

# Releasing Phosphorus from Calcium for Struvite Fertilizer Production from Anaerobically Digested Dairy Effluent

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**ABSTRACT:** Being a non-renewable resource and a source of potential water pollution, phosphorus could be recovered from animal manure in the form of struvite ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ) to be used as a slow-release fertilizer. It was found recently that the majority of phosphorus in anaerobically digested dairy effluent is tied up in a fine suspended calcium-phosphate solid, thus becoming unavailable for struvite formation. Acidification and use of a chelating agent were investigated for converting the calcium-associated phosphorus in the digested effluent to dissolved phosphate ions, so that struvite can be produced. The results demonstrated that the phosphorus in the effluent was released into the solution by lowering the pH. In addition, the phosphorus concentration in the solution increased significantly with increased ethylenediaminetetraacetic acid (EDTA) concentration, as EDTA has a high stability constant with calcium. Most of the phosphorus (91%) was released into the solution after adding EDTA. Further, the freed phosphorus ion precipitated out as struvite provided that sufficient magnesium ions ( $\text{Mg}^{2+}$ ) were present in the solution. Furthermore, the phase structure of the solid precipitate obtained from the EDTA treatment matched well with standard struvite, based on the data from X-ray diffraction analysis. These results provide methods for altering the forms of phosphorus for the design and application of phosphorus-removal technologies for dairy wastewater management. *Water Environ. Res.*, **82**, 34 (2010).

**KEYWORDS:** phosphorus, struvite, calcium, wastewater, dairy effluent, ethylenediaminetetraacetic acid, anaerobic digestion.

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## Introduction

Phosphorus is an important non-substitutable macronutrient. Existing in nature as phosphates in various inorganic or organic forms, phosphorus compounds range from simple to complex, in terms of molecular structure. Because phosphorus is essential for all biological processes, there are concerns that the exploitation of this non-renewable resource to meet current demands is not sustainable. Two major opportunities exist for conserving the world's phosphorus resources—recycling from waste materials and more efficient use of phosphorus in agriculture as fertilizers.

One of the main sources of phosphorus for recycling is animal manure, as it has a high phosphorus content. A practice of manure management for concentrated animal feeding operations is the use of anaerobic digestion technology. Anaerobic digestion has several major advantages over direct land disposal in treating animal manures, such as biogas production, odor reduction, pathogen removal, and stabilization of organic solids. However, because anaerobic digestion does not remove any nutrients during the waste transformation process, the digested effluent still has a high phosphorus concentration (Sung and Santha, 2003; Zhang et al., 2000). Ideally, if the phosphorus in the effluent can be recovered to be exported from the animal farm to be used as fertilizer elsewhere, the excess nutrient problems in the animal farm can be solved, and associated water quality concerns can be addressed.

Generally, phosphorus-removal technologies applied to wastewater treatment include chemical and biological processes. A recently developed chemical technology for phosphorus removal and recovery is crystallization of phosphorus in the form of struvite (magnesium ammonium phosphate hexahydrate, or  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ) (Battistoni et al., 1997, 2001, 2006; Burns et al., 2001; Jeong and Hwang, 2005; Liberti et al., 1986; Wrigley et al., 1992). Struvite can be used as a slow release fertilizer, and its crystalline structure formation is well-suited to be produced in a crystallizer. Different types of crystallization reactors have been tested, such as a mechanical stirring reactor (Pastor et al., 2008; Stratful et al., 2004; Yoshino et al., 2003), a gas-agitated fluidized-bed reactor (Bowers and Westerman, 2005a, 2005b; Jaffer et al., 2002; Le Corre et al., 2007), and a water-agitated fluidized-bed reactor (Adnan et al., 2003; Battistoni et al., 2001).

Struvite formation requires three soluble ions in the solution (magnesium [ $\text{Mg}^{2+}$ ], ammonium [ $\text{NH}_4^+$ ], and phosphate [ $\text{PO}_4^{3-}$ ]) to react, forming precipitates with low solubility (pKsp of 12.6). Several factors can affect struvite precipitation, such as pH and supersaturation of the three ions ( $\text{Mg}^{2+}$ ,  $\text{NH}_4^+$ , and  $\text{PO}_4^{3-}$ ) in the solution and the presence of impurities (e.g., calcium) (Doyle and Parson, 2002; Nelson et al., 2003). For example, higher pH (e.g., pH 8.5) is favorable to struvite formation; thus, increasing solution pH was used as a method to enhance struvite formation (Doyle and Parson, 2002). However, calcium, as an impurity, could be a negative factor for struvite formation. Calcium presence at high levels in synthesized wastewater would inhibit struvite formation, because calcium-phosphorus precipitates also could be formed (Le Corre et al., 2005).

Phosphorus recovery using a struvite crystallization process has been demonstrated successfully in laboratory-, pilot-, and full-

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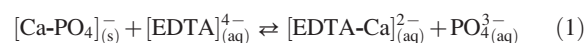
scale models using swine wastewater (Adnan et al., 2003; Bowers and Westerman, 2005a, 2005b; Suzuki et al., 2005). High total phosphorus removal (approximately 80%) has been obtained in field-scale tests (Bowers and Westerman, 2005b), indicating that this struvite crystallization process can be used for phosphorus recovery from a certain type of animal wastewater.

Struvite precipitation, however, has not been proven effective in anaerobically digested dairy wastewater. Phosphorus recovery from flushed dairy manure wastewater was evaluated using crystallization in a cone-shaped fluidized-bed reactor (Harris et al., 2008). The phosphorus products obtained in that study were verified in the form of calcium phosphate—not struvite—by X-ray diffraction (XRD), scanning electron microscopy, and elemental analysis. The results suggested that the phosphorus was not available in the phosphate ionic form required for struvite formation.

Phosphorus specification and phase distribution in dairy manure play an important role in struvite formation. The phosphorus in animal manure often has been characterized into inorganic, organic, phospholipid, and extracted fractions (Barnett, 1994a, 1994b; Dou, Knowlton, Kohn, Wu, Satter, Zhang, Toth, and Ferguson, 2002; He and Honeycutt, 2001; Leinweber et al., 1997; Sharpley and Moyer, 2000). The phosphorus distribution was characterized in 13 dairy manures representing a range in storage types and bedding options, and it was reported that the largest portion of total phosphorus was in the water-extractable fraction, with an inorganic phosphorus content of 12 to 44% and an organic phosphorus content of 2 to 23% (He et al., 2004). Sharpley and Moyer (2000) also observed that inorganic phosphorus in manure was the majority of the total phosphorus. In addition, inorganic phosphorus is predominantly particulate-bound (Gerritse and Vriesema, 1984). Particulate phosphorus could be calcium-phosphorus compounds with low solubility because of the high calcium content in dairy manure. The high calcium level results from the cows' diet, with a molar ratio of calcium to phosphorus of 1.66 to 2.43 (Güngör and Karthikeyan, 2008). Several studies on phosphorus extraction strongly support that inorganic phosphorus in animal manure is predominantly in calcium-phosphorus and/or magnesium-phosphorus bound form (Chapuis-Lardy et al., 2003; Dou, Toth, Galligan, Ramberg, and Ferguson, 2002; Güngör and Karthikeyan, 2005a, 2005b; Kleinman et al., 2002). Recently, Güngör and Karthikeyan (2008) evaluated phosphorus dynamics during anaerobic digestion of dairy manure, to determine phosphorus speciation and phase distribution in both influent and effluent. They reported that less than 20% of total phosphorus was in a dissolved form in both undigested and anaerobically digested dairy manure. Total dissolved phosphorus (TDP) constituted approximately 12% of total phosphorus in the influent, while approximately 7% of total phosphorus was in a dissolved form in the effluent. Their results suggested the mineralization of dissolved unreactive phosphorus (DUP) during anaerobic digestion and subsequent partitioning of dissolved phosphate ions into a particulate-bound form, resulting in a slight increase in the particulate phosphorus content of digested manure. Therefore, the majority of the phosphorus in the digested dairy manure was in a suspended solid form. The high calcium level probably contributed to the presence of phosphorus as a particulate, by forming a calcium-phosphorus suspended solid.

One logical hypothesis is that struvite fertilizer still could be produced with the anaerobically digested dairy wastewater, if the

calcium-phosphorus suspended solids are converted to dissolve phosphate ions that become available to struvite formation. In theory, this can be accomplished by adding a chelating agent, such as ethylenediaminetetraacetic acid (EDTA). The EDTA could sequester calcium, because EDTA is a chelating agent to calcium, with a high stability constant of  $[\text{EDTA-Ca}]^{2-}$  as  $10^{+10.7}$  (Martell and Hancock, 1996). Thus, EDTA should exhibit stronger binding to calcium. Both calcium-EDTA complex and released dissolved reactive phosphorus (DRP) would dissolve in the solution, resulting in an increased phosphorus concentration in the solution after EDTA addition. The release of phosphorus can be predicted according to eq 1. If calcium were present in the solid form of  $[\text{Ca-PO}_4]^-$ , EDTA added into the solution would react with the calcium. The reaction products would be soluble ions of  $[\text{EDTA-Ca}]^{2-}$  and  $\text{PO}_4^{3-}$ . Thus, concentrations of calcium as the  $[\text{EDTA-Ca}]^{2-}$  form and phosphorus as phosphate ions in the solution increase after EDTA addition.



Where s and aq represent solid and aqueous solution, respectively.

The purpose of the study was to test the hypothesis that struvite precipitation could be formed from dairy effluent if phosphorus were released into solution, as reactive phosphate ions, and become available for struvite formation. The liberation of phosphorus from calcium-phosphate solids was investigated using different methods, such as acidification and sequestering calcium with a chelating agent. The effect of various conditions, such as pH change, on the liberation of phosphorus and calcium also was investigated. An improved process for phosphorus recovery from anaerobically digested dairy effluent through struvite crystallization was proposed. The process also was tested with a pilot-scale reactor. In addition, the solid product obtained after phosphorus liberation and reacted for struvite precipitation was analyzed using XRD for confirming the struvite phase structure.

## Materials and Methods

**Dairy Effluent.** The effluent samples in this study were collected from a full-scale anaerobic digester at a dairy farm located in Washington State. The dairy operation used a scrape system for manure handling. Solid-liquid separation of anaerobically digested manure was achieved using a mechanical screen separator. After separation, the liquid portion (named *raw effluent* here) then was discharged to a lagoon. The raw effluent before discharging was collected and used in all of the experiments.

**Treatments for the Raw Effluent.** Two types of treatment were performed to liberate phosphorus in the dairy effluent—acidification and EDTA treatment.

**Acidification.** The first treatment of the effluent samples was acidification. Acidification aimed to negate the interfering effect of calcium, attempting to dissolve the phosphorus into the solution as soluble phosphate ions by protonating the phosphate ions. The reduced concentration would lower the calcium-phosphate ionic product below the equilibrium solubility product for calcium phosphates, resulting in the dissolution of solid calcium phosphate.

Concentrated hydrochloric acid (36.5 to 38.0%) was added to the effluent samples to depress the pH to various targeted levels, from its original pH 7.8 to 3.8, for dissolving the calcium-phosphate solids. The samples were mixed by magnetic stirring for approximately 60 minutes, to reach equilibrium. Then, the

samples were centrifuged at approximately 10 000 rpm for 10 minutes. The TDP, DRP, and calcium amounts in the supernatant were determined for the calculation of concentrations of phosphorus (mmol/L) as  $\text{PO}_4^{3-}$  and calcium (mmol/L) as  $\text{Ca}^{2+}$  ions. The TDP is defined as the total phosphorus in the supernatant, because the particulate phosphorus was removed by centrifugation. The DUP is defined as the difference between the TDP and the DRP in the supernatant. The DUP component comprises mainly polyphosphate (condensed phosphorus) and organic phosphorus.

It is noted that acidification typically dissolves inorganic phosphorus into the solution. Although the majority of total phosphorus is in the form of inorganic phosphorus, the specific phosphorus speciation present in dairy effluent is not clear. It was suggested that dicalcium phosphate dihydrate (DCPD,  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ), dicalcium phosphate anhydrous (DCPA,  $\text{CaHPO}_4$ ), octacalcium phosphate [OCP,  $\text{Ca}_8\text{H}(\text{PO}_4)_3 \cdot 3\text{H}_2\text{O}$ ], newberyite ( $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ ), and struvite were probable solid phases in both the anaerobic digester influent and effluent (Güngör and Karthikeyan, 2008).

**EDTA Treatment.** The second type of treatment was to add a chelating agent, EDTA, into the effluent. Rather than dissolving the calcium and phosphorus in solution, as in the acidification process, the purpose of using EDTA was to sequester calcium from the calcium-phosphorus solids. The EDTA, with final concentrations from 0 to 70 mmol/L, was added to the effluent samples. Then, the samples were mixed at approximately 120 rpm for 1 hour on a shaker, to ensure a complete reaction between the EDTA and calcium-phosphorus, and further centrifuged at approximately 10 000 rpm for 10 minutes.

An additional procedure was performed after the EDTA addition and centrifuging, but before the analysis. Specifically, the pH in the effluent was increased to 8.5, to encourage formation of phosphate solids, and then centrifuged again before analysis.

To evaluate the effect of the treatment, the concentrations of TDP, DRP, calcium, and magnesium in the supernatants were determined. It should be pointed out that the DRP concentration of TDP could indicate the potential of struvite formation, as only DRP can be used to form struvite.

**Struvite Formation.** At higher EDTA levels in the above experiments, it was anticipated that magnesium also would be tied up and unable to contribute to precipitating the phosphorus as struvite. Thus, magnesium chloride (0 to 155.4 mmol/L) was added to increase the  $\text{Mg}^{2+}$  ion molarity at EDTA levels of 40 and 70 mmol/L. The TDP concentrations in the solutions were analyzed after centrifugation. The resultant concentrations of TDP in solution decreased significantly after precipitation of struvite enabled by excess  $\text{Mg}^{2+}$  ions.

To verify struvite formation, the precipitated solid was collected after centrifugation and subjected to XRD analysis for phase structure. In addition, the composition of the solid was determined according to the contents of  $\text{PO}_4^{3-}$ ,  $\text{NH}_4^+$ , magnesium, and calcium, according to the analytical methods described in the Analytical Methods section.

Experiments were performed in triplicate. Experimental errors were determined and were typically less than 10%.

**Pilot Study for Struvite Crystallization.** Struvite formation was further investigated at the pilot scale through releasing the phosphorus in a continuous crystallizer. A cone-shaped fluidized-bed struvite crystallizer (Bowers and Westerman, 2005a, 2005b)

was developed for reducing the phosphorus content of swine wastewater. The system achieves a fast reaction and produces a desirable, granular product, by keeping both the small and large particles well-fluidized in the reaction zone. The crystallizers were operated at residence times ranging from 4.8 minutes to as low as 1.2 minutes, with swine lagoon wastewater, at both laboratory and field scales. Removal of total phosphorus reached 65% in the laboratory tests and 82% in the field test (Bowers and Westerman, 2005a, 2005b).

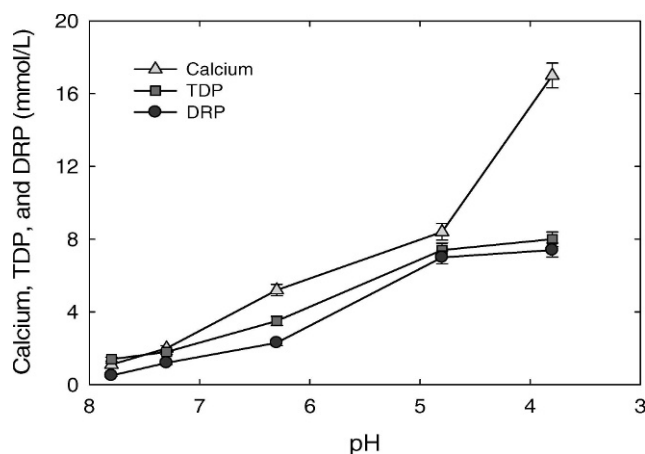
The same crystallizer also was used in this pilot study on a dairy farm site. The main crystallizer cone of this system was 2.3 m in height and 0.46 m in diameter at the top. Pretreatment (see the Process Improvement for Struvite Production section) was done in either three 1235-L tanks or one 5700-L plastic tank, all equipped with clamp-on agitators to provide stirring. Pumping of pretreated liquid to the crystallizer cone was accomplished by a Watson-Marlow-Bredel industrial hose pump (Watson-Marlow-Bredel Inc, Wilmington, Massachusetts), and the treated wastewater overflow from the cone passed through a 190-L dropout tank before exiting to the lagoon. A peristaltic pump was used for metering caustic soda solution into the cone bottom for pH adjustment. Struvite material, screened to include only particles between #8 and #24 standard sieve size, was loaded into the cone to serve as the initial bed material.

The flowrate of the cone of the effluent was between 1.7 and 2.1 L/min in this study. The dairy effluent was pumped from the pretreatment tank at various flowrates. The discharge of the pump was directed into the crystallizer cone bottom through flexible tubing. The liquid, after treatment in the cone, overflowed at the cone top through a wide flexible hose.

Caustic soda (sodium hydroxide [ $\text{NaOH}$ ]) for pH-boosting, required for struvite crystallization, was pumped by a diaphragm-style metering pump from a 175-L polyethylene tank into taps distributed around the bottom of the cone. Ammonia also can be used for pH-boosting, and it flowed from a portable cylinder through a pressure regulator, flow-control valve, and high-pressure tubing into the bottom of the crystallizer. The pretreating liquids (acids and solutions of EDTA, see the Process Improvement for Struvite Production section) were pumped by a diaphragm pump and a peristaltic pump, from another polyethylene tank, through tubing, to the pretreatment tank.

The struvite bed granules developed as the system operated and were harvested periodically by opening a valve at the bottom of the cone. Struvite product from the crystallizer settled from the bottom of the cone into the product collector during harvesting. The collector consisted of a watertight enclosure containing a removable receiver basket.

**Analytical Methods.** Analytical methods for the determination of TDP (P mmol/L as  $\text{PO}_4\text{-P}$ ), DRP (P mmol/L as  $\text{PO}_4\text{-P}$ ), total phosphorus (P mmol/L as  $\text{PO}_4\text{-P}$ ), ammonia-nitrogen (N mmol/L as  $\text{NH}_4\text{-N}$ ), and pH were adopted from *Standard Methods* (APHA et al., 2005). The TDP (method 4500-P F) and DRP (given by orthophosphate, method 4500-P G) in the supernatant were determined using the automated ascorbic acid method. The supernatant samples were passed through a 0.45- $\mu\text{m}$  filter before the analysis of TDP and DRP. The total phosphorus in the effluent samples was determined using method 4500-PF. Ammonia-nitrogen was determined using the titrimetric method (method 4500-NH<sub>3</sub> C). The concentrations of calcium and magnesium in the supernatants were measured using the atomic absorption



**Figure 1—Concentrations of calcium, TDP, and DRP in the supernatant after acidification.**

method with an air-acetylene flame on a spectrometer (Varian 220, Varian Inc., Palo Alto, California). Before the analysis of calcium and magnesium, concentrated hydrochloric acid (HCl) was added to the samples to adjust the pH to 1.0 to 2.0. This adjustment should have solubilized calcium and magnesium into a solution if calcium and magnesium were in a particulate form.

Contents of the total phosphorus, calcium, and magnesium in the raw effluent determined using these methods ranged from 6.7 to 10.5 mmol/L (or 208 to 326 mg/L), 12.0 to 26.0 mmol/L (or 480 to 1040 mg/L), and 5.0 to 16.0 mmol/L (or 121 to 389 mg/L), respectively.

The XRD analysis was run on an X-ray powder diffractometer (D500, Siemens, Munich, Germany). Operating conditions were 35 kV and 30 mA with a sealed copper anode X-ray (CuK $\alpha$ ) radiation. Samples were scanned from 10 to 70 degrees (2-theta) with 0.02 degrees and 1.5 seconds per step. The XRD powder diffraction analysis is a method by which X-rays of a known wavelength are passed through a sample to identify the crystal structure, such as struvite (JCPDS, 1986). The wave nature of the X-rays means that they are diffracted by the lattice of the crystal to give a unique pattern of peaks of “reflections” at differing angles and of different intensity, just as light can be diffracted by a series of suitably spaced lines.

## Results and Discussion

**Liberation of Phosphorus by Acidification.** Figure 1 presents the results of the acidification to dissolve phosphorus and Ca<sup>2+</sup> ions in solution. The concentrations of Ca<sup>2+</sup>, TDP, and DRP increased significantly with a decrease in pH, as a result of the addition of acid—evidence that the acid released phosphorus and Ca<sup>2+</sup> into the solution. For example, the concentrations of Ca<sup>2+</sup>, TDP, and DRP of 1.1, 1.4, and 0.5 mmol/L at an initial pH of 7.8 were increased to 17, 8.0, and 7.4 at pH 3.8, respectively. These results demonstrated that more phosphorus was solubilized into solution as the pH decreased, and the majority of phosphorus in the original dairy manure effluent at pH 7.8 must have been in a suspended-solid form.

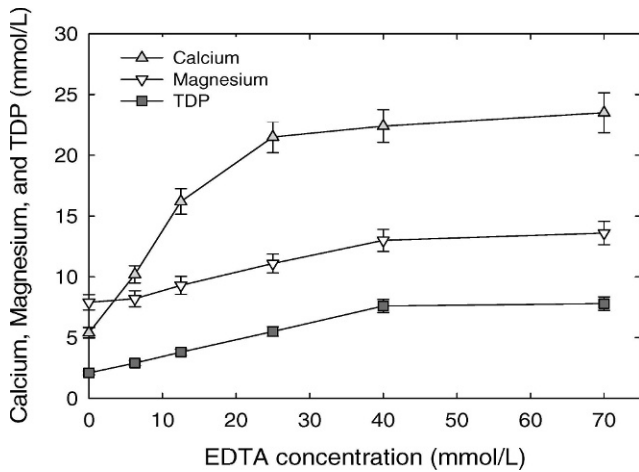
The released phosphorus, as phosphate ions, in a low pH solution, could have formed struvite or returned back to calcium-phosphate particles when the solution pH rose to the original pH of 7.8, as concentrations of the constituent ions in the probable

calcium-phosphorus species were likely to exceed their equilibrium solubility. The equilibrium of the probable calcium-phosphorus species competes with that of struvite for released phosphate ions. If the calcium content was so high that the equilibrium moved toward the calcium-phosphorus compounds, calcium-phosphorus solids would be formed. Struvite also could be formed if high concentrations of constituent ions (NH<sub>4</sub><sup>+</sup> and Mg<sup>2+</sup>) of struvite were present in the solution and crystal seeds that would support the spontaneous formation of new particles.

Although acidification can dissolve inorganic phosphorus into a solution, the specific phosphorus speciation present in the dairy manure effluent was not clear. To understand phosphorus speciation, geochemical equilibrium modeling with software Mineql+ (Massachusetts Institute of Technology, Cambridge, Massachusetts) was used to determine the probable types of phosphorus. The Mineql+ simulation suggested that dicalcium phosphate dehydrate, dicalcium phosphate anhydrous, octacalcium phosphate, newberyite, and struvite were probable solid phases in both the digester influent and effluent (Güngör and Karthikeyan, 2008). It was noted that anaerobic digestion did not influence the solid phosphorus type and stability (Güngör and Karthikeyan, 2008). Another study, using a kinetic model, investigated using calcium and magnesium carbonate and phosphate mineral aeration treatment of anaerobic digestion liquors (Musvoto et al., 2000). The kinetic model described an anaerobic digestion system of three phases (solid–liquid–gas) comprised of water, carbonate, phosphate, short-chain fatty acid and ammonia; ion pairing; and so on. From these modeling results, the precipitated minerals, in decreasing proportion of precipitated mass, were as follows: struvite (82 to 89%), amorphous phosphate (5 to 15%), calcium carbonate (0 to 6%), magnesium carbonate (0 to 5%), and newberyite (MgHPO<sub>4</sub>) (0.1 to 0.3%). However, the calcium content in the Musvoto et al. (2000) study was much lower than that in the anaerobic digester effluent of our current study, and the high calcium might change the predicted results from the model.

It should be noted that manure characteristics (i.e., ionic composition) could vary among different dairy operations and even seasonally within the same operation. This variation would influence the Mineql+ simulation and further determination of the phosphorus solid phases (Güngör and Karthikeyan, 2008). Thus, the solid phosphorus species in digested effluent could vary from one dairy operation to another.

Although the above studies predicted the probable phosphorus phase as struvite, nucleation and growth stages of the struvite crystals are complex; these stages are affected by several factors, such as thermodynamics of the liquid–solid equilibrium, phenomena of matter transfer between solid and liquid phases, kinetics of reaction, solution pH, supersaturation, mixing energy, temperature, and presence of impurity ions (Le Corre et al., 2005). Impurities to struvite, such as calcium, could inhibit the growth rate of struvite crystals, as a result of the blocking of active growth sites by adsorption on the crystal surfaces. The effect of calcium on struvite crystal size, shape, and purity using pure chemicals was investigated by Le Corre et al. (2005). The results show that the presence of calcium ions had a significant effect on struvite crystallization. The increase of calcium concentration inhibited struvite growth and led to the formation of an amorphous substance rather than a crystalline struvite. At a molar ratio of magnesium to calcium of approximately 1:1 and above, a

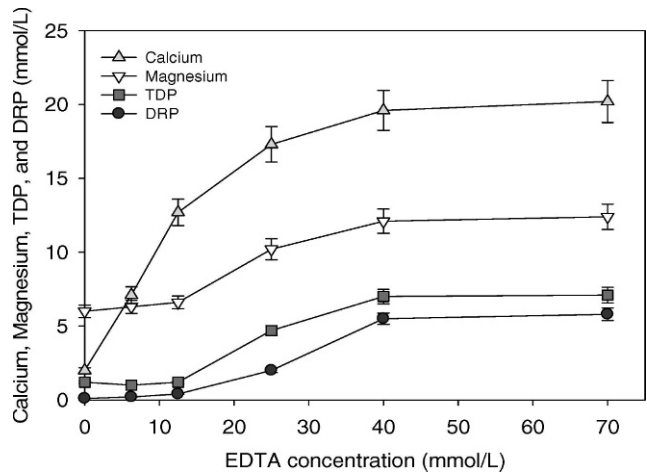


**Figure 2—Concentrations of calcium, magnesium, and TDP in supernatants after EDTA addition, without pH adjustment.**

substance identified as an amorphous calcium phosphate—not a crystalline struvite—was formed. In the current study, the molar ratio of magnesium to calcium was approximately 1:2.1, suggesting that it was difficult to form crystalline struvite.

**Effect of EDTA Addition on Phosphorus Liberation.** The results demonstrated that EDTA was successful in liberating phosphorus into the solution (Figure 2). As the amount of EDTA addition increased, more calcium and phosphorus dissolved in the solution. This is consistent with the hypothesis that EDTA tied up calcium, releasing both calcium and calcium-bound phosphorus into the solution. For instance, without EDTA addition, most of the calcium and phosphorus were present in the solids, as expected, leaving little in the final treated liquid. However, with 40 mmol/L EDTA addition, slightly exceeding the sum of the calcium and magnesium molarity in the raw sample, most of the calcium (93%) was released. The total phosphorus in the raw effluent was 8.6 mmol/L. The TDP was 7.8 mmol/L in the presence of 70 mmol/L EDTA. Thus, most of the total phosphorus (91%) was released into the solution by adding EDTA. The release profiles of phosphorus and magnesium were similar, but magnesium lagged behind somewhat. This lag can be explained by the fact that EDTA preferentially binds to calcium first. Because the stability of the  $[\text{EDTA-Ca}]^{2-}$  complex is 2 orders of magnitude greater than that of the  $[\text{EDTA-Mg}]^{2-}$  complex, EDTA binds magnesium only when almost all of the calcium has been bound. Therefore, the phosphorus was released into the solution from calcium solids. It should be noted that a high dose (40 to 70 mmol/L) of EDTA is too expensive to use in a commercial system and was used here only to test the concept of calcium tie-up.

In addition, the results (Figure 3) obtained with an increasing pH were similar to those without pH adjustment. As expected, calcium, magnesium, and phosphorus in both TDP and DRP were released into the solution. For example, at high levels of EDTA (>40 mmol/L), the calcium binding effect of the EDTA blocked the ability of calcium to combine with phosphorus to form solids, even with the pH at 8.5, leaving most of the calcium and phosphorus in solution. However, the release of phosphorus did not occur at this pH until the EDTA addition exceeded the calcium molarity. This effect was assumed to result from the tendency of EDTA to bind calcium first, leaving any magnesium in the

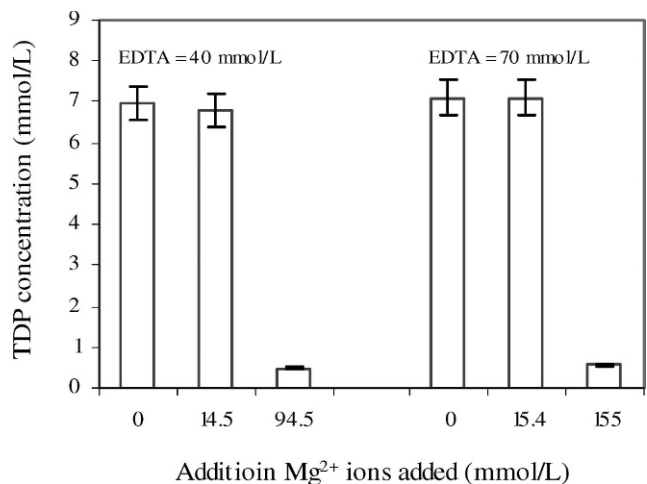


**Figure 3—Phosphorus, calcium, and magnesium in solution after EDTA addition, with adjustment of pH = 8.5.**

solution available to precipitate phosphorus as struvite, as phosphorus is released from the calcium phosphate solids by the EDTA.

However, EDTA, at a high concentration, also can bind with magnesium as an  $[\text{EDTA-Mg}]^{2-}$  complex with stability constants  $10^{+8.7}$ , resulting in the reduction of free  $\text{Mg}^{2+}$  ions available for struvite formation. Therefore, at high EDTA levels, magnesium is bound up and unable to precipitate the phosphorus as struvite. In fact, more complete phosphorus liberation was observed at the high EDTA levels shown in Figures 2 and 3.

Struvite formation also requires free  $\text{Mg}^{2+}$  ions, as they are constituent ions of struvite. To verify this hypothesis with the dairy effluent, magnesium chloride was added to increase the magnesium ion molarity at different levels. At sufficient levels of  $\text{Mg}^{2+}$  ions, all EDTA would bind up with the  $\text{Mg}^{2+}$  ions. Therefore, chemical equilibrium leads to the formation of struvite—not calcium-phosphorus compounds—because of the high concentrations of  $\text{Mg}^{2+}$  and  $\text{PO}_4^{3-}$  ions available with the  $\text{NH}_4^+$  ions present in solution. If this hypothesis is true, the phosphorus concentration would be significantly decreased after struvite formation. Figure 4 shows the effects of  $\text{Mg}^{2+}$  ions added



**Figure 4—TDP in supernatant after both EDTA and additional  $\text{Mg}^{2+}$  ions added (pH = 8.5).**

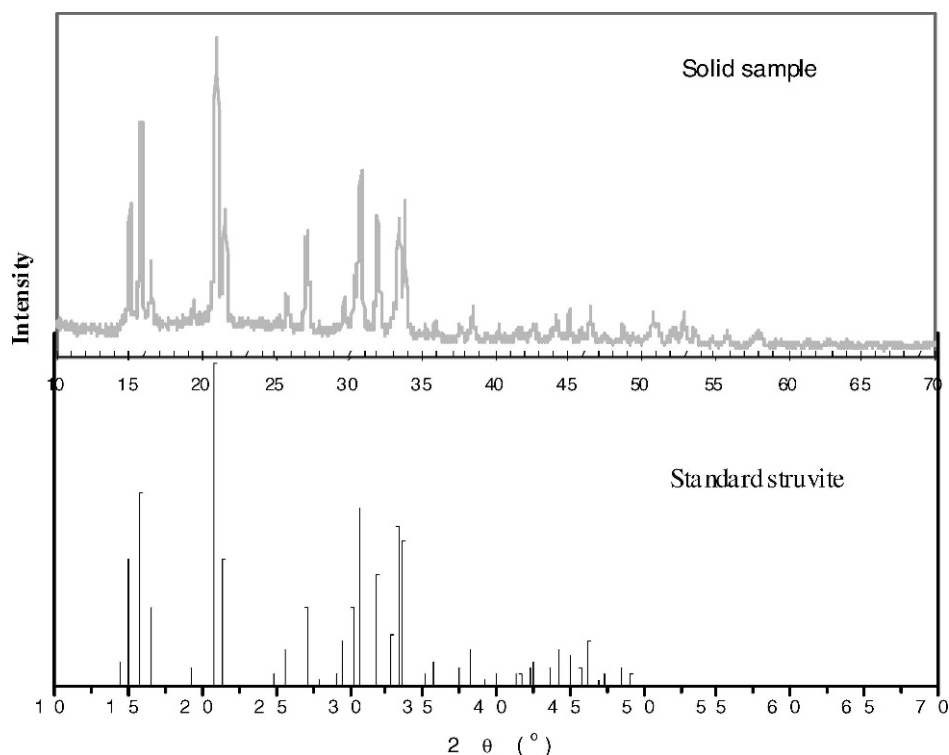


Figure 5—XRD pattern from the solid product compared with standard struvite.

at different levels at EDTA concentrations of 40 and 70 mmol/L. These results verified the above hypothesis. The phosphorus concentration in the solution had no significant change at the  $Mg^{2+}$  ion concentration of 14.5 mmol/L compared with that of zero  $Mg^{2+}$  ions added at the EDTA concentration of 40 mmol/L. These results indicated that EDTA tied up all  $Mg^{2+}$  ions, leaving no free  $Mg^{2+}$  ions for a struvite-forming reaction. However, when the  $Mg^{2+}$  ion concentration increased to 94.5 mmol/L, which was much higher than the concentration of EDTA of 40 mmol/L, the excess  $Mg^{2+}$  ions combined with the phosphorus to form struvite precipitates, resulting in a sharp reduction of phosphorus concentration in the solution. Similar results were obtained at an even higher EDTA level of 70 mmol/L. The resulting concentrations of phosphorus were consistent with the precipitation of struvite.

**Precipitate Identification.** Figure 5 shows the result of XRD analysis of the precipitated solid compared with that of standard struvite. It was clear that the precipitated solid's pattern matched well with the unique pattern of standard struvite (JCPDS, 1986) for both angles (diffraction angles  $2\theta$ ) and intensities. Thus, from the XRD pattern, the solid was identified as struvite.

In addition, the solid composition analysis results listed in Table 1 show the composition of the solid product compared with pure struvite. The results of phosphorus, nitrogen, and magnesium demonstrated a molar ratio of phosphorus to nitrogen to

magnesium of 1:1.02:1.02, which is close to the theoretical ratio of 1:1:1. The relative purity was approximately 78% compared with pure struvite. Therefore, both the XRD pattern and the composition analysis suggested that a majority (78%) of the product obtained was struvite.

#### Process Improvement for Struvite Production

The performance of phosphorus removal by the crystallizer is summarized in Table 2. Generally, total phosphorus removal was poor, with reduction never exceeding 15%. In all of the runs that exceeded 10% removal, raw effluent was acidified to below pH 7.0. Acidification of the raw effluent seemed to improve the performance slightly.

The poor phosphorus reduction results with the dairy effluent contrast sharply with the high reduction (82%) with swine wastewater (Bowers and Westerman, 2005b) obtained from the same crystallizer. The results confirmed that the phosphorus in the dairy effluent was not available for struvite formation. Struvite crystallization requires the availability of reactive phosphate, whereas the calcium-phosphate solids, with low solubility, provided little reactive phosphate, thereby blocking struvite crystallization and thus resulting in poor phosphorus reduction in the dairy effluent. Therefore, freeing the phosphorus to be in the phosphate ion form before struvite formation is required.

Table 1—Composition of the solid sample compared with pure struvite.

Sample	Phosphorus (% wt)	Nitrogen (% wt)	Magnesium (% wt)	Molar ratio of P:N:Mg	Calcium (% wt)	Product purity (%)
Solid product	10.1	4.6	7.8	1:1.02:1.02	0.9	78
Pure struvite	12.9	5.9	9.9	1:1:1	0	100

**Table 2—Phosphorus removal in crystallizer from dairy effluent.**

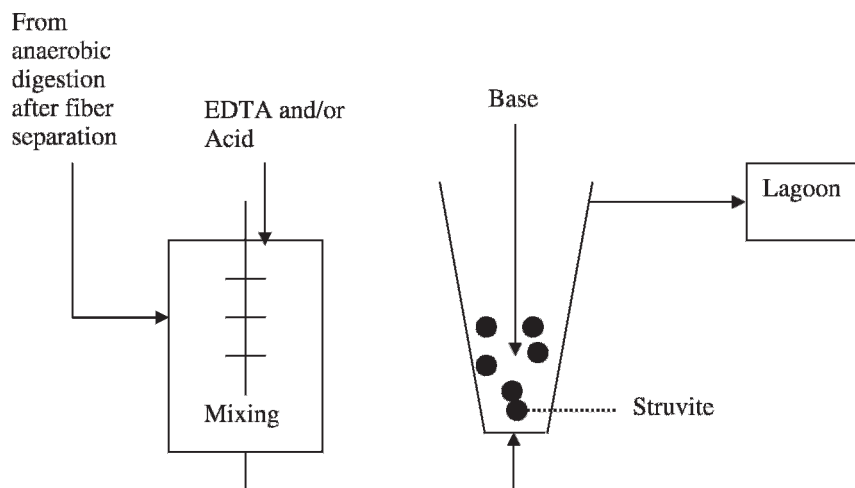
Run number	Sample	Total phosphorus (mg/L)	Total phosphorus reduction (%)	Flowrate (L/min)	pH (raw)	pH (crystallizer)
1#	Raw	275	3	1.7	7.0	7.9
	Treated	268				
2#	Raw	302	11	1.7	6.4	8.0
	Treated	270				
3#	Raw	293	4	1.7	6.5	7.5
	Treated	281				
4#	Raw	293	11	1.9	6.5	8.5
	Treated	262				
5#	Raw	290	13	1.9	6.0	8.0
	Treated	251				
6#	Raw	317	1	2.1	8.0	8.0
	Treated	315				
7#	Raw	317	5	1.9	8.0	8.25
	Treated	300				
8#	Raw	288	1	2.1	7.5	7.5
	Treated	285				
9#	Raw	288	8	1.9	7.5	8.0
	Treated	265				

A modified process was proposed to improve struvite crystallization in the pilot study. The schematic process is shown in Figure 6. A unit is required for a pretreatment to release the phosphorus before the crystallizer. The EDTA should be added in the pretreatment unit, not as a cone reagent (possibly because it takes longer to react than the cone residence time). The pretreatment might include acidification.

This modified process was tested for struvite crystallization. The flowrate of the digester effluent through the system was 7.5 to 7.7 L/min. Digester effluent was directed into the pretreatment tank(s), where it was mixed with EDTA to bind calcium and hydrochloric acid, to prevent premature precipitation of struvite from the supersaturated solution that develops upon addition of EDTA. Upon startup of the system, rapid growth of the bed was observed, indicating struvite precipitation. Table 3 summarizes operating conditions and the results for the first four runs, from which samples were taken and analyzed. The first two runs used nearly identical operating conditions; the next used similar

conditions, except for a higher initial pH; and the next used a lower pH in the cone. Compared with the results in Table 2, the performance improvement is evident. In the pilot tests, low dosages of EDTA were added to reduce its cost. For example, the molar ratio of EDTA to calcium was 1:1. On a weight base, this corresponds to an EDTA concentration of 7.3 g/L, if the calcium concentration is 25 mmol/L, as in a typical effluent. The current EDTA market price is US \$0.95/kg according to the Chemical Marketing Report ([http://www.icispricing.com/il\\_shared/il\\_splash/chemicals.asp](http://www.icispricing.com/il_shared/il_splash/chemicals.asp)). Thus, EDTA will cost approximately \$6.90 for treating 1000 L of the effluent. This EDTA dose seems to be too expensive to be practical. For possible commercial use, other organic acid anions are being explored in the authors' laboratory, such as oxalate, which is much less expensive. The oxalate would be added in quantities no greater than the calcium content of the effluent, leading to conversion of the oxalate to calcium oxalate.

In addition to a concern of high EDTA costs, another critical issue is the environmental effects resulting from any additive into

**Figure 6—Schematic process of improvement for struvite crystallization.**

**Table 3—Phosphorus removal in crystallizer from dairy effluent, using EDTA.**

Run number	Sample	Total phosphorus (mg/L)	Total phosphorus reduction (%)	Flowrate (L/min)	pH (raw)	pH (crystallizer)
E-1#	Raw	239	70	7.4	5.2	7.3
	Treated	71.5				
E-2#	Raw	169	82	7.6	5.1	7.5
	Treated	31.1				
E-3#	Raw	122	30	7.5	5.75	7.6
	Treated	84.8				
E-4#	Raw	149	62	7.4	5.1	6.75
	Treated	57.2				

the effluent. The EDTA has wide industrial applications, involving the sequestration of metal ions in aqueous solution, such as in textiles, pulp and paper, foods, cosmetics, and so on. The EDTA is also on the U.S. Environmental Protection Agency (Washington, D.C.) (U.S. EPA) list of inert pesticide ingredients (list 4B). This list contains ingredients for which EPA has sufficient information to reasonably conclude that the current use pattern in pesticide products will not adversely affect public health or the environment. Thus, EDTA should not have any adverse effect on a dairy farm when it is added to the effluent.

### Conclusions

Phosphorus, as suspended calcium phosphate solids in anaerobic digestion dairy manure effluent, was liberated into a solution as phosphate ions by either acidification or adding an EDTA chelating agent. Approximately 91% of the total phosphorus and 93% of the calcium were released into the solution by the addition of EDTA. The liberated phosphorus was precipitated as struvite, by ensuring that sufficient free  $Mg^{2+}$  ions remained present in the solution.

### Credits

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