Journal of Environmental Management 267 (2020) 110626

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: http://www.elsevier.com/locate/jenvman

Research article

Assessment of nutrient fluxes and recovery for a small-scale agricultural waste management system

Kevin D. Orner[a,*,1], Fabricio Camacho-Céspedes[b], Jeffrey A. Cunningham[a], James R. Mihelcic[a]

[a] Department of Civil & Environmental Engineering, University of South Florida, Tampa, FL, 33620, USA
[b] Tropical Science Center, Monteverde, P.O. Box 55-5655, Puntarenas, Costa Rica

ARTICLE INFO

Keywords:
Resource recovery
Food security
Biogas
Sustainable agriculture
Manure
Wastewater

ABSTRACT

The efficiencies of removing or recovering nitrogen and phosphorus in widely implemented small-scale tubular anaerobic digesters are not well understood, as the technology is primarily promoted for its recovery of energy, not nutrients. The purpose of this study was to use nutrient mass balances to assess the fate of nitrogen and phosphorus in two tubular anaerobic digesters, specifically designed to digest animal manure, that were integrated with a conical batch reactor to precipitate struvite ($MgNH_4PO_4$) from the digester effluent. The field study showed that locally available products, bittern and soda ash, can be used as a magnesium source and for pH adjustment (respectively) in the struvite precipitation reactor. Results from the mass balances showed that PO_4^{3-} and NH_4^+ were released from the manure during anaerobic digestion, increasing the concentrations of PO_4^{3-} and NH_4^+ in the liquid phase (by 130% and 120%, respectively). Despite this increase in liquid-phase concentrations, average removals were 25% for total phosphorus and 4% for total nitrogen via sedimentation in the digesters. The digesters also removed an average of 87% of total suspended solids and 84% of chemical oxygen demand from the influent waste stream. During struvite precipitation, an average of 79% of PO_4^{3-}–P and 14% of NH_4^+-N was removed from the digester effluent. Harvested precipitate comprised (by mass) 9.9% Mg, 2.4% N, and 12.8% P, consistent with struvite formation. The treatment system offers dual benefits: improved sanitation and recovery of nutrients as a fertilizer that may also indirectly reduce surface water and groundwater degradation. Quantifying nutrient recovery from small-farm-generated agricultural waste and understanding recovery mechanisms can improve environmental management and facilitate progress toward the achievement of multiple Sustainable Development Goals by improving sanitation, promoting sustainable management of wastes and natural resources, improving food security, and supporting the ecological restoration of local agroecosystems.

1. Introduction

The United Nations Sustainable Development Goal (SDG) 6 contains specific targets that include providing access to adequate and safe sanitation for all, increasing recycling and safe water reuse, and improving water quality by reducing water pollution (UN, 2018). Consistent with this and other SDGs, a developing paradigm in managing wastewater is that wastewater contains recoverable valuable resources such as nutrients, energy, and water (Guest et al., 2009; Ren and Umble, 2016; Orner and Mihelcic, 2018). This resource recovery paradigm can fulfill multiple SDGs related to sustainable management of wastes and natural resources, while improving food security through increased productivity from community agriculture practices that also support local ecosystems (Zhang et al., 2016; Orner et al., 2017).

However, resource recovery from agricultural waste may be challenging in the many parts of the world for which such waste is typically not treated before disposal. For example, in China, 90% of manure was not treated before land application (Wang, 2003); similarly, of 93,000 farms in Costa Rica (the location of this study), 79,000 have no treatment of their agricultural waste (Costa Rica Ministerio de Ambiente y Energía, 2015). This is important not only in terms of resource recovery, but also because absence of appropriate management of agricultural waste can lead to public health issues, eutrophication of surface waters, and greenhouse gas emissions.

Opportunities exist to recover nutrients, energy, and water from agricultural waste utilizing tubular anaerobic digesters. The potential

* Corresponding author.
E-mail address: korner@mail.usf.edu (K.D. Orner).
[1] Current Affiliation: Department of Civil and Environmental Engineering, University of California. 760 Davis Hall, Berkeley, CA 94720, USA.

https://doi.org/10.1016/j.jenvman.2020.110626
Received 29 January 2020; Received in revised form 16 April 2020; Accepted 16 April 2020
Available online 1 May 2020
0301-4797/

impact of such recovery is considerable given that over 48 million digesters are estimated to be implemented worldwide (Bruun et al., 2014). In particular, tubular anaerobic digesters produce a biogas that can be directly used for producing electricity, heat, and cooking fuel. Furthermore, if pathogens in the agricultural waste are inactivated during digestion, the accumulated biosolids can be used as a soil amendment or as compost optimization agents (Camacho-Céspedes et al., 2018), and the nutrient-rich liquid effluent leaving the anaerobic digester can be land-applied (Pognani et al., 2012; Stoknes et al., 2016). This is beneficial for plants, which prefer mineralized forms of nitrogen and phosphorus rather than the organic forms found in raw manure (Moser, 1998). However, land application systems can be overloaded during rain events, resulting in runoff of ammonium and phosphate to water bodies. Therefore, recovering ammonia and phosphate in the form of a slow-release fertilizer would both recover a beneficial product that can support food security and reduce nutrient pollution directly from the digester. Unfortunately, the efficiencies of removing or recovering nitrogen and phosphorus in tubular anaerobic digesters are not well understood, as the technology is primarily promoted for its recovery of energy, not nutrients. Some nitrogen and phosphorus can be removed from the influent stream via transfer to the solid phase (sludge), but the rates of nutrient transfer are not well understood (Kinyua et al., 2016). Amini et al. (2017) measured no decrease in total nitrogen and a 43% decrease of total phosphorus in the liquid phase in a 30-L pilot scale digester. Neither of these two studies constructed mass balances to determine material flows of nitrogen or phosphorus. Therefore, tubular anaerobic digesters offer benefits of biogas production and mineralization of nutrients, but the fate of N and P in these systems is, for the most part, not understood.

One technology that has been used to recover nutrients from anaerobic digester effluent (digestate) is the precipitation of struvite ($MgNH_4PO_4$) (Battistoni et al., 2000; Doyle and Parsons, 2002). Targeted waste streams generally contain relatively high concentrations of ammonium and phosphate, in which case magnesium is the limiting reagent for struvite precipitation; thus, magnesium is added to obtain a 1:1:1 M ratio of Mg:N:P. The technology is able to produce a commercial struvite fertilizer from digestate at several large-scale wastewater treatment plants (Ostara, 2018). However, existing struvite precipitation technologies (Celen and Turker, 2001; Munch and Barr, 2001; Ostara, 2018) using an influent of digestate require electricity and equipment that may not be appropriate for small rural farms in low- and middle-income countries. Therefore, the potential for struvite precipitation from anaerobic digestion in rural agricultural settings is, as yet, untested.

The recovery of ammonium and phosphate from struvite precipitation has been studied in several other source streams including human urine (Ishii and Boyer, 2015), landfill leachate (Huang et al., 2014), industrial wastewater (Matynia et al., 2013), and swine wastewater (Liu et al., 2011). Previously, Etter et al. (2011) developed a low-cost struvite reactor design for human urine influent, but the design has yet to be tested for other influents such as digestate. It has thus not yet been determined if the nitrogen and phosphorus exiting a tubular digester can be recovered through struvite precipitation using low-cost, locally available materials without the input of electricity. Such a technology would allow farmers to self-sufficiently produce a slow-release, nutrient-rich fertilizer that has similar properties to conventional synthetic fertilizer (Ahmed et al., 2006) and also reduce nutrient inputs to surface waters and groundwater.

Therefore, the overall goal of this study was to determine the nutrient recovery potential of tubular anaerobic digesters that are integrated with a locally produced pilot-scale struvite precipitation reactor. The three specific objectives were to: 1) quantify the efficiency of nutrient removal in two tubular digesters that receive agricultural waste by conducting mass balances for nitrogen and phosphorus, 2) quantitatively estimate the rate of solids digestion in the two tubular digesters, and 3) construct a low-cost, locally produced pilot-scale struvite precipitation reactor that receives effluent from the two tubular digesters, and assess the efficiency of nitrogen and phosphorus recovery of the precipitation process. Improving environmental management of agricultural waste through an integrated resource recovery system could provide multiple benefits to a community: improved sanitation, removal of nutrient loading to the environment to reduce eutrophication risks, and recovery of struvite as a potential fertilizer to support local food security.

2. Materials and methods

2.1. Site description

The study took place in the rural Costa Rican community of San Luis de Monteverde, a community of approximately 500 people who primarily work in agriculture and tourism. Farmers raise chickens, swine, and dairy cows and grow coffee, fruit, vegetables, and some medicinal plants. In Costa Rica, discharge of agricultural wastes has directly led to higher levels of bacteria and nutrients in surface waters (Shahady and Boniface, 2018).

The University of Georgia-Costa Rica (UGA-CR) maintains a working farm that allows for testing of treatment technologies to reduce the impacts of agricultural wastes. The system for managing farm waste, shown in Fig. 1, includes the treatment of feces from an average of eight dairy cows milked twice per day and eight swine of different ages using two digesters. Each morning, a maintenance worker opens several valves to drain swine waste by gravity into the two digesters. Then the worker uses a water hose to sluice any remaining large fecal matter to the digesters. Fecal matter from dairy cows is sluiced into digester #1.

The operating parameters of the two digesters are shown in Table 1. The flow into digester #1 is greater than digester #2 because higher volumes of water are used during and after milking of dairy cows. Prior to the construction and implementation of the struvite precipitation reactor, the effluent from both digesters flowed by gravity to four storage lagoons, the last of which held tilapia grown for aquaculture. Discharge from the aquaculture lagoon flows out a discharge pipe into a nearby field. Because digester effluent is known to be rich in NH_4^+ and PO_4^{3-}, a key part of this study was the construction and assessment of a pilot-scale struvite precipitation reactor to manage the digester effluent before discharge (as shown in Fig. 1), thereby lowering the eutrophication risk while simultaneously recovering valuable nutrients that can potentially be used as fertilizer.

2.2. Construction and operation of struvite reactor

A 200-L struvite precipitation reactor was constructed for this study based on a previous design used for the precipitation of struvite from human urine (Etter et al., 2011). Goals were to use appropriate materials and to provide beneficial resources for local farmers. The cost of the materials of the galvanized metal reactor was approximately US $660. The reactor was operated in batch mode seven times between July and October 2018. The digester effluent was received in a newly constructed storage container (covered with a cloth filter cover to reduce solids from entering) before the liquid was manually poured into the struvite precipitation reactor. Although up to 200 L of digester effluent could be processed for each batch, each batch typically contained 50 L due to practical considerations of the study, such as lifting and taking measurements.

Inducing the precipitation of struvite requires the addition of magnesium and a base. Therefore, 100 mL of bittern, a liquid byproduct from salt production (17 g/L Mg, 11 g/L K, 29 g/L Na, 13 g/L S), was added to provide sufficient magnesium. The bittern was obtained from a salt production facility located approximately 60 km away from the study location. Because a common base like NaOH was not locally available and would have to be ordered from a specialty manufacturer, soda ash (Na_2CO_3) was used to raise the pH in the reactor. Soda ash is produced

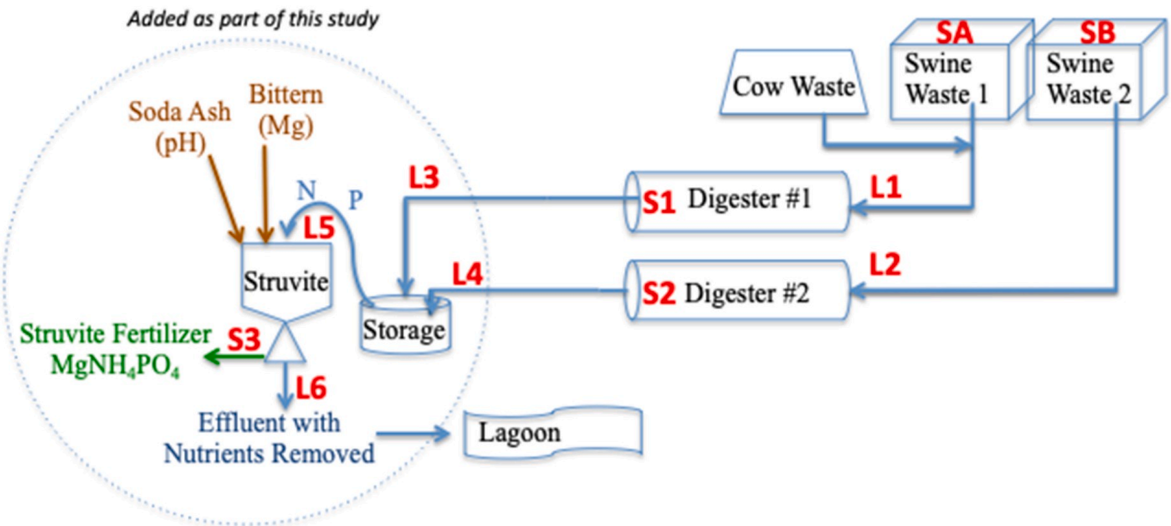

Fig. 1. Overall process for resource recovery from two tubular digesters integrated with a struvite precipitation reactor. Abbreviations that begin with S and L are sampling locations for solids (S) and liquids (L), respectively.

Table 1
Tubular digesters' operating parameters.

Parameter	Unit	*n*	Digester #1	Digester #2
Volume	L		12,000	12,000
Temperature of Digester Contents	°C	19	21.1±1.7	21.1±1.6
Flow Rate (time-averaged over 24 h)	L/d	10	840±270	670±200
Hydraulic Residence Time	d		14.3	17.9

along with carbon dioxide and water when baking soda (available locally) is heated.

Once the magnesium and base were added to the reactor, a stirring mechanism was rotated by hand at approximately 60 RPM for 5 min to promote mixing and precipitation of struvite. A filter bag made of manta, a cloth used in Costa Rica to collect coffee grounds before drinking coffee, was placed under the reactor to collect contents once the valve was opened. The cloth filtered struvite (and any other solids) from the liquid exiting the reactor through the effluent pipe. Effluent liquid emptied into the second storage lagoon. The filter bag was hung for drying near an air vent for one day, and then the struvite powder was removed from the bag with a brush and stored in a plastic container.

2.3. Sampling and analysis

Liquid samples were obtained from the two tubular digesters and from the struvite precipitation reactor at the six locations shown in Fig. 1. These samples were collected during 15 sampling campaigns that occurred approximately once every two weeks between February and October 2018. Liquid samples were analyzed on-site for five-day biochemical oxygen demand (BOD_5), total solids (TS), volatile solids (VS), total suspended solids (TSS), and volatile suspended solids (VSS) using standard methods (APHA, 2012). Chemical oxygen demand (COD) was measured on-site (TNT 82206) with a Hach portable colorimeter (Loveland, CO). Hach kits were also used to measure total nitrogen (TN; kit TNT 827) and total phosphorus (TP; kit TNT 845) off-site using a PG Instruments T60 Visible Spectrophotometer (Leicestershire, United Kingdom) located at the Universidad Estatal a Distancia (UNED) laboratory in San José. Samples were also analyzed at the University of Costa Rica (UCR) laboratory in San José to determine concentrations of NO_3^-, PO_4^{3-}, Mg^{2+}, Ca^{2+}, and NH_4^+ using Inductively Coupled Plasma Atomic Emission Spectroscopy. Other water quality parameters such as pH, conductivity, temperature, dissolved oxygen, and NH_4^+ were measured on-site using a YSI multiprobe (Yellow Spring, OH). Solid samples (swine manure, digester sludge, struvite) were collected on-site and analyzed at the University of Costa Rica for percent solids, percent nitrogen, and percent phosphorus. A two-sample *t*-test with a $p = 0.05$ significance level was performed on the percent reductions in TP, PO_4^{3-}-P, TN, and NH_4^+-N data to determine if the reduction percentages in the two tubular digesters were significantly different from one another.

2.4. Mass balances for solids and nutrients in tubular digesters

Mass-balance equations were produced for each of the two tubular digesters (Table 2) in equations (1)–(6). Flow rates and concentrations were either measured (as described above) or else estimated from the mass balance equations. Table S1 in the supplementary material provides additional details on the symbols, symbol description, units, and how each parameter was determined.

For each digester, the influent is a combination of the initial water and liquid waste (sampled at L1, L2 in Fig. 1) that enters the digester by gravity when a valve is manually opened each morning, along with animal feces that enter the digester by washing (SA, SB). Some phosphorus, nitrogen, and solids accumulate in the digester sludge (S1, S2) while the remainder leaves in the digester effluent (L3, L4). Additionally, some solids are digested, converting organic phosphorus and nitrogen into inorganic phosphate and ammonium, respectively.

Multiple processes affecting the solids concentration occur in the digester, including digestion, biological growth, and precipitation (Metcalf and Eddy, 2003). These three processes are combined into the digestion term, R_{digest}, in the solids mass balance (Table 2, Equations (3) and (6)). In addition, the solids (feces or cells in the case of biological growth, or struvite or other precipitate in the case of chemical precipitation) are separated from the liquids through sedimentation.

Several assumptions were made to generate the mass balance

Table 2
Mass Balance Equations for Digester #1 and Digester #2. Terms in equations are defined in Table S1 in the supplementary material. μ_{S1}, μ_{S2}, $R_{digest,1}$, and $R_{digest,2}$ are unknown variables (i.e. estimated from mass balance, and not measured).

Location	Equation #	Balance	Equation
Digester #1	1	TP	$\mu_{S1}\,TP_{S1} = \mu_{SA}\,TP_{SA} + Q_{L1}\,TP_{L1} - Q_{L3}\,TP_{L3}$
	2	TN	$\mu_{S1}\,TN_{S1} = \mu_{SA}\,TN_{SA} + Q_{L1}\,TN_{L1} - Q_{L3}\,TN_{L3}$
	3	TSS	$\mu_{S1} = \mu_{SA} + Q_{L1}\,TSS_{L1} - Q_{L3}\,TSS_{L3} - R_{digest,1}$
Digester #2	4	TP	$\mu_{S2}\,TP_{S2} = \mu_{SB}\,TP_{SB} + Q_{L2}\,TP_{L1} - Q_{L4}\,TP_{L4}$
	5	TN	$\mu_{S2}\,TN_{S2} = \mu_{SB}\,TN_{SB} + Q_{L2}\,TN_{L1} - Q_{L4}\,TN_{L4}$
	6	TSS	$\mu_{S2} = \mu_{SB} + Q_{L2}\,TSS_{L2} - Q_{L4}\,TSS_{L4} - R_{digest,2}$

equations. In Equations (1)–(6), it is assumed there are no loss terms for N and P, i.e. all N and P that enter the digester either exits in the effluent or is accumulated in the sludge. For instance, it is assumed that no N is lost through nitrification/denitrification because the digester is anaerobic, so nitrification is not expected to occur. In contrast to N and P, the mass of suspended solids may be reduced through digestion. Equations (3) and (6) indicate that solids enter the digester in one of two ways (in the daily emptying of the waste by opening a valve, or in the hose washing that follows), and that the solids that enter can either settle to the sludge, exit as suspended solids in the effluent stream, or be broken down via digestion. In Equations (1)–(6), the terms μ_{S1} (mg/d) and μ_{S2} (mg/d) represent the rate at which solids accumulate in the sludge layer of the respective digester (i.e., via sedimentation of solids). These accumulation rates cannot be directly measured and therefore must be estimated by solving Equations (1), (2) and (4), or (5). Estimates of μ_{S1} and μ_{S2} are then put in to the solids balances, allowing the digestion rate (g/d) (R_{digest}) to be estimated in Equations (3) and (6).

2.5. Struvite reactor efficiency

During this study, the struvite reactor was operated in batch mode with a batch volume of 50 L, as described in Section 2.2. In the reactor, chemical precipitation converts ammonium and phosphate into struvite, which is separated from the liquid and captured via filtration. The struvite reactor has one influent (L5 in Fig. 1), but two effluents, as some phosphorus and nitrogen are precipitated into solid struvite (S3), while the remaining nutrients leave in the liquid effluent (L6). By measuring the phosphorus and nitrogen concentrations in the influent and effluent liquid streams, the removal efficiency achieved by the reactor is calculated.

These calculated removal efficiencies can then be combined with known digester effluent flow rates and concentrations to estimate the N and P mass fluxes that might be expected if a full-scale struvite reactor were deployed in place of the pilot-scale reactor. The hypothetical full-scale struvite reactor mass loadings are based on an assumption of continuous operation, i.e., all digester effluent is treated in the struvite precipitation reactor prior to discharge. Thus, the influent nitrogen loading to the (hypothetical) full-scale struvite reactor is $Q_{L3}\ TN_{L3} + Q_{L4}\ TN_{L4}$, and the influent phosphorus loading is $Q_{L3}\ TP_{L3} + Q_{L4}\ TP_{L4}$. For the purposes of this analysis, it is assumed that the nitrogen and phosphorus removal percentages observed in the pilot-scale reactor would also apply to a full-scale struvite reactor.

3. Results and discussion

3.1. Measured liquid influent and effluent characteristics in two digesters and struvite precipitation reactor

Average measured liquid concentrations for several water quality parameters that were inputs for the digester mass balance equations are found in Table 3. Average measured liquid concentrations for several water quality parameters entering and exiting the struvite precipitation reactor are found in Table 4. In the struvite precipitation reactor, the pH rose from 7.25 in the influent to 8.52 in the effluent as base was added to promote precipitation of struvite. The TS rose from 1200 to 2700 mg/L, indicating that some precipitate was not captured by the locally sourced cloth filter and left in the effluent. A finer locally sourced cloth could likely capture more struvite solids. The analysis of the fate of phosphorus, nitrogen, and solids in the two digesters and the struvite precipitation reactor is included in subsequent sections.

3.2. Measured elemental composition of solids in two digesters and struvite precipitation reactor

Table 5 provides information about the elemental composition of solid constituents. Solid sludge was collected from inside the digesters and analyzed. Additionally, the solid precipitate was collected from the dried filter cloth of the struvite precipitation reactor and subsequently analyzed. Composition from these solids can be compared to the composition of other common solids such as synthetic fertilizer, pure struvite, and bacterial biomass. As seen from Table 3, the concentrations of TN and TP in the liquid phase decreased between the digester influent

Table 4
Average Influent and Effluent Characteristics in the Struvite Precipitation Reactor. The first number is the arithmetic mean of *n* measurements and the second number is the standard deviation of the measurements.

Parameter	Unit	*n*	Influent	Influent + Mg + Base	Effluent	% Reduction
TP	mg P/L	4	48±26	48±26	19±6	60%
PO_4^{3-}–P	mg PO_4^{3-}-P/L	3	24±10	24±10	5±3	79%
TN	mg N/L	3	205±20	205±20	185±10	10%
NH_4^+–N	mg NH_4^+-N/L	15	165±66	168±71	145±64	14%
pH		19	7.3±0.2		8.5±0.2	
TS	mg/L	4	1210±284		2700±258	

Table 3
Average Influent and Effluent Characteristics of Tubular Digesters. The liquid digester influent flow measurements do not include the influent solid feces terms (SA and SB). Negative percentages indicate increased values in the effluent due to, for example, release of nutrients from manure during digestion. The first number is the arithmetic mean of *n* measurements and the second number is the standard deviation of the measurements.

Parameter	Unit	*n*	Digester #1			Digester #2		
			Influent	Effluent	% Reduction	Influent	Effluent	% Reduction
TP	mg P/L	5	31 ± 8.6	22 ± 5.5	31%	48 ± 16.5	53 ± 9.8	−11%
PO_4–P^{3-}	mg PO_4–P^{3-}/L	3	6.4 ± 2.6	13 ± 2.4	−100%	23 ± 4.3	32 ± 2.7	−40%
TN	mg N/L	3	140 ± 36	120 ± 40	15%	250 ± 130	290 ± 32	−19%
NH_4^+–N	mg NH_4^+-N/L	22	76 ± 37	98 ± 28	−29%	123 ± 53	235 ± 67	−91%
TS	g TS/L	11	2.2 ± 1.6	0.8 ± 0.4	61%	3.2 ± 1.3	1.5 ± 0.4	53%
VS	g VS/L	11	1.4 ± 1.3	0.4 ± 0.2	70%	1.8 ± 0.9	0.8 ± 0.2	53%
TSS	g TSS/L	10	1.1 ± 0.8	0.2 ± 0.2	83%	1.8 ± 1.5	0.2 ± 0.1	90%
VSS	g VSS/L	10	0.7 ± 0.4	0.2 ± 0.1	74%	1.3 ± 1.0	0.2 ± 0.1	87%
BOD_5	g/L	10	1.5 ± 1.1	0.2 ± 0.2	86%	1.3 ± 0.6	0.3 ± 0.2	79%
COD	g/L	7	2.6 ± 1.4	0.3 ± 0.1	87%	2.8 ± 1.3	0.6 ± 0.1	80%
pH		30	6.9 ± 0.9	7.0 ± 0.2		7.4 ± 0.7	7.2 ± 0.3	

Table 5
Measured Percentages of Constituents from Field Samples from Digesters and Struvite Reactor. Theoretical percentages are indicated with an *. $n = 1$.

Element	% Mg	%N	%P	% K	% Ca	%C	N:P molar ratio
Digester #1	0.3	2.8	0.7	0.3	1.5	26.8	9.4
Digester #2	0.3	5.1	1.2	0.7	1.9	42.6	9.9
Struvite Reactor	9.9	2.4	12.8	9.9	1.7	10.8	0.4
Synthetic Fertilizer*		10	30	10			0.7
100% Struvite*	9.9	5.7	12.6				1.0
Biomass ($C_{60}H_{87}O_{23}N_{12}P$)*		12.4				53.1	12

and the digester effluent. This indicates that N and P were transferred from the liquid phase to the solid phase within the digesters. Two possible mechanisms are consistent with this process: either N and P were assimilated into bacterial biomass, or N and P precipitated as struvite within the digesters. In either case, subsequent sedimentation of the solid phase would result in the observed TN and TP removal from the liquid phase. Because struvite is expected to exhibit a 1:1 M ratio of N:P, but the sludge in the digester exhibited molar ratios of above 9:1 (see Table 5), we conclude that N and P removal from the liquid phase was due to biological assimilation, not due to struvite precipitation.

Approximately 5 g of dry solids were recovered for every 50 L of liquid entering the struvite reactor. An analysis of the solid powder revealed mass percentages of 9.9% Mg, 12.8% P, 1.7% Ca, and 10.8% C

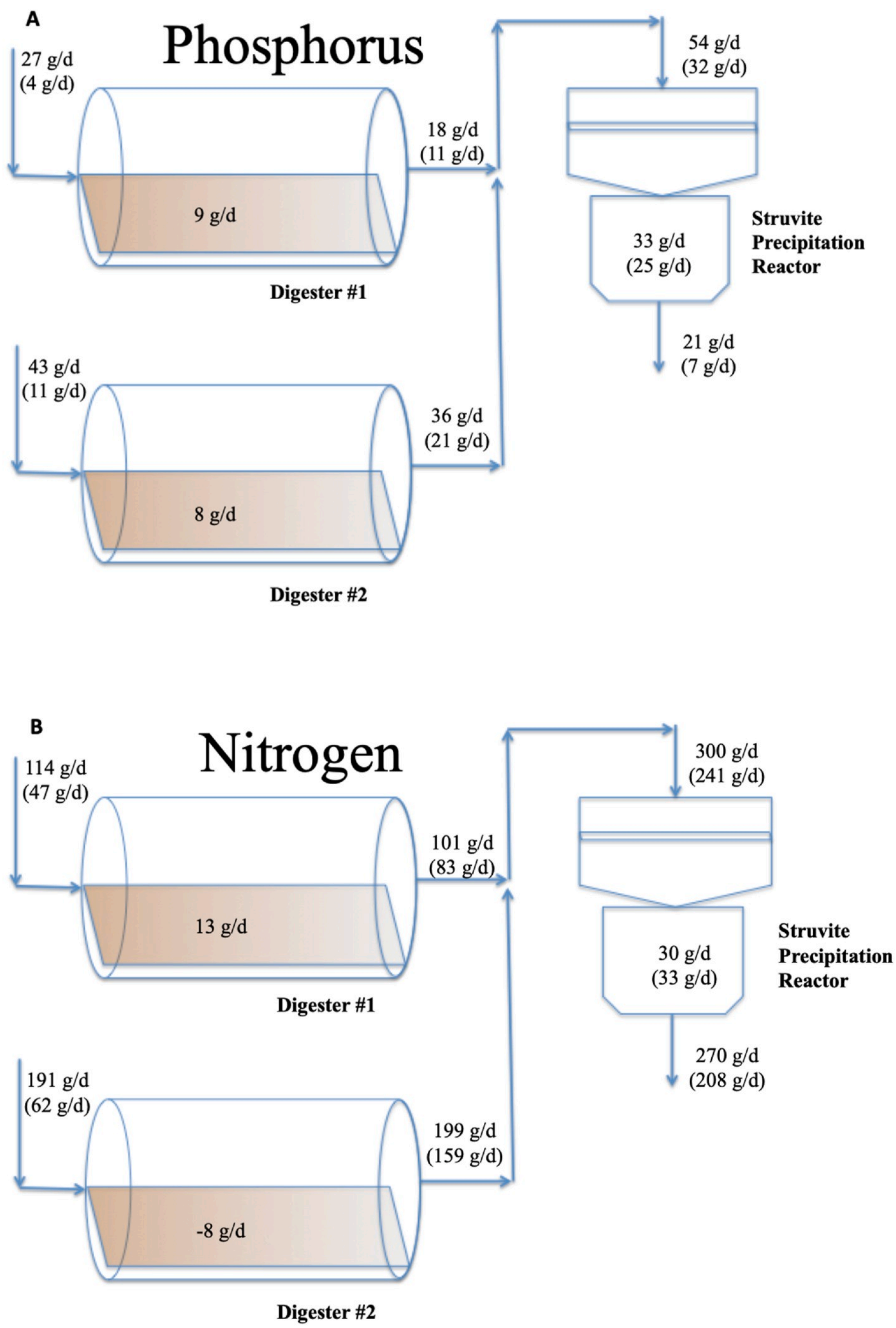

Fig. 2. A) Fate of Phosphorus and B) Nitrogen in Digester #1, Digester #2, and Struvite Precipitation Reactor. The numbers in parentheses are PO_4^{3-}-P and NH_4^+-N. The numbers not in parentheses are Total Phosphorus and Total Nitrogen. Loadings of the struvite reactor influent and effluent are estimates assuming full-scale operation (i.e. all digester effluent is treated) as discussed in Section 2.5.

(Table 5) when soda ash was used as the base for raising pH. This corresponds to a Mg:P molar ratio of 1:1, which indicates struvite formation. An analysis of the solid struvite powder revealed a nitrogen mass fraction of 2.4%. This is lower than the expected nitrogen mass fraction of 5.7% for pure struvite. This could possibly indicate that the solid formed is not struvite. However, it is more likely that the measured value of 2.4% is lower than the actual composition because the solid was heated at 100 °C, and it is known that such heating releases N in the form of ammonia (Bhuiyan et al., 2008). The 9.9% mass fraction of potassium indicates that K-struvite ($KMgPO_4{\bullet}6H_2O$) may also have been recovered, but this typically occurs only once nitrogen has been depleted (Jagtap and Boyer, 2018). The presence of C in the collected solids indicates that some organics were mixed together with the struvite. Even though the precipitate included some K-struvite and organic matter, the main finding is that the harvested precipitate appears to consist principally of struvite.

3.3. Fate of phosphorus in the two tubular digesters

Measured liquid water quality data from Table 3 and solid characteristics from Table 5 were integrated into equations (1) and (4) for digester #1 and digester #2, respectively, to determine influent and effluent phosphorus loadings shown in Fig. 2A.

The phosphate in the liquid effluent was an average of 131% higher than the influent phosphate due to digestion and release of particulate P into soluble P; in digester #1, the effluent was 176% higher (4–11 g P/d), and in digester #2 the effluent was 86% higher (11–21 g P/d). It is well known that digestion releases P from organic solids (Metcalf and Eddy, 2003); however, little literature exists on phosphorus release from animal manure in tubular anaerobic digesters. Two other studies on tubular anaerobic digesters found an increase in phosphate concentration of 16% and 24% (Lansing et al., 2008a, 2008b), much lower than the increase found in this study.

However, even though the phosphate concentration in the liquid phase increases, the total phosphorus (TP) loading decreases from the digester influents to the digester effluents, putatively due to sedimentation of solids in the digesters. Because digester #1 receives influent from four smaller swine and four dairy cows and digester #2 most often receives influent from six larger swine, the TP loading (g/d) in digester #1 (27 g P/d) is approximately half that of digester #2 (43 g P/d). The difference in loading rate and feces source and composition may explain the significant difference between the two tubular digesters in TP reduction percentage (*t*-test, p-value<0.01). However, it cannot be concluded with 95% confidence that phosphate reduction percentages are different ($p = 0.06$). The effluent TP from digester #1 decreased 33% to 18 g P/d and from digester #2 decreased 18% to 36 g P/d. This TP reduction percentage is close to the 36% and 43% decreases measured by Lansing et al. (2008b) and Amini et al. (2017), respectively, but is less than the 92% TP reduction from a previous investigation of digester #1 (Kinyua et al., 2016). The reduction of TP is likely due to biological assimilation (as discussed in Section 3.2), followed by sedimentation of the bacterial cells.

3.4. Fate of nitrogen in the two tubular digesters

Measured liquid water quality data from Table 3 and solid characteristics from Table 5 were integrated into equations (2) and (5) for digester #1 and digester #2, respectively, to determine influent and effluent nitrogen loadings shown in Fig. 2B.

The ammonium increased from the digester influent to the effluent an average of 116%; digester #1 increased 78% (47 g NH_4^+–N/d to 83 g NH_4^+–N/d), whereas digester #2 had a much larger increase of 154% (63 g NH_4^+-N/d to 159 g NH_4^+-N/d). It is well known that digestion increases NH_4^+ concentrations by converting organic N into NH_4^+ (Metcalf and Eddy, 2003), but the efficiency of tubular digesters in effecting this conversion is not well characterized. Two studies of tubular digesters in Costa Rica by Lansing et al. (2008a, 2008b) reported 67% and 78% increases in ammonium, whereas a previous investigation of digester #1 found a 62% reduction in total ammonia nitrogen (TAN) (140 mg NH_4^+-N/L to 53 mg NH_4^+-N/L) (Kinyua et al., 2016). Because nitrification is not expected to convert NH_4^+ into NO_3^- due to lack of oxygen in the digester, an increase in NH_4^+ is more likely.

However, even though the ammonium concentration in the liquid phase increases considerably, the total nitrogen (TN) loading is about the same in the digester influents and effluents. Total nitrogen decreased by an average of 4%, similar to the 0% reduction found by Amini et al. (2017). There was a significant difference in TN (*t*-test, $p = 0.03$) and ammonium ($p < 0.01$) reduction percentages, likely due to differences in nutrient loading. In digester #1, TN loading dropped by 11% (114 g N/d to 101 g N/d). The decrease in TN is likely due to biological assimilation (as discussed in Section 3.2), followed by sedimentation of the bacterial cells. In digester #2, TN loading increased by 4% (191 g N/d to 199 g N/d), possibly due to resuspension of sludge from a sediment layer into the bulk liquid phase, or possibly indicating a mild underestimation of the influent TN loading. Although this evidence suggests that nitrogen was removed by biological assimilation in the tubular digester, that does not mean that the same mechanisms are dominant in the struvite precipitation reactor, which will be discussed in section 3.7.

3.5. Fate of solids in the two tubular digesters

Measured liquid water quality data from Table 3 and solid characteristics from Table 5 were integrated into equations (3) and (6) for digester #1 and digester #2, respectively. The resulting estimates for the fate of solids are shown in Table S2. The average daily solids loading to digester #1 of 984 g/d was much less than the loading to digester #2 of 1659 g/d because digester #2 received influent from more mature swine that produced more mass of manure each day. This larger mass of manure from the more mature swine was less likely to exit the pens by gravity to digester #2, thus the higher percentage of influent wash solids (46%). The TS, VS, TSS, and VSS decreased on average by 57%, 61%, 87%, and 81%, respectively, between the digester influent and the digester effluent. The solids reduction values in both digesters in this study are similar to those of other tubular digesters assessed in Costa Rica (Lansing et al., 2008a, 2008b; Kinyua et al., 2016). The solids reduction results indicate that the digesters are performing as expected and are effective in removing the majority of TSS, either through sedimentation into the sludge solids or hydrolysis of the solids during digestion.

There was a large difference in the estimation of daily sludge solids generation for both digester #1 (equations (1) and (2)) and digester #2 (equations (4) and (5)). This consequently affected the daily estimation of digestion in digester #1 (equation (3)) and digester #2 (equation (6)). Because the phosphate and ammonium concentrations in the digester effluents increased by an average of 131% and 116%, respectively, it is clear that digestion is occurring and a negative digestion rate is not likely. Therefore, for digester #1, the N data from equation (2) were used and not the P data from equation (3). Consequently, the digester #1 estimated sludge sedimentation rate of 467 g/d was used from equation (2), which resulted in a digestion estimate of 364 g/d from equation (3). For digester #2, both the P data from equation (4) and N data from equation (5) were reasonable. Consequently, the digester #2 estimated sludge sedimentation rate of 259 g/d was generated as an average of the estimates generated from equation (4) (666 g/d) and equation (5) (−148 g/d). Putting 259 g/d into equation (6), the digestion rate estimate for digester #2 is 1284 g/d.

The digestion rates in this study are similar to digestion rates from existing studies (Kinyua et al., 2014). Given working volumes of 12,000 L in each digester, the estimated digestion rates become 0.03 g TSS/L-d in digester #1 (37% of the influent of 0.08 g TSS/L-d) and 0.11 g TSS/L-d (77% of the influent of 0.14 g TSS/L-d) in digester #2. Overall, digester #1 had a lower digestion rate (364 g TSS/d, 0.03 g TSS/L-d) and a higher sludge sedimentation rate (467 g TSS/d) than digester #2 (digestion of 1691 g TSS/d, 0.11 g TSS/L-d and sludge sedimentation rate of 259 g/d). One hypothesis is that while digester #2 only receives influent from swine, digester #1 receives swine influent as well as wash from the cow milking area. In this area, cows and maintenance workers bring in recalcitrant materials like sand, which are more likely to settle in the digester and are less likely to be digested. This leads to a higher solids sedimentation rate but a lower solids digestion rate in digester #1.

3.6. Fate of phosphorus in the struvite reactor

The estimations of daily phosphorus loadings for the struvite reactor (Fig. 2A) are based on the hypothetical case of full-scale continuous operation, as discussed in Section 2.5. The estimated struvite reactor influent loadings of 54 g TP/d and 32 g PO_4^{3-}–P/d are the sum of the effluent loadings from digester #1 (13 g TP/d, 11 g PO_4^{3-}–P/d) and digester #2 (36 g TP/d, 21 g PO_4^{3-}–P/d). The estimated struvite reactor effluent loadings of 21 g TP/d and 7 g PO_4^{3-}/d were calculated based on the measured percent reductions of 60% TP and 79% PO_4^{3-} in the pilot-scale reactor (Table 4). The 79% phosphate reduction is close to the range of 85–97% phosphorus recovery in previous studies that performed struvite precipitation on swine digester effluent (Perera et al., 2007; Song et al., 2011; Amini et al., 2017). However, only 60% of TP was removed (estimated loading reduction from 54 g TP/d to 21 g TP/d), meaning that an estimated 33 g TP/d would be in the solid form and 21 g TP/d would remain in the effluent, of which 7 g TP/d would be in the form of phosphate (Fig. 2A). Of the estimated 22 g/d of influent phosphorus not in the form of phosphate, about 64% (14 g/d) is expected to remain in the effluent.

The anticipated high reduction of phosphorus, especially phosphate, would be especially beneficial for farms with agricultural waste managed near freshwater lakes and in phosphorus-limited watersheds. The struvite precipitation reactors could be strategically placed in such regions to reduce the quantity of bio-available phosphate and thus mitigate the chances of harmful algae blooms while providing the benefit of a slow-release fertilizer.

3.7. Fate of nitrogen in the struvite reactor

The estimations of daily nitrogen loadings for the struvite reactor (Fig. 2B) are based on the hypothetical case of full-scale continuous operation, as discussed in Section 2.5. The estimated struvite reactor influent loadings of 300 g TN/d and 241 g NH_4^+-N/d are the sum of the effluent loadings from digester #1 (101 g TN/d, 83 g NH_4^+-N/d) and digester #2 (199 g TN/d, 159 g NH_4^+-N/d). The estimated struvite reactor effluent loadings of 270 g TN/d and 208 g NH_4^+-N/d were calculated based on the measured percent reductions of 10% TN and 14% NH_4^+-N in the pilot-scale reactor (Table 4). The 14% ammonium reduction is slightly higher than the 7% ammonium removal observed during a previous struvite precipitation study using an influent of swine digester effluent (Amini et al., 2017). The estimated 33 g/d of ammonium removal and 30 g/d of TN removal suggest minimal removal of nitrogen not in the form of ammonium.

The 10% nitrogen reduction was low, but is expected given similar low nitrogen reduction efficiencies during sidestream struvite precipitation (Mehta et al., 2015). The removal of nitrogen via struvite precipitation is the intended result, and is in contrast to the removal mechanism of biological assimilation implicated in the tubular digester. The low nitrogen reduction may be less than desired for coastal regions and nitrogen-limited watersheds. In such cases, additional nitrogen removal may be necessary through treatment technologies such as nitrification/denitrification or ion exchange.

3.8. Implications for environmental management

One implication from the pilot-scale demonstration is the need to better manage the effluent products of the tubular digester. Just as releasing biogas leads to increased global warming potential through the release of methane, releasing NH_4^+ and PO_4^{3-} in the liquid digester effluent directly to land that hydrologically connects to surface water or shallow groundwater not only wastes a valuable resource, but also may cause harm to the environment and public health. This study also supports a multiple resource recovery strategy that can be implemented in low- and middle-income countries, of not only recovering biogas, but also recovering nutrients as fertilizer from small-scale tubular anaerobic digester systems. Struvite, a slow-release fertilizer, should be stored in a cool, dry location like synthetic fertilizers. Struvite precipitation coupled with a small-scale digester should thus reduce environmental loadings of mineralized phosphorus and nitrogen to local sources of water. A life cycle assessment and life cycle cost analysis are currently being performed to provide insight into the environmental and economic sustainability of the integrated system.

The ability of tubular anaerobic digesters integrated with a struvite precipitation reactor to remove contaminants and recover multiple resources from small-farm-generated agricultural waste facilitates progress towards the achievement of multiple SDGs. The integrated treatment system contributes to multiple targets within SDG 6 such as improving water quality, increasing safe water reuse, reducing untreated wastewater, and protecting water-related ecosystems (UN, 2018). Additionally, the ability of small rural farms in low- and middle-income countries to recover energy and fertilizer also contributes to SDG 1 (No Poverty), SDG 2 (Zero Hunger), SDG 7 (Affordable and Clean Energy), SDG 10 (Reduced Inequalities), SDG 12 (Responsible Consumption and Production), and SDG 13 (Climate Action) (UN, 2018).

4. Conclusions

The overall goal of this study was to determine the nutrient recovery potential of tubular anaerobic digesters that are integrated with a locally produced pilot-scale struvite precipitation reactor. The system can be used to manage agricultural waste to enhance recovery of resources and thus facilitate the achievement of multiple SDGs and reduce nutrient loading to local waters. Overall, if all digester effluent was directed through the struvite precipitation reactor, it is estimated that unmanaged TP loading to the environment would decrease by 70% and unmanaged TN loading would decrease by 12% from the digester influent to the struvite effluent. Results indicate that an average of 25% of P and 4% of N was removed in the digester effluent through sedimentation. Additionally, 79% of remaining PO_4^{3-}–P and 14% of remaining NH_4^+-N were removed from the liquid effluent of the two digesters in a struvite precipitation reactor. The digesters averaged 87% reduction in TSS and 84% reduction in COD.

The recovered solid in the struvite reactor appears to be struvite as the Mg:P ratio is 1:1; however, the recovered solid's N/P/K mass fractions of 2.5/12.9/9.9 are less than the current synthetic fertilizer's N/P/K mass fractions of 10/30/10. However, struvite may be preferable over synthetic fertilizer given that it is less soluble than synthetic fertilizer, meaning that its nutrients are disseminated to the plants over a longer period of time, reducing the amount of fertilizer needed.

Another promising result of this study was the demonstration of using locally available materials for reactor construction and chemical inputs. A magnesium source, which may be a barrier to struvite production in low and middle income settings due to its high cost, was found as a locally produced waste product. Likewise, a base was produced from soda ash by heating locally purchased baking soda.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Kevin D. Orner: Conceptualization, Methodology, Formal analysis, Investigation, Writing - original draft, Writing - review & editing, Visualization. **Fabricio Camacho-Céspedes:** Conceptualization, Resources. **Jeffrey A. Cunningham:** Conceptualization, Methodology, Validation, Writing - review & editing, Supervision, Funding acquisition. **James R. Mihelcic:** Conceptualization, Methodology, Validation, Writing - review & editing, Supervision, Funding acquisition.

Acknowledgements

This material is based upon work supported by the National Science Foundation under grant 1243510. This material was also made possible by a Fulbright Study/Research Grant to the contact author. The contact author wishes to thank the University of Georgia-Costa Rica for hosting his visit for ten months and Ronald Sánchez Brenes and staff at Universidad Estatal a Distancia (UNED) for use of their analytical laboratory.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2020.110626.

References

Ahmed, S.Y., Shiel, R.S., Manning, D.A.C., 2006. Use of struvite, a novel P source derived from wastewater treatment. In: Wheat Cultivation. 18th World Congress of Soil Science. Philadelphia.
Amini, A., Aponte-Morales, V.A., Wang, M., Dilbeck, M.P., Lahav, O., Zhang, Q., Cunningham, J.A., Ergas, S.J., 2017. Cost-effective treatment of swine wastes through recovery of energy and nutrients. Waste Manag. 69, 508–517.
Apha, 2012. Standard Methods for the Examination of Water and Waste Water, twenty-second ed. American Public Health Association, Washington, DC.
Battistoni, P., Pavan, P., Prisciandaro, M., Cecchi, F., 2000. Struvite crystallization: a feasible and reliable way to fix phosphorus in anaerobic supernatants. Water Res. 34, 3033–3041.
Bhuiyan, M.I.H., Mavinic, D.S., Koch, F.A., 2008. Phosphorus recovery from wastewater through struvite formation in fluidized bed reactors: a sustainable approach. Water Sci. Technol. 57, 175–181.
Bruun, S., Jensen, L.S., Vu, V.T.K., Sommer, S., 2014. Small-scale household biogas digesters: an option for global warming mitigation or a potential climate bomb? Renew. Sustain. Energy Rev. 33, 736–741.
Camacho-Céspedes, F., Uribe Lorio, L., Newcomer, Q., Masters, K., Kinyua, M., 2018. Bio-optimization of compost with cultures of mountain microorganisms (MM) and digested sludge from bio-digester (LDBIO). UNP Res. J. 10, 330–341.
Celen, I., Turker, M., 2001. Recovery of ammonia as struvite from anaerobic digester effluents. Environ. Technol. 22, 1263–1272.
Costa Rica Ministerio de Ambiente y Energia, 2015. (Compendio de Estadisticas ambientales: Costa Rica 2015) compendium of environmental statistics: Costa Rica 2015. http://www.inec.go.cr/sites/default/files/documetos-biblioteca-virtual/puambientalcompendioisticas-2015-01.pdf. (Accessed 13 July 2018).
Doyle, J.D., Parsons, S.A., 2002. Struvite formation, control and recovery. Water Res. 36, 3925–3940.
Etter, B., Tilley, E., Khadka, R., Udert, K.M., 2011. Low-cost struvite production using source-separated urine in Nepal. Water Res. 45, 852–862.
Guest, J.S., Skerlos, S.J., Barnard, J.L., Beck, M.B., Daigger, G.T., Hilger, H., Jackson, S. J., Karvazy, K., Kelly, L., Macpherson, L., Mihelcic, J.R., Pramanik, A., Raskin, L., van Loosdrecht, M.C.M., Yeh, D., Love, N.G., 2009. A new planning and design paradigm to achieve sustainable resource recovery from wastewater. Environ. Sci. Technol. 43, 6126–6130.
Huang, H., Xiao, D., Zhang, Q., Ding, L., 2014. Removal of ammonia from landfill leachate by struvite precipitation with the use of low-cost phosphate and magnesium sources. J. Environ. Manag. 145, 191–198.
Ishii, S.K.L., Boyer, T.H., 2015. Life cycle comparison of centralized wastewater treatment and urine source separation with struvite precipitation: focus on urine nutrient management. Water Res. 79, 88–103.
Jagtap, N., Boyer, T.H., 2018. Integrated, multi-process approach to total nutrient recovery from stored urine. Environ. Sci. Water Res. Technol. 4, 1639–1650.
Kinyua, M.N., Cunningham, J., Ergas, S.J., 2014. Effect of solids retention time on the use of anaerobically digested swine waste as a substrate for denitrification. Bioresour. Technol. 152, 14–20.
Kinyua, M.N., Zhang, J., Camacho-Cespedes, F., Tejada-Martinez, A., Ergas, S.J., 2016. Use of physical and biological process models to understand the performance of tubular anaerobic digesters. Biochem. Eng. J. 107, 35–44.
Lansing, S., Botero, R., Martin, J.F., 2008a. Waste treatment and biogas quality in small-scale agricultural digesters. Bioresour. Technol. 99, 5881–5890.
Lansing, S., Viquez, J., Martinez, H., Botero, R., Martin, J., 2008b. Quantifying electricity generation and waste transformations in a low-cost, plug-flow anaerobic digestion system. Ecol. Eng. 34, 332–348.
Liu, Y.H., Kwag, J., Kim, J., Ra, C., 2011. Recovery of nitrogen and phosphorus by struvite crystallization from swine wastewater. Desalination 277, 364–369.
Matynia, A., Wierzbowska, B., Hutnik, N., Mazienczuk, A., Kozik, A., Piotrowski, K., 2013. Separation of struvite from mineral fertilizer industry wastewater. Procedia Environ. Sci. 18, 766–775.
Mehta, C.M., Khunjar, W.O., Nguyen, V., Tait, S., 2015. Technologies to recover nutrients from waste streams: a critical review. Crit. Rev. Environ. Sci. Technol. 45, 385–427.
Metcalf and Eddy, 2003. Wastewater Engineering, fourth ed. McGraw-Hill, Boston.
Moser, M.A., 1998. Anaerobic Digesters Control Odors, Reduce Pathogens, Improve Nutrient Manageability, Can Be Cost Competitive with Lagoons, and Provide Energy Too. Resource Conservation Management, Inc. http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.591.2479&rep=rep1&type=pdf. (Accessed 13 July 2018).
Munch, E.V., Barr, K., 2001. Controlled struvite crystallization for removing phosphorus from anaerobic digester sidestreams. Water Res. 31, 151–159.
Orner, K.D., Mihelcic, J.R., 2018. A review of sanitation technologies to achieve multiple Sustainable Development Goals that promote resource recovery. Environ. Sci. Water Res. Technol. 4, 16–32.
Orner, K.D., Ozcan, O., Saetta, D., Boyer, T.H., Yeh, D.H., Anderson, D., Cunningham, J. A., 2017. House of quality planning matrix for evaluating wastewater nutrient management technologies at three scales within a sewershed. Environ. Eng. Sci. 34, 773–784.
Ostara, 2018. Ostara Overview North America. http://ostara.com/wp-content/uploads/2018/04/Ostara-Overview-Handout-180424.pdf. (Accessed 4 May 2018).
Perera, P.A., Han, Z.-Y., Chen, Y.-X., Wu, W.-X., 2007. Recovery of nitrogen and phosphorus as struvite from swine waste biogas digester effluent. Biomed. Environ. Sci. 20, 343–350.
Pognani, M., Barrena, R., Font, X., Sanchez, A., 2012. A complete mass balance of a complex combined anaerobic/aerobic municipal source-separated waste treatment plant. Waste manage 32, 799–805.
Ren, Z.J., Umble, A.K., 2016. Water treatment: recover wastewater resources locally. Nat 529, 25.
Shahady, T., Boniface, H., 2018. Water quality management through community engagement in Costa Rica. J. Environ. Soc. Sci. 8, 488–502.
Song, Y.-H., Qiu, G.-L., Yuan, P., Cui, X.-Y., Peng, J.-F., Zeng, P., Qian, F., 2011. Nutrients removal and recovery from anaerobically digested swine wastewater by struvite crystallization without chemical additions. J. Hazard Mater. 190, 140–149.
Stoknes, K., Scholwin, F., Krzesinski, W., Wojciechowska, E., Jasinka, A., 2016. Efficiency of a novel "Food to waste to food" system including anaerobic digestion of food waste and cultivation of vegetables on digestate in a bubble-insulated greenhouse. Waste Manag. 56, 466–476.
United Nations (UN), 2018. Transforming our world: the 2030 agenda for sustainable development. https://sustainabledevelopment.un.org/content/documents/21252030AgendaforSustainableDevelopmentweb.pdf. (Accessed 13 July 2018).
Wang, X., 2003. Diffuse pollution from livestock feeding in China. Agriculture 3B. Diffuse Pollution Conference, Dublin.
Zhang, Q., Prouty, C., Zimmerman, J.B., Mihelcic, J.R., 2016. More than Target 6.3: a systems approach to rethinking Sustainable Development Goals in a resource-scarce world. Eng. Times 2, 481–489.