations (activities) of Mg^{2+} and Ca^{2+} by 68%, NH_4^+ by 25%, and PO_4^{3-} by 92%. Therefore, the molar ratio of monovalent ammonium or divalent magnesium and calcium to trivalent orthophosphate activities was much higher than that of ion concentrations. Moerman et al. (2009) suggested using $\text{Ca}^{2+}:\text{PO}_4^{3-}$ molar ratio as a determinative parameter when observing calcium interference to struvite precipitation. The $\text{Ca}^{2+}:\text{PO}_4^{3-}$ molar ratio in ADDM filtrate increased from 1.5:1 to 6.1:1 when considering activity instead of concentration. The percentage of struvite in formed precipitates began to

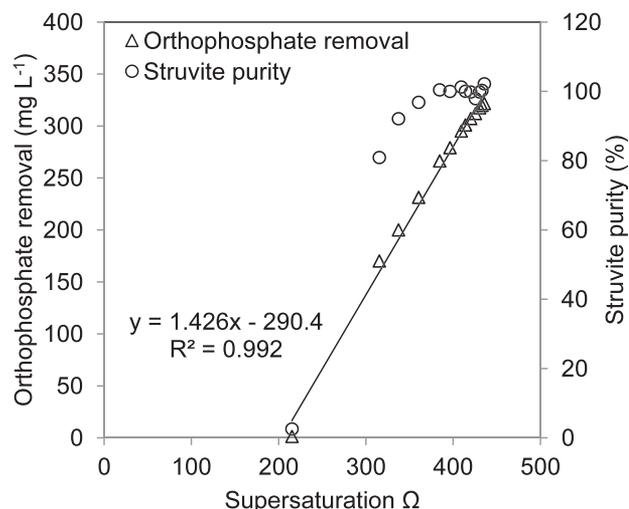


Figure 3—Supersaturation index (Ω) effect on orthophosphate removal and purity of struvite recovered from mixtures of anaerobically digested dairy manure filtrate and synthetic wastewater at pH 9.

decrease when more than 30% ADDM filtrate was present in the synthetic filtrate sample or $\text{Ca}^{2+}:\text{PO}_4^{3-}$ activity ratio was 1.1 (Figure 1b). As the $\text{Ca}^{2+}:\text{PO}_4^{3-}$ activity ratio increased to more than 1, struvite purity reduced considerably. This finding is consistent with work done by Moerman et al. (2009), which concluded that the $\text{Ca}^{2+}:\text{PO}_4^{3-}$ molar ratio should be less than 1.0 for effective struvite formation. Similarly, Wang et al. (2005) concluded that the $\text{Ca}^{2+}:\text{PO}_4^{3-}$ molar ratio should be less than 0.5 to maximize struvite purity. Nevertheless, component ion activity ratios rather than concentration ratios should be used as a determinative factor when dealing with high ionic-strength wastewater.

High ionic strength can lower orthophosphate availability for struvite formation (Zeng and Li, 2006). Struvite supersaturation index was highest in synthetic filtrate and decreased as more ADDM filtrate was added to the sample or as ionic strength increased. Orthophosphate removal increased linearly as the supersaturation index increased (Figure 3), suggesting hindrance of ionic strength to phosphate precipitation. However, struvite purity was only affected by ionic strength when the supersaturation index was less than 360 (Figure 3) or ionic strength was greater than 0.145. Although ionic strength varied between ADDM filtrate and synthetic wastewater, the difference was small (0.07 M) and was therefore unlikely to cause the large difference in orthophosphate removal efficiencies (99.9 vs. 0.8%).

Identifying Calcium Interference. Orthophosphate removal was high (99.7 to 99.9%) at pH 9 for the tested $\text{Ca}^{2+}:\text{Mg}^{2+}$ molar ratios (0 to 1.14). However, as $\text{Ca}^{2+}:\text{Mg}^{2+}$ molar ratio increased, orthophosphate was preferentially removed with calcium instead of magnesium (Figure 4). The experiments indicated that Ca^{2+} alone does not hinder phosphorus recovery; however, it does reduce struvite purity. It appeared that more calcium phosphates were precipitated from solutions with high initial free calcium concentrations. Recovered precipitates from the sample containing a $\text{Ca}^{2+}:\text{Mg}^{2+}$ molar ratio of 1.14 were observed with scanning electron microscopy (SEM) to have similar amorphous qualities to other recovered calcium phos-

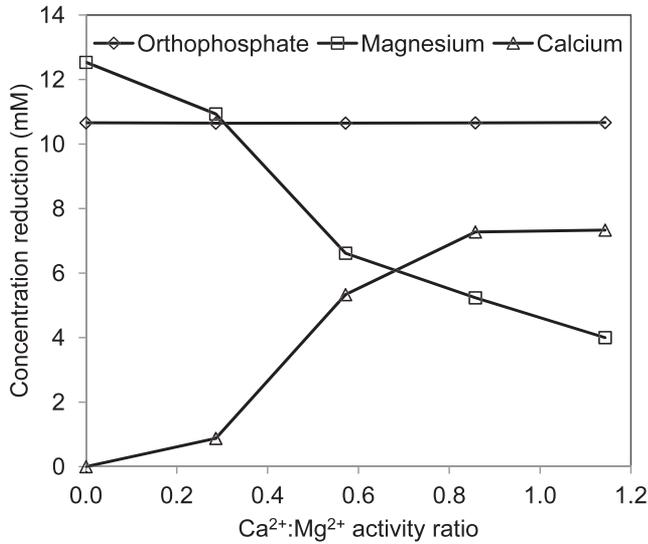


Figure 4—Effect of $\text{Ca}^{2+}:\text{Mg}^{2+}$ activity ratio on constituent ion reduction in synthetic manure filtrate at pH 9.

phates in the literature (Le Corre et al., 2005; Shen et al., 2010; Wang et al., 2005). Assuming calcium was removed as calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$ and the remainder of the removed orthophosphate was formed into struvite, calcium phosphates were observed to dominate formed precipitates when the $\text{Ca}^{2+}:\text{Mg}^{2+}$ activity ratio was approximately 0.5:1 and greater (Figure 5) (Wang et al., 2005). This finding is consistent with the literature (Bhuiyan and Mavinic, 2008; Le Corre et al., 2005; Shen et al., 2010). This study found that struvite precipitation was hindered when the $\text{Ca}^{2+}:\text{Mg}^{2+}$ activity ratio was higher than 0.2:1, no longer dominant when the ratio was higher than approximately 0.5:1, and completely suppressed when the ratio was greater than 0.75:1 (Figure 5). The $\text{Ca}^{2+}:\text{PO}_4^{3-}$ molar ratio also has been used as a determinative parameter for struvite purity. Calcium phosphates were responsible for decreasing struvite purity when the $\text{Ca}^{2+}:\text{PO}_4^{3-}$ molar ratio was greater than zero; greater decreases occurred with purity greater than 0.5 to 1.0. This finding is also consistent with the literature (Hao et al., 2008; Wang et al., 2005).

Because struvite is more valuable than calcium phosphates, it is important to maintain the highest purity struvite possible (Wang et al., 2005). There is a tradeoff between maximum phosphorus removal and greatest struvite purity in calcium-containing wastewaters (Jordaan et al., 2010). This situation can be remedied by adding excess Mg^{2+} to force out precipitation of struvite or by reducing inhibitory effects of Ca^{2+} (Zeng and Li, 2006). Adding significant amounts of Mg^{2+} as magnesium salts, however, presents additional challenges in real applications because of high chemical costs, excessive residual Mg^{2+} in effluent, and environmental effects resulting from excessive chloride loads. Chelation treatment (EDTA, oxalic acid) to form complexes with Ca^{2+} was found to improve struvite purity in ADDM. Crystal morphology, however, was inconsistent with other recovered struvite (Shen et al., 2010). Additionally, chelating chemicals have been found to be too expensive for phosphorus recovery in ADDM, and their discharge introduces additional environmental effects (Ferguson and McCarty, 1971; Zhang et al., 2010). Therefore, an alternative method to

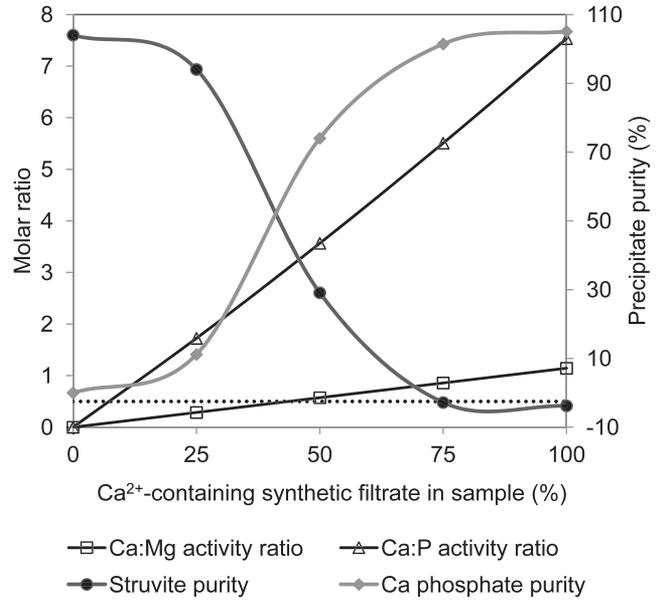


Figure 5—Variation of precipitates formed with $\text{Ca}^{2+}:\text{Mg}^{2+}$ and $\text{Ca}^{2+}:\text{PO}_4^{3-}$ activity ratios in synthetic manure filtrate at pH 9.

supplementing excessive Mg^{2+} or chelating calcium needs to be developed to reduce hindrance of Ca^{2+} for successful struvite recovery in high- Ca^{2+} wastewaters.

Overcoming Calcium Interference. Calcium removal increased as ADDM filtrate pH was increased from 7.7 to 8.2 to approximately 10; however, calcium concentration was observed to increase when pH was decreased to neutral (Figure 6). Higher $\text{Ca}^{2+}:\text{PO}_4^{3-}$ molar ratio samples typically showed higher calcium precipitation at pH 9 to 10. No relationship between $\text{Mg}^{2+}:\text{PO}_4^{3-}$ and calcium precipitation was found, even when supplementing Mg^{2+} so that $\text{Mg}^{2+}:\text{PO}_4^{3-}$ was 14.4:1. An average of 4.8% of orthophosphate was removed with precipitation. By increasing the pH of ADDM filtrate, up to 74% Ca^{2+} was

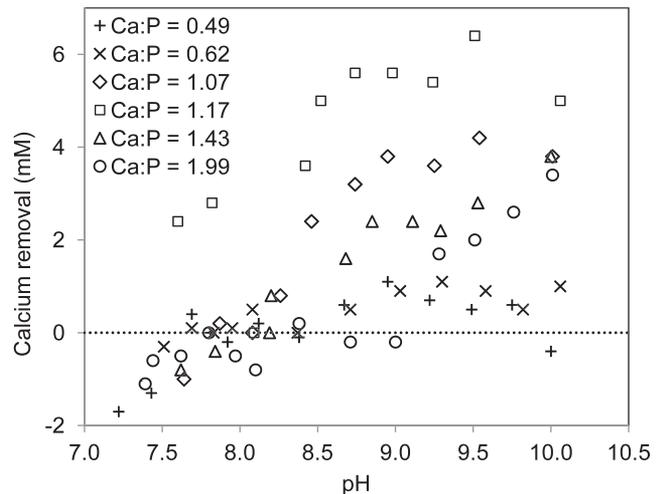


Figure 6—Effect of pH on calcium concentration reduction after precipitation tests using anaerobically digested dairy manure filtrate.

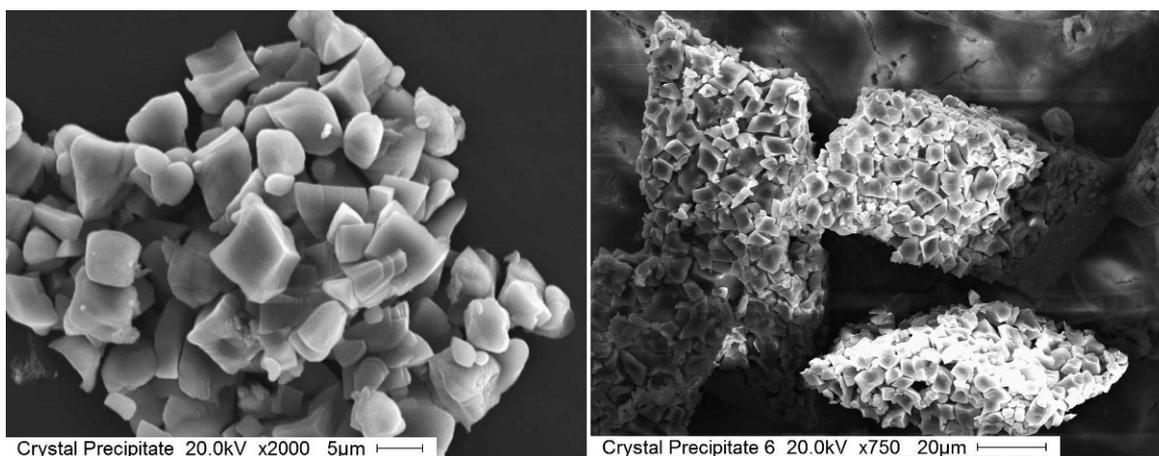


Figure 7—Scanning electron microscopic image of precipitates recovered from real anaerobically digested dairy manure filtrate at (a) zoom = 2000 \times and (b) zoom = 750 \times .

removed at the highest pH tested (10). Average Ca^{2+} removal was 22% at pH 8 to 9 and 46% at 9 to 10 pH. Decreasing pH caused dissolution of solid-phase calcium-containing particles, thereby increasing Ca^{2+} concentration. Similarly, the mass of formed suspended solids increased as pH was increased to 10, while solids tended to dissolve when pH was decreased to neutral. The SEM imagery (Figure 7) and EDS spectrographs suggested recovered particles to be primarily calcium carbonate (CaCO_3) with little to no struvite or calcium-phosphate precipitation (MFA Scientific Research Laboratory, 2009). Additionally, elemental quantification of recovered precipitates from three samples (pH 9.0, 9.5, 10.0) indicated an average $\text{Ca}:\text{O} = 0.346 \pm 0.039$, suggesting precipitation of CaCO_3 . Ryzner indices of the samples were less than 5.5 when pH was greater than 8 (Figure 8a), confirming heavy CaCO_3 deposition. Struvite supersaturation index was 54 to 264, which was less than 360, confirming little struvite precipitation (Figure 3).

Calcium carbonate has been reported to precipitate in real and synthetic wastewaters in alkaline conditions (Cao and Harris, 2008; Ferguson and McCarty, 1971; Jordaan et al., 2010). Along with low orthophosphate removal in this experiment, these observations suggest that calcium carbonate precipitation may be a feasible pretreatment technique to reduce calcium interference and retain orthophosphate in solution for struvite precipitation.

High concentrations of alkalinity are reported in centrifuged undigested dairy manure (9300 mg/L as CaCO_3) and in anaerobically digested cattle manure (11470 mg/L as CaCO_3) (Shen et al., 2010; Zeng and Li, 2006). Alkalinity was measured to be 4938 mg/L as CaCO_3 in ADDM filtrate. When pH is increased to 9 to 10, enough CO_3^{2-} is stoichiometrically available in ADDM filtrate (from alkalinity) to precipitate all Ca^{2+} as CaCO_3 .

As discussed above, it is imperative to reduce ADDM $\text{Ca}^{2+}:\text{PO}_4^{3-}$ and $\text{Ca}^{2+}:\text{Mg}^{2+}$ molar ratios as much as possible for producing high purity struvite. Increasing pH to 9.5 reduced $\text{Ca}^{2+}:\text{PO}_4^{3-}$ and $\text{Ca}^{2+}:\text{Mg}^{2+}$ molar ratios in the ADDM filtrate by 40.3 and 38.7%, respectively (Figure 8b). By precipitating CaCO_3 and decreasing the molar ratio of Ca^{2+} to struvite component

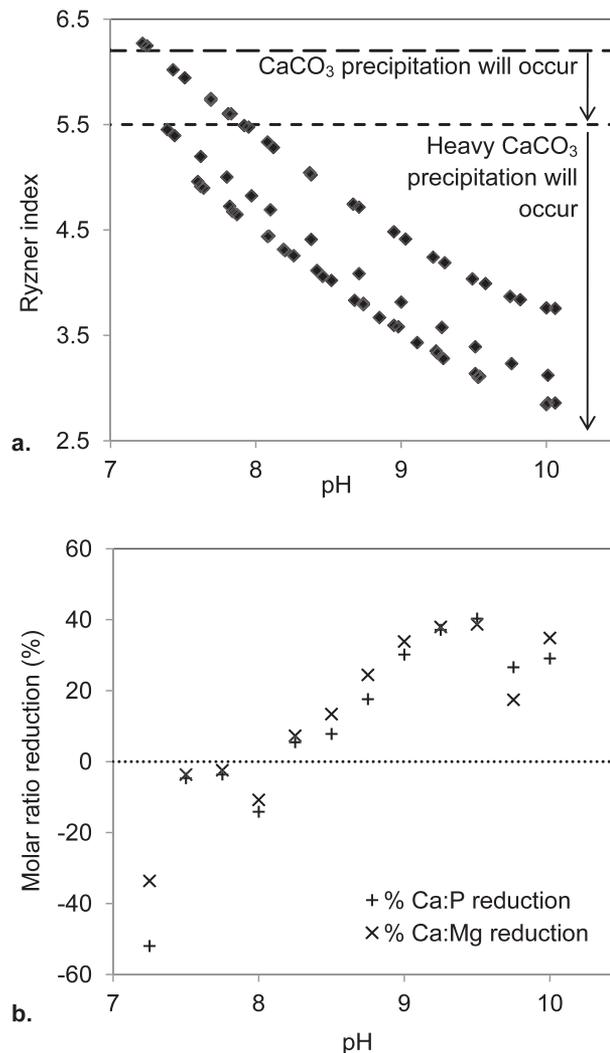


Figure 8—Effect of pH on (a) Ryzner index and (b) $\text{Ca}^{2+}:\text{PO}_4^{3-}$ and $\text{Ca}^{2+}:\text{Mg}^{2+}$ molar ratio reduction, after precipitation tests using anaerobically digested dairy manure filtrate.

ions, the resulting ADDM filtrate will be able to produce higher purity struvite.

By removing dissolved calcium via chemical precipitation at an elevated pH, $\text{Ca}^{2+}:\text{PO}_4^{3-}$ and $\text{Ca}^{2+}:\text{Mg}^{2+}$ activity ratios can be reduced to less than 1 and 0.5, respectively, for acceptable struvite precipitation conditions. In two subsequent experiments using low-calcium ADDM, however, batch struvite precipitation tests showed no struvite recovery. Following the methods described earlier for calcium removal by calcium-carbonate precipitation, solid-phase calcium was separated using centrifugation. The ADDM centrate had a supersaturation index below 215, the threshold for struvite recovery from ADDM (Figure 3). Therefore, high dissolved-calcium concentration is not the only interfering factor. Interference from ionic strength, alkalinity, or other factors needs to be identified and overcome before efficient recovery of struvite is possible from real ADDM.

High Mg^{2+} is required to precipitate struvite in high-alkalinity wastewaters (Cao and Harris, 2008). This is thought to be caused by formation of stable aqueous phase MgCO_3 (aq) in high-alkalinity wastewaters, rendering most magnesium unavailable for struvite formation (Cao and Harris, 2008; Shen et al., 2010). It has been reported, however, that the presence of magnesium increases the solubility of calcium carbonate (Ferguson and McCarty, 1971). Supplemental Mg^{2+} , if required to precipitate struvite, should be introduced after calcium carbonate precipitation pretreatment.

Conclusions

Anaerobically digested dairy manure filtrate is supersaturated with Mg^{2+} , NH_4^+ , and PO_4^{3-} for potential struvite recovery. Struvite formation likely is hindered, however, by high Ca^{2+} concentration, $\text{Ca}^{2+}:\text{PO}_4^{3-}$ or $\text{Ca}^{2+}:\text{Mg}^{2+}$ molar ratio, ionic strength, alkalinity, or a combination of these.

High Ca^{2+} concentration in alkalinity-deficient, synthetic dairy manure filtrate had no significant interference with orthophosphate removal (greater than 99%); whereas, amorphous calcium phosphates were preferentially precipitated over struvite.

Precipitation can significantly reduce Ca^{2+} when increasing pH to 9 to 10 while orthophosphate and magnesium are retained in manure filtrate. The $\text{Ca}^{2+}:\text{PO}_4^{3-}$ and $\text{Ca}^{2+}:\text{Mg}^{2+}$ molar ratios are reduced for suitable struvite formation conditions.

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References

American Public Health Association; American Water Works Association; Water Environment Federation (1998) *Standard Methods for the Examination of Water and Wastewater*, 20th ed.; American Public Health Association: Washington, D.C.; American Water Works Association: Denver, Colorado; Water Environment Federation: Alexandria, Virginia.

Bhuiyan, M. I. H.; Mavinic, D. S. (2008) Assessing Struvite Precipitation in a Pilot-Scale Fluidized Bed Crystallizer. *Environ. Technol.*, **29** (11), 1157–1167.

Borgerding, J. (1972) Phosphate Deposits on Digestion Systems. *J. Water Pollut. Control Fed.*, **44** (5), 813–819.

Cao, X.; Harris, W. (2008) Carbonate and Magnesium Interactive Effect on Calcium Phosphate Precipitation. *Environ. Sci. Technol.*, **42** (2), 436–442.

Davies, C. W. (1962) *Ion Association*; Butterworths: Washington, D.C.

de-Bashan, L. E.; Bashan, Y. (2004) Recent Advances in Removing Phosphorus from Wastewater and its Future Use as Fertilizer (1997–2003). *Water Res.*, **38** (19), 4222–4246.

Ferguson, J. F.; McCarty, P. L. (1971) Effects of Carbonate and Magnesium on Calcium Phosphate Precipitation. *Environ. Sci. Technol.*, **5** (6), 534–540.

Güngör, K.; Karthikeyan, K. G. (2008) Phosphorus Forms and Extractability in Dairy Manure: A Case Study for Wisconsin On-Farm anaerobic digesters. *Bioresour. Technol.*, **99** (2), 425–436.

Hao, X. D.; Wang, C. C.; Lan, L.; van Loosdrecht, M. C. M. (2008) Struvite Formation, Analytical Methods and Effects of pH and Ca^{2+} . *Water Sci. Technol.*, **58** (8), 1687–1692.

Harris, W. G.; Wilkie, A. C.; Cao, X.; Sirengo, R. (2008) Bench-Scale Recovery of Phosphorus from Flushed Dairy Manure Wastewater. *Bioresour. Technol.*, **99** (8), 3036–3043.

Jin, Y.; Hu, Z.; Wen, Z. (2009) Enhancing Anaerobic Digestibility and Phosphorus Recovery of Dairy Manure through Microwave-Based Thermochemical Pretreatment. *Water Res.*, **43** (14), 3493–3502.

Jordaan, E. M.; Ackerman, J.; Cicek, N. (2010) Phosphorus Removal from Anaerobically Digested Swine Wastewater through Struvite Precipitation. *Water Sci. Technol.*, **61** (12), 3228–3234.

Le Corre, K. S.; Valsami-Jones, E.; Hobbs, P.; Parsons, S. A. (2005) Impact of Calcium on Struvite Crystal Size, Shape and Purity. *J. Cryst. Growth.*, **283** (3–4), 514–522.

Metcalf and Eddy, Inc. (2003) *Wastewater Engineering: Treatment and Reuse*, 4th ed.; McGraw Hill: New York.

Museum of Fine Arts (MFA) Scientific Research Laboratory (2009) Material Name: calcium carbonate. http://cameo.mfa.org/browse/record.asp?key=2171&subkey=1652&materialname=c&browse=1&search_start=41&page=3&material_page=images (accessed October 2011).

Moerman, W.; Carballa, M.; Vandekerckhove, A.; Derycke, D.; Verstraete, W. (2009) Phosphate Removal in Agro-Industry: Pilot- and Full-Scale Operational Considerations of Struvite Crystallization. *Water Res.*, **43** (7), 1887–1892.

Ohlinger, K. N.; Young, T. M.; Schroeder, E. D. (1998) Predicting Struvite Formation in Digestion. *Water Res.*, **32** (12), 3607–3614.

Pan, S. H.; Lo, K. V.; Liao, P. H.; Schreier, H. (2006) Microwave Pretreatment for Enhancement of Phosphorus Release from Dairy Manure. *J. Environ. Sci. Health., Part B*, **41** (4), 451–458.

Qureshi, A.; Lo, K. V.; Liao, P. H. (2008) Microwave Treatment and Struvite Recovery Potential of Dairy Manure. *J. Environ. Sci. Health., Part B*, **43** (4), 350–357.

Saidou, H.; Moussa, S. B.; Amor, M. B. (2009) Influence of Airflow Rate and Substrate Nature on Heterogeneous Struvite Precipitation. *Environ. Technol.*, **30** (1), 75–83.

Schuling, R. D.; Andrade, A. (1999) Recovery of Struvite from Calf Manure. *Environ. Technol.*, **20** (7), 765–768.

Shen, Y.; Ogejo, J. A.; Bowers, K. E. (2010) Reducing the Effects of Calcium on Struvite Precipitation in Liquid Dairy Manure. *Proceedings of the 2010 American Society of Agricultural and Biological Engineers Annual International Meeting*; Pittsburgh, Pennsylvania, June 20–23; American Society of Agricultural and Biological Engineers: St. Joseph, Michigan.

Uludag-Demirer, S.; Demirer, G. N.; Chen, S. (2005) Ammonia Removal from Anaerobically Digested Dairy Manure by Struvite Precipitation. *Process Biochem.*, **40** (12), 3667–3674.

U.S. Department of Agriculture (USDA) (2009) *Manure Use for Fertilizer and for Energy*; Report to Congress; U.S. Department of Agriculture: Washington, D.C.

-
- Wang, J.; Burken, J. G.; Zhang, X.; Surampalli, R.; (2005) Engineered Struvite Precipitation: Impacts of Component-Ion Molar Ratios and pH. *J. Environ. Eng.*, **131** (10), 1433–1440.
- Wang, C.; Hao, X.; Guo, G.; van Loosdrecht, M. C. M. (2010) Formation of Pure Struvite at Neutral pH by Electrochemical Deposition. *Chem. Eng. J.*, **159** (1–3), 280–283.
- Zeng, L.; Li, X. (2006) Nutrient Removal from Anaerobically Digested Cattle Manure by Struvite Precipitation. *J. Environ. Eng. Sci.*, **5** (4), 285–294.
- Zhang, T.; Bowers, K. E.; Harrison, J. H.; Chen, S. (2010) Releasing Phosphorus from Calcium for Struvite Fertilizer Production from Anaerobically Digested Dairy Effluent. *Water Environ. Res.*, **82** (1), 34–42.