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Timothy A. Shepherd
Iowa State University

Robert T. Burns
Iowa State University

Lara B. Moody
Iowa State University

D. Raj Raman
Iowa State University, rajraman@iastate.edu

Kenneth J. Stalder
Iowa State University, stalder@iastate.edu

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Development of an Air Sparged Continuous Flow Reactor for Struvite Precipitation from Two Different Liquid Swine Manure Storage Systems

T. A. Shepherd, R.T. Burns, L.B. Moody, D.R. Raman, K.J. Stalder
Agricultural and Biosystems Engineering Department, Iowa State University

Abstract: Forced precipitation of struvite (MgNH₄PO₄·6H₂O) has been demonstrated to be an effective method to reduce dissolved reactive phosphorus (DRP) from swine manure. The development of a robust and flexible continuous flow struvite precipitation reactor is essential to the application of this method to modern livestock operations. Swine manure generally requires pH adjustment, magnesium amendment and a sufficient reaction time to create optimum conditions for struvite precipitation. A bench-scale (14-L) continuous flow reactor was developed to force struvite precipitation and reduce DRP. The bench scale system was developed to quantify system performance prior to building a much larger pilot-scale unit. The bench-scale reactor used air sparging to provide pH adjustment and mixing. Influent manure slurry was continuously amended with magnesium chloride (MgCl₂·6H₂O) to promote maximum DRP removal. During continuous flow operation, a 10-minute hydraulic retention time was provided for struvite precipitation. This paper discusses the design and development of the continuous flow air sparged tank reactor (ASTR) and reports on the reactor’s DRP reduction capabilities on manure collected from two commercially utilized swine manure storage systems; 1) a concrete storage tank with a permeable cover, and 2) a shallow under floor pit manure collection system. Continuous flow ASTR treatment provided a 95% reduction of DRP from the covered storage tank manure and a 78% reduction of DRP from the under floor pit manure.

Keywords: Manure, Phosphorus, Struvite, Swine

Introduction

Growing concerns about water quality and land management have resulted in new requirements for the land application of manure, often in the form of legislation; these regulations often limit the application of manure based on crop nutrient needs, such as phosphorus (Shober and Simms, 2003). Developing a treatment system designed to remove phosphorus from manure slurries prior to land application offers an alternative method to reduce the amount of phosphorus applied to the land. One such method is the forced precipitation of the crystalline precipitate struvite (magnesium ammonia phosphate hexahydrate, MgNH₄PO₄·6H₂O). Forced precipitation of struvite has been shown to significantly reduce the amount of soluble phosphorus from manure slurries and has the ability to concentrate phosphorus for recovery and future use (Bowers and Westerman, 2005a; Burns et al., 2000; Munch and Barr, 2001; Ohlinger et al., 2000). In laboratory and field tests, forced struvite precipitation has been shown to typically remove around 90% of dissolved reactive phosphorus (DRP) from swine manure (Burns et al. 2001). Recovered struvite can be used as a slow-release commercial or agricultural fertilizer, offering potential as an added value byproduct (de-Bashan and Bashan, 2004). Furthermore, controlling the amount of phosphorus removed during treatment can provide a manure that is a balanced fertilizer in terms of nitrogen and phosphorus for a specific crop.

In a pure solution, a 1:1:1 (Mg²⁺: NH₄⁺: PO₄³⁻) molar ratio will form struvite (Burns et al., 2001). The amount of phosphorus which can be removed from liquid manure is related to the availability of magnesium, ammonia and phosphate in the liquid manure. If magnesium or ammonia isn’t present in sufficient quantities, struvite formation will stop before the desired amount of DRP has been removed. The degree of struvite precipitation depends upon the conditional solubility product (Ksp) of struvite. The
conditional solubility product of struvite is directly proportional to the product of Mg$^{2+}$, NH$_4^+$, and PO$_4^{3-}$ ions in solution and is highly dependent on solution pH (Ohlinger et al. 2000); increasing any one ion concentration increases the Ksp, creating better conditions for struvite formation and DRP removal. As pH increases, the amount of struvite which can be precipitated increases until it reaches its maximum precipitation point at a pH of 9.0 (Buchanan et al., 1992).

In typical manure slurries, Mg$^{2+}$ is the limiting ion for optimized struvite formation; this requires the addition of magnesium to maximize DRP removal. Furthermore, in complex organic solutions, such as manures, magnesium can form complexes with other ions in solution, reducing magnesium's contribution to the Ksp of struvite, requiring a higher than stoichiometric magnesium addition to overcome the competing reactions and achieve the desired DRP removal rates (Burns et al., 2003). Phosphorus can also complex with other ions in solution forming precipitants such as calcium phosphates, brushite, and monetite, effectively reducing the amount of struvite which can be formed (Celen et al., 2007).

Currently, there are several treatment systems that apply struvite precipitation techniques for phosphorus removal in municipal and industrial wastewaters (Munch and Barr 2001; Ohlinger et al. 2000). Full-scale struvite reactors have been incorporated into municipal and industrial wastewater treatment systems in Japan and Europe; however, their implementation is not common practice in livestock production facilities (Burns et al., 2003).

Bowers and Westerman (2005a) developed a cone-shaped fluidized bed reactor for treatment of swine wastewater. Their system utilized a fluidized bed containing struvite to promote the growth of struvite crystals within the reactor. Modeling and testing indicated that the reactor operated under plug flow conditions with a completely mixed fluidized bed. Field tests provided removal rates of DRP ranging from 13% to 80%. Under certain operating conditions, testing provided evidence of spontaneous nucleation and seeding. Spontaneous nucleation and seeding decreased the bed particle size and reduced phosphate removal performance due to struvite becoming entrained with the effluent and wash out of the reactor. Bowers and Westerman (2005b) reduced the flow rate through the reactor to maintain struvite settling in order to ensure that struvite and bed washout did not occur.

Munch and Barr (2001) modeled and tested a pilot-scale fluidized bed struvite reactor based on the Phosnix process developed by Unitika Ltd (Japan) (Brett et al. 1997). Munch and Barr’s (2001) reactor utilized a struvite seed material to develop the fluidized bed and promote further precipitation upon the surface of the bed material. They used a municipal wastewater with low TS conditions, achieving a DRP removal rate of 94%. Fine struvite crystals were found in the effluent of the reactor. This provided higher concentrations of suspended solids in the effluent than the influent and accounted for increased effluent TP. If struvite precipitates spontaneously, the upflow velocity within the system may be great enough to push small struvite particles out of the reactor, increasing the effluent suspended solids and reducing the overall phosphorus removal performance.

With the inconsistent nature of agricultural wastewaters, a rapid increase in TS of the manure has the potential to create a similar washout affect in fluidized bed reactors and thus provide lower than expected phosphorus removal rates. Organic matter and other suspended particles could interfere with the struvite bed particles and reduce the precipitation potential of struvite on the bed particles by promoting the spontaneous nucleation of fine struvite particles which can become entrained in the effluent.

Fluidized bed reactors are complex in design, fabrication, and operation. Bench and pilot-scale fluidized designs have provided significant phosphorus removal efficiencies (Bowers and Westerman 2005ab, Munch and Barr 2001). The transition of bench and pilot-scale fluidized bed reactors to full-scale, on-farm systems may be limited because of their complexity; furthermore, modifications to achieve high flow rates required to make this type of system applicable for use with large modern pork production operations may not be economically feasible.

Manure treatment systems that can perform at relatively high flow rates under variable environmental conditions are desirable for implementation within existing swine production systems. When treating swine manure, the most convenient point for treatment occurs during the land application of the slurry. The characteristics of the manure slurry (solids content, nutrient concentrations, etc.) can change during field application events. The changes in manure characteristics during a field application event require a treatment system that is robust, tolerant of variable influents, and flexible. Furthermore, manure land application systems typically apply manure slurries at rates ranging from 1,900 – 5,700 L min$^{-1}$ (500-1,500 gpm). This relatively high volume application rate requires comparable flow rates within a treatment system designed to work during application, necessitating short retention times to avoid excessively large reactors. A flexible system requires a design that can be easily modified to accommodate differences between manure management strategies and characteristics from different liquid manure storage systems involving a variety of livestock species.
Continuous flow stirred tank reactors (CSTR) inherently buffer shock loading (Benfield and Randall, 1987), thus the phosphorus removal efficiency will be less susceptible to changes in the manure slurries, providing a robust system. Continuous flow stirred tank reactors are relatively simple in design, and their sizing is well defined (AWWA, 1999). The simple design parameters also provide operational and maintenance benefits associated with startup and process changes that may not be available with fluidized bed reactors.

The objective of this study was to develop and test a short-retention-time bench-scale CSTR, capable of effectively and reliably reducing DRP from swine manure slurries.

Materials and Methods

Bench-scale design

A 19-L (5-gal) plastic bucket was chosen as the platform for the bench-scale air sparged continuous flow tank reactor (ASTR). Figure 1 provides a diagram of the 14-L ASTR with dimensions. Figure 2 shows the constructed ASTR. A fine bubble EDI PermaCap 5 diffuser (Environmental Dynamics Inc., Columbia, MO) was mounted at the bottom to provide the highest air bubble contact time available. The volume of manure at steady-state operation was set at 14 L, requiring a 1.4 L/min flow rate to achieve the desired 10-minute HRT. Manure was injected with a Wayne utility pump (Model 75982, Wayne Water Systems, Harrison, OH) through 0.6 cm copper tubing located directly above the diffuser plate to provide rapid mixing. Magnesium chloride was injected with a Masterflex peristaltic pump (Model 7518-10, Cole Palmer, Vernon Hills, IL) through 0.3 cm copper tubing located directly above the diffuser plate to provide incorporation with the manure slurry. The effluent outlet was located near the center of the ASTR to discourage short-circuiting within the reactor.

Three commercial and one fabricated air diffusion plates were tested to determine the gas transfer characteristics and mixing capabilities. Three PermaCap 5 (Environmental Dynamics Inc., Columbia, MO) diffuser types provided fine, medium, or coarse air bubble sizes at similar flow rates. Diffusers were tested to identify the pH adjustment capabilities for air flow rates between 15-35 L/min.

The ASTR system does not provide a mechanism for the recovery of the precipitated phosphorus. Struvite has a specific gravity of 1.7, while liquid swine manure has a specific gravity near 1.0; this difference may allow for the use of gravity separation for the ultimate removal and recovery of precipitated phosphorus from the manure.

Up-flow clarifiers (UFC) are commonly used in municipal wastewater treatment systems to separate solids from liquids in continuous flow (AWWA, 1999). A UFC is designed to reduce the up-flow velocity of the liquid to allow for the gravitational settling of suspended particles, such as struvite. The use of gravitational settling allows UFCs to maintain low operating costs, while achieving continuous flow solids separation. A UFC following the ASTR was introduced to determine the system TP reduction capabilities. A custom fabricated UFC was integrated in series with the ASTR as shown in Figure 3. The UFC used had a diameter of 0.36 m with a total volume of 36.6 L. Flow from the ASTR was split to 0.7 L/min of treated wastewater providing the UFC with a 52 min detention time. The weir was designed to provide a surface overflow rate of 32 m³/day/m² based on design parameters provided by Metcalf and Eddie (1991).

For simplicity during initial testing of the test reactor, magnesium was applied in excess to insure maximum phosphate removal. The magnesium injection rate was determined from initial DRP analysis and then adjusted to achieve a Mg²⁺:PO₄³⁻ ratio of 1.6:1.

Manure sources

Manure used for testing the phosphorus removal capabilities of an ASTR and UFC was collected from two different swine production facilities utilizing different manure storage systems. The first manure tested was collected from a commercial finishing facility located near Ames, Iowa. Manure from the commercial finishing facility was collected from a storage tank covered with light expanded clay aggregate (LECA) rock designed to store manure produced in a one year period. The second manure tested was collected from the Iowa State Swine Teaching Facility (Ames, Iowa), which is a swine finish facility. Manure from the Iowa State Swine Teaching Facility was collected directly from an under floor shallow-pit in the finishing barn, prior to transfer to the secondary storage tank.

Sample Analysis

Chemical analysis methods were as follows; dissolved reactive phosphorus - Standard Method 4500-P E (APHA, 1998), total phosphorus - Standard Method 965-17 (AOAC, 2002), total Kjeldahl nitrogen (TKN) - Standard Method 2001-11 (AOAC, 2000), and ammonium (NH₄⁺) - Standard Method 4500-NH₄ B & C for (APHA, 1998), total solid analysis - Standard Method 2540 B (APHA, 1998), and pH - an Orion 4-Star pH/Conductivity probe (Thermo Fisher Scientific, Waltham, MA). The probe was calibrated with 7.0 and 10.0 standard pH solution was performed before each treatment.
Bench Scale Operation

Treatment of swine manure for DRP reduction in the bench-scale ASTR proceeded in two steps; Figure 4 provides a operational flow chart for the pre-aeration and continuous flow sequence of the ASTR operation. The untreated manure was first pre-aerated to provide and approximate pH increase of 1.0 units; the pre-aeration step was then followed by continuous flow operation to force the precipitation of DRP. Pre-aeration consisted of applying diffused air at a flow rate of 20 L/min for 30 minutes to provide the initial pH adjustment in 14 L of untreated manure. The ASTR was then operated in a continuous flow mode. During continuous flow operation, untreated manure was injected at 1.4 L/min, MgCl₂ was continuously injected at a rate determined from laboratory analysis to achieve a 1.6:1 Mg²⁺:PO₄³⁻ ratio, air sparging proceeded at 20 L/min, and treated manure was continuously extracted at 1.4 L/min.

To test the ASTR-UFC system capability for removal of precipitated phosphorus, the UFC was first filled with ASTR treated manure (the ASTR was operated as previously described). The ASTR and UFC were then operated continuously in series. The ASTR-UFC continuous flow treatment time was extended from 30 minutes in the ASTR treatment to 80 minutes. The time extension was provided to identify changes in DRP and TP due to accumulation of struvite in the UFC, and to test the sustainability of the ASTR’s DRP reduction performance. Samples of the ASTR and UFC effluents were collected for analysis of DRP and TP for the duration of continuous flow operation. Table 1 provides the initial waste characteristics of the manure tested.

During ASTR and ASTR-UFC treatments, samples were collected from the raw manure, after pre-aeration but before magnesium addition, and at timed intervals for the duration of the continuous flow operation. However, during the first duplicate of the ASTR treatment, magnesium injection was initiated prior to sampling of the aerated manure; a sample was collected shortly after magnesium injection was initiated from the ASTR effluent port, this has been noted in Figure 4.
Figure 4. Operational flow chart indicating the pre-aeration and continuous flow sequences of the ASTR for the precipitation of phosphorus from liquid swine manure.

Experiments and Results

ASTR Performance

Table 1 provides the nutrient analysis of the two, untreated manures utilized in the treatments. Initial testing of the aeration system indicated that the commercial diffusers outperformed the fabricated diffuser, and the fine bubble diffuser provided the best gas transfer. The fine bubble diffuser appeared to provide adequate mixing in the ASTR.

Table 1. Chemical analysis of two untreated manure sources: Dissolved reactive phosphorus (DRP), Total Phosphorus (TP), Total Kjeldhal Nitrogen (TKN), Ammonium (NH₄), Total Solids (TS)

<table>
<thead>
<tr>
<th>Source</th>
<th>DRP, mg/L as PO₄³⁻</th>
<th>TP, mg/L as PO₄³⁻</th>
<th>TKN, mgN/L</th>
<th>NH₄, mg NH₄-N/L</th>
<th>TS, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISU Teaching Shallow Pit</td>
<td>264 ± 26</td>
<td>2190 ± 35</td>
<td>2950 ± 60</td>
<td>1460</td>
<td>3.9 ± 0.1</td>
</tr>
<tr>
<td>Ames Producer Covered Storage</td>
<td>770 ± 19</td>
<td>990 ± 80</td>
<td>--</td>
<td>--</td>
<td>4.6 ± 0.1</td>
</tr>
</tbody>
</table>

ASTR-UFC Performance

Manure collected from the covered storage tank at the commercial swine production site (Ames, IA) was used for the 110-minute treatment with the ASTR-UFC system for the reduction of DRP during pre-aeration and continuous flow operation, and TP removal performance of the UFC. Pre-aeration provided a pH increase from 7.64 to 8.15 in the ASTR. Figure 5 provides the analysis of DRP and TP for the duration of the 110-minute treatments. The ASTR-UFC system indicated that the ASTR provided an average DRP reduction of 95% with manure from the covered storage for the 80 minutes of continuous flow operation. There was no increase in phosphorus reduction in the ASTR using the longer 80 minute run-time when compared to the 30 minute run time. As such, the extended continuous flow treatment time did not affect the ASTR’s ability to precipitate struvite. The sample collected after pre-aeration and prior to magnesium injection provided a 68% reduction in DRP. Total phosphorus comparisons of the ASTR influent and UFC effluent indicated that there was no significant removal of total phosphorus through the system.
**Discussion**

The test of the ASTR treatment system provided an average DRP reduction of 78% with the manure from the shallow pit storage under continuous flow operation. The test of the ASTR-UFC system indicated that the ASTR provided an average DRP reduction of 95% with manure from the covered storage for the duration of continuous flow operation. The difference between DRP reduction rates between the two manures tested is most likely due to the amount DRP available for struvite precipitation and its relation to the conditional solubility product of struvite. Manure from the covered storage tank had a higher initial DRP content (770mg/L) than the manure collected from the shallow pit storage (264 mg/L). Ohlinger et al. (2000) indicated that a decrease of any contributing species decreases the conditional solubility product of the system and reduces the precipitation potential of struvite. If DRP is reduced significantly, the conditional solubility product and struvite precipitation potential will also decrease. This indicates that the reduction of DRP within the ASTR can limit the precipitation potential of struvite and thus limit the overall phosphorus removal capabilities. The ASTR treatment provided an average DRP effluent concentration of 41 mg/L using the manure from covered storage and 64 mg/L using the manure from the under floor shallow pit.

The initial step in struvite precipitation is pH adjustment. Ohlinger et al. (2000) also found that the solubility of struvite was highly pH dependant; as pH increases within a system, the precipitation potential of struvite is increased. Changes in solution pH affect the solubility of struvite and ammonia availability. Burns et al. (2003) indicated that raising the pH of swine wastes provided much better phosphorus removal through struvite precipitation; however, consideration of chemical and energy costs should be accounted for when determining the pH adjustment level to provide the most economically feasible treatment system while maintaining appropriate phosphorus removal rates. Burns et al., typically increased swine manure pH by one unit during their study. Typical swine manures usually have a pH near 7.5, indicating a pH increase of one unit is required. The ASTR provided an adjustment of 0.5 units; further pH adjustment may achieve higher phosphorus removal rates.

The analysis of the manure from the two different storage facilities following ASTR treatment indicates that the pre-aeration step provided a significant reduction of DRP without magnesium addition, (50% and 68% in samples tested). Two mechanisms can be identified that account for this reduction: magnesium was present prior to treatment allowing for struvite formation after pH adjustment, or phosphate was precipitated as another species such as calcium phosphate, brushite, or monetite. Magnesium is common in most ground water sources and is associated with water hardness; furthermore, some magnesium salts, albeit small amounts, are commonly used in swine rations. Laboratory analysis of magnesium in the raw manure was not performed and X-ray diffraction was not used to identify the precipitated species. Further investigation during pilot-scale studies should include initial magnesium analysis of raw manures and may provide sufficient quantities of recoverable precipitants for quantification of precipitant species.

Several chemicals can be utilized for phosphate removal in wastewaters. The most common include lime, ferric and aluminum salts, magnesium hydroxide (Mg(OH)₂), magnesium oxide (MgO), and magnesium chloride (MgCl₂). Adding lime or metal salts does not precipitate struvite; however they do complex with phosphate to from precipitants under the same principles. Magnesium hydroxide, MgO, MgCl₂, are all viable magnesium sources to force struvite formation. Magnesium hydroxide and MgO have low solubility characteristics and would require dissolving in water (slaking) prior to amendment similar to lime softening systems for effective implementation. Without slacking prior to amendment, the reaction times required for struvite precipitation would be significantly increased due to the low solubility of Mg(OH)₂ and MgO, 0.0012 g/100g H₂O and 0.00062 g/ 100g H₂O, respectively. Slaking systems are difficult to operate with consistency and can create issues with amendment accuracy. Miles and Ellis (2001) utilized Mg(OH)₂ and MgO to force precipitation; however, the low solubility and precipitation potential of Mg(OH)₂ prior to amendment reduced amendment accuracy. Magnesium hydroxide and MgO increase the pH of the solution, reducing the pH adjustment requirement for optimized struvite precipitation. Magnesium chloride has a high solubility, 54.2 g/100g H₂O, which makes it easier to handle and reduces the required reaction time in comparison to Mg(OH)₂ and MgO (Burns et al. 2001). However, MgCl₂ is acidic and may reduce solution pH, requiring greater pH adjustment to optimize struvite precipitation. For agricultural applications, the use of MgCl₂ can reduce equipment cost and labor while increasing the accuracy of dosing when compared to the use of less soluble magnesium compounds.
The incorporation of the UFC did not provide a significant reduction of TP. These results indicate that the settling characteristics of the manure and particle characteristics of the precipitated phosphorus did not allow for continuous removal of phosphorus with the ASTR-UFC system. Phosphorus removal strategies that could be incorporated with the ASTR system include operating the ASTR as a sequencing batch reactor, or providing forced gravitational separation in place of the UFC. Further experimentation with other methods of struvite recovery, such as centrifuging the ASTR treated manure will be conducted in the future to identify the capability for solids separation and TP reduction following treatment.

Methods of struvite recovery, such as centrifuging the ASTR treated manure will be conducted in the future or providing forced gravitational separation in place of the UFC. Further experimentation with other techniques and their ability to remove struvite and precipitated phosphorus from ASTR treated manure slurries and determine the economic feasibility of ASTR manure treatment.

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