Extraction of Soluble Phosphorus from Swine Wastewater

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Abstract. Manure phosphorus (P) 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 was developed for removal of phosphorus from livestock wastewater. It includes nitrification of wastewater and increasing the pH of the nitrified wastewater by adding an alkaline earth metal-containing compound to precipitate phosphorus to form an effluent having a specified nitrogen:phosphorus ratio that is useful as a balanced fertilizer or a low P fertilizer for remediation of contaminated soils. The presence of infectious microorganisms is reduced in the useable effluent. The precipitated phosphorus is recovered in a marketable form.

Keywords. Phosphorus removal, animal waste treatment, swine wastewater, N/P ratio, pathogens, CAFO, manure P, hog lagoons, sprayfield remediation.
Introduction

Manure nutrients in excess of the assimilative capacity of land available on farms are an environmental concern often associated with confined livestock production. For the USA as a whole, in 1997 about 20% of the 929 million pounds of farm-level excess phosphorus (P) exceeded the assimilative capacity at the county level (Kellogg et al., 2000). This means that a substantial amount of manure P needs to be moved at least off the farms and that some needs to be transported longer distances beyond county limits to solve distribution problems of this nutrient.

One of the main problems in sustainability of animal production is the imbalance between nitrogen (N) and P in the waste (Cochran et al., 2000; USEPA, 2001). Nutrients in manure are not present in the same proportion needed by crops. For example, the mean N:P ratio (4:1) in manure is generally lower than the mean N:P ratio (8:1) taken up by major grain and hay crops (USDA, 2001). Therefore, when manure is applied based on a crop’s nitrogen requirement, there is a P buildup in soil and increased potential for P losses through runoff and subsequent eutrophication of surface waters (Edwards and Daniel, 1992; Heathwaite et al., 2000; Sharpley et al., 2000).

Past research efforts on P removal from wastewater using chemical precipitation have been frustrating due to the large chemical demand and limited value of by-products, such as alum and iron sludges, or to both the large chemical demand and large losses of ammonia at the high pH that is required to precipitate phosphorus with calcium (Ca) and magnesium (Mg) salts (Loehr et al., 1973; Westerman and Bicudo, 1998). Other methods used for phosphorus removal include flocculation and separation of solids using polymer addition and filtration or settling (Vanotti and Hunt, 1999). Although polymer treatment is effective for removal of organic P forms in liquid manure, it is not effective for removal of the soluble P. This presents a problem in systems that use lagoons or other digestion or settling processes where most of the P in the liquid effluent is in the form of soluble phosphates.

In order to solve these problems, we have developed and filed a patent on a process to remove soluble phosphorus from animal wastewater (Vanotti et al., 2001). The process requires minimal chemical addition, reduces problems of ammonia emissions during separation of phosphorus from the aqueous phase, and recovers phosphorus in a reusable form. The process also enables precision control of the N:P ratio of the treated waste to desired levels to solve problems of phosphorus accumulation in soil or remediation of contaminated sprayfields.

Enhanced Phosphorus Removal with a Nitrification Pretreatment

We found that soluble phosphorus can be easily removed from animal wastewater, which has had a nitrification pre-treatment, in the form of an alkaline earth metal-containing phosphate that can be used as a fertilizer. In the process, carbonate and ammonium buffers contained in liquid waste must be at least reduced or eliminated during the nitrification pretreatment. This substantially reduces the overall chemical demand needed for optimum phosphorus precipitation and removal. With our process the amount of phosphorus removed, and consequently the Nitrogen:Phosphorus (N:P) ratio of the effluent, can also be adjusted to precisely match the N:P ratio needed by the growing crop or to remediate a sprayfield having excessive soil phosphorus levels by increasing the N:P ratios above the present crop requirement. This technology not only solves current problems with excessive accumulation of phosphorus in soils receiving liquid manure, it also produces a valuable phosphorus fertilizer material and at least reduces the presence of infectious microorganisms. The aspect of reuse is important because, unlike nitrogen, the world phosphorus reserves are limited.
Theory

The alkaline earth metal-containing compound reacts with the bicarbonate alkalinity of animal wastewater to form a carbonate; with ammonium to form ammonia and with phosphate to precipitate phosphate compounds (Loehr et al., 1973; Tchobanoglous and Burton, 1991). Using calcium hydroxide as an example, the following equations define the reactions:

\[ \text{Ca(OH)}_2 + \text{Ca(HCO}_3\text{)}_2 \rightarrow 2\text{CaCO}_3 \downarrow + 2\text{H}_2\text{O} \quad (1) \]

\[ 5 \text{Ca}^{++} + 4\text{OH}^- + 3\text{HPO}_4^{2-} \rightarrow \text{Ca}_6\text{OH(PO}_4\text{)}_3 \downarrow + 3\text{H}_2\text{O} \quad (2) \]

The reaction in equation 1 is complete above a pH of about 9.5, while that of equation 2 starts above about a pH of 7 but is very slow below about a pH of 9. As the pH value of the wastewater increases beyond about 10, excess calcium ions will then react with the phosphate, as shown in equation 2, to precipitate calcium phosphate compounds. Not expressed in equation 1 is the fact that in wastewater containing high ammonia concentration, the lime dose required to elevate the pH is also increased due to the ammonium-ammonia reaction that neutralizes the hydroxyl ions (equation 3):

\[ \text{Ca(OH)}_2 + 2\text{NH}_4^+ \rightarrow 2\text{NH}_3 \downarrow + \text{Ca}^{++} + 2\text{H}_2\text{O} \quad (3) \]

Therefore, precipitation of phosphate in animal wastewater using an alkaline earth metal-containing compound such as lime is very difficult due to the inherently high buffer capacity of these wastes (\(\text{NH}_4\text{-N} \geq 200 \text{ mg/L} \) and alkalinity \(\geq 1200 \text{ mg/L} \)). This buffer prevents rapid changes in pH (as shown in the control treatment in fig. 2). However, this problem is solved using a pre-nitrification step that eliminates both ammonia (equation 4) and bicarbonate alkalinity (equation 5):

\[ \text{NH}_4^+ + 2\text{O}_2 \rightarrow \text{NO}_3^- + 2\text{H}^+ + \text{H}_2\text{O} \quad (4) \]

\[ \text{HCO}_3^- + \text{H}^+ \rightarrow \text{CO}_2 \downarrow + \text{H}_2\text{O} \quad (5) \]

As a result, the buffering problem of ammonia (equation 3) is crossed out with ammonia oxidation (equation 4) and the problem of carbonate buffers (equation 1) is crossed out with the acid produced during nitrification (equation 5), leaving an un-buffered system that promotes phosphate removal (equation 2) when smaller amounts of lime are added.

Process Description

The first step of the process is the nitrification pre-treatment of animal wastewater. Any nitrification process can be performed, such as suspended-growth nitrification, attached-growth nitrification, etc. Biological removal of nitrogen through the process of nitrification is regarded as the most efficient and relatively low cost means of removing ammonia from wastewater (Tchobanoglous and Burton, 1991). In suspended-growth nitrification, a nitrifying sludge composed of free bacteria is mixed with the wastewater liquid by the aeration or agitation of the liquid. The commonly used activated-sludge process is a suspended growth process that combines bacterial biological oxygen demand (BOD) removal and bacterial nitrification treatment (nitrogen removal) that are performed by separate bacteria. In other cases, carbon oxidation and nitrification functions are done in separate tanks.

Attached-growth nitrification uses various media so that the nitrifying bacteria attach to the surface of the media; examples include trickling filters, rotating biological contactors, packed-bed reactors, etc. Another type of attached-growth system is intermediate between suspended- and attached-growth and that is a fluidized bed biological reactor. In this type of reactor, nitrifying pellets remain suspended in the fluid; i.e., fluidized by the drag forces associated with
the upward flow of air and water. The nitrifying bacteria are entrapped in polymeric porous materials made of polyvinyl alcohol (PVA) or polyethylene glycol (PEG). One of the advantages of using such nitrifying pellets is that the number of microorganisms in the reactor can be increased, thus removing the ammonia more quickly (Vanotti and Hunt, 2000). Whether a fluidized bed biological reactor (a six hour process) or suspended growth process (a two day process) is used, the changes in water characteristics after treatment are the same.

Nitrifiers are autotrophic microorganisms that consume ammonia, oxygen, and carbon dioxide and produce oxidized nitrogen (nitrate and nitrite) and acidity. In the present system, the nitrification process is used to remove both carbonate alkalinity and ammonia from wastewater and increase acidity. In general, any nitrification processes will work provided bacteria are adapted to operate at high ammonia concentrations.

After the nitrification step in which at least about 50% of the initial ammonia and alkalinity in animal wastewater are consumed, the preferred amount being greater than about 90% disappearance of nitrogen and bicarbonate alkalinity, the liquid is transferred to a separate vessel.

The second step is to at least increase the pH of the nitrified wastewater. This is accomplished by adding an alkali such as sodium hydroxide, potassium hydroxide, etc., and alkaline earth metal salts such as calcium chloride, magnesium chloride, etc., and mixtures thereof, to precipitate the soluble phosphorus in the nitrified wastewater. The amount of alkali and/or salt added depends on the degree of phosphorus removal desired and is preferably added in the minimum quantity necessary to balance the Nitrogen:Phosphorus ratio of crops or to remediate sprayfields. Automation can be provided with a pH controller to maintain a selected treatment pH of the liquid. The alkali can be delivered to batch or continuous flow systems, and it can be added in dry forms or in water mixtures.

The second step can include adding an alkaline earth metal-containing compound to the nitrified animal wastewater, which both increases the pH and precipitates phosphorus. The alkaline earth metal-containing compound includes for example calcium or magnesium oxide, calcium hydroxide such as hydrated lime, caustic lime, slaked lime, magnesium hydroxide, dolomite hydrated lime, dolomite lime oxide, etc., and mixtures thereof.

The third step is to mix and react the chemical with the phosphate in the wastewater so that an insoluble phosphate compound is produced. The chemical is mixed with the liquid using static on-line mixers or moving mixers. Mixing time is that needed to dissolve the lime in the wastewater and varies with mixing apparatus. After dissolution, reaction time is typically about 1 to 5 minutes, but precise duration should be determined for specific cases. Visual inspection can be used since the reaction is normally complete when clear precipitate flocs are evident in the mixed liquid.

In the fourth and final step, treated wastewater is passed through a sludge clarifier to remove the precipitate. Settling for at least about 20 minutes to about 240 minutes is allowed to insure that at least most if not all of the phosphorus precipitate has settled out.

The third step (mixing and reaction) and the fourth step (clarification) can be performed in separate vessels or combined in the same vessel. The phosphorus precipitate can be dewatered and used as a fertilizer or can be mixed with other materials or treated to produce useful phosphorus products such as calcium orthophosphates (superphosphates), ammonium phosphates, or feed additives. To obtain a high-purity material, the liquid after the nitrification step is passed through a clarifier (settling unit, membrane filtration unit, etc.) before reaction with lime.
Laboratory Experiment

Lagoon wastewater from a swine operation was treated in a fluidized bed biological reactor during a 16-hour period. The reactor contained nitrifying bacteria immobilized in pellets made of polyvinyl alcohol (PVA) polymer and aeration that provided oxygen and fluidization of the immobilized pellets (Vanotti and Hunt, 2000). The nitrifying pellets increased microbial population in the vessel, which reduced total treatment time of nitrification. During this nitrification pre-treatment, the natural carbonate alkalinity of 1890 mg CaCO₃/L of the wastewater was essentially consumed in the process of ammonia oxidation (approximately 300 mg nitrogen/L). Only an alkalinity of 63 mg CaCO₃/L remained and the pH decreased from about 8.1 to approximately 6.1. The pH of the wastewater is initially lowered with the acid produced by the nitrifying bacteria. However, since the wastewater is low in ammonia and carbonate buffers, the total amount of chemical needed to increase the pH above 9 is substantially reduced. We were thus able to effectively obtain the pH higher than 9 needed to optimize precipitation of soluble phosphorus using Ca and Mg based compounds.

To illustrate that a single compound can be used to elevate pH and at the same time provide the extra Ca or Mg needed to precipitate phosphorus, hydrated lime [Ca(OH)₂] was used for the chemical addition step. After nitrification, the liquid was transferred to a separate laboratory vessel where it was treated with hydrated lime at rates of 151, 753, and 1506 mg/L to obtain Ca:P molar ratios of 1.0, 5.0, and 10.0, respectively (fig. 1). The rates of calcium were calculated based on the initial orthophosphate concentration in the wastewater (63 mg phosphorus/L or 2.03 mmol phosphorus/L). Identical lime treatments were also applied to the control. The nitrification step was omitted in the control. All experiments were duplicated.

![Graph showing P removed from liquid (mg/L) with nitrification and control](image)

Figure 1. Phosphorus removal from swine wastewater using hydrated lime. **Initial conditions:** PO₄-P = 63 mg/L, pH = 8.05, alkalinity = 1890 mg/L, NH₄-N = 300 mg/L. **After nitrification:** PO₄-P = 63 mg/L, pH = 6.06, alkalinity = 63 mg/L, NH₄-N = 61 mg/L. Corresponding pH changes are shown in fig. 2.

Fixed amounts of lime corresponding to each treatment were added to reaction vessels containing either nitrified wastewater or wastewater that had not been nitrified (control) and mixed with a stirrer for one minute. Treated wastewater was sampled in the supernatant after about a 0.5 hour gravity sedimentation period and analyzed for nutrients using Standard Methods (APHA, 1998).
Figure 2. Changes in pH of swine wastewater after treatment with hydrated lime. The control is lagoon liquid with the following characteristics: PO₄-P = 63 mg/L, pH = 8.05, alkalinity = 1890 mg/L, NH₄-N = 300 mg/L. After nitrification treatment, the carbonate alkalinity and ammonia concentrations are substantially reduced (pH = 6.06, alkalinity = 63 mg/L, NH₄-N = 61 mg/L) and addition of lime rapidly increases pH, thereby promoting calcium phosphate precipitation and P removal (fig. 1).

Results showed that the pH in the control was not significantly increased by treatment; it varied little from 8.05 to 8.27 (fig. 2). As a consequence, phosphorus removal rates were low (about < 34%; fig. 1). This illustrates that precipitation of phosphate in animal wastewater using an alkaline earth metal-containing compound such as lime for example is very difficult due to the inherently high buffer capacity of these wastes (NH₄-N and alkalinity), which prevents rapid changes in pH as shown in the control treatment in fig. 2. This contrasts with results obtained in the nitrification/phosphorus removal sequence; the pH increased 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.

Field Prototype

A system was evaluated in a swine operation. The system consisted of a nitrification reactor (Vanotti et al., 2000), a 100-gallon tank with a conical bottom, a mixer to precipitate the phosphorus from the nitrified effluent (P-reactor), a smaller 30-gallon tank to prepare (mix) the chemical with water, a pump to inject the chemical solution into the P-reactor, and a pH controller (fig. 3). Hydrated lime (2% Ca(OH)₂ in water) was injected into the stirred tank containing nitrified lagoon wastewater; a pH controller stopped injection when pH of mixed liquid reached a set point of 9.0, 9.5, 10, or 10.5 (Treatments 1-4, respectively). Once the desired treatment pH was reached, the precipitated solids were removed from the bottom of the tank after about a 30-minute settling period. The precipitated solids were analyzed for phosphorus content after filtration and drying. A total of 20 batch runs were conducted consisting of a total of four pH treatment levels and four replicates.
Results shown in table 1 indicate that the P removal performance of the system obtained under field conditions was consistent with results obtained in the laboratory. Since ammonia nitrogen has been converted to nitrate, increased pH does not result in 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, using data from Edwards and Daniel (1992), 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 < 1 Ca:P molar ratio treatment (table 1). Higher N:P ratios would be prescribed to clean phosphorus-polluted sprayfields. This remediation uses a negative mass phosphorus balance between phosphorus applied and phosphorus removed by harvestable plant materials that is achieved with irrigation of treated wastewater having N:P ratios > 15 (table 1). The higher this ratio number, the shorter the time would be needed by a succession of crops to deplete soil phosphorus and bring back soil phosphorus test values to environmentally acceptable levels.

Other cases are possible where sufficient land for effluent disposal is not available or land application of nitrogen and phosphorus is not desirable. Accordingly, denitrification processes may be employed to convert the nitrate-nitrogen into nitrogen gas (N₂) and provide an effluent virtually free from nutrients, so that its final acceptability for discharge is enormously improved.
Table 1. Performance of field prototype used to remove and recover phosphorus from lagoon swine wastewater (Duplin Co., N.C.).

<table>
<thead>
<tr>
<th>Treatment</th>
<th>pH</th>
<th>Ca(OH)₂</th>
<th>Alkalinity</th>
<th>Suspended Solids</th>
<th>NH₄- N</th>
<th>Total N</th>
<th>Total P</th>
<th>N:P Ratio†</th>
<th>Ca:P Molar Ratio‡</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Applied</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Influent (Lagoon liquid)</td>
<td>0</td>
<td>7.7</td>
<td>--</td>
<td>1738(90)</td>
<td>327(41)</td>
<td>278(4)</td>
<td>320(9)</td>
<td>71.9(4.7)</td>
<td>4.45</td>
</tr>
<tr>
<td>Treated effluent with nitrification-Ca extraction process</td>
<td>1</td>
<td>9.0</td>
<td>141(5)</td>
<td>511(20)</td>
<td>83(8)</td>
<td>8(4)</td>
<td>303(14)</td>
<td>25.5(2.8)</td>
<td>11.9</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>9.5</td>
<td>271(28)</td>
<td>570(41)</td>
<td>94(7)</td>
<td>8(4)</td>
<td>301(14)</td>
<td>11.1(0.2)</td>
<td>27.1</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>10.0</td>
<td>344(2)</td>
<td>557(42)</td>
<td>85(5)</td>
<td>6(3)</td>
<td>299(15)</td>
<td>3.3(0.9)</td>
<td>90.6</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>10.5</td>
<td>433(14)</td>
<td>545(22)</td>
<td>89(13)</td>
<td>5(3)</td>
<td>299(15)</td>
<td>1.6(0.7)</td>
<td>186.9</td>
</tr>
</tbody>
</table>

* Treatment: Hydrated lime (2% Ca(OH)₂ in water) was injected into a stirred tank containing nitrified lagoon wastewater; a pH controller stopped injection when 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. The precipitated solids were filtered with a glass filter, dried, and analyzed for phosphorus content (table 2).

† N:P ratio = Total N concentration : Total P concentration. Total N of treated effluent is mostly nitrate-N.

‡ Ca:P molar ratio = Applied Ca : P in the influent.

¶ Data are the average of four batch runs. Values in parentheses are standard errors.

Table 2. Phosphorus content in solids produced from swine lagoon liquid using the nitrification-lime precipitation process (Duplin Co. farm).

<table>
<thead>
<tr>
<th>Treatment pH</th>
<th>Dewatered Solids Produced Per m³ of Liquid Treated (g)</th>
<th>Phosphorus Grade (% P₂O₅)</th>
<th>Total P Recovered in the Precipitate (g)</th>
<th>P Recovery* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.0</td>
<td>560</td>
<td>17.5</td>
<td>43.0</td>
<td>93</td>
</tr>
<tr>
<td>9.5</td>
<td>750</td>
<td>17.2</td>
<td>56.6</td>
<td>93</td>
</tr>
<tr>
<td>10.0</td>
<td>910</td>
<td>16.1</td>
<td>64.0</td>
<td>93</td>
</tr>
<tr>
<td>10.5</td>
<td>970</td>
<td>15.7</td>
<td>66.4</td>
<td>94</td>
</tr>
</tbody>
</table>

* P Recovery = Percent ratio of total P recovered in precipitate and total P removed from liquid by nitrification - lime precipitation process. Water quality characteristics of clarified effluent shown in table 1.
More than 90% of the P removed from the liquid was recovered in the solids as shown in the solids analyses (table 2). Although the amount of precipitate substantially increased with lime application, phosphorus grade of the precipitate changed little (16-17% \( \text{P}_2\text{O}_5 \)) indicating that most of the chemical was selectively used to precipitate P. The phosphorus precipitate can be dewatered and used as a fertilizer or can be mixed with other materials or treated to produce useful phosphorus products such as calcium orthophosphates (superphosphates), ammonium phosphates, or feed additives (Vanotti et al., 2001).

In addition to the phosphorus removal aspect, the high pH used in the process destroys the pathogens in liquid swine manure. Results obtained in a lagoon-less system showed that P removal process via nitrification-calcium precipitation at pH 10.5 produces a sanitized effluent free of salmonellae, enterococci, and other pathogen indicators evaluated (Vanotti et al., 2002).

Conclusions

One of the main problems in sustainability of animal production is the imbalance between N and P in the waste. When manure is applied based on N, there is a P buildup in soil and increased potential for P losses through runoff and subsequent eutrophication of surface waters. The technology presented was developed to solve this problem by removing soluble P from animal wastewater. Phosphorus is selectively precipitated using an alkaline earth metal after carbon and ammonia buffers are reduced with a nitrification pretreatment. Collectively, our findings indicate:

- Once ammonia and carbonate alkalinity concentrations in swine wastewater are substantially reduced with a nitrification pre-treatment, the subsequent addition of lime rapidly increases the pH of the liquid, thereby promoting formation of P precipitate with small amounts of chemical added.
- Since ammonia nitrogen has been converted to nitrate, increased pH does not result in 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 or remediate sprayfields.
- The final product is calcium phosphate (> 15% \( \text{P}_2\text{O}_5 \)) that can be reused as fertilizer.
- The high pH in the process also destroys pathogens in the wastewater.

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