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Method for Recovery of Phosphorus from Animal Wastewater

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ABSTRACT

A wastewater treatment process and systems were developed to extract and concentrate phosphates from livestock wastewater. The research was conducted over a 10-year period and went from initial bench studies to pilot module development to full-scale demonstrations of the phosphorus module on swine farms and current licensing and commercialization by industry. The basic process is based on the distinct chemical equilibrium between phosphorus and calcium ions when natural buffers are substantially eliminated, which substantially reduces chemical addition. The precipitated phosphorus is recovered in a marketable form. The concentration grade obtained during full-scale demonstration was 24.4 ± 4.5% P_2O_5. The recovered calcium phosphate can be recycled into a marketable fertilizer without further processing due to its high content (> 90%) of plant available phosphorus. The process has several positive implications. Removing phosphorus from wastewater can cut down on any excess, which is not absorbed from the soil by plants and instead washes away as runoff into streams and rivers. Large amounts of the nutrient can lead to oxygen depletion in water bodies. During processing, hydrated lime precipitates most of the phosphorus in the wastewater as a solid and converts it into a marketable calcium phosphate fertilizer. This phosphorus could be very useful to the fertilizer industry because world reserves of the nutrient are limited. Another benefit is that the high pH achieved by the P module destroys disease-causing pathogens present in the leftover manure liquid. A second generation system includes simultaneous separation of solids and phosphorus from wastewater and industrial effluents. The combined separation process is more efficient in terms of equipment needs and chemical use. Thus, it reduced installation and operational cost of phosphorus treatment.

KEYWORDS: Phosphorus recovery, calcium phosphate, swine wastewater, soluble phosphate

INTRODUCTION

The aspect of phosphorus (P) reuse is important for crop producers because of increasing demand and cost of inorganic fertilizers. The merging of food and fuel economies has increased the demand of mineral P fertilizer, and its price increased over 200% in 2007 (Trostle, 2008). The increased P demand may stimulate new technologies and economic opportunities for P recovery from manure, especially using technologies that produce concentrated byproducts with nutrient values that compete with mineral fertilizers.

Although solids-liquid separation is effective for removal of organic P forms in liquid manure, it is not effective for removal of the soluble P. Techniques for P removal from wastewater by precipitation of calcium phosphate are classified into three groups: crystallizers, fluid bed reactors, and the P precipitation process inventions described in this paper (Reindl, 2007). The technology was developed to remove soluble P from animal wastewater and other high-ammonia strength effluents and has the advantage over the previous art of requiring minimal chemical addition and producing a valuable by-product (Vanotti *et al*. 2005, Vanotti *et al*. 2010, Bauer *et al*. 2007). It is based on the distinct chemical equilibrium between phosphorus and calcium ions when natural buffers (NH_4-N and alkalinity) are substantially eliminated.

Another method of removing P by chemically treating the wastewater is through struvite ($MgNH_4PO_4.6H_2O$) precipitation. Struvite forms from 1:1:1 ratios of Mg, NH_4 and PO_4 in theory compared to typical ratios of 1:16:1.2 in liquid manure. Addition of $MgCl_2$ and NaOH or $MgCl_2$ and NaOH + phosphate have been used to balance the stoichiometric ratio and optimize struvite precipitation.

While various systems have been developed for removing P from wastewater, there still remains a need for improved systems that remove and recover the P in concentrated purified forms. A wastewater treatment process and systems were developed to extract and concentrate phosphates from livestock wastewater. The research was conducted over a 10-year period and went from initial bench studies to pilot module development to full-scale demonstrations of the P module in swine farms and current commercialization by industry. The objective of this paper is to summarize the research process in this development from bench to full-scale.

BASIC PROCESS CONFIGURATION

The basic process (US Patent 6,893,567, Vanotti et al. 2005) comprises 1) a first step of providing wastewater having reduced levels of carbonate and ammonium buffers, and reduced levels of suspended solids to a reactor vessel; and 2) a second step that consists of adding an alkaline earth base to said wastewater to precipitate soluble phosphate. The alkaline earth base can be selected from the group consisting of calcium hydroxide, magnesium hydroxide, calcium oxide, magnesium oxide, and their mixtures.

In wastewaters containing phosphate and ammonia, an effective way to remove the carbonate and ammonium buffers is through nitrification (Figure 1). In another embodiment of US Patent 6,893,567, the process involves 1) providing a nitrified wastewater having reduced levels of suspended solids to a reactor vessel; and 2) adding Ca or Mg hydroxide to said nitrified wastewater to increase pH of the nitrified wastewater to at least about pH 9 to precipitate and recover phosphate (Vanotti *et al.* 2005). In this situation, since NH_4^+ is mostly converted to NO_3^-, increased pH during P precipitation does not result in significant gaseous N loss of ammonia. The final product is a Ca phosphate-rich sludge that can be used as P fertilizer.

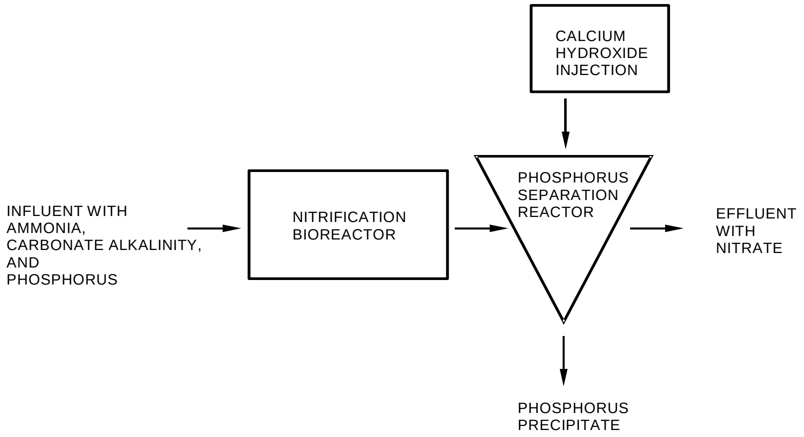


Figure 1. Schematic showing the basic configuration of the P removal process (Vanotti *et al.* 2005).

PROCESS CHEMISTRY

Animal wastewater is a mixture of urine, water, and feces. Livestock urine usually contains more than 55% of the excreted N of which more than 70% is in the form of urea (Sommer and Husted, 1995). Hydrolysis of urea by the enzyme urease produces NH_4^+ and carbonate according to the following reaction:

$$CO(NH_2)_2 + 2H_2O \rightarrow 2NH_4^+ + CO_3^{2-} \qquad (1)$$

Therefore, a substantial part of the inorganic carbon in liquid manure is produced during decomposition of organic compounds. Carbonate and NH_4^+ alkalinity are the most important chemical components in liquid manure contributing to the buffering capacity in the alkaline pH range (Fordham and Schwertmann, 1977; Sommer and Husted, 1995). Alkaline pH is necessary to form a P precipitate with Ca and Mg compounds (House, 1999). When a Ca or Mg hydroxide is added to liquid manure, the hydroxide reacts with the existing bicarbonate to form carbonate, with NH_4^+ to form ammonia (NH_3), and with phosphate to form phosphate precipitate compounds (Loehr *et al.* 1976; Tchobanoglous and Burton, 1991). For instance, using Ca hydroxide as an example, the following equations define the reactions:

$$Ca(OH)_2 + Ca(HCO_3)_2 \rightarrow 2CaCO_3 \downarrow + 2H_2O \qquad (2)$$

$$5\,Ca^{++} + 4OH^- + 3HPO_4^= \rightarrow Ca_5OH(PO_4)_3 \downarrow + 3H_2O \qquad (3)$$

The reaction in equation 2 is complete at $pH \geq 9.5$, while that of equation 3 starts at $pH > 7.0$, but the reaction is very slow at $pH \leq 9.0$. As the pH value of the wastewater increases beyond 9.0, excess Ca ions will then react with the phosphate, to precipitate as Ca phosphate (eq. 3). Not expressed in equation 2 is the fact that in wastewater containing high NH_4^+ concentration, large amounts of lime are required to elevate the pH to required values since NH_4^+ reaction tends to neutralize the hydroxyl ions according to equation 4:

$$Ca(OH)_2 + 2NH_4^+ \rightarrow 2NH_3\uparrow + Ca^{++} + 2H_2O \qquad (4)$$

Consequently, precipitation of phosphate in animal wastewater using an alkaline compound such as lime is very difficult due to the inherent high buffering capacity of liquid manure (NH_4-N $\geq$ 200 mg L^{-1} and alkalinity $\geq$ 1200 mg L^{-1}). The buffer effect prevents rapid changes in pH.

However, this problem is solved using a pre-nitrification step that reduces the concentration of both NH_4^+ (eq. 5) and bicarbonate alkalinity (eq. 6) (Vanotti *et al.* 2005):

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O \qquad (5)$$

$$HCO_3^- + H^+ \rightarrow CO_2\uparrow + H_2O \qquad (6)$$

The buffering effect of NH_4^+ (eq. 4) is reduced by biological nitrification of the NH_4^+ (eq. 5). Simultaneously, the buffering effect of bicarbonate (eq. 2) is greatly reduced with the acid produced during nitrification (eq. 6). These two simultaneous reactions leave a less buffered liquid in optimum pH conditions for phosphate removal with the addition of small amounts of lime (eq. 3).

The experiment shown in Figure 2 summarizes the process chemistry described above. The pH in the control (without nitrification pre-treatment) was not significantly increased by lime treatment; it varied little from 8.05 to 8.27. As a consequence, phosphorus removal rates were low (about < 34%; Figure 2). This illustrates that precipitation of phosphate in animal wastewater using an alkaline earth metal-containing compound, such as hydrated lime for example, is very difficult due to the inherently high buffer capacity of these wastes (NH_4-N and alkalinity. This contrasts with results obtained by biologically treating the wastewater and subsequently chemically treating the clarified wastewater that is low in solids and natural buffers; the pH increased significantly up to about 12 and phosphorus removal increased to about 100% using exactly the same lime rates of the control. Thus, once ammonia and carbonate alkalinity concentrations are substantially reduced with a nitrification pre-treatment, the subsequent addition of $Ca(OH)_2$ rapidly increases the pH of the liquid above 9, thereby promoting formation of calcium phosphate precipitate with small amounts of chemical added.

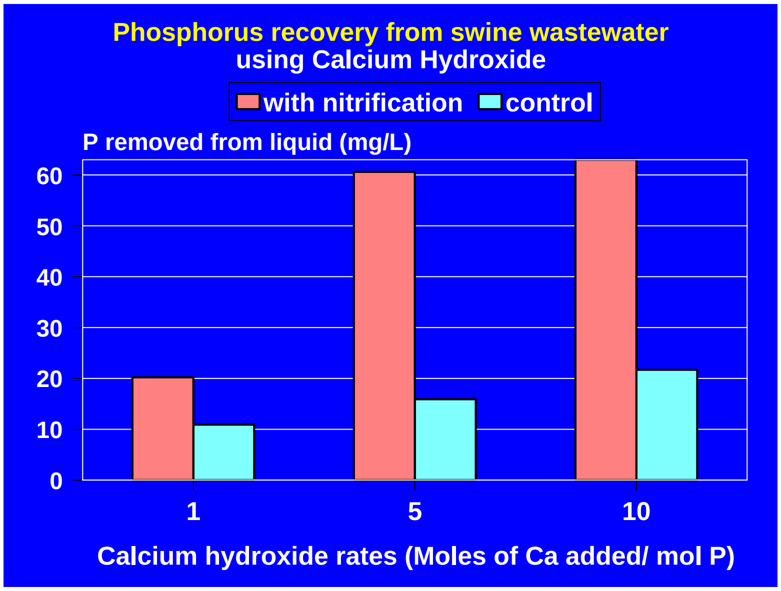


Figure 2. Effect of nitrification and hydrated lime addition on phosphorus removal from swine lagoon wastewater. The control is lagoon liquid without nitrification. Initial wastewater characteristics (control): pH 8.05, alkalinity 1890 mg/L, ammonia-N 300 mg/L. After nitrification: pH 6.06, alkalinity 63 mg/L, ammonia-N 61 mg/L. Highest bar is 100% P removal (Vanotti *et al.* 2005).

CASE EXAMPLE 1: PHOSPHORUS RECOVERY FROM WASTEWATER SWINE LAGOONS

A pilot demonstration was conducted at a swine production facility using lagoon liquid and the system shown in Figure 3. In this livestock system with anaerobic lagoons (or other anaerobic digesters), the anaerobically digested supernatant liquid, rich in NH_4-N and alkalinity, is nitrified and P is subsequently removed by adding hydrated lime. The pilot biological reactor was described by Vanotti *et al*. (2003). It consisted of a 0.34-m^3 contact aeration tank used to lower influent BOD, followed by a 0.18-m^3 sedimentation tank, and a 1.3-m^3 aerated fluidized tank for nitrification. The phosphorus reactor was placed after the nitrification reactor to precipitate and separate the phosphorus from the nitrified effluent. It consisted of a 379-L plastic tank with conical bottom and a mixer. A smaller 114-L tank and mixer was used to prepare the lime milk (2% hydrated lime mixture in water). A peristaltic pump connected to a pH controller was used to transfer the lime milk into the P-reactor. The chemical was a high ~~-~~purity, hydrated lime powder containing 98.5% $Ca(OH)_2$.

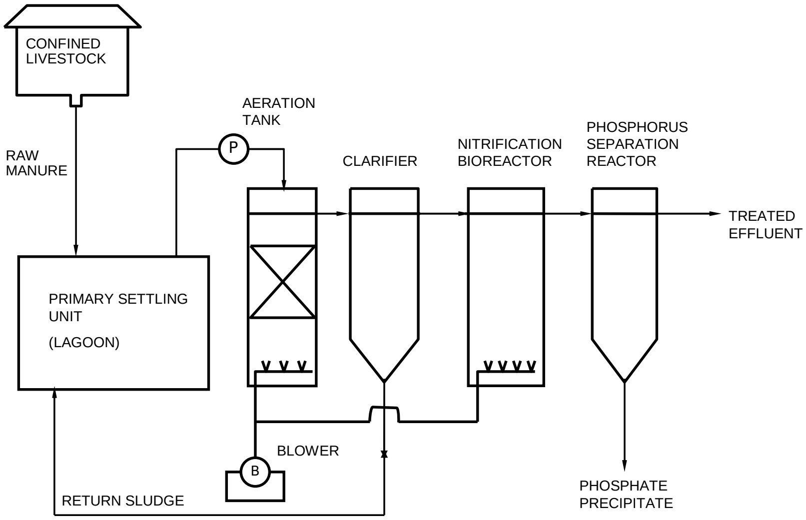


Figure 3. Schematic of the pilot unit used to remove phosphorus from swine lagoon liquid using a nitrification-lime application treatment sequence (Vanotti *et al*. 2003).

Phosphorus removal performance of the pilot system under field conditions was consistent with results obtained in the laboratory (Table 1). Phosphorus concentration was significantly decreased with treatment. Phosphorus removal efficiencies of 95% and 98% were obtained with pH treatment levels of 10.0 and 10.5, respectively, and corresponding Ca:P molar ratios of 2 and 2.5. In practice, the level of treatment added will depend on the degree of phosphorus removal desired and should be preferably added in the minimum quantity necessary to balance the N:P ratio of crops or to remediate sprayfields. Since ammonia nitrogen has been converted to nitrate, increased pH does not result in significant gaseous nitrogen loss. Therefore, the amount of phosphorus removed, and consequently the N:P ratio of the effluent, can also be adjusted in this process to match the N:P ratio needed by the growing crop to which it will be applied. For example, a final N:P ratio of 10.7:1 and 13.4:1 would be needed to match wheat and coastal bermudagrass specific nutrient uptake needs, respectively, which can be delivered with about < 1 Ca:P molar ratio treatment (Table 1). Although the amount of precipitate substantially increased with lime application, phosphorus and calcium content of the precipitate changed little (16-17% P_2O_5 and 22-28% Ca) indicating that most of the chemical applied was selectively used to precipitate P.

Table 1. Performance of field prototype used to remove and recover phosphorus from lagoon swine wastewater in Duplin County, N.C., using biological treatment and chemical phosphorus precipitation (Vanotti *et al*. 2005)

Treatment (a)	pH	$Ca(OH)_2$ Applied mg/L	Ca:P Molar Ratio (b)	Alkalinity mg/L	NH_4-N mg/L	Total N mg/L	Total P mg/L	N:P Ratio (c)
Influent (Lagoon liquid)								
	7.7	--	--	1738	278	320	71.9	4.45
Effluent after Nitrification Pre-treatment								
	7.7	--	--	532	10	300	65.4	4.59
Effluent after Phosphorus Precipitation								
1	9.0	141	0.82	511	8	303	25.5	11.9
2	9.5	271	1.58	570	8	301	11.1	27.1
3	10.0	344	2.00	557	6	299	3.3	90.6
4	10.5	433	2.52	545	5	299	1.6	186.9

(a)Treatment: Hydrated lime liquid was injected into a stirred tank containing nitrified lagoon wastewater; a pH controller stopped injection when the pH of mixed liquid reached a set point of 9, 9.5, 10, or 10.5 (treatments 1 through 4, respectively). Once the desired treatment pH was reached, the precipitated solids were removed from the bottom of the tank after a 30-minute settling period.

(b) Ca:P molar ratio = Applied Ca : P in the influent.

(c) N:P ratio = Total N concentration : Total P concentration. Total N of treated effluent is mostly nitrate-N.

CASE EXAMPLE 2: PHOSPHORUS RECOVERY COMBINED WITH SOLIDS-LIQUID SEPARATION AND BIOLOGICAL N REMOVAL ON A PIG FARM

In another embodiment of the invention (US Patent 6,893,567, Vanotti *et al*. 2005), the phosphorus removal process is used in conjunction with liquid-solid separation and denitrification linked together into a practical system that provides total nitrogen (N) removal in addition to the P removal. It was developed to replace anaerobic lagoon technology commonly used in the USA to treat swine waste (Vanotti *et al*. 2007). This system for wastewater treatment comprises (Figure 4):

(a) a solid separation unit, wherein flocculants are used to clump suspended solids and increase separation efficiency,

(b) a denitrification unit in direct fluid communication with a clarified effluent from the solid separation unit,

(c) a nitrification unit in fluid communication with the denitrification unit,

(d) a phosphorus separation reactor unit in fluid communication with a liquid effluent from the nitrification unit, and

(e) a clarification unit in fluid communication with said nitrification unit and said phosphorus separation unit.

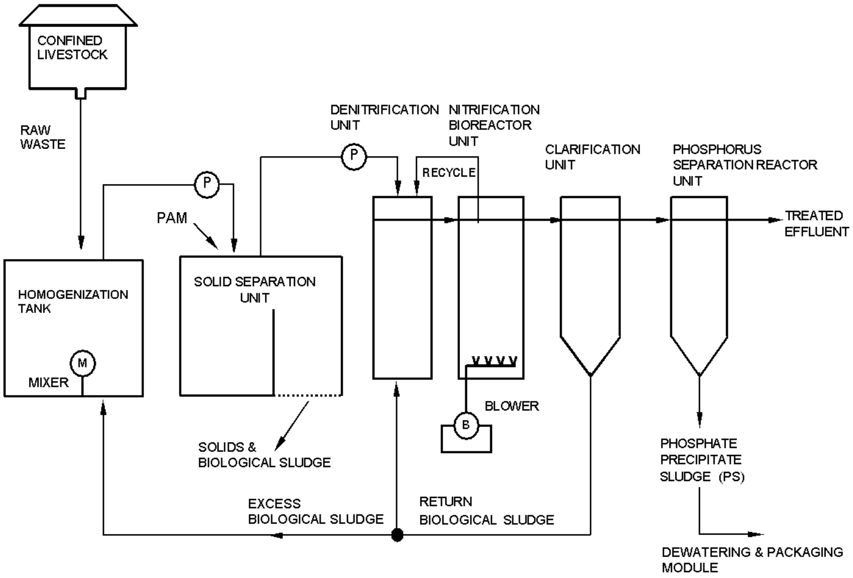


Figure 4. Schematic drawing of the swine waste treatment system without lagoon. The soluble P is removed after liquid-solid separation and ammonia removal (Vanotti *et al.* 2007).

This configuration was tested full-scale on a finishing swine farm in North Carolina with removal efficiencies of 94% for soluble P (Vanotti *et al.* 2007). In this complete system, raw liquid manure is first treated through an enhanced solid-liquid separation process with polymers to remove most of the carbonaceous material from the wastewater. The separated water is then treated with the nitrification/denitrification; the liquid is clarified and then chemically treated to remove the soluble P.

The separation of solids from raw flushed manure was done using polyacrylamide (PAM) polymer flocculant. Prior to entering the solid-liquid separation unit, the raw flushed manure was well mixed in a 388-m^3 homogenization tank. Solids were separated using a solid-liquid separation module (Selco MC, Castellon, Spain) that included injection of cationic PAM, removal of flocculated solids in a rotary screen, dewatering solids in a belt press, and further separation of residual solids in a dissolved air flotation unit. The separated manure solids were transported off-site to a centralized solids processing facility and converted to organic plant fertilizer, soil amendments, and plant growth media, or used for energy production. The second process unit treated the liquids after solid separation using a biological N removal system. The project used the Biogreen process (Hitachi Plant Engineering & Construction Co., Tokyo, Japan) that removed N via nitrification/denitrification (NDN) processes. Nitrification was performed in an aeration tank (110-m^3) that used nitrifying bacteria immobilized in polymer gel pellets (12-m^3) to increase concentration and effectiveness of bacterial biomass. Air was provided with an 11.2 kW, rotary lobe blower. Hydraulic retention time (HRT) of nitrification averaged 2.8 d. Nitrification transformed NH_4-N into NO_3-N and depleted > 80% of bicarbonate alkalinity. A pre-denitrification configuration transformed NO_3-N into N_2 gas where nitrified wastewater was continually recycled to a 263-m^3 anoxic denitrification tank at a rate average of 4.4 times the inflow rate. In this tank, suspended denitrifying bacteria (3-6 g L^{-1} mixed liquor suspended solids) used soluble manure carbon contained in the separated liquid to remove the NO_3^- . Thus, elimination of ammonia and reduction of carbonate buffering during biological N removal treatment allowed the recovery of P from the liquid when small amounts of lime were added in the third treatment module (Vanotti et al., 2005).

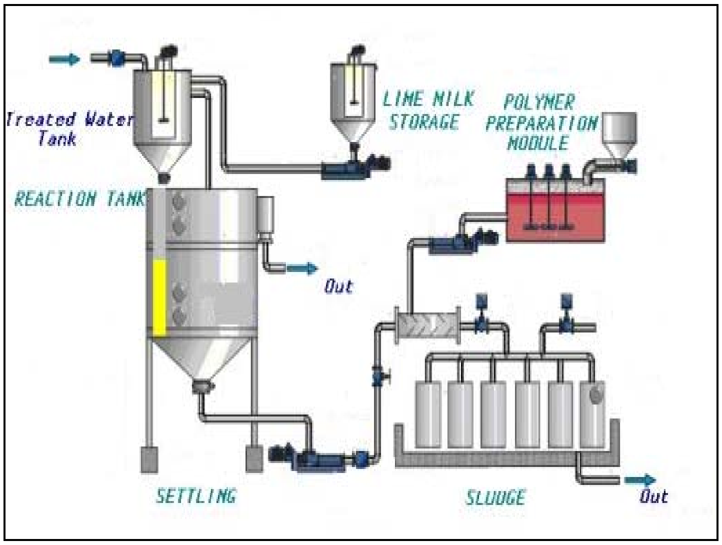


Figure 6. Schematic diagram of phosphorus precipitation and dewatering module used on pig farm.

Figure 7. Phosphorus precipitation and dewatering module on pig farm. Pictures above show reaction chamber and settling tank, and pictures below show dewatering and bagging of the phosphorus precipitate.

After biological N treatment, the effluent was discharged into a 299-m^3 tank that stored water needed to recharge pits under the barns after barns were flushed. Excess water flowed by gravity from this storage tank into the phosphorus separation module (Figures 6 and 7). This was the third and final process unit in the system. It was designed to recover soluble P (as calcium phosphate) and destroy pathogens by alkaline pH. In this module, liquid was first mixed with hydrated lime slurry in a reaction chamber. The lime slurry was a 30% $Ca(OH)_2$ suspension supplied in standard tote containers and ready to use (Chemical Lime Company, Charlotte, NC). A pH probe and controller linked to the lime injection pump kept the process pH at 10.5. The liquid and precipitate were subsequently separated in a 9-m^3 settling tank. The precipitated calcium phosphate was removed from the bottom of the tank with a pump and it was further dewatered using a 12-filter bag Draimad unit that also bagged the sludge (Teknobag-Draimad, Aero-Mod, Inc., Manhattan, KS). Anionic polymer was added in-line to the P precipitate to enhance separation by filter bags (Szogi et al., 2006). Bags containing the wet calcium phosphate were left to dry on a drying concrete pad and removed from the farm on a monthly basis. Process automation was provided by sensors integrated to a programmable logic controller (PLC) for 24 hours per day operation. Treatment parameters such as process pH or frequency of sludge transfer were set by the operator using a tactile screen located in the plant control panel. Clarified effluent from the P module was stored in the existing lagoon before use in crop irrigation.

Results obtained at full-scale on a 4360-swine farm showed removal efficiencies of the soluble P of 94.7% for wastewater containing 76 to 197 mg L^{-1} soluble P (Figure 8). On average, the advanced treatment system reduced total N (TKN + NO_3-N) concentration from 1503 to 261 mg L^{-1} (83% reduction) and TP from 566 to 26 mg L^{-1} (95% reduction) (Table 2). In addition to substantial reductions in land requirement due to the reduced N and P loads after advanced treatment, the N:P ratio of the liquid was improved from 2.65 to 10.04. This higher N:P ratio resulted in a more balanced effluent from the view of crop utilization. The biological N removal step eliminated 97% of the NH_4^+-N and substantially reduced bicarbonate alkalinity (from 5,001 to 624 mg/l) which, in turn, affected the succeeding P separation step by promoting formation of calcium phosphate with smaller amounts of lime added. The average lime consumption to reach the set point pH of 10.5 was 567 g/m^3. Although a high pH in the phosphorus removal process is necessary to produce calcium phosphate and kill pathogens, the treated effluent is poorly buffered, and the high pH decreases readily once in contact with the CO_2 in the air. For example, short-term (2.5-h) aeration treatment of the effluent could create enough acidity to lower the pH from 10.5 to 8.5. However, natural aeration during storage may be equally effective to lower pH (Vanotti and Szogi, 2008).

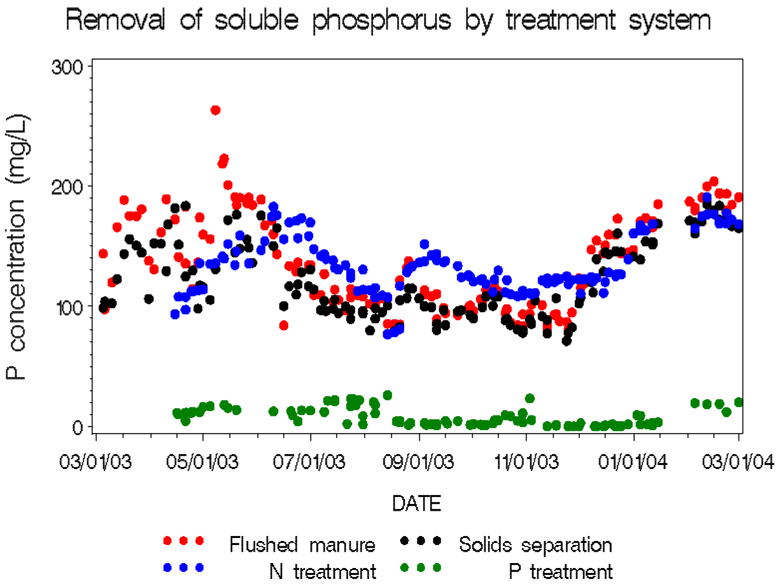


Figure 8. Removal of soluble phosphorus from flushed swine manure (red) as it passes through the treatment system that used solid-liquid separation (black), biological N removal (blue), and phosphorus removal (green). One year period at full scale (4,360 pigs).

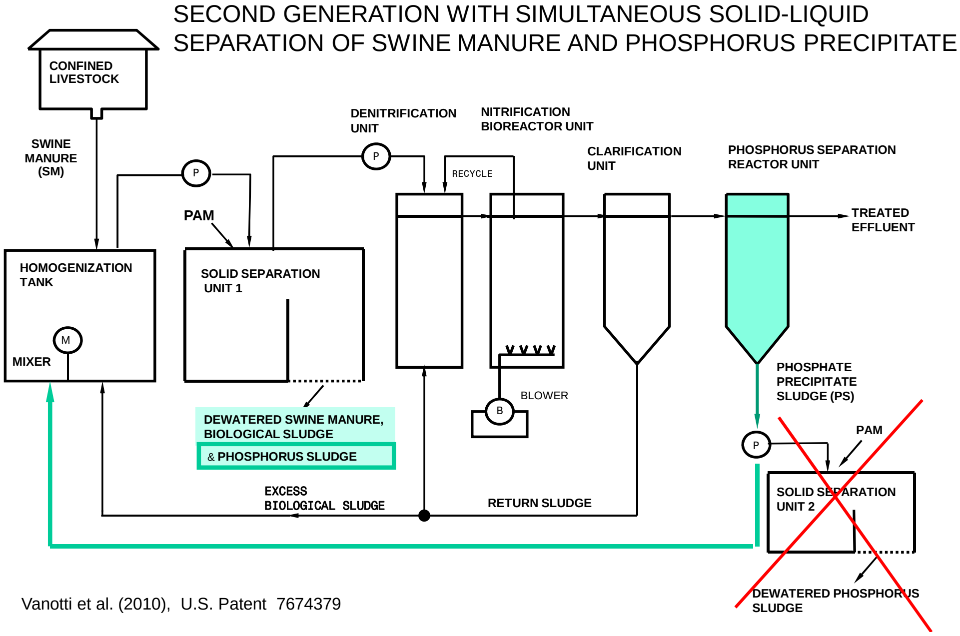
A total of 285 bags of calcium phosphate product containing 526 kg of P was produced and left the farm during a 9-month period. The concentration grade was 24.4 ± 4.5% P_2O^5. Each bag weighed an average of 34.8 kg and contained 23.3% solids. The phosphorus was > 90% plant available based on standard citrate P analysis used by the fertilizer industry.

Table 2. Wastewater treatment plant performance and system efficiency at Goshen Ridge Farm, North Carolina. Data are means (± s.d) for 18-month period (Vanotti and Szogi, 2008)

		Treatment Step			
Water Quality Parameter	Raw Flushed Swine Manure	After Solid-Liquid Separation	After Biological N Treatment	After Phosphorus Treatment	System Efficiency
	------------------------------mg L^{-1} ‡		----------------------------		%
TSS	11,612± 6746	811 ± 674	134 ± 75	232 ± 152	98.0
BOD_5	3046±2341	923 ± 984	40 ± 44	10 ± 16	99.7
TKN	1501 ± 567	895 ± 298	43 ± 34	26 ± 25	98.3
NH_4-N	838 ± 311	796 ± 297	31 ± 34	14 ± 19	98.3
NO_2+NO_3-N	1.5 ± 4.5	0.4 ± 2.6	228 ± 110	235 ± 116	--
TP	566 ± 237	168 ± 53	149 ± 33	26 ± 16	95.4
Soluble P	131 ± 39	116 ± 33	138 ± 28	7 ± 7	94.7
Alkalinity	5001±1695	4154± 1463	624 ± 470	763 ± 353	84.7
pH	7.64 ± 0.22	7.93 ± 0.26	7.29 ± 0.70	10.53 ± 0.63	--

CASE EXAMPLE 3: PHOSPHORUS PRECIPITATION AND SIMULTANEOUS SOLIDS-LIQUD SEPARATION OF SWINE MANURE SOLIDS AND PHOSPHORUS PRECIPITATE

One possible simplification of the foregoing system is to simultaneously separate and dewater the phosphorus sludge (PS) and liquid swine manure (SM), producing only one solids stream consisting of manure solids enriched with P (Figure 9). The modification retains all the system's environmental benefits of removing soluble P and pathogens from the final liquid effluent using the P removal module. However, the main advantage of this innovation is the reduction of capital and operational expenses that results from having one solid-liquid separation unit in the treatment plant vs. two solid-liquid separation units (one for SM and another for PS). However, characteristics of SM and PS are so different that the type of polymer recommended for solid-liquid separation of each material is also very different. For example, flocculation and separation of SM are optimized with positively charged (cationic) PAM, and neutral or negatively charged (anionic) PAMs are not useful for this application (Vanotti and Hunt, 1999). By contrast, flocculation and separation of alkaline calcium phosphate sludge (PS) are optimized with anionic PAM (Szogi et al., 2006).



Vanotti et al. (2010), U.S. Patent 7674379

Figure 9. Schematic drawing of a wastewater treatment system with simultaneous separation of phosphorus and manure solids (Vanotti *et al.* 2010).

We conducted bench-scale research to determine the feasibility and optimize the conditions for the simultaneous separation of SM and PS with PAM (Garcia *et al.* 2007). These and other improvements were incorporated into a second-generation system to lower equipment and operational costs (Vanotti *et al*. 2009, 2010).

Feasibility of Simultaneous Separation of Phosphorus Sludge and Manure Solids in Bench Tests

Our objectives were to evaluate if it is technically feasible to flocculate and dewater both the phosphorus sludge (PS) and raw swine manure (SM) in a simultaneous operation, using the same dewatering equipment and producing only one stream of solids. The simultaneous separation concept was tested in a laboratory prototype using PS and SM materials from a first-generation version of the system without a lagoon installed on a swine farm in North Carolina (Figure 9). Compared with SM, the PS material had a higher pH (10.1 vs. 7.5), about 5 times more total suspended solids (TSS) (29.5 vs. 5.7 g L^{-1}), and 9 times the total P (2.7 vs. 0.3 g L^{-1}).

We found that the calcium phosphate precipitate generated with the soluble P removal process does not re-dissolve when mixed with SM; therefore, it is amenable for simultaneous separation with PAM. Although SM and PS solids have contrasting chemical characteristics, they can be efficiently (>90%) separated using a single polymer application of cationic PAM. The simultaneous separation process did not increase the amount of PAM that would normally be used to effectively treat SM alone. The same dosage of PAM (60 mg L^{-1}) was effective even when the mixture contained 43% more TSS and 94% more TP as a result of PS addition (up to 150 mL L^{-1}). PAM effectiveness in terms of TSS or TP increased with the simultaneous separation process, from 108 to 160 g TSS g^{-1} PAM, and from 4.7 to 11.4 g TP g^{-1} PAM. Mass removal efficiencies at the higher PS rate were 96.8% for TSS and 94.7% for TP.

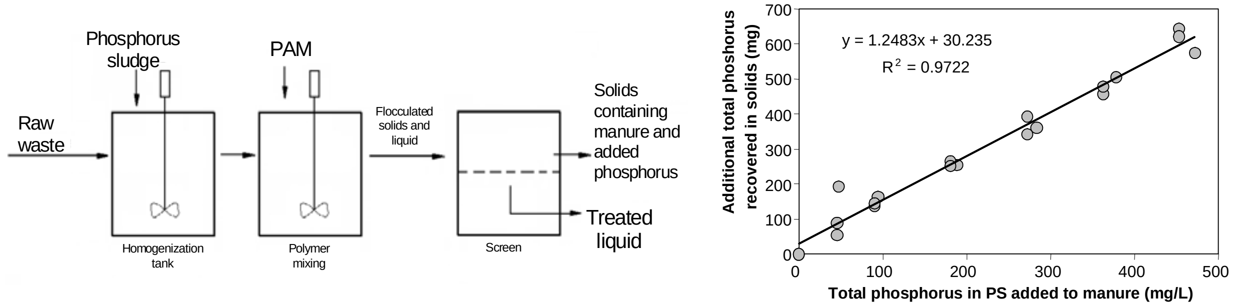


Figure 10. Schematic drawing of bench experiment that mixed raw swine manure (SM) and phosphorus precipitate sludge (PS) and used polymer flocculation (PAM) to dewater the mixture. Results showed quantitative recovery of the phosphorus contained in the phosphate precipitate sludge without additional PAM usage (Garcia *et al*. 2007).

When one considers only the incremental P recovery in the solids (above that originally contained in the manure), the simultaneous separation process produced a quantitative recovery of the P in the PS that was added to the SM (Figure 10). The quality of the treated liquid in terms of TSS, COD, and TP concentrations was also improved, and the P content of the separated solids was significantly increased (from 9.5% to 16.9% P_2O_5). Our results indicate that simultaneous separation of two contrasting sludges with PAM is technically feasible, and that the combined separation process is more efficient in terms of polymer use and equipment needs compared with a situation in which two dewatering units are used to separate the same amount of solids. Thus, its implementation can reduce installation and operational costs of the overall treatment system.

Phosphorus Precipitation and Simultaneous Solid-liquid Separation Demonstration in Full-scale Pig Operation

The lower-cost, second generation version of the technology (U.S. Patent No. 7,674,379, Vanotti *et al*. 2010) was evaluated at full-scale as part of Environmentally Superior Technology (EST) demonstration (Vanotti et al., 2009). The system used solids separation, nitrification/denitrification, and phosphorus removal/disinfection (Figures 11 and 12) and was demonstrated at full-scale on a 5,145-head swine farm during three production cycles (15 months). The plant was constructed and operated by Terra Blue Inc. (Clinton, N.C.).

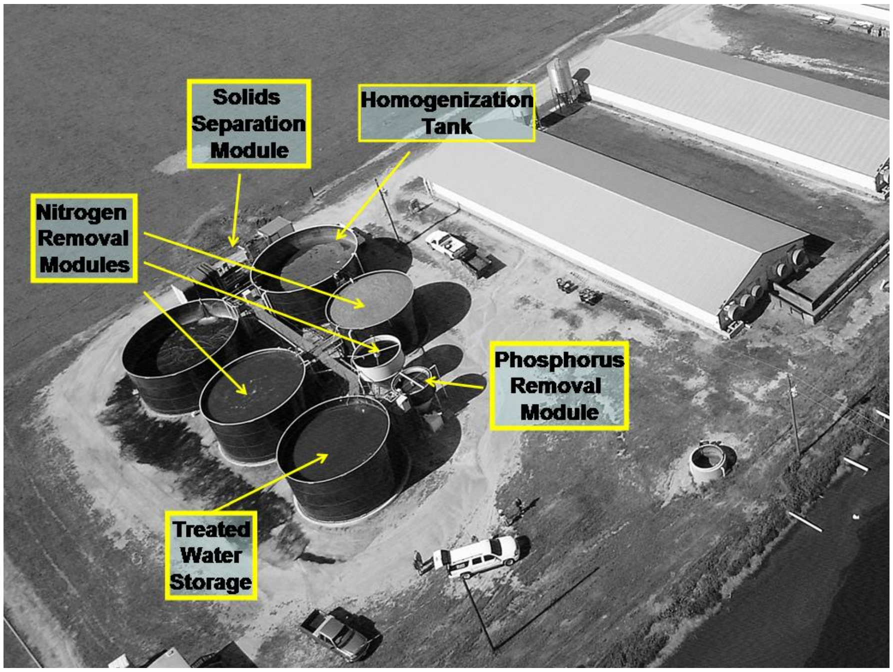


Figure 11. Aerial view of second generation swine waste treatment system with simultaneous separation of phosphorus and manure solids.

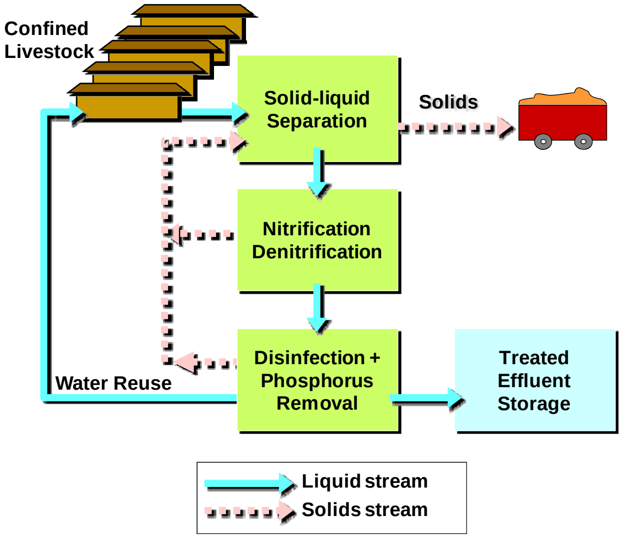


Figure 12. Schematic diagram of second generation swine waste treatment system with simultaneous separation of phosphorus and manure solids.

The separation process used polyacrylamide (PAM) flocculation to enhance the separation of fine suspended particles (Vanotti and Hunt 1999). Solids were separated with a rotary press separator. The polymer dosage was 128 mg L^{-1}. The separated wastewater was treated continuously in a nitrogen removal unit that used nitrification/denitrification (NDN). Nitrification was performed in an aeration tank (227 m^3) that used a high-performance nitrifying bacterial sludge (HPNS) adapted to high strength wastewater and cold temperatures (Vanotti *et al*. 2011). Air was supplied continuously with a 10-HP positive displacement lobe blower. A pre-denitrification configuration transformed NO_3 into N_2 gas where the nitrified wastewater was continuosly recycled into a 277-m^3 anoxic denitrification tank (DN) (Figure 9). The denitrification tank contained a submersible mixer. A settling tank (14.3 m^2) was used to clarify the effluent and return the suspended biomass solids to the DN tank (or wasting excess biomass to the separation module) (Figure 12). The height of the liquid in these tanks was 4 m. The rates of sludge and nitrified liquid recycling into the DN tank were 3.5 and 0.5 times the inflow rate, respectively. The clarified effluent was stored in a 277-m^3 clean water tank and re-used as needed to recharge barn pits after they were flushed. Excess water flowed by gravity from this storage tank into the third and last stage.

In the third stage, P was precipitated as a calcium phosphate solid, and pathogens were reduced by the alkaline environment). The effluent was mixed with hydrated lime slurry [12% $Ca(OH)_2$] in a 0.3-m^3 reaction chamber (Figure 13). The pH of the process was maintained at 9.5-9.7 by a pH probe and controller linked to the lime injection pump. The P precipitate was separated in a settling tank (8.8 m^2) (Figure 13), further dewatered using the solids separation unit in the first unit of the system (Garcia et al., 2007), and combined with the manure solids for off-farm transport (Figure 12). Clarified effluent from the P module was stored in the existing lagoon before use in crop irrigation.

Figure 13. View of reaction chamber, precipitate settling tank, and lime mixing tank in a phosphorus separation module at second generation project treating manure from 5145 pigs.

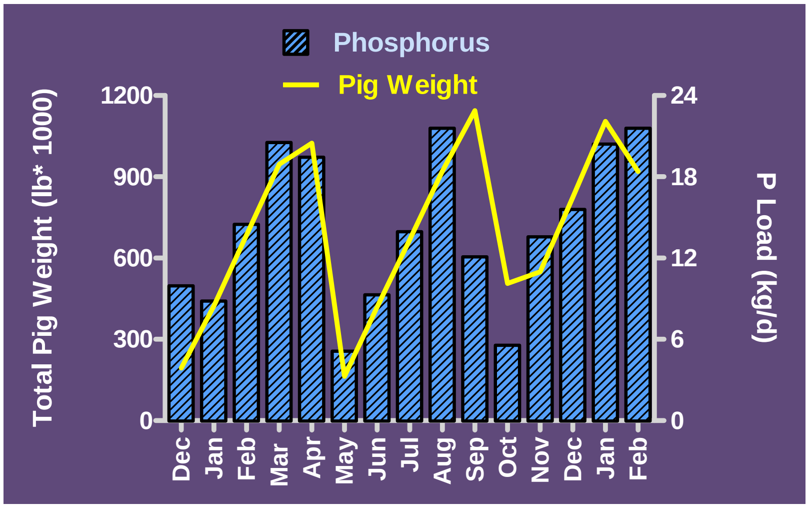


Figure 14. Changes in total phosphorus load (kg d^{-1}) into the wastewater treatment plant related to the changes in total weight of the pigs on the farm (5,145 pigs).

Table 3. Wastewater treatment plant performance and system efficiency at Tyndall Farm (5,145 pigs), North Carolina. Data are means (± s.d) of a 15-month evaluation period during three pig growing cycles (Vanotti *et al*. 2009)

Water Quality Parameter	Raw Flushed Swine Manure	Treatment Step After Solid-Liquid Separation	 After Biological N Treatment	 After Phosphorus Treatment	System Efficiency
	------------------------------mg L^{-1}		----------------------------		%
TSS	11,113± 6194	1212 ± 1032	219 ± 205	226 ± 225	97.1
BOD$_5$	6820±6084	3032 ± 2694	52 ± 50	38 ± 47	99.4
TKN	2007 ± 769	1414 ± 553	121 ± 127	83 ± 111	95.9
NH$_4$-N	1251 ± 616	1190 ± 455	103 ± 128	43 ± 79	96.6
NO$_2$+NO$_3$-N	1 ± 5	0	229 ± 182	156 ± 148	--
TP	494 ± 228	170 ± 79	85 ± 28	35 ± 21	92.9
Soluble P	86 ± 49	79 ± 37	73 ± 28	18 ± 16	79.5
Alkalinity	6883±2188	5372± 1540	1288 ± 875	1547 ± 815	77.5
pH	7.85 ± 0.33	7.81 ± 0.22	7.96 ± 0.53	9.71 ± 0.70	--

Data in Figure 14 shows the changes in total P load (kg d^{-1}) going into the wastewater treatment plant as affected by the changes in total weight of the pigs on the farm during three cycles of production (5,145 pigs). Removal efficiencies by the overall system were 98% suspended solids, 97% ammonia, 95% phosphorus, 99% copper and zinc (Table 3). In addition, the system removed 99.9% odors and 99.99% pathogens (Vanotti *et al.* 2009). The system met EST standards at 1/3 the cost of the previous version.

The biological N removal step eliminated >90% of the NH_4^+-N and substantially reduced bicarbonate alkalinity (from 5,372 to 1,288 g L^{-1}) which, in turn, affected the succeeding P separation step by promoting formation of calcium phosphate with smaller amounts of lime added. Removal efficiencies of the soluble phosphate using the P-removal unit (process pH = 9.5) averaged 75% for wastewater containing 13 to 125 mg L^{-1} PO_4-P (Table 3). They are lower than efficiencies of 94% obtained in Case Example 2 (Table 2) that used a process pH of 10.5. In the second generation project, we lowered process pH to economize lime use because a very high level of P treatment was not needed. To meet the EST standard for TP, a 50% reduction was sufficient. An important contribution of the P-removal unit with regards to meeting EST standards was helping meet the pathogen standard (4-log reduction) due to the high pH that, in addition to precipitate calcium phosphate, disinfects the effluent (Vanotti *et al.* 2005b)

SUMMARY AND CONCLUSIONS

Manure phosphorus in excess of the assimilative capacity of land available on farms is an environmental concern often associated with confined livestock production. A wastewater treatment process and systems of wastewater treatment were developed for removal of phosphorus from livestock wastewater as calcium phosphate. It includes biologically treating the wastewater to remove the ammonia and carbonate buffers and increasing the pH of the clarified wastewater by chemically treating it with an alkaline earth metal-containing compound to precipitate phosphorus. Since ammonia nitrogen has been mostly converted to nitrate or N_2, the increased pH does not result in significant gaseous nitrogen loss. The amount of phosphorus removed, and consequently the N:P ratio of the effluent, can be adjusted in this process to match specific crop needs. We tested three configurations of the technology on pig farms showing consistent results. In addition to the phosphorus removal aspect, the high pH used in the process destroys pathogens in liquid swine manure. The final product is calcium phosphate that has the potential to be reused as fertilizer or processed to produce phosphate concentrates.

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REFERENCES

Bauer, P., Szogi, A.A., and Vanotti, M.B. (2007) Agronomic effectiveness of calcium phosphate recovered from liquid swine manure. *Agron. J.* **99**(5):1352-1356.

Fordham, A.W., and Schwertmann, U. (1977) Composition and reactions of liquid manure (gulle), with particular reference to phosphate: III. pH-buffering capacity and organic components. *J. Environ. Qual.* **6**(1):140–144.

Garcia, M.C., Vanotti, M.B., and Szogi, A.A. (2007) Simultaneous separation of phosphorus sludge and manure solids with polymers. *Trans. ASABE* **50**(6):2205-2215.

House, W.A. (1999) The physico-chemical conditions for the precipitation of phosphate with calcium. *Environ. Technol.* **20**(7):727–733.

Loehr, R.C., Prakasam, T.B.S., Srinath, E.G., and Yoo Y.D. (1976) Development and demonstration of nutrient removal from animal wastes. U.S. Environmental Protection Agency, Washington, DC.

Reindl, J. (2007) Phosphorus removal from wastewater and manure through hydroxylapatite. An annotated bibliography. Available at: http://danedocs.countyofdane.com/webdocs/PDF/lwrd/lakes/hydroxylapatite.pdf

Sommer, S.G., and. Husted. S. (1995) The chemical buffer system in raw and digested animal slurry. *J. Agric. Sci. Cambridge* **124**(1):45–53.

Szogi, A.A., Vanotti, M.B., and Hunt, P.G. (2006) Dewatering of phosphorus extracted from liquid swine waste. *Bioresour. Technol.* **97**(1):183-190.

Tchobanoglous, G., and Burton, F.L. (1991) *Wastewater engineering: Treatment, disposal, and reuse*. Irwin/McGraw-Hill, Boston, MA.

Trostle, R. (2008) Global agricultural supply and demand: Factors contributing to the recent increase in food commodity prices. USDA – Economic Research Service, Outlook WRS-0801.

Vanotti, M. B., and Hunt, P.G. (1999) Solids and nutrient removal from flushed swine manure using polyacrylamides. *Trans. ASAE* **42**(6):1833-1840.

Vanotti, M. B., Szogi, A.A., and Hunt, P.G. (2003) Extraction of soluble phosphorus from swine wastewater. *Trans. ASAE* **46**(6):1665-1674.

Vanotti, M.B., Szogi, A.A., and Hunt, P.G. (2005) Wastewater treatment system. US Patent No. 6,893,567, Issued May 17, 2005. *U.S. Patent & Trademark Office*, Washington, D.C., USA.

Vanotti, M.B., Millner, P.D., Hunt, P.G., and Ellison, A.Q. (2005b) Removal of pathogen and indicator microorganisms from liquid swine manure in multi-step biological and chemical treatment. *Biores. Technol.* **96**:209-214.

Vanotti M.B., Szogi, A.A., Hunt, P.G., Millner, P.D., and Humenik, F.J. (2007) Development of environmentally superior treatment system to replace anaerobic swine lagoons in the USA. *Bioresour. Technol.* **98**(17):3184-3194.

Vanotti, M.B. and Szogi, A.A. **(**2008) Water quality improvements of CAFO wastewater after advanced treatment. *J. Environ. Qual.* **37**:S86-S96.

Vanotti, M.B., Szogi, A.A., Millner, P.D. and Loughrin, J.H. (2009) Development of a second-generation environmentally superior technology for treatment of swine manure in the USA. *Biores. Technol.* **100**(22):5406-5416.

Vanotti, M.B., Szogi, A.A., and Fetterman, L. (2010) Wastewater treatment system with simultaneous separation of phosphorus sludge and manure solids. U.S. Patent No. 7,674,379 B2. *U.S. Patent & Trademark Office*, Washington, D.C., USA.

Presentation at WEFTEC 2012, 85th Annual Water Environment Federation Technical Exhibition and Conference, New Orleans, Oct. 3, 2012.

Vanotti, M.B., Szogi, A.A., and Ducey, T.F. (2011) High performance nitrifying sludge for high ammonium concentration and low temperature wastewater treatment. US Patent Publication No. US2011/0000851. *U.S. Patent & Trademark Office*, Washington, DC.