REDUCING DAIRY EFFLUENT PHOSPHORUS CONTENT THROUGH STRUVITE PRODUCTION

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ABSTRACT

Forced precipitation of struvite (magnesium ammonium phosphate hexahydrate, $MgNH_4PO_4{\bullet}6H_2O$) in wastewater treatment has recently received increased attention as a method of phosphorus (P) recycling. Dairy lagoon P concentrations can be lowered, and the recovered struvite has the potential to be marketed and used as a fertilizer. Struvite may even be useful in organic production on calcareous soils, where rock P (PR) is not an option.

A new organic treatment method, based on an existing process using a cone-shaped fluidized-bed reactor, was developed and field-tested using dairy wastewater. Wastewater pH was adjusted within the reactor using acetic acid and KOH. Input and output samples were analyzed with ICP-AES. The new process yielded a mean total P (TP) removal of 12% (±3%) at a 95% confidence limit (n=34). Magnesium (Mg) reduction of 12% (±2%) was also observed.

The granular product was examined semi-quantitatively using SEM-EDS, which confirmed the presence of amorphous Mg phosphates with approximately a 1:1 molar ratio of Mg:P. Wastewater and product analysis are ongoing, and greenhouse trials are scheduled to test the effectiveness of the recovered P as a fertilizer at various soil pH levels.

INTRODUCTION

The recovery and use of P by crystallization from municipal and agricultural wastewater has the potential to improve treated effluent quality while decreasing sludge volume and creating relatively pure, useful byproducts. While it is unclear exactly how long existing PR reserves will last, P is a limited resource and its reuse is necessary for the long-term sustainability of agricultural and industrial production (Driver et al., 1999). Most efforts have focused on wastewater treatment plants (WWTPs), where spontaneous struvite precipitation can be destructive to WWTP facilities (de-Bashan and Bashan, 2004; Shu et al., 2006). Additionally, P releases from WWTPs can cause eutrophication of surface water bodies, resulting in strict limits on treated effluent. Given the scale and expense of a WWTP, it is easier to justify capital investment in new P removal technologies, so these facilities have naturally been a focus of research. There exist several full-scale, working examples of WWTPs using crystallization processes for P removal. Depending on the process, the product is either calcium (Ca) phosphate (apatite) or Mg phosphate (struvite) (van Dijk and Braakensiek, 1984; Driver et al., 1999; de-Bashan and Bashan, 2004).

Comparatively little work has been done regarding on-site P removal from agricultural wastewater. Greaves et al. (1999) noted that P is typically more concentrated in manures than in sewage, making manure an ideal target for P recovery. According to the same review, while land application is the preferable method of manure P reuse, application of manure to meet crop nitrogen (N) needs results in a significant P surplus. P recovery through crystallization could be used to correct this imbalance. The product would also be easily dried, easily handled, marketable, and transportable at a fraction of the cost of manure or compost.

However, there are significant constraints for on-site P removal processes that must be met in order for the technology to be practical. Recovery technology must be economical on a smaller scale than P removal at a typical WWTP. Additionally, the system cannot require extensive monitoring, maintenance, or material inputs, and treated effluent must remain suitable for spreading on crops (Greaves et al., 1999). This last requirement imposes the most stringent limitation, as it precludes the use of processes common to P recovery at WWTPs, such as NaOH addition and raising pH to very alkaline levels. High sodium concentrations or high pH would render the effluent unsuitable for land application, so these techniques cannot be used to treat agricultural wastewater. Only a relatively inexpensive technology that maintains the suitability of effluent for application is practical for on-site P removal in an agricultural setting.

The cone-shaped fluidized bed reactor designed by Bowers and Westerman (2005a) is one such technology. In laboratory and field-scale experiments, P was recovered as crystalline struvite from wastewater generated in swine production. The uniquely shaped reactor was used in combination with Mg addition and pH increase using ammonia to reduce TP concentration in treated effluent, with mean concentration reductions of up to 82% for TP (Bowers and Westerman, 2005b). X-ray diffraction (XRD) analysis confirmed the presence of struvite.

Unfortunately, few applications for recovered struvite have been developed. Its chemical composition makes it impractical as a raw material in the modern P industry (Driver et al., 1999; Schipper et al., 2001). Its potential for use as a slow-release fertilizer has been known for decades, but until recently little scientific work has been conducted. Johnston and Richards (2003) evaluated different recovered phosphates, comparing their relative effectiveness as fertilizer in a greenhouse setting, and found recovered struvite to be an effective fertilizer for ryegrass. Struvite crystallization was also carried out on landfill leachate in Hong Kong, and the product was found to be as effective as commercial fertilizer for vegetables (Li and Zhao, 2003).

Previous studies have examined struvite as a fertilizer on acidic or neutral soils. The development of an effective alternative for P fertilization on calcareous soils using recovered P could improve the sustainability of both livestock and crop production in semi-arid areas such as the western United States. By recovering P using a method based on Bowers and Westerman (2005a) that is in accordance with the letter and spirit of the regulations for organic food production, the product could be even more valuable. The use of recovered P in conventional or organic production on alkaline soils could help to alleviate P loading in areas with large numbers of livestock, and provide producers with a valuable resource and potential source of revenue.

METHODS

Wastewater Treatment and Water Analysis

Wastewater treatment using the University of Idaho pilot-scale struvite crystallizer was performed in August and September 2006 at two separate dairies in northern Colorado. Two different processes were used; the “conventional” process which utilizes HCl and anhydrous ammonia for pH adjustment, and the “new” process which replaces these chemicals with acetic acid and KOH. By using KOH rather than NaOH, treated wastewater remains suitable for land application. The chemicals in the new process are also usable in some areas of organic agriculture, and the product might one day be certified as well.

The primary components of the fluidized-bed crystallizer system are a 250 gal holding tank and a large, inverted conical reactor vessel. The reactor cone is initially seeded with a bed of PR material to provide sites for the growth of struvite crystals. During operation, wastewater is pumped from the holding tank into the base of the reactor cone through a manifold. Inside the manifold, other substances such as Mg solution, hydroxide solution, or gaseous ammonia can be combined with the effluent stream. Effluent then enters the cone, and passes through the bed of material at its base. Treated effluent drains back into the lagoon from the top of the cone.

Wastewater was pumped from an anaerobic lagoon into the holding tank, and adjusted to a pH of 5.2. Acidification increased the concentration of orthophosphate (OP) in the effluent by dissolving inorganic phosphate complexes already present in the water. Liquid in the tank was continuously mixed by a pump at its base, and electrodes were used to monitor pH. Once the target pH was reached, acidified wastewater was pumped at a rate of 1.8 to 2 gal min^{-1} through the manifold, where either NH_3 or KOH solution was added to rapidly increase the pH to 7.5-8.3 to encourage the precipitation of phosphates as the effluent passed through the seed material.

Wastewater samples were taken at three points in the process: prior to entering the holding tank, immediately prior to entering the manifold, and at the top of the reactor vessel. Samples were analyzed at the Colorado State University Soil, Water, and Plant Testing Laboratory. OP was evaluated using the ascorbic acid method (Kuo, 1996). Samples were digested with nitric and perchloric acid, and TP and metals were determined using ICP-AES (Thermo Jarrell Ash IRIS Advantage, high resolution, dual view). Basic statistical analysis was completed using Microsoft Excel 2003 (full analysis will be performed using SAS).

Reactor Product Analysis

Samples of product harvested from the reactor bed were sent to the Colorado School of Mines for XRD analysis. Product was further inspected using a scanning electron microscope in conjunction with energy dispersive spectroscopy (SEM-EDS). Carbon paint was applied to the face of small aluminum cylinders, and the product was sprinkled on the carbon paint while wet. Cylinders were allowed to dry for one week prior to examination with SEM-EDS.

RESULTS AND DISCUSSION

Wastewater Analysis Results

Wastewater samples were collected at the reactor input and output during operation in order to track and analyze reactor performance. Selected preliminary results for both the conventional and new methods are presented in Table 1.

Table 1. Mean concentrations and removal efficiency for selected elements of the influent and treated effluent using the conventional and new processes. (Conventional n=5, new n=30).

	conventional, input (ppm)	conventional, output (ppm)	conventional removal %	new, input (ppm)	new, output (ppm)	new removal %
OP (as P)	25.5	4.77	81	60.3	31.3	48
TP (as P)	94.9	81.0	14	78.4	67.2	14
total Mg	154.2	136.0	12	175.6	152.1	13
total Ca	299.2	303.2	-1.3	313.8	292.8	7

The different processes were tested at separate dairies due to difficulties pumping the effluent at the first location. Mg and OP concentrations were greater in the effluent used for the new process, while TP concentration was greater in the wastewater used for the conventional process. Additionally, the effluent used for the new process was diluted with irrigation water prior to the last five hours of operation, yielding lower concentrations for this period (not shown in Table 1). This period had notably lower TP removal efficiency. Including these four samples, the mean TP removal efficiency for the new process was 12%, with a 95% confidence interval of ±3%. Mean Mg removal efficiency was also 12%, with a 95% confidence interval of ±2%.

A reduction in both Mg and TP was observed for both the conventional and new processes, with considerably more Mg being removed than P on a molar basis. On a molar basis, 1.6 to 3 times more Mg was removed than P. OP reductions were also much greater than TP on an absolute and relative basis. Ca concentration increased slightly with the conventional method, while it decreased with the new method. Although TP reduction was similar in both processes, the conventional process resulted in greater relative OP reduction than the new process.

Product Analysis Results

Samples of reactor products made using both the conventional and new methods were analyzed using XRD, but a crystalline struvite phase could not be identified. PR samples were also examined using XRD, and showed strong correlation with database spectra for carbonate fluorapatite as well as quartz, dolomite, and calcite.

When the product was examined with SEM-EDS, semi-crystalline and amorphous particles having an approximately 1:1 ratio of Mg:P were identified from the new and conventional methods (Figures 1 and 2, respectively). While EDS data is only semi-quantitative, it suggests a strong association between Mg and P in these materials. The structure of the magnesium phosphate particles examined using SEM-EDS was highly variable, but in all cases fairly large amounts of both P and Mg were present.

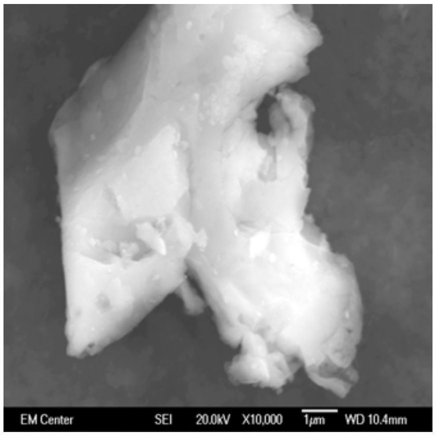

Figure 1. Particle produced using the acetic acid/KOH method. EDS analysis showed atomic composition of 16.25% P, 15.14% Mg, 65.25% O, 1.37% K, 0.77% Al, 0.79% Si, and 0.43% Ca.

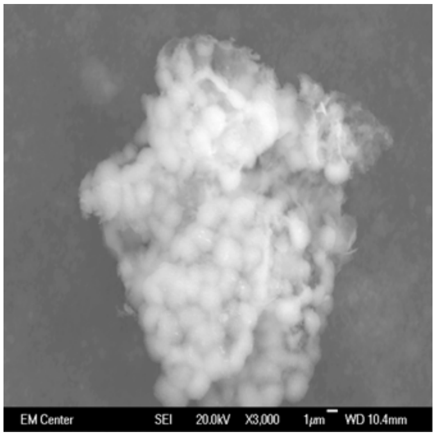

Figure 2. Particle produced using the HCl/NH_3 method. EDS analysis showed atomic composition of 12.91% P, 9.99% Mg, 5.17% Ca, 66.18% O, 2.02% Si, and trace Fe, K, and Cu.

DISCUSSION

The mean TP removal efficiency of 12% did not match the 66% removal efficiency observed by Bowers and Westerman (2005b) in experiments with swine wastewater and no added Mg, but was comparable to results obtained by Bowers et al. (2005) for treatment of dairy wastewater in Idaho and Washington (14% reduction in Idaho and 15% in Washington) using the conventional acidified process. Reported Mg and P concentrations in the Idaho dairy wastewater (Bowers et al., 2005) were similar to the concentrations observed in this study. Wang et al. (2005) concluded that the ideal Ca:Mg molar ratio for struvite precipitation is 0.5 or less, and that a ratio greater than 1.0 in wastewater significantly inhibits struvite formation. The Ca:Mg ratio in the current study ranged from 1.04 to 1.21. Bowers and Westerman (2005b) found that a Mg:TP ratio greater than one may reduce efficiency. The molar ratio of Mg:TP in the current study ranged from 2.0 to 3.8, without supplemental Mg. It is possible that high concentrations of Ca or Mg inhibited struvite formation in the reactor. However, Huang et al. (2006) found that Mg:TP ratios as high as 3.3:1 with Ca:Mg ratios of up to 6:1 were conducive to struvite production in WWTPs. Even given these conflicting results, the Ca:Mg or Mg:TP ratio in the wastewater may not be optimal for struvite crystallization and could explain the low observed efficiency.

Even at decreased efficiency, the observed simultaneous reduction of P and Mg levels in the effluent suggests that magnesium phosphates were indeed precipitated from reactor effluent. On a molar basis, 1.6 to 3 times more Mg was removed than P, so other Mg compounds were probably produced in the reactor in addition to phosphates.

According to Bowers and Westerman (2005a), all OP is theoretically available for recovery through struvite crystallization. The TP reduction they observed was sometimes greater than this theoretical maximum. In the current study, however, TP reduction was notably lower than OP reduction. This indicates that some potentially recoverable phosphate is being discharged in the treated effluent stream prior to crystallization in the reactor bed, or that some of the bed particles themselves are being expelled from the reactor. The net result is that large decreases in OP concentration result in smaller than expected TP reduction. Bowers and Westerman (2005b) reported that with a similar setup and flow rates of 1.5 gal min^{-1} and 2.5 gal min^{-1}, the slower flow rate resulted in greater P removal efficiency in field-scale experiments. It is possible that a slower flow rate and correspondingly longer reaction time would improve performance and product characteristics over those reported in the current study.

SEM-EDS data shows that amorphous Mg phosphates were formed in the reactor, rather than the crystalline morphology observed in laboratory and fieldwork in Bowers and Westerman (2005b). The struvite particles in the SEM images bear no resemblance to recovered struvite crystals in Li and Zhao (2003), for they lack any regular structure. EDS analysis was only possible on very small particles due to the lack of electrical ground on larger particles, so no comparison can be made with larger struvite particles shown in Huang et al. (2006). However, XRD analysis would likely have identified crystalline phases of struvite if they were present in detectable amounts. This indicates that either the large particles are not crystalline phosphates, or that they are not present in high enough concentration to be identified by XRD.

Observed removal efficiency in the current study is lower than previous studies (Bowers and Westerman, 2005b), and strong evidence exists that the recovered magnesium phosphates are in amorphous rather than crystalline form. These differences could be due to high Mg or Ca concentration, other ions in the wastewater, or incomplete crystallization. A longer reaction time might improve removal efficiency and the crystalline structure of recovered material.

SUMMARY

Low removal efficiency compared to that observed in Bowers and Westerman (2005b) and the amorphous nature of the Mg phosphate particles examined in the current study point to the necessity to elucidate the reactions occurring under field conditions. Previous studies have shown that P can be recovered by producing struvite crystals in a cone-shaped fluidized bed reactor, but the observed performance and product characteristics in the current study do not match those of previous studies. Further work is needed to improve removal efficiency and regularity of precipitate characteristics using actual wastewater under field conditions.

Though removal efficiencies are comparatively low, the data suggest that Mg phosphates were precipitated from the wastewater in the reactor. Struvite production at dairies can help to correct nutrient imbalances in the western United States while providing a useful byproduct.

ACKNOWLEDGEMENTS

The authors would like to thank the NRCS, Farm Pilot Project Coordination, Inc., and Applied Chemical Magnesias Corp. for financial support. The authors are grateful for the assistance of dairy owners in Colorado, Dr. J.R. Self, K. Doesken, A. Elliott, and M. Smith.

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