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Bench-scale recovery of phosphorus from flushed dairy manure wastewater

Willie G. Harris *, Ann C. Wilkie, Xinde Cao, Roy Sirengo

Soil and Water Science Department, University of Florida, Gainesville, FL 32611, USA

Abstract

Recovery of phosphorus (P) from flushed dairy manure in an easily-dewatered form would enable farmers to manage P as a resource rather than land-apply it in excess at environmental risk. The purpose of this study was to evaluate (i) the feasibility of P recovery and (ii) the form of recovered P from flushed dairy manure wastewater using crystallization in a fluidized-bed reactor. Wastewater was pumped directly from a dairy farm reservoir and continuously fed in parallel through four bench-scale fluidized-bed reactors deployed on-site. Chemical additives (NaOH and $MgSO_4$) required for recovery were injected directly into the zone of fluidization. Recovered P forms were assessed by X-ray diffraction, scanning electron microscopy, and micro-elemental analysis. Recovery of P as poorly-crystalline hydroxylapatite (HAP) was documented in coatings ultrasonically removed from quartz seed grains following fluidization at elevated pH in conjunction with $MgSO_4$ injection. Addition of $MgSO_4$ was required to prevent $CaCO_3$ precipitation upon pH elevation and hence enable calcium phosphate precipitation. It is likely that $MgSO_4$ inhibited $CaCO_3$ via formation of $MgCO_3$ (aq). Periclase (MgO), which also served as an effective seed material, generated sufficient alkalinity at grain surfaces to precipitate abundant $CaCO_3$ and in some cases detectable Ca phosphate even without NaOH addition to elevate pH of bulk solution.
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Keywords: Dairy manure wastewater; Phosphorus; Nutrient recovery; Fluidized-bed crystallization; Hydroxylapatite (HAP)

1. Introduction

Dairies face the prospect of increasingly stringent environmental regulations arising from concerns that phosphorus (P) from dairy manure can impact vulnerable water resources (Mansell et al., 1995; McDowell and Sharpley, 2004; McFarland and Hauck, 2004). Many dairies use hydraulic flushing for manure management, followed by primary treatment (mechanical screening or sedimentation, or both) to remove coarse solids. The liquid fraction of flushed dairy manure after settleable solids are removed is referred to as flushed dairy manure wastewater (Wilkie et al., 2004). In Florida, the most common manure management system utilizes short-term holding ponds for

flushed dairy manure wastewater storage, with subsequent pumping to sprayfields to supply fertilizer nutrients and irrigation water for production of forage crops (Wilkie, 2003). Sprayfield application of the wastewater has the advantage of on-site recycling of nutrients, but presents a nutrient- and waste-management dilemma. Application rates based on crop nitrogen (N) requirement generally result in a P rate that is more than double the crop requirement. Addition of P beyond plant uptake is wasteful and the excess P constitutes an environmental risk, especially on soils with low P retention. On the other hand, basing application rates on P uptake requires supplemental N and at least twice the land area.

Recovery of a sufficient amount of P from dairy wastes in a form that can be managed conservatively by dairy farmers would help resolve conflicting agricultural and environmental interests. Recovered P in an easily dewatered form could be stored and applied as a slow-release

* Corresponding author. Tel.: +1 352 392 1951x251; fax: +1 352 392 3902.
E-mail address: apatite@ufl.edu (W.G. Harris).

fertilizer in accordance with crop needs. Recovering P from waste streams is also a sustainable strategy to conserve P resources. Global reserves of high-quality mined phosphate deposits are being gradually depleted. It is estimated that there are seven billion tons of phosphate rock as P_2O_5 remaining in reserves that could be economically mined. The human population consumes as much as 40 million tons of P as P_2O_5 each year (Shu et al., 2006) and P demand will increase by 1.5% each year. It is predicted that the resource could be exhausted in as little as 100–250 years (Shu et al., 2006).

Currently, the methods applied to remove P from wastewater are based on the formation of phosphate precipitates. Phosphate can be precipitated as Ca phosphate and struvite ($MgNH_4PO_4$) under conditions of high pH and with sufficient excess of Ca^{2+}, Mg^{2+}, and NH_4^+ ions (Momberg and Oellerman, 1992; Valsami-Jones, 2001). Elevated pH can be accomplished by alkali addition or in some cases by sparging with air to remove carbon dioxide (Battistoni et al., 1997). Previous studies showed that carbonate and Mg^{2+} ions normally encountered in wastewaters can interfere with the Ca precipitation process (Kibalczyc et al., 1990; Seckler et al., 1996). Calcium carbonate precipitation can reduce or prevent P recovery by reducing Ca^{2+} activity (Seckler et al., 1996), and Mg^{2+} can inhibit crystallization of Ca phosphate (Ferguson and McCarty, 1971; Kibalczyc et al., 1990). However, results of the present study show that an interactive effect of CO_3^{2-} and Mg^{2+} can enable Ca phosphate precipitation at elevated pH (>9).

A technology based on nucleated crystallization has been developed to recover P from municipal wastewater within a fluidized-bed reactor (van Dijk and Braakensiek, 1984; Morse et al., 1998; Woods et al., 1998). Several researchers have applied this technology to examine struvite formation in swine and livestock wastewater (Burns et al., 2003; Suzuki et al., 2005; Bowers and Westerman, 2005a). Burns et al. (2003) indicated that $MgCl_2$ can force the precipitation of P from swine manure but seeding the reaction did not significantly enhance the recovery process. Bowers and Westerman (2005b) developed a novel concept for an effective crystallizer, consisting of a continuously operating cone-shaped fluidized-bed. This design offers a lot of advantages over other means for precipitating P, e.g., it provides a high ratio of crystal surface area to reactor volume which allows use of a small reaction vessel, lowering cost (Bowers and Westerman, 2005a). However, we are aware of no report of P recovery from dairy wastewater using fluidized crystallization in a cone-shaped fluidized-bed reactor. Flushed dairy manure poses a greater challenge for P recovery than municipal wastewater because of high dissolved organic carbon, carbonate, and Mg content. This study was conducted to determine (i) the feasibility of P recovery and (ii) the form of recovered P from flushed dairy manure wastewater using crystallization in a cone-shaped fluidized-bed reactor.

2. Methods

2.1. Dairy wastewater sampling and characterization

This research was conducted primarily at the Dairy Research Unit (DRU) of the University of Florida, in Hague, Florida using flushed dairy manure wastewater. Solids in the flushed manure had already been removed using a mechanical solids separator, followed by a solids-settling basin. Thus, the wastewater was very dilute, containing ~0.5% total solids. Effective solids removal is likely required for optimal P recovery. Daily composite samples of the wastewater were collected for three days. These three composite samples were chemically analyzed for the following dissolved elements after 0.45-μm filtration using analytical procedures described in Section 2.4: Ca, Mg, Na, K, P, Zn, Cu, Mn, Al, Fe, NH_4, and NO_3 (Table 1).

2.2. Fluidized-bed reactor design

Four fluidized-bed reactors (R1, R2, R3, and R4) were set up in a continuous ("on-line") flow mode at the DRU (Figs. 1 and 2). The function of each reactor was to produce an expanded bed of "fluidized" seed grains within the wastewater, such that the grain surfaces could serve as nucleation sites for nutrient precipitation. The structural support of the reactor system was constructed of wood (Fig. 1). The drain and feed lines into the reactors were made from PVC pipes. Schedule 40, 1/2-in. PVC was used for the feed lines whereas Schedule 40, 2-in. PVC was used for the drainage section. All other connections were made using flexible tubing. Ball valves were provided in three

Table 1

Concentrations of ionic constituents and other chemical characteristics of the flushed dairy manure wastewater samples composited daily from the Dairy Research Unit (DRU) of the University of Florida

Sample	Alkalinity (mg/L)	pH	EC[a]	Eh[b]	P[c]	Ca[c]	Mg[c]	K[c]	Na[c]	NH_4^{+c}
1	1317	7.15	2540	−340	19	116	69	254	77	156
2	1521	6.74	2510	−364	38	166	65	258	77	152
3	1209	7.01	2470	−374	26	131	58	233	71	135

Fe, Al, and NO_3 were not included due to their very low concentrations.
[a] Electrical conductivity, in μmhos/cm.
[b] Redox potential, in mV.
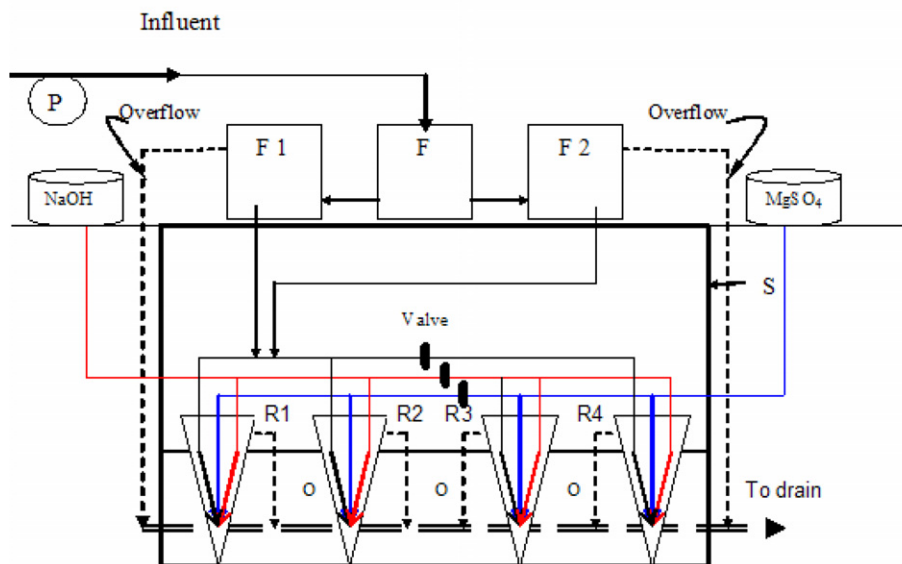[c] Total soluble concentrations, in mg/L.

Fig. 1. Reactor system diagram for the fluidized crystallization study. R1, R2, R3, and R4: reactors; F1, F2 and F: feed reservoirs; P: peristaltic pump; S: wooden support frame; O: overflow.
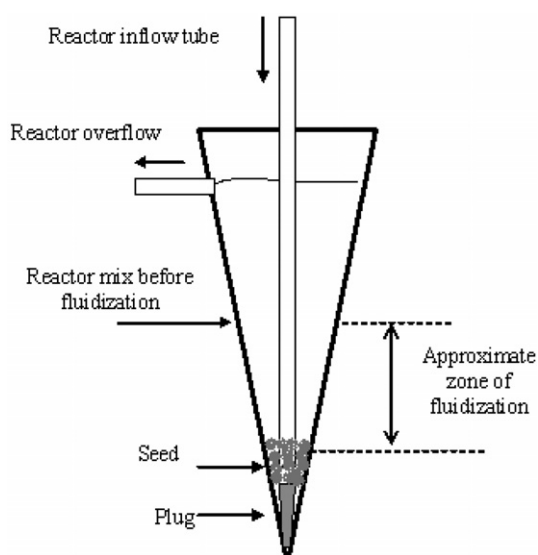

Fig. 2. Simple schematic drawing of the 1-L cone-shaped fluidized-bed reactor.

influent lines to route the feed to either of two sets of reactors, such that two treatments could be replicated simultaneously with the same wastewater source. Three 20-L nalgene carbuoys (F, F1, and F2) were modified to serve as feed reservoirs (Fig. 1). Wastewater was pumped into the central reservoir (F) and then discharged equally by gravity into reservoirs F1 and F2. The carbuoy taps were sized down with plastic barbs to reduce the outflow to a rate that permitted effective control of flow to the reactors within the range of the delivery rate of the variable-speed peristaltic pump. A constant head was accomplished by pumping at a rate high enough to maintain overflow through overflow drains at the top of the carbuoys. Imhoff cones (Fisher Scientific, Inc.) were modified to serve as

reactors (Fig. 2). This 1-L cone, constructed of clear, impact-resistant plastic, is externally graduated from 0 to 1000 mL for easy reading and fitted with a removable plug at the tapered end. Twenty grams of quartz-dominated bedding sand or periclase (MgO) grains (0.25–0.50 mm) served as seed material. The grains were fluidized (suspended by hydraulic flow) by influent feed.

Selection of bedding sand as a seeding material was based on its availability and familiarity to dairy farmers, as well as reports of successful use by others (Valsami-Jones, 2001). Magnesium oxide was selected to test the possibilities (i) that its surface alkalinity could obviate the need for bulk pH elevation using alkali and (ii) that it could favor struvite and hence recovery of N as well as P.

2.3. Treatment operations

Experimental variables included (i) different seed materials (sand and periclase), (ii) pH (controlled by NaOH additions), and (iii) additions of $MgSO_4$. Four treatments with two replicates were conducted: Treatment 1 (T1), MgO seed + no pH elevation; Treatment 2 (T2), MgO seed + pH elevation; Treatment 3 (T3), sand seed + pH elevation; and Treatment 4 (T4), sand seed + pH elevation + $MgSO_4$ addition. Additives (NaOH and $MgSO_4$) were stored in 2-L nalgene containers (Fig. 1), and delivered to the bottom of the reactors via a small semi-rigid plastic tube (internal diameter approximately 1 mm). The actual delivery rate of the 2 M NaOH was determined in field trials by monitoring and confining the pH roughly to 8.5–9.5. The delivery rate of concentrated $MgSO_4$ solution was set at 12 mL/min per reactor. The reactors were operated for approximately 2.5 h at an influent flow rate of approximately 2 L/min (residence time of about 30 s) during data collection for this study, with two replicates per treatment

(two reactors in parallel receiving influent from the same wastewater reservoir).

Seed grains were loaded into the reactors, and the reservoirs were allowed to fill, with the feed pump operating at approximately 8 L/min. The time at which the spigots of reservoirs F1 and F2 were opened was noted as time zero. A grab sample was collected from the feed reservoir at time zero. Slurry samples were collected at 1 h and 2 h near the outflow of the reactor by immersing a 20 mL scintillation vial. Samples were then immediately stored in a cooler and subsequently analyzed for total P (TP) and dissolved reactive P (DRP). Precipitates from the surface of the seeding agent were removed via ultrasound and air-dried for the solid-state phase characterization, as described in Section 2.4.

An air-sparging experiment was conducted to verify that pH of the wastewater could be elevated from the stripping of CO_2 from the wastewater. Air was delivered to a 100 mL batch of wastewater via a fine stone at three relative flow rates to produce small bubbles and attain a high gas-liquid contact surface area for CO_2 exchange.

2.4. Analytical procedure

All metals were analyzed by inductively-coupled plasma spectroscopy. Total P was analyzed with the alkaline oxidation method (Dick and Tabatabai, 1977) and soluble reactive P using EPA method 365.2 (USEPA, 1979). NH_4 and NO_3 were determined colorimetrically (EPA Methods 350.1 and 353.2, respectively). Alkalinity was determined by titration, and pH and electrical conductivity were determined using a standard pH/conductivity meter (Roades, 1982). These data were modeled using a chemical speciation program MINTEQA2 (Allison et al., 1991) to determine if conditions would be thermodynamically favorable for precipitation of calcium phosphate minerals or struvite.

Two factors to evaluate P recovery effectiveness, i.e., conversion efficiency (α) of DRP from the liquid to the solid and recovery efficiency (β) of TP from the liquid, were calculated as:

$$\alpha = \frac{C_{0,DRP} - C_{DRP}}{C_{0,DRP}} \times 100 \qquad (1)$$

$$\beta = \frac{C_{0,TP} - C_{TP}}{C_{0,TP}} \times 100 \qquad (2)$$

where $C_{0,DRP}$ represents the initial concentration of dissolved reactive P, C_{DRP} stands for the concentration of dissolved reactive P at sampling time, $C_{0,TP}$ gives the initial concentration of total P, and C_{TP} is the concentration of total P at sampling time. Conversion efficiency indexes the percentage reduction of DRP, whether it is recovered by retention on seed sands or lost by being transported as particulates from the reactor. Recovery efficiency indexes TP retained in the reactor, a true measure of recovery.

Solid phases formed on the seed grains were analyzed using X-ray diffraction (XRD) and scanning electron microscopy (SEM) in conjunction with energy dispersive X-ray fluorescence elemental spectroscopy (EDS). For XRD analysis, step-scanned data were collected between angles (2θ) of 2° and 50° at a rate of 1.8°/min using a computer-automated diffractometer. The X-ray source was a Cu anode operating at 35 kV and 20 mA using Cu Kα radiation with a diffracted beam graphite-monochromator. Minerals were identified from XRD using techniques described in Whittig and Allardice (1986). Selected samples were further examined by using SEM-EDS to determine the mineral morphology and element composition.

3. Results and discussion

Poorly-crystalline hydroxylapatite (HAP) was recovered using both MgO grains and bedding sand grains as seeds, as documented by XRD (Figs. 3 and 4) and SEM (Fig. 5a and b) in conjunction with EDS (Fig. 5c). Chemical modeling based on analytical results for the composite wastewater samples indicated that all but the most soluble forms of Ca phosphates (e.g., brushite) would be supersaturated and hence potentially recoverable. Modeling also showed that the wastewater was supersaturated for struvite, but the degree of supersaturation was less than that of HAP. Thus, although struvite precipitation is possible, it is thermodynamically less favored than Ca phosphate precipitation. In effect, the "theoretical" predictions are relatively consistent with the reactions observed in our recovery experiments.

The conditions required for P recovery differed between the two seed materials. Quartz in the bedding sand nucleated only $CaCO_3$ when pH was elevated (Fig. 4 T3) due to the high dissolved CO_3^{2-} load, or alkalinity, of the
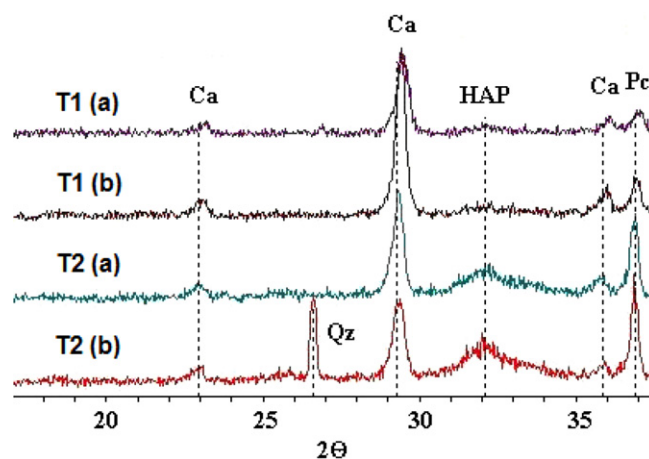

Fig. 3. XRD patterns of the material removed from two treatments T1 and T2 with MgO as seed grain in two replicates (a and b) for each treatment. T1: no pH elevation, showing greater calcite precipitation on grains; T2: pH elevated using NaOH, showing less calcite precipitation and poorly crystalline HAP. Reactors for each replicated treatment were fed simultaneously from the same reservoir. Minerals with peaks labeled: Ca, calcite ($2\theta = 23.1$, 29.2, and 36.1); Qz, quartz ($2\theta = 26.7$); HAP, hydroxylapatite ($2\theta = 32.1$); and Pc, periclase ($2\theta = 37$). The quartz in the bottom pattern probably resulted from an incidental contaminant entrained in the flushed manure.
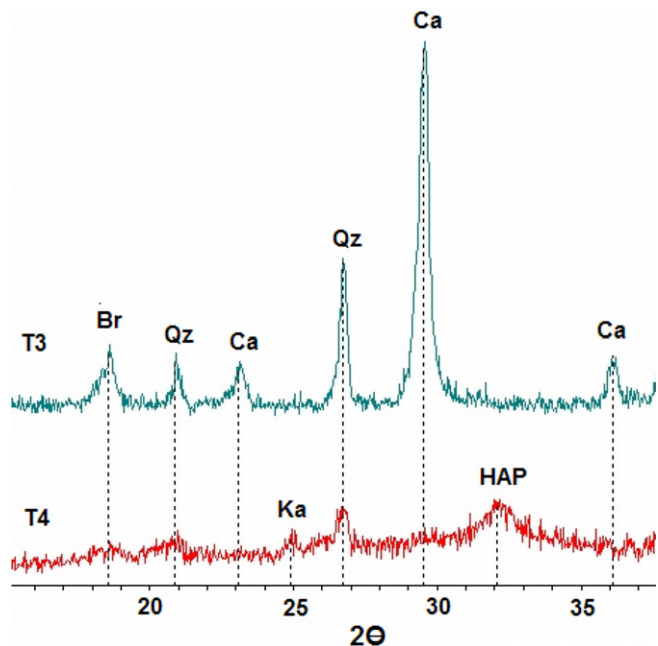
Fig. 4. XRD patterns of the material removed from treatments T3 and T4 with sand as seed grains. T3: pH elevation and T4: pH elevation + MgSO$_4$ addition. Minerals with peaks labeled: Br, brucite ($2\theta = 18.5$); Qz, quartz ($2\theta = 20.9$, 26.7); Ca, calcite ($2\theta = 23.1$, 29.2, and 36.1); Ka, kaolinite ($2\theta = 24.9$), and HAP, hydroxylapatite ($2\theta = 32.1$). Note almost complete suppression of carbonate on the bedding sand grains by the magnesium sulfate. Small amounts of entrained kaolinite and quartz probably did not get removed in the elutriation prior to ultrasound treatment.
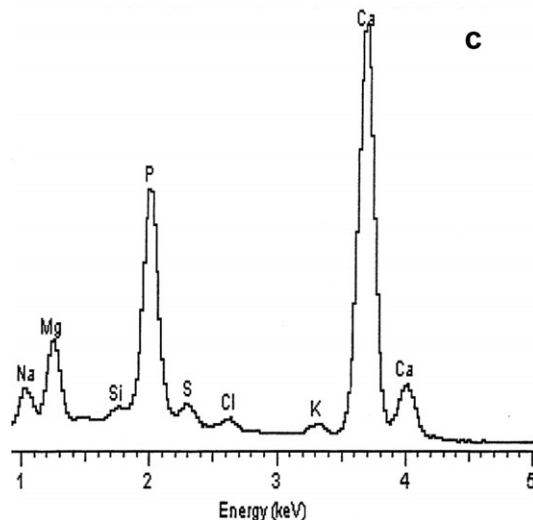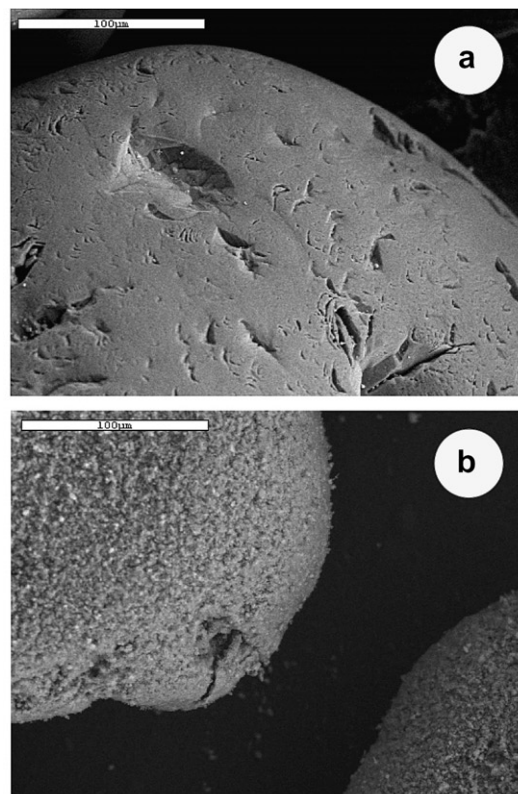

Fig. 5. (a) SEM image of the clean quartz grain used for the seed material in the reactor, showing a smooth surface of the quartz grain; (b) SEM image of the quartz grain in the treatment T4 with sand seed + pH elevation + MgSO$_4$ addition following 2 h fluidization, showing the grain surface covered with mainly X-ray amorphous precipitate material; (c) EDS spectrum of the amorphous precipitate material, revealing the precipitate material dominated by Ca and P.

wastewater (mean of 1349 mg L^{-1} expressed as CaCO$_3$ for three daily composite samples, Table 1). An additive, Mg^{2+} (added as dissolved MgSO$_4$), was found to be effective at preventing CaCO$_3$ precipitation and enabling HAP recovery (Fig. 4 T4). In order to verify the inhibiting effect of Mg^{2+} on CaCO$_3$ precipitation, we conducted a lab experiment with a pure aqueous system under a chemical condition similar to the flushed manure wastewater, but varying Mg concentration (P = 1.1 mM, Ca = 3.0 mM, CO$_3$ = 15 mM, Mg = 1.0–30.0 mM, and pH = 9.2 ± 0.1). The experiments were conducted on Ca + PO$_4$, Ca + PO$_4$ + CO$_3$, and Ca + Mg + PO$_4$ + CO$_3$ systems. Similar results as those in the bench-scale phosphate recovery experiments were observed: Mainly amorphous calcium phosphate (ACP) formed in the system Ca + PO$_4$ (Fig. 6a), but no CaCO$_3$ formed. The presence of CO$_3$ resulted in CaCO$_3$ formation (Fig. 6c). When MgSO$_4$ was added in sufficient proportion (Mg/Ca > 0.1), CaCO$_3$ precipitation was suppressed and only ACP was formed (Fig. 6b). We believe the effect related to the rapid formation of MgCO$_3$ (aq), hence tying up CO$_3^{2-}$ and leaving Ca^{2+} free to react with PO$_4^{3-}$. Also, in some cases, Mg serves as an inhibitor of Ca phosphate crystallization (Ferguson and McCarty, 1971; Kibalczyc et al., 1990), but the presence of abundant CO$_3^{3-}$ apparently can mitigate this effect.

Elevating bulk pH to about 9.0–9.5 from pH ∼7.5 in the wastewater was required for the most effective P recovery using MgO grains (Fig. 3, T2 a and b). However, some

"runs" of the treatment without pH elevation (pH ∼7, Table 1) also produced an XRD-detectable amount of poorly-crystalline HAP coatings on the MgO grains (Fig. 3, T1 a and b), probably due to MgO hydrolysis which produced localized alkalinity near the grain surface. This surface alkalinity of MgO grains was evidenced by the precipitation of CaCO$_3$ even without elevating bulk pH
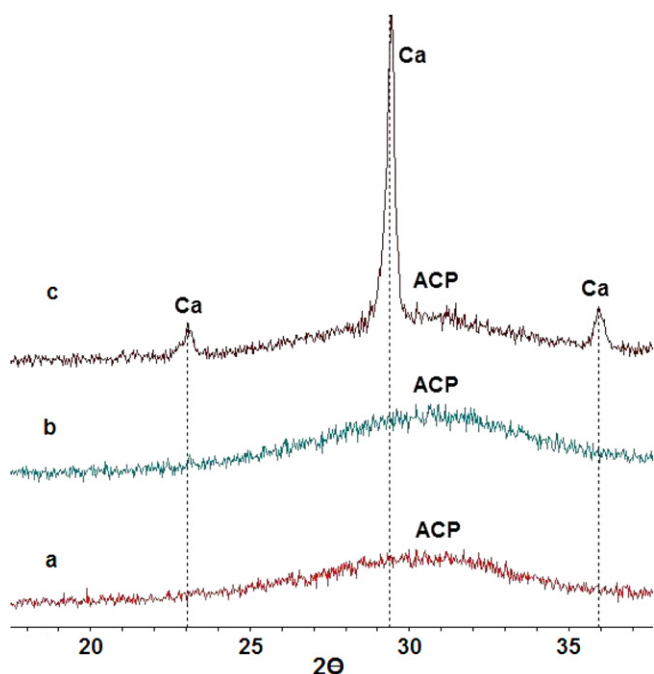
Fig. 6. XRD patterns of the precipitates from the pure Ca + PO$_4$ aqueous systems (pH = 9.2) and the systems with presence of CO$_3$ and Mg. (a) Ca + PO$_4$; (b) Ca + PO$_4$ + CO$_3$ + Mg; (c) Ca + PO$_4$ + CO$_3$. Minerals with peaks labeled: Ca, calcite (2θ = 23.1, 29.2, and 36.1); ACP, amorphous calcium phosphate (2θ between 25 and 35).

with NaOH (Fig. 3 T1) and by there being minimal bulk pH elevation (about 0.5 pH units) as measured during the operation. Hence, the local pH elevation at the grain surface in some cases was apparently enough to precipitate Ca phosphate as well as CaCO$_3$, though the latter was much more prevalent. Also, we were unsuccessful in significantly suppressing CaCO$_3$ precipitation on MgO grains, even with additions of dissolved MgSO$_4$ that accomplished this suppression for bedding sand seed grains (data not shown).

High alkalinity of the wastewater poses a problem for P recovery in addition to CaCO$_3$ precipitation. It results in the buffering of pH such that elevating pH requires a large amount of NaOH addition. Sparging with air is an alternative means of elevating pH that would be cost effective if it is accomplished with the practical hydraulic retention inter-

val of the reactor. Also, sparging would eliminate two undesirable consequences of NaOH additions: elevated Na and permanent pH elevation (Battistoni et al., 1997). The pH would naturally revert to a lower pH following the sparging process. Sparging effectively elevated the pH of DRU wastewater (data not shown), but not fast enough in the bench-scale reactors to successfully recover phosphate on seed grains. The prospect of success with sparging would likely increase with scale of operations; larger scales would enable longer hydraulic retention times.

This study was designed to maximize P loading and hence the relative rate of phosphate accumulation on seed grains, rather than to optimize efficiency of recovery. The objective was to document P recovery and the nature of phosphate phases recovered using solid-state techniques and to relate these findings to the chemistry of the wastewater. Collection of sufficient material on grains for these solid-state assessments within a practical time limit and at a small scale required a high rate of flow through the reactor (i.e., short hydraulic residence time and high nutrient loading rate). However, we did conduct limited assessment of P conversion efficiency (α) and recovery efficiency (β) by analyzing DRP and TP in the reactor inflow and outflow (Table 2). The T1 treatment with MgO as seed grain but no pH elevation showed minimal recovery and conversion. When pH was increased to ~9.5 in the T2 treatment with MgO as seed grains, TP and DRP were significantly reduced, resulting in 24–28% of P recovery and 63–70% of DRP conversion (Table 2), indicative of the necessity for pH elevation to improve P recovery. As expected, addition of MgSO$_4$ in the T4 treatment with bedding sand as seed grains suppressed CaCO$_3$ and enhanced P precipitation, leading to a significant reduction of DRP, with as much as 72–80% of P conversion from liquid to solid (Table 2). No time effect was evident on the TP, DRP, and P recovery and conversion efficiencies at two samplings (Table 2).

Several factors may limit P recovery efficiency from flushed dairy manure wastewater. About half of the TP is in organic form (Wilkie et al., 2004) which is not subject to precipitation, and heterogeneous nucleation of colloidal Ca phosphate may result in transport of particulate P from the reactor. Since the treatment was in a continuous-flow system, the short residence time of our small reactors

Table 2
Dissolved reactive P (DRP), total P (TP), pH, P conversion efficiency (α), and P recovery efficiency (β), in T1, T2, and T4 treatments

Time (h)	T1					T2					T4		
	pH	TP (mg/L)	DRP (mg/L)	α (%)	β (%)	pH	TP (mg/L)	DRP (mg/L)	α (%)	β (%)	pH	DRP (mg/L)	α (%)
0	7.42[a]	53.0	26.0	0	0	7.42	53.0	26.0	0	0	7.07	25.5	0
1	7.38	50.0	25.0	3.85	5.66	9.41	40.0	9.50	63.5	24.5	8.95	7.00	72.5
2	7.23	48.0	25.5	1.92	9.43	9.61	38.5	8.00	69.2	27.3	8.75	5.00	80.4

T1, MgO seed grains without pH elevation; T2, MgO seed grains with NaOH-induced pH elevation; and T4, bedding sand seed grains plus MgSO$_4$ addition with NaOH-induced pH elevation. Time "0" means the beginning of the reaction; Times "1" and "2" indicate a continuous operation at 1 and 2 h, respectively.
[a] Average of two replicates ($n = 2$).

probably limited conversion and recovery efficiency. The P that can potentially be recovered via fluidized-bed technology is limited to DRP, so any process that increases the proportion of DRP (e.g., anaerobic digestion) would enhance recovery potential. During anaerobic digestion, nutrients contained in the organic matter are conserved and mineralized to more soluble and chemically available forms. While TP concentrations per se are conserved during the process, anaerobic mineralization of organic P results in an effluent with a higher P fraction in the soluble phase as dissolved inorganic P, facilitating P recovery (Wilkie, 2005).

4. Conclusions

Results of this study verify that P can be recovered from flushed dairy manure wastewater in the form of calcium phosphate. Interference of P recovery by $CaCO_3$ can be eliminated by adding Mg, which suppresses $CaCO_3$ precipitation. Results of the present study show an interactive effect of CO_3^{2-} and Mg^{2+} on Ca phosphate precipitation when they co-exist; i.e., addition of $MgSO_4$ can suppress carbonate precipitation and enhance Ca phosphate precipitation at elevated pH (>9). Seeding materials can be a factor in the recovery, as exemplified by the effects of bedding sand (quartz) versus MgO. The quartz-dominated bedding sand provides a surface for P nucleation and retention in easily-dewatered form, but the quartz surface does not otherwise significantly affect the chemical environment in its vicinity. Hydrolysis of MgO grains, on the other hand, produces alkalinity near the grain surface to allow for precipitation of $CaCO_3$ and (though not consistently) small amounts of calcium phosphate. There may be a way to exploit this inherent alkalinity to avoid bulk pH elevation in P recovery, but this study was only minimally successful to this end. An important consideration is that only dissolved inorganic P is recoverable. Hence, any processing of the wastewater that mineralizes organic P (e.g., anaerobic digestion) would improve P recovery efficiency. Sparging to elevate pH may be an advantageous approach for P recovery at larger scales because it would avoid liabilities from alkali additions.

Acknowledgements

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