Geochemical Aspects of Phosphate Recovery from Livestock Manure

By

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A dissertation submitted to the

Graduate School-Newark

Rutgers, The State University of New Jersey

In partial fulfillment of requirements

For the degree of

Doctor of Philosophy

Graduate Program in Environmental Sciences

Written under the direction of

Ashaki Rouff

and approved by

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Newark, New Jersey

May 2021
Abstract of the dissertation

**Geochemical Aspects of Phosphorus Recovery from Livestock Manure**

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Dissertation Director:

Ashaki A. Rouff

Accumulation of excess phosphorous from livestock manure application to crop soil is a major driver for harmful algal bloom formation in surface waters. While this practice as part of a crop nutrition management plan is agronomically sound, it is driving P deposition into vulnerable watersheds and thus in incurring stricter limitation on livestock manure soil application. The process of struvite (MgNH₄PO₄·6H₂O) production out of livestock manure liquids at alkaline condition (pH 8-10) is an expanding practice for P recovery and removal, but high concentration of dissolved organic matter and calcium hinders struvite precipitation and limits the recovery treatment effectivity. In addition, calcium in livestock manure forms insoluble phosphate minerals such as hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂) during the recovery treatment. Due to long residence time of livestock manure effluent in storage lagoons, ≤ 90 % of its phosphate content is complexed to colloids and unavailable for recovery. Common practices to improve phosphate recovery as struvite are acidification and anaerobic digestion pretreatments and magnesium dosing during treatment to suppress
hydroxyapatite formation, all of these significantly increase operation costs. Another disadvantage of alkaline struvite production is high pH of effluent discharge that may harm crop or soil fertility and high overall residual nutrients content. This study evaluated applying aerated fluidized bed reactor approach for struvite recovery from LWE, together with aerobic pretreatment to free up complex phosphate and a combined aeration plus constructed wetland treatment post-treatment. It was hypothesized that this synergic approach will: Effectively recover phosphate without the need for digestion or acidification pretreatment of livestock manure effluent; apply post treatment to address the high pH of discharge effluent and supplement other nutrients removal. In order to further elucidate the geochemistry of interaction between struvite, dissolved organic matter and calcium, a constant composition model simulated struvite precipitation with various dissolved low molecular weight organics and calcium in simulated livestock wastewater effluents. Results from bench and pilot scale aerated fluidized bed reactor trials found an improved phosphate recovery rate when lower calcium and dissolved organic matter occurred, and that high calcium and dissolved organic matter also increased the time needed for phosphate precipitation as struvite in aerated fluidized bed reactor. This was further corroborated by constant composition model showing that the anionic low molecular weight phenol and benzoate increased struvite growth rate by an order of magnitude and suppressed the hinderance effect of calcium on struvite growth. Optimization of magnesium dosing for phosphate recovery from livestock manure found that minimal dosing was sufficient to maximize struvite content in recovered solids and that the thermal stability of ammonium (NH₄) in recovered struvite improved by ≤ 34%. Finally, an evaluation of supplement treatments found that application of aerobic microbial
pretreatment for cattle manure increased the content of recoverable phosphate by up to 92%, and aeration of alkaline effluent from aerated fluidized bed reactor neutralized its pH values.
Acknowledgement

To my wife Dana, my chief editor and supporting partner. This could not have happened without you, thanks for accepting dirty dairy farmer boots, hearing nothing but struvite for many years and all the long days and weekends.

I wish to thank foremost to my dissertation advisor, Ashaki Rouff for her enduring faith in my research and for the opportunity to explore this expansive and sometime non-conventional journey. Thank you for keeping an open mind for the crazy department while keeping it in check. I appreciate the unique opportunity you gave me to work at your lab and for your mentorship and guidance. Thank you boss, for all the effort you put into the success of this dissertation.

I wish to thank my committee members: Beni Lew, Dimitrios Ntarlagiannis, Evert Elzinga and Joseph Heckman, for contributing their time and experience to support this research. Thanks to Beni Lew for his assistance with developing the aerated-FBR and the microbial pretreatments for nutrient recovery, Evert Elzinga for facilitating and mentoring my FTIR and XRD experimental work, and to Joseph hackman for all his support and hosting of field research looking into the use of recovered struvite as fertilizer.

To my lab mates over the years: Amy cannon, Karen Juarez Marlon Ramlogan, Omanjana Goswami, and Suah Yekeh. It has been a long journey and I appreciate all the wisdom you have shared with me, your significant contributions along the way and the opportunity to work together.
Special thanks to Robert Fulper and all the amazing people at Fulper Farm, for believing in this project and for hosting the pilot research on their dairy farm for so many years.

I wish to thank Alexander Gates from the department of earth and environmental science at Rutgers University Newark for supporting the initial set-up of the aerated-FBR research through the GS-LSAMP program.

I wish to acknowledge the contributions of Lee Blaney from the department of chemical, biochemical and environmental engineering at the University of Maryland and his students to the research of low molecular weight organics interaction with struvite, and the for use of his HPLC resources. Also, I wish to acknowledge Deb Jaisi and Mingjing Sun from the department of plant and soil sciences at the University of Delaware, for their support with evaluating inorganic phosphate content in cattle manure and the use of their HPIC resources.

Finally, I wish to thank all the kind people who lend me their time and helped me get to the finish line: To my brother Oren Rabinovich who put up his boots and helped me set up the pilot site experiment in the dead of winter and was always there when I needed a hand; Kyle Gabriel for his enormous work on setting up the open source automation apparatus with MyCodo software; Clint Burgher from Rutgers Animal research farm for support with manure sampling; Candice Huber and the Northeast SARE team for facilitating the field work part of this thesis; Mike Kalczynski and Nathan Rabideaux from the Department of Earth and Environmental Science at Rutgers University Newark for their technical support and good advice.
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<tr>
<td>AFO</td>
<td>animal feed operation</td>
</tr>
<tr>
<td>AMCSD</td>
<td>American mineralogist crystal structure database</td>
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<tr>
<td>ANOVA</td>
<td>analysis of variance</td>
</tr>
<tr>
<td>ATR</td>
<td>attenuated total reflectance</td>
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<tr>
<td>BOD</td>
<td>biochemical oxygen demand</td>
</tr>
<tr>
<td>C</td>
<td>carbon</td>
</tr>
<tr>
<td>N</td>
<td>nitrogen</td>
</tr>
<tr>
<td>Ci</td>
<td>carbon link numerator (i=1,2..n)</td>
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<tr>
<td>CAFO</td>
<td>concentrated animal feeding operation</td>
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<tr>
<td>CCW</td>
<td>counter clockwise</td>
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<td>CI</td>
<td>confidence interval</td>
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<td>CIF</td>
<td>crystallographic information file</td>
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<td>CM</td>
<td>cattle manure</td>
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<td>clockwise</td>
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<td>constructed wetland treatment</td>
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<tr>
<td>DB9</td>
<td>d shell breakout 9 port</td>
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<tr>
<td>DCPA</td>
<td>dicalcium phosphate anhydrous</td>
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<td>DI</td>
<td>deionized water</td>
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<td>DL</td>
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<tr>
<td>DOC</td>
<td>dissolved organic carbon</td>
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<td>dissolved organic matter</td>
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<td>DSC</td>
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<td>differential thermogravimetric scan</td>
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<td>DW</td>
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<td>EDTA</td>
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<td>ground</td>
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<td>GOF</td>
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<td>GPIO</td>
<td>general-purpose input output</td>
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<td>HAB</td>
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<td>HAT</td>
<td>Hardware Attached</td>
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<td>high density polyethylene</td>
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<td>high performance liquid chromatography</td>
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<td>HRT</td>
<td>hydraulic retention time</td>
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<tr>
<td>HS</td>
<td>humic substance</td>
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<tr>
<td>HT</td>
<td>high temperature</td>
</tr>
<tr>
<td>Iᵢ</td>
<td>inflow</td>
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<tr>
<td>I²C</td>
<td>inter-integrated circuit</td>
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<tr>
<td>IAP</td>
<td>ion activity product</td>
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<tr>
<td>ICP</td>
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IP₆ - inositol hexaphosphate
IR – infrared
J- joule
K - equilibrium constant
L – liter
LM - livestock manure
LMW - low molecular weight
LT - low temperature
LW - livestock wastewater
LWE - livestock wastewater effluent
M - mole liter
MAP - monoammonium phosphate
MHC - monohydrocalcite
MHz – megahertz
MS - mass spectroscopy
N - nitrogen element
N₂ - nitrogen gas
NH₃ – ammonia
NO₂ – nitrite
NO₃ – nitrate
NPK - nitrogen phosphate potassium ratio
NPT - national standard pipe thread
O₂ - oxygen gas
OCP - octacalcium phosphate
OES - optical emission spectrometry
OH – hydroxide
ORP - oxidation reduction probe
P – phosphorous
PES - Polyether sulfone
PFR - plug flow reactor
PID - proportional integral derivative
PO₄ – phosphate
PTFE - polytetrafluoroethylene
PVC - polyvinyl chloride
PWM - pulse width modification
PWR - power source
Q – volumetric flow rate
R – replicate
R² - coefficient of determination
RX - receiving data port
S – sample
SBC - single board computer
SBP - small bioreactor process
SD - standard deviation
SEM - scanning electron microscopy
shADP5 - short human-derived amelogenin-derived peptide 5
SI - saturation index
STA - simultaneous thermal analysis
SVDV - synchronous vertical dual view
SW - swine wastewater
SWW - simulated wastewater
TCP - tricalcium phosphate
TG – thermogravimetric
TMP - trimagnesium phosphate
TMT – treatment
TOC - total organic carbon
TSS - total suspended solids
TX - transmit data port
UV – ultraviolet
VDC - volt direct current
VSB - vegetated submerged bed
VVM - volume air per volume reactor minute
WWE - wastewater effluent
XRD - x-ray diffraction
1. Introduction

1.1 Overview

Most animal feed operations (AFO) generate wastewater effluents with high content of water fouling biochemical oxygen demand (BOD) and total suspended solids (TSS) from manure and urine excrement. Addressing the potential harm from these requires that all livestock wastewater effluents (LWE) or livestock manure (LM) leaving the AFO will be retained in lagoons, tanks, etc. to separate them from reaching watersheds as a point source contaminant.\(^1\) Disposal of LWE or LM in the United States (U.S.) is done mainly by applying it to crop soil as part of a crop nutrition management plan,\(^2\) whereby it becomes a non-point source of contamination that is permissible for soil application by most U.S. local environmental regulations.\(^3\) While this approach is mostly suitable to mitigate harm from BOD and TSS, it often falls short in resolving the harmful effect of LWE nutrients deposition primarily of phosphorous (P) and nitrogen (N), from crop soil to surface water where it promotes growth of harmful algal bloom (HAB).\(^4\) The growth of HAB in surface waters is greatly dependent on the availability of P that is often the growth limiting nutrient, and to lesser extent on the presence of nitrogen (N) and other nutrient contaminants.\(^5,6\) Current research has demonstrated that transport of the highly bio-available\(^7\) organic phosphorous (Org-P) and phosphate (PO\(_4\)-P)\(^8,9\) from crop soil to water occurs not only by particulate deposition (aeolian, wash off),\(^10-12\) but also through sub surface flow transport in saturated vadose zones or by fast transport pathways such as cracked soils, indicating that the scope of P transport is more expansive than previously estimated.\(^13\) The growing economical toll of HABs and its negative impact on localities quality of life,\(^14\) are driving stricter regulation that limit LWE or LM compost soil application by means such as
establishing no application buffer zone near waterways and restricting permissible application rated in nutrient management plans. Recovery of P from LWE is also motivated by the recognition that it is a perishable earthen mineral resource essential for food production and industrial applications, where an estimate of $10^7$-26 ton of P is deposited annually to surface waters from manure mostly as PO$_4$-P. This has a significant impact on future security of food production where an improvement in nutrient retention is needed to meet the forecasted deficit between the estimated mineral PO$_4$-P reserves and production demands rise due to growing population. Current trajectories of rock phosphate mineral supplies predicts that such a shortage will begin taking effect by 2035 with a maximum negative economic impact by 2050-2100. In order to mitigate the systematic loss of P from AFO’s along the production process by recovering PO$_4$-P from livestock waste, several approaches are currently applied on a commercial scale (Table 1.1).

Table 1.1. Approaches to mitigation of nutrient loss from AFO

<table>
<thead>
<tr>
<th>PO$_4$-P sources within AFO systems</th>
<th>Method for P Nutrient Management</th>
</tr>
</thead>
<tbody>
<tr>
<td>a. Feed$^{20,21}$</td>
<td>Adding phytase (Phy) enzyme to feed to improve feed conversion of IP$_6$ by cattle and reduced P excretion in CM.</td>
</tr>
<tr>
<td>b. Yard runoff$^{22}$</td>
<td>Limit yard runoff with fuller cover and drain collection to mitigate P losses to wash-off and leaching.</td>
</tr>
<tr>
<td>c. Crop soil$^{23,24}$</td>
<td>Soil and manure inoculation with phytase expressing Bacillus sp. bacteria for conversion of Org-P to bioavailable PO$_4$-P. Cover crop and sub surface LWE application</td>
</tr>
<tr>
<td>d. Solid separation$^{25}$</td>
<td>Separation and composting of LM to stabilize P into a less soluble form that is less likely to be lost in wash-off processes.</td>
</tr>
<tr>
<td>e. Lagoon/Tank$^6$</td>
<td>Spraying on fields for nutrient and waste disposal and/or precipitation of LWE P as struvite salt fertilizer (7-29-0; Mg 10)</td>
</tr>
</tbody>
</table>
1.2 Recovery of orthophosphate and other nutrients from livestock wastewater

When addressing PO₄-P recovery from the AFO waste stream starting with a LM from the livestock yard, bedding, etc. through LWE and separated solids composting pathways and onto soil application, the retention of PO₄-P can be done either by mechanical or chemical separation methodologies such as struvite (MgNH₄PO₄·6H₂O) production (Figure 1.1).

Mechanical separation of PO₄-P is done by removing the particulate matter that carries it either as IP₆ biomass or as complexed colloidal with mixed sorbent or precipitate P (mostly Ca-PO₄) that is part of the TSS. Belt screen press, screw press, disc centrifuges, geotextiles and settling pools are widely used as a mean to separate the bulkier particles (>25 µm) with a removal of up to ≤ 30% w/w of LWE TSS. Evaluation of PO₄-P content in the total solids of LWE (swine, cattle) showed that ≤ 90 % was present in the TSS phase and ≤ 50 % was in particles larger than 500 µm diameter. An alternative or supplement approach for retention of LWE nutrients in soils application is the use of
cover crops as a mean to prevent the soil erosion that leads to PO4-P deposition. In areas where ground slope is steeper than the effective retention capacity of cover crops, a more conservative approach of sub-surface manure application may be applied by utilizing plow injection incorporation.

1.3 Geochemical challenges of struvite precipitation in livestock wastewater

Chemical recovery of PO4-P from LW is primarily applied either by wet chemistry or more recently by milling processes. The process of milling utilize mechanical friction energy to promote crystallization of struvite, while wet chemistry use coagulation-flocculation or precipitation to extract nutrients as solids from the LWE liquid phase. The most widely used P precipitation process currently is the production of struvite as described in eq. 1.1 for the precipitation of PO4-P, ammonium (NH4-N), and magnesium (Mg), whereby:

\[
\text{Mg}^{2+}_{\text{aq}} + \text{HPO}_4^{2-}_{\text{aq}} + \text{NH}_4^+_{\text{aq}} \leftrightarrow \text{MgNH}_4\text{PO}_4\cdot6\text{H}_2\text{O(s)} + \text{H}^+_{\text{aq}} \quad \text{(Eq. 1.1)}
\]

Precipitation of struvite is pH dependent with a maximum saturation index (SI) occurring at pH 7-11, since at acidic pH the speciation of HPO42- and PO3- is minimal while at high alkalinity (pH > 11) Mg2+aq and NH4+aq concentrations are minimal. When dissolved potassium (K) concentration in LWE is high (K:NH4-N > 1:5) the isomorph K-Struvite (KMgPO4·6H2O) is likely to coprecipitate, and the mineral dittmarite MgNH4PO4·H2O can often coprecipitate with struvite however the driving mechanism for its formation in LWE is not well described. The value of struvite SI is defined by the ion activity product (IAP) of its components and Ksp of struvite:

\[
\text{SI} = \log_{10} \left[ \frac{\text{IAP}}{\text{Ksp}} \right] = \log_{10} \left[ \frac{\left(\text{Mg}^{2+}\right)\left(\text{PO}_4^{2-}\right)\left(\text{NH}_4^+\right)}{10^{-13.26}} \right] \quad \text{(Eq. 1.2)}
\]
In order to predict struvite formation, kinetic considerations for the rate of precipitation are also needed. Theses involve the rate of struvite formation by nucleation and growth, as well as competition from struvite components coprecipitation into other thermodynamically favorable mineral phases (Table 1.2).

Table 1.2. Representative group of the mineral phases occurring during the wet chemistry alkaline nutrients recovery process for LWE treatment

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formation</th>
<th>Ksp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dittmarite</td>
<td>( \text{Mg}^{2+} + \text{H}<em>{2}\text{PO}</em>{4}^- + \text{NH}_4^+ + \text{H}_2\text{O} \leftrightarrow \text{MgNH}_4\text{PO}_4\cdot\text{H}_2\text{O} + 2\text{H}^+ )</td>
<td>(10^{-13.26})</td>
</tr>
<tr>
<td>K-struvite</td>
<td>( \text{Mg}^{2+} + \text{H}_{2}\text{PO}_4^- + \text{K}^+ \leftrightarrow \text{MgNH}_4\text{PO}_4\cdot6\text{H}_2\text{O} + 2\text{H}^+ )</td>
<td>(10^{-11})</td>
</tr>
<tr>
<td>HAP</td>
<td>(5\text{Ca}^{2+} + 3\text{PO}_4^{3-} + \text{OH}^- \leftrightarrow \text{Ca}_5(\text{PO}_4)_3\text{OH} )</td>
<td>(10^{-58.62})</td>
</tr>
<tr>
<td>(\beta)-TCP</td>
<td>(3\text{Ca}^{2+} + 2\text{PO}_4^{3-} \leftrightarrow \text{Ca}_3(\text{PO}_4)_2 )</td>
<td>(10^{-28})</td>
</tr>
<tr>
<td>Newberyite</td>
<td>( \text{Mg}^{2+} + \text{HPO}_4^{2-} + 3\text{H}_2\text{O} \leftrightarrow \text{MgHPO}_4\cdot3\text{H}_2\text{O} )</td>
<td>(10^{-5.8})</td>
</tr>
<tr>
<td>Monetite</td>
<td>(3\text{Ca}^{2+} + 2\text{PO}_4^{3-} \leftrightarrow \text{Ca}_3(\text{PO}_4)_2 )</td>
<td>(10^{-6.9})</td>
</tr>
<tr>
<td>Nesquehonite</td>
<td>( \text{Mg}^{2+} + \text{CO}_3^{2-} + 3\text{H}_2\text{O} \leftrightarrow \text{CaCO}_3\cdot3\text{H}_2\text{O} )</td>
<td>(10^{-4.67})</td>
</tr>
</tbody>
</table>

Since the ratio of dissolved nutrients in most LWE is \( \text{NH}_4^{+\text{aq}} >> \text{Mg}^{2+\text{aq}} > \text{PO}_4^{3-\text{aq}} \), great consideration is applied in chemical nutrients recovery processes to the formation of Ca-P04 minerals that suppress struvite formation by lowering its IAP values as \( \text{PO}_4 \) is often the limiting constituent. The rate of struvite precipitation is also greatly affected by dissolved organic matter (DOM) in LWE, where higher DOM concentration was shown to reduces the rate of struvite precipitation. In contrast, slight to moderated increase in the concentration of TSS in LWE improves struvite nucleation and growth as it provide an abundance of localized sites favorable for ion complexation and thus reduce the
nucleation energy making it more favorable.\textsuperscript{52} However, from an engineering perspective, very high TSS values greatly reduce the size of struvite particles (≤ 5 µm) due to dispersed precipitation sites, preventing its settling for an effective separation from the LWE and tend to result in poor recovery.\textsuperscript{53}

1.3.1 Hindrance for struvite formation and potential benefits associated with Ca and other polyvalences cations

In livestock LWE, high contents of polyvalence cations and carbonates promotes the coprecipitation of calcium carbonates (CaCO\textsubscript{3}·nH\textsubscript{2}O), magnesium carbonates (CaCO\textsubscript{3}·nH\textsubscript{2}O), calcium phosphates (Ca-PO\textsubscript{4}) or magnesium phosphates (Mg-PO\textsubscript{4}) mineral during the alkaline nutrient recovery process.\textsuperscript{26,31} Carbonates are a viable soil amendment treatment for acidic soils (liming) that is a key to preventing phytotoxicity stress.\textsuperscript{54} Within LWE solution under alkaline conditions, The speciation between the formation of calcite (CaCO\textsubscript{3}) and monohydrocalcite (CaCO\textsubscript{3}·H\textsubscript{2}O) depends on Mg\textsuperscript{2+\textsubscript{aq}} concentration, where as it increases (Mg\textsuperscript{2+}\textsubscript{aq}:Ca\textsuperscript{2+} > 1.2 ) monohydrocalcite will form.\textsuperscript{55} At a higher still concentrations of Mg\textsuperscript{2+\textsubscript{aq}} magnesite (MgCO\textsubscript{3}) followed by nesquehonite (MgCO\textsubscript{3}·3H\textsubscript{2}O) will form.\textsuperscript{56,57} Minerals of Ca-PO\textsubscript{4} commonly forming in LWE treated for alkaline nutrient recovery are hydroxyapatite (Ca\textsubscript{10} (PO\textsubscript{4})\textsubscript{6}(OH)\textsubscript{2}; HAP), tricalcium phosphate (β-TCP; Ca\textsubscript{3}(PO\textsubscript{4})\textsubscript{2}) and monetite (CaHPO\textsubscript{4}). These are less likely to precipitate when excess Mg is applied to LWE, usually by supplementing > 100 mg L\textsuperscript{-1} Mg.\textsuperscript{57,58} In the process of PO\textsubscript{4}-P recovery from livestock wastewaters for nutrients recycling, suppressing the formation of HAP is desirable as it is insoluble (equilibrium solubility product; K\textsubscript{sp} 10^{-58})\textsuperscript{59} and therefore not effective as fertilizer. In contrast, monetite and TCP are effective...
fertilizers but tend to have poor recovery rates in the LWE treatment apparatus due to their flaky morphology resulting in high buoyancy. The formation of Mg-PO$_4$ trimagnesium phosphate (Mg$_3$(PO$_4$)$_2$; TMP) and bobbierite (Mg$_3$(PO$_4$)$_2$·8H$_2$O) occurs in LWE where higher concentration of Mg are present and tend to be less kinetically favorable than the formation of Ca-PO$_4$ minerals when no Mg supplementation applied.

Both PO$_4$ minerals and carbonates have high affinity for polyvalent cations sorption, where the sorption of Zinc (Zn), Manganese (Mn), Cobalt (Co), copper (Cu) nickel (Ni) and iron (Fe) can facilitate reclamation of micronutrients from LWE. The uptakes reported for these recovered micronutrients from LWE were mostly withing the environmentally safe margin for soil application (120-600 mg kg$^{-1}$).

1.3.2 Hindrance for struvite formation associated with DOM in LWE

The composition of DOM in LM and subsequently in downstream LWE is highly heterogeneous depending on the livestock source (cattle, hogs, poultry, etc.), feed or process (storage in lagoon / tank, solid separation, post-treatment type). Therefore, with some degree of generalization DOM in LWE is often classified either by: dalton (Da) molecular mass size; chemical group composition (Org-P; N, Lipids, etc.); geochemical stability ranging from highly stable humic substance (HS) to short term stability of low molecular weight DOM; or by ratio of aliphatic to cyclic carbon in ultraviolet (UV) radiation absorption at a specific wavelength (nm) such as the UV$_{254nm}$ analyses. Prior research has shown that at lower concentrations of DOM, hindrance to both nucleation and growth of struvite is limited, but at higher concentrations (> 500 mg L$^{-1}$) longer nucleation times and slower growth rates of up to 1-2 orders of magnitude
from a 1-20 µ mole min\(^{-1}\) at pH 9 and 0.2 < SI \(_{\text{struvite}}\) < 2 were observed.\(^{77-79}\) Complexation of DOM with struvite components, PO\(_4\)-P, Mg, NH\(_4\)-N will either reduce its IAP and in effect its SI, or form an energetic barrier that will lower the kinetic of struvite agglomeration rate. On the other hand, the high affinity of DOM-Ca complexation might be advantageous to struvite formation, due to the high degree of Ca hinderance to struvite formation. It is worth noting that while it is expected that co-chelation of Mg will occur simultaneously with Ca, the high ratio of Mg >> P in most LWE reduces the consequent reduction in struvite SI.\(^{48,77,80,81}\)

1.4 Design of aerated-FBR reactor

There are as many unique designs of novel reactors for struvite precipitation as there are laboratories who study this subject, these can mostly be classified as either: plug flow reactors (PFR); continuous stirred-tank reactor (CSTR), or a hybrid of the two methods (Figure 1.2). The majority of CSTR or PFR use the principle of fluidized bed (FB) to separate the precipitating solids from the LWE flow. Inside a FB separator, vertical expansion of the flow pathway reduce the effluent flux in proportion to Bernoulli principle.\(^{82}\) As a result of the flux reduction, the buoyancy of suspended struvite particles decreases, they no longer travel with the LWE leaving the reactor and a fluidized bed layer of suspended solids is formed. For improved nutrients recovery in any of these reactor designs, an increased hydraulic shear pressure greatly improve the rate of struvite precipitation by an exponent power relation.\(^{83,84}\) Shear pressure within the reactor can be achieved by influent jet geometry in PFR such as rearranging the feeding nozzles position or shape for an increased hydraulic shock,\(^{85}\) and by using variable mixer agitator shapes and rounds per minute (rpm) setting in CSTRs.\(^{57,58,86}\) The time of reaction per unit of
influent is described as hydraulic retention time (HRT) and can be simplified for most applicable purposes as the relation between reaction volume V and flow rate Q:

\[ \text{HRT} = \frac{V}{Q} \]  

(eq. 1.3)

Solids from either of the three reactor designs, PFR, CSTR or aerated-FBR are collected by gravimetric separation, mostly through lowering of the flow rate and collecting the high solid content fraction of the reactor volume followed by sieving and air drying.

![Diagram of reactor designs](image)

Figure 1.2. Common struvite reactor designs: a. plug flow reactor (PFR) allow separation by FB along the expansion of pathway (v2). Nozzle design in v1 allow for shear mixing of influent to promote growth; b. in continuous stir tank reactor (CSTR) shear mixing is independent of the inflow rate and design is more compact comparing to PFR. Separation for recovered solids is not integral to the CSTR and further treatment is needed; c. the aerated-FBR integrate CSTR with PFR for a compact design.

1.5 Optimizing struvite production through aerated-FBR treatment

1.5.1 Supplement of Mg for inducing struvite formation in treated LWE

Supplement Mg application\textsuperscript{87,88} to struvite recovery process in LWE treatment has two goals, pH titration above pH 8 when MgO is applied\textsuperscript{89,90} in addition to suppressing Ca-P minerals precipitation through which can be achieved through any Mg source (mineral salt...
MgCl₂, Seawater Mg, etc.).\textsuperscript{91,92} When MgO is applied to LWE, the hydrolyzed product Mg(OH)₂ drive the effluent pH upwards, which satisfy both the alkalinity needed and Mg dosing for struvite production.

1.5.2 Aeration of LWE for reduced struvite production costs

Carbon dioxide stripping\textsuperscript{93} is used in the aerated-FBR reactor to achieve alkaline conditions without OH\textsuperscript{57,58} or magnesium oxide (MgO) application.\textsuperscript{87} In this process, excess aeration saturates the effluent with soluble gases from the air, or strip them out of the effluent in proportion to the concentration difference between the gas and liquid phases (primarily: oxygen gas; O\textsubscript{2g}, carbon dioxide; CO\textsubscript{2g}, nitrogen; (N\textsubscript{2g}).\textsuperscript{94,95} Removal of CO\textsubscript{2} from LW will raise the liquid pH by condensation of carbonic acid (H\textsubscript{2}CO\textsubscript{3}) in proportion to:

\[\text{HCO}_3^{-\text{aq}} + \text{H}^+ \leftrightarrow \text{H}_2\text{CO}_3^0 \text{aq} \leftrightarrow \text{H}_2\text{O} + \text{CO}_2^{\text{aq}} \leftrightarrow \text{CO}_2^{\text{g}}\]  
\text{(eq. 1.4)}\textsuperscript{96}

As the liquid phase is aerated, the interface of air water is equilibrating the partial pressure (X\textsubscript{gas-phase}) of both phases for the dissolved CO\textsubscript{2}, where X\textsubscript{CO2-water}>> X\textsubscript{CO2-air} and CO\textsubscript{2} is stripped from the aqueous phase. The rate of pH increase is governed primarily by the system alkalinity (buffer) content, temperature, aeration geometry and ratio of volume air to volume liquid per minute (VVM).\textsuperscript{93,95} Aeration will raise pH by lowering CO\textsubscript{2aq} partial pressure in proportion to henry constant (k\textsubscript{H}) up to an approximate maximum X\textsubscript{CO2} effect on pH change at pH 9-9.5 depending on the solution ionic strength and alkalinity buffer.

1.5.3 Open-source automation applications for aerated-FBR treatment of LWE

Utilizing a single board processor (SBP) computer such as Raspberry Pi 3 B+ (R-Pi) is suitable for field and lab geochemical research applications such as titration, datalogging, mixing and sample processing. Using single board design, the R-Pi is a compact and low
cost (U.S.$ 35) apparatus that operate in field conditions without losing capabilities. R-Pi use 40 pin port for 0 / 3.3 VDC logic, 5 VDC power output, I²C communication and two cord (RX / TX) data communication with external accessories. Since the R-Pi does not currently support analogic data processing, an analog to digital (bit conversion) intermediate device is needed. For geochemical applications, Atlas Scientific data processors are designated for pH, ORP, etc. electrode sensors readers. An environmental engineering program (MyCodo) installed on R-Pi is used to control geochemical equipment, log sensor reading and automate. Key accessories components for geochemical research applications are: a. powering of equipment, b. signal processing, c. datalogging.

a. powering of equipment: The R-Pi SBC support pulse width modification (PWM), and in combination with logic outputs (0 / 3.3 VDC) can operate devices that support external / remote control. Most conventional remote controllers require a high (~1-5 VDC; 20-70 mA) signal for an “on/start” command and a PWM for output modification of motor speed. Additional pins operate counter/ forwards and other esoteric conditions. The R-Pi 26 designated GPIO can operate simultaneously delivering 3.3 VDC at ~70 mA.

b. signal processing: Since R-Pi SBC does not support analog input, a data acquisition processor is needed to convert signal mV; mA to bit input (analog to digital). Another consideration is needed for circuit isolation for pH, ORP, EC, etc. reading. Once isolated the R-Pi software Mycodo can handle data processing, or a simple python code can be applied.

c. datalogging: The most useful application of the MyCodo – R-Pi system is its datalogger, with an advance function control. As such in addition to a relatively high frequency data recording, integrated operations can be run simultaneously with minimal user input. This
includes PID functions, titration, time dosing, auto sampling, mechanical agitation and more. The large sensor library allows use of a wide range of available methods and combine products from various manufactures.

1.6 Post treatment for LWE with CWT

The use of constructed wetland treatment (CWT) is of growing interest as a cost-effective approach to disposal of LWE, especially in regions where soil application of LWE is limited by regulations.97-99 Two types of CWT are vegetated submerged bed (VSB) and free water surface (FWS),100 where FWS can hold either emerging / floating or submerged vegetation. VSB are considered more effective for water conservation with lower evapotranspiration (ET) comparing to FWS, as it is primarily a sub-surface flow with lesser plant roots mass and water – air interface.101 Another benefit of the VSB system is a very high surface area for LWE contact with microbial biofilm that is an effective driver of BOD sequencing and TSS retention.102-104 In FWS system, the majority of BOD and TSS removal occur on surface areas provided by wetland plants epidermis, adjunct biofilms to plant surfaces, as well as nutrient exchange with the wetland plants. Pools of FWS with submerged plants is a unique subgroup of FWS wetland used as a finishing treatment for considerably cleared LWE where oxygenating plants and high ultraviolet radiation from exposed water surface eliminate excess microbial population.103

Considerations of CWT design to treat LWE accounts primarily for the available area for CWT placement, need for water preservation, load of TSS in the LWE and the risk of overflow failure due to storm related flooding (Table 1.3).103 CWT application for nutrients removal targets both nutrient retention and nutrient recycling. The retention of nutrients is aimed primarily N and P,105 where transition from anaerobic to aerobic
conditions drives different metabolic cycles and frees N, P for plant or biofilm ingestion (nitrification, denitrification, organophosphate hydrolysis, etc.) 

97,104,106. The N nutrients in LWE are primarily NH4-N, NO3-N and NO2-N, and an applied sequence of transition from aerobic, anaerobic conditions and so forth promotes the conversion of N into the NO3-N that is highly bioavailable for plants roots uptake and improve retention, while ratio of C >> N in LWE improve biofilm retention of N. 107,108 Retention of P from LWE in CWT is primarily a by-product of TSS retention, as most of LWE P is in complexed form either as Ca-P insoluble salts or surface complexation with colloidal material. 109 Long term research has demonstrated that in similarity to P accumulation in soils, as colloidal P build up in CWT, it can over time pass the CWT retention capability and leach into surface waters or be washed away during flooding events. 110,111

A nutrient recycling approach for CWTs involves periodical harvesting of plant biomass from the CWT as a means to both recycle nutrients and clear the CWT from excess N, P or biomass that hinder flow. The plant cattail (Typha) is a widely used emerging plant in FWS CWT due to its salt tolerance (≤ 15 ppt) and ability to withstand a wide wetting ranged from high water table to +24 inch submersion. 103 The shoots system of Cat tail is rich in starch and protein 112-114 and can be milled into animal feed with an expected yield of 7-12 kg shoots m^2 CWT, making it a potentially viable approach to recycling LWE nutrients into feed. 114,115 Another similar approach utilized harvesting of algae or submerged plants into feed as a mean to recycle nutrients out of CWT. 116,117
### Table 1.3. Comparison of VSB and FWS design for CWT

<table>
<thead>
<tr>
<th>Design consideration</th>
<th>VSB</th>
<th>FWS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area requirement</td>
<td>Low, very high surface area</td>
<td>High</td>
</tr>
<tr>
<td>Cost of installation</td>
<td>High, require upkeep for accumulated TSS</td>
<td>Low, initial investment in earthen pools and plants</td>
</tr>
<tr>
<td>Mode of operation</td>
<td>Primarily anaerobic</td>
<td>Aerobic to anaerobic as a function of pool depth and plants population</td>
</tr>
<tr>
<td>Flood resilience</td>
<td>Lower, tend to overflowing bypass and require a retaining pool backup</td>
<td>High, emerging plants serve as a flow energy breaker and pool design takes storm surge into account</td>
</tr>
</tbody>
</table>

### 1.7 Microbial treatments for improved PO₄-P recovery as struvite

Microbial activity in LM is key in mineralizing Org-P and other organic nutrients, where exocellular expression of enzymes by LM microbiome is effective at converting the Org-P inositol hexaphosphate (IP₆) into PO₄-P. This in turn prevents accumulation of relatively mobile IP₆ from LM soil application. Therefore, while there are many phosphatase enzymes, the activity of the enzyme phytase (Phy) in LM is recognized as a significant factor in reducing the harm from P in LWE and LM soil application.
The application of microbial treatment for nutrient recovery is mostly done by anaerobic digestion that is beyond the scope of this thesis or by aerobic digestion, both are used as a pretreatment for nutrient recovery as struvite or other approaches. Microbial treatment to LWE can be applied either by dosing as activated sludge, inoculation or as an immobilized biological reactor (Figure 1.3).

![Microbial bioreactor designs: a. activated sludge from concentrated dewatering separation is reintroduced to LW and preventing dilution of treatment; b. constant microbial suspension dosing treatment; c. suspended SBP capsules are placed withing LW solution](image)

In activated sludge, a targeted microbiome slurry sample is collected from the previously treated effluent and re-introduced into the treated LW to promote the desired nutrient removal reaction. Similarly, inoculation introduce an external cultured microbial slurry into LW for the same effect. Immobilized microbial treatment used small bioreactor process (SBP) to encapsulate the applied bacteria within a membrane, thus immobilizing it within the flow through of treated LW. The benefits of using the SBP are its ability to isolate the applied bacteria within the permeable membrane (0.4-1.2 μm), thus protecting it from predatory stress and damage from suspended solids. Capsulation placement of SBP eliminates the need for dosing or inoculation, as it is retained within the LWE flow and not diluted by continuous volume exchanges. The SBP apparatus is consisted of an outer
membrane and an inner carrier agar bar to supplement microbial nutrition. As the supplement nutrients is depleted and additional environmental stress hinder the growth of SBP bacteria it becomes ineffective, usually withing 1-3 months.

1.8 Methodology

The geochemical research questions outlined is this chapter revolved primary on how can struvite formation be better induced in the presence of Ca and non-descript DOM in LWE. A review of the current state of the art indicated that mitigation of these hinderances rely on acidification for de-complexation of PO₄-P from Ca, and anaerobic digestion for DOM elimination. These approaches leave room for improvement of process efficiency and evaluation of applying aerobic alternative for PO₄-P recovery. The key gaps of knowledge identified regarded the geochemical nature of the synergic interaction between Ca, DOM and struvite components during induced precipitation, and consequently the effects of Ca and DOM on struvite coprecipitation with other minerals, its thermal stability and the mineral morphology. These research questions were then integrated into the four dissertation hypotheses outlined in the hypotheses segment, out of which the individual objectives executed in the dissertation chapters two through six were derived.
1.8.1 Hypotheses

This research looks into the geochemistry of struvite formation in LWE, where high Ca and DOM conditions are not ideal for its nucleation and growth. It is hypothesized that:

I. Aerated-FBR, a hybrid reactor design can be an effective mean for PO$_4$-P recovery as struvite from LWE.

II. Combined treatment of aerated-FBR and CWT can provide a cost effective nutrient mitigation treatment for LWE of small – medium farm operations.

III. While overall DOM in LWE hinder struvite growth, the presence of dissolve ionic LMW organics counteracts it and promote struvite growth.

IV. Recovery of PO$_4$-P as struvite from LWE using bacillus sp. pretreatment to mineralize organic P for CM can prevent Ca-P complexation that hinder struvite recovery.

1.8.2 Objectives

The following objectives were developed for the dissertation research chapters in order to investigate the hypotheses listed in section 1.8.1 of the methodology.

Chapter 2 objectives: Aerated Fluidized Bed Treatment for Phosphate Recovery from Dairy and Swine Wastewater

1. Evaluate the use of aerated-FBR system for PO$_4$-P recovery from swine and dairy LWE in a bench scale

2. Compare struvite production from a DOM free synthetic LWE to sampled LWE from dairy and swine AFO to assess the synergic effect of DOM and Ca on struvite precipitation
**Chapter 3 objectives:** Nutrient Recovery and Constructed Wetland Treatments for Dairy Lagoon Effluent: A Pilot Scale Evaluation

1. Evaluate PO\textsubscript{4}-P recovery from dairy LWE in a pilot scale
2. Compare the use of VSB and FWS CWT’s for post aerated-FBR treatment of dairy LWE

**Chapter 4 objectives:** Magnesium Supplementation for Improved Struvite Recovery from Dairy Lagoon Wastewater

1. Compare the geochemical effects of Mg dosing rates and reaction pH on struvite recovered from dairy LWE.
2. Evaluate the minerology, micronutrient uptake and thermal stability of the mixed phase struvite carbonate fertilizer recovered from dairy LWE treated with aerated-FBR.

**Chapter 5 objectives:** Effect of Phenolic Organics in Simulated Dairy Wastewater on Struvite Precipitation

1. Assess the synergic effect of Ca and phenol LMW as a DOM model on struvite nucleation and growth

**Chapter 6 objectives:** Formation of Struvite in the Presence of Low Molecular Weight Organics

1. Compare struvite nucleation and growth in the presence of wide range of LMW functional groups modeling DOM in simulated LWE.

**Chapter 7 objectives:** Enhanced phosphorus recovery from cattle manure with aerobic *bacillus sp.* mineralization treatment

1. Compare aerobic microbial and enzymatic pretreatments to enhance struvite recovery from cattle LWE.
2. Evaluate the use of SBP to immobilize microbial pretreatment for CM for struvite nutrient recovery with aerated-FBR treatment.

1.9 Synopsis of thesis work

The thesis work outlined in the methodology section (chapter 1.8) was not laid as a single experimental design but rather evolved throughout the discovery process. The initial set of research questions focused on the design and applications of the aerated-FBR system for nutrients recovery as outlined in chapters 2-3. This work started with a wider scope looking into struvite production from both cattle and hog wastewaters, but as it became clear that the mineral complexity of precipitate from cattle wastewater posed a more significant case study it became the primary research interest. The key geochemical interests as identified in chapters 4-6 were the effects of magnesium dosing, pH and individual LMW organics functional groups on the formation of struvite. This work evaluated the effect of Mg dosing on the thermal stability and minerology of recovered solids from treated cattle LWE, as well as the relation between LMW organics, struvite nucleation and growth in simulated LWE. Another interest pursued outlined in chapter 3 and 7 was the application of CWT and aerobic microbial treatments of LWE to enhance the outcomes of the nutrient recovery process. The goal of CWT application was to supplement the nutrient removal done by the aerated-FBR treatment, while an aerobic microbial pretreatment enhanced the availability of PO₄-P by mineralizing Org-P.
2. Aerated Fluidized Bed Treatment for Phosphate Recovery from Dairy and Swine Wastewater

Abstract:

An aerated fluidized bed reactor (aerated-FBR) was used for recovery of orthophosphate (PO$_4$−P) from dairy wastewater (DW) and swine wastewater (SW) by struvite (MgNH$_4$PO$_4$·6H$_2$O) precipitation. Model wastewater solutions (S-model, D-model) free of organic material were also treated. The maximum PO$_4$−P recovery for treated livestock wastes was 94% for SW and 63% for DW. The PO$_4$−P recovery did not improve for S-model compared to SW, but increased to 81% for D-model relative to DW, suggesting that the high organic content of DW may hinder the recovery process. X-ray diffraction (XRD) analysis of recovered solids revealed that treated SW produced mostly struvite (95–98%) while DW yielded a mixture of struvite (28–33%), calcite (CaCO$_3$; 17−55%), and monohydrocalcite (CaCO$_3$·H$_2$O; 13–42%). The Fourier transform infrared (FTIR) spectra of the solids confirm the presence of vibrational bands associated with these minerals. Simultaneous thermal analysis (STA) indicated that all solids, except for DW, show thermogravimetric (TG) trends consistent with the struvite and calcium carbonate content. The DW solids had additional TG steps, possibly due to high organic and colloidal content, and slightly improved ammonium stability. The aerated-FBR treatment is an effective method to reduce PO$_4$−P from livestock wastewater through precipitation of pure struvite and struvite/calcium carbonate mixtures.

This chapter is published under:
2.1 Introduction

Livestock wastewater is nutrient-rich with high concentrations of orthophosphate (PO$_4$-P) and ammonium (NH$_4$-N), both extensively used by agronomic crop producers.$^{17,47}$ In wastewater, phosphorus (P) is present as PO$_4$-P and organic P, such as phytic acids, that eventually degrade into PO$_4$-P.$^{125}$ The NH$_4$-N is mostly from excess proteins in livestock feed that are excreted as urea in urine.$^{132}$ The United States (U.S.) livestock population consists mostly of poultry, hogs, and cattle. The hog and cattle industries with $\sim$70-90 million animals per year contribute 40% of overall nitrogen (N) and P emitted through livestock waste.$^{133,134}$

The majority of livestock in the U.S are raised in concentrated animal feeding operations, which are regulated as contaminant point sources. Thus, all of their wastewater effluents are contained in lagoons or storage tanks, and commonly discharged to topsoil as fertilizer through spraying.$^{135}$ Wastewater discharged in this manner, done as part of an overall nutrition management plan, has limited benefit as fertilizer because application is imprecise and the nutrients are not in slow release form.$^{136}$ Effluent spraying also results in unnecessary water losses and contributes to greenhouse gas emissions.$^{137,138}$ Furthermore, in some soils types such application, similarly to excess manure application, may result in a reduction in crop yield due to excess PO$_4$-P, salinity, and micronutrient accumulation over time.$^{139,140}$ Excess nutrients in soils degrade water quality through eutrophication of surface waters via runoff, and leaching into groundwater by nitrification.$^{141,142}$
Agricultural wastewater can be treated for nutrient recovery by the aerated fluidized bed reactor (aerated-FBR) method that precipitates PO$_4$-P and NH$_4$-N as struvite (MgNH$_4$PO$_4$·6H$_2$O), a viable slow release fertilizer $^{58,143}$

$$\text{Mg}^{2+} + \text{NH}_4^+ + \text{HPO}_4^{2-} + 6\text{H}_2\text{O} \leftrightarrow \text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O} + \text{H}^+ \quad \text{(eq. 2.1)}$$

Struvite precipitation is predicted from its saturation index (SI), a function of the ion activity product (IAP) of constituent ions, and the mineral solubility product (Ksp) (Appendix A, Figure A.1). The SI is influenced by pH, Mg$^{2+}$, NH$_4$-N and PO$_4$-P concentrations, with a maximum SI, and optimized precipitation at pH 9-10 $^{38,144,145}$ For aerated-FBR treatment, struvite precipitation can be induced by raising the wastewater pH from a typical value of pH 6-8 to pH 8-9 by carbon dioxide (CO$_2$(g)) stripping with aeration and sodium hydroxide (NaOH) titration $^{58}$ In this pH range other PO$_4$-P salts, such as hydroxyapatite (Ca$_5$(PO$_4$)$_3$OH; HAP) are also supersaturated $^{146}$ Addition of struvite seeding can promote rapid mineralization around nucleation sites, increasing the rate of struvite formation relative to other PO$_4$-P minerals $^{83}$ Although struvite components are required at an equimolar ratio (eq. 2.1), raising the Mg$_{\text{aq}}^{2+}$:PO$_4$-P$_{\text{aq}}$ molar ratio to ~2:1 by Mg$^{2+}$ addition further reduces the precipitation of competing PO$_4$-P minerals $^{147}$ At high dissolved potassium (K) concentrations, isomorphic substitution for NH$_4^+$ may form K-struvite (KMGPO$_4$·6H$_2$O) $^{148}$

Struvite recovery can be hindered by dissolved organic carbon (DOC), and high Ca$^{2+}$ content that lowers the Mg$^{2+}$:Ca$^{2+}$ ratio and oversaturates HAP $^{149}$ Calcite (CaCO$_3$) and monohydrocalcite (CaCO$_3$×H$_2$O) are other Ca-bearing minerals that can form at high carbonate concentrations. Struvite recovery can be hindered by dissolved organic carbon (DOC), and high Ca$^{2+}$ content that lowers the Mg$^{2+}$:Ca$^{2+}$ ratio and oversaturates HAP $^{149}$
Calcite (CaCO₃) and monohydrocalcite (CaCO₃·H₂O) are other Ca-bearing minerals that can form at high carbonate concentrations. Monohydrocalcite forms at Mg²⁺:Ca²⁺ ratios >1:1.2, a common condition in wastewaters. Complexation of Ca²⁺ with PO₄-P, and calcite formation reduces the struvite growth rate, and produces poorly crystalline struvite. Similarly, high DOC concentration slows struvite growth and creates amorphous solids with PO₄-P polymers. Smaller crystals and/or amorphous, flake-like particles are difficult to separate from wastewaters due to low density and higher buoyancy, and have poor aerated-FBR recovery.

Struvite production from swine wastewater (SW) is well described, but fewer studies have investigated struvite production from dairy wastewater (DW), and the impact of DOC on struvite recovery from DW is somewhat unclear, where several studies looked into improving P recovery by wastewater digestion methods. This study evaluates the formation of struvite in both DW and SW by aerated-FBR treatment at variable hydraulic retention times (HRT). Comparison of P recovery between treated livestock wastewater and model solutions with similar inorganic compositions to the wastewaters, and no added DOC (S-model, D-model) were also evaluated (Appendix A, Table A1). The extent of P removal and the mineralogical, chemical and physical properties of recovered solids were used to determine the effect of wastewater type and composition, specifically Ca and DOC content, on P recovery. Results elucidate the viability of aerated-FBR treatment of livestock wastewater for struvite production as an alternative to direct application of wastewaters to soils, and for sustainable use of nutrient resources.
2.2 Materials and Methods

Wastewater and model solutions

Effluents of dairy and swine lagoon wastewater were collected from Fulper Farm, Lambertville New Jersey, and the Rutgers New Brunswick New Jersey Agricultural Experiment Station, respectively. Effluents were characterized for total P (measured as PO₄-P mg L⁻¹ by acid persulfate digestion), NH₄-N, NO₃-N, alkalinity (as CaCO₃), Cl and DOC using colorimetry (Hach, DR-3900), and for trace and major elements by inductively coupled plasma optical emission spectroscopy (ICP-OES; Agilent, 5110 SVDV). Visual MINTEQ software¹⁵⁴ was used for equilibrium modeling of wastewater composition to determine ionic strength, speciation and struvite saturation (Appendix A; Figure A.1). The complexation of Ca with DOC was estimated using a Gaussian model, assuming normal distribution of ligand sites.¹⁵⁵ The organic molecular weight was input as 1500 Da, based on the 1-3000 Da range observed for organics in livestock waste¹⁵⁶ (Appendix A Table A.2, Figure A.2). Model solutions of dairy (D-model) and swine (S-model) wastewaters were prepared with similar concentrations of major ions at the wastewater ionic strength (Table 2.1). Solutions were prepared in deionized water (DI) using KCl, MgCl₂·6H₂O, (NH₄)₂HPO₄, NH₄HCO₃, NaNO₃, NH₄Cl and CaCl₂·2H₂O reagents (ACS grade, Thermo Fisher; Arcos Organics).

Aerated fluidized bed reactor

A 14 L polyvinyl carbonate aerated-FBR was constructed with two chambers: a continuous flow stirred-tank reactor (CSTR) and a fluidized bed (FB) canal, connected by a 0.5” gap at the base of their shared wall (Figure 2.1). For CO₂(g) purging, air flow is applied to the CSTR at 42 L air L⁻¹ reactor volume hr⁻¹, and a vacuum tube removes foam
formed by aeration. NH$_4$-N losses as ammonia gas (NH$_3$) emission is a negative side effect of aeration, but at tested aerated-FBR setting such losses were negligible and did not lower struvite SI (Appendix A; Figure A.3). Additional details on aerated -FBR design and aeration are available elsewhere. Influent solutions are added to the reactor using peristaltic metering pumps (Masterflex, Cole Parmer; Peristaltic, Fisher). Air flow and influent stirring generates sufficient agitation for homogenization, and to prevent solid settling. The FB chamber has an inverted trapezoid profile that expands at its top, where an outflow tube is placed. The upward expansion of the FB canal reduces the effluent flow velocity, forcing free fall of larger suspended solids, thereby separating the effluent leaving the reactor from the solids formed in the CSTR.

Figure 2.1. Schematic of aerated -FBR: a. CSTR 11 L reaction chamber, b. overhead mixer (A20, Fisher) with PTFE coated 2.5 inch shaft, c. effluent level, d. PVC air frit with 10 L/min air flow regulator (Key instrument), e. wall mounted pH meter (PT100, Cole-Parmer), f. narrow 0.5 inch slit passage from CSTR to FB chamber, g. solid collection drain valve, h. effluent flow direction (arrows), i. depiction of solid crystals (dots) forming a fluidized bed, j. effluent exit tube, k. vacuum tube for foam removal for livestock wastewater samples.
Phosphate recovery experiment

The aerated -FBR treatment of wastewaters and model solutions was performed in batch then steady state flow-through mode. In batch mode, wastewater or model solution influent was added to the reactor and aerated for the duration of one HRT:

\[
\text{HRT} = \frac{\text{[total reactor volume (14 L)]}}{\text{[influent flow rate (L min\(^{-1}\)])}} \quad (\text{eq.2.2})
\]

Aeration raised pH to 8-8.5 (Appendix A; Figure A.3), and NaOH used to titrate to pH 9. In flow-through mode, magnesium chloride (Mg\(^{2+}\)) was added to the influent flow, and struvite seed at 0.1g/L reactor volume was applied. Influent pumping rates were 880, 400 or 200 mL/min wastewater or model solution plus 28, 12 or 6 mL min\(^{-1}\) Mg\(^{2+}\) solution, for 15, 35 or 68 min HRT. Aeration of 35 min was chosen as a baseline for retention time, with either a double or halved additional HRT treatment, in order to observe the effect of HRT treatment on trends in P recovery. A small volume of 2.5 N NaOH was titrated continuously to maintain pH at 9. Six samples were collected for each aerated -FBR treatment: influent wastewater/model (\(S_0\)), aerated batch mode effluent (\(S_{0a}\)), and four flow-through effluent samples (\(S_1-S_4\)). To ensure steady state conditions in flow-through mode, the treatment was carried out for three HRTs (treating three reactor volumes of 14 L) before collecting the first sample (\(S_1\)). Treatment was continued for three additional HRTs, with samples taken at the end of each HRT (\(S_2-S_4\)). All samples were collected from the FB chamber outlet, filtered through a 0.45 µm membrane and analyzed for P (as PO\(_4\)-P) and NH\(_4\)-N by colorimetric analysis. For statistical evaluation, the software module JMP 12.0 (SAS) was used to compare P removal between aerated -FBR experiments (Appendix A; Table A.1). The percent P removal was calculated as 1-(\(S_i/S_0\))×100, where \(S_i\) is the mean P concentration of \(S_1-S_4\) and \(S_0\) is the influent P concentration. To compare multiple
treatments, an analysis of variance (ANOVA) was applied together with a Tukey-Kramer comparison of means\textsuperscript{157} at a 0.95 confidence level.

**Solid characterization.**

Solid samples were collected from the aerated -FBR and air-dried. A small fraction was dissolved in 5\% HCl and filtered through a 0.45 µm membrane to separate the insoluble solid fraction. The filter residue was air-dried and weighed to determine recovered mass. The filtrate was analyzed by ICP-OES and colorimetry for elemental composition, PO\textsubscript{4}-P and NH\textsubscript{4}-N. Solids were analyzed by X-ray diffraction (XRD; D8 Advance, Bruker) from 5-60 °2θ at 0.016 °2θ resolution. TOPAS 4.2 software (Bruker) was used to estimate the mineralogy as a mineral phase distribution by semi-quantitative analysis of the XRD patterns using a convolution based profile fitting fundamental parameters approach ),\textsuperscript{158} combined with phase analysis. Degree of crystallinity was estimated using EVA software (Bruker). Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR; Perkin Elmer, Spectrum 100) scans were collected from 650-4000 cm\textsuperscript{-1} at 4 cm\textsuperscript{-1} resolution for additional mineralogical characterization and evaluation of functional groups. Simultaneous thermal analysis (STA) and evolved gas analysis (EGA) (Netzsch, Perseus STA 449 F3, Bruker Alpha FTIR) was performed from 28-1060 °C at a 20°C min\textsuperscript{-1} heating rate in a nitrogen (N\textsubscript{2}(g)) atmosphere. FTIR spectra for EGA were collected from 600-4000 cm\textsuperscript{-1} at 8 cm\textsuperscript{-1} resolution. Temperature ranges for ammonia (NH\textsubscript{3}(g)), water vapor (H\textsubscript{2}O\textsubscript{(g)}) and CO\textsubscript{2}(g) evolution were determined from the corresponding gas absorption peaks at 966, 1510 and 2360 cm\textsuperscript{-1}, respectively. A Gram-Schmidt (GS) process of orthonormalizing was used to relate the total FTIR scan to the gas signal intensity. This
data was compared to results from differential scanning calorimetry (DSC) to determine the enthalpies of decomposition for gas release.

2.3 Results and Discussion

aerated-FBR P Recovery

The percent of P recovery was compared for wastewater and model solutions (Figure 2.2a), and the significance of observed trends confirmed by Tukey Kramer statistical analysis (Figure 2.2b). More P removal was observed for SW (92-94%) than DW (46-64%), with no effect of HRT on removal from SW, and ~18% improvement for DW-68 compared to DW-35. Since DW has higher DOC (800 mg L\(^{-1}\)) and Ca (5 mM) than SW (Table 2.1) (200 mg/L and 1mM respectively), and these are known to inhibit struvite formation, both the amount of P and the rate of removal are lower. Comparing SW and S-model, similar P removal was observed for S-model-35 and SW samples. However, S-Smodel-15 has the lowest P removal of all treated samples (44%). In SW, the Ca concentration is low, so complexation with DOC may sufficiently reduce free Ca\(^{2+}\) (Appendix A; Table A.2), limiting any inhibitory effect on struvite formation. For S-model, in the absence of complexing organic ligands, Ca effectively reduces the rate of removal, requiring a longer HRT for recovery commensurate with SW. The D-model solutions showed no effect of HRT on P removal. However, P removal is enhanced for DW, D-model-35 relative to DW, D-wastewater-35, but is comparable for D-model-68 and DW-68. Therefore, either higher DOC concentration, or its composition in DW,\(^{79}\) lowers the rate of P removal. These results provide insight into the influence of DOC and Ca on struvite precipitation. When the Ca and DOC concentration is low, as in SW, complexation between the two appears to mitigate inhibitory effects of both components on the P removal rate. However, for DW,
higher DOC inhibits P removal, as the presence of Ca alone in D-model does not have an effect on P removal.

Table 1.1. Chemical composition and other chemical properties of livestock wastewater and model solutions.

<table>
<thead>
<tr>
<th>Influent</th>
<th>DW</th>
<th>SW</th>
<th>D-model</th>
<th>S-model</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Major constituents (mM)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH4-N</td>
<td>37</td>
<td>21</td>
<td>45</td>
<td>26</td>
</tr>
<tr>
<td>P</td>
<td>0.3</td>
<td>0.6</td>
<td>0.3</td>
<td>0.6</td>
</tr>
<tr>
<td>Mg</td>
<td>5</td>
<td>1</td>
<td>15</td>
<td>11</td>
</tr>
<tr>
<td>Cl</td>
<td>29</td>
<td>7</td>
<td>63</td>
<td>40</td>
</tr>
<tr>
<td>CO3(^2-)</td>
<td>41</td>
<td>13</td>
<td>41</td>
<td>13</td>
</tr>
<tr>
<td>NO3(^-)</td>
<td>1</td>
<td>3</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>K</td>
<td>19</td>
<td>5</td>
<td>20</td>
<td>5</td>
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<tr>
<td>Na</td>
<td>14</td>
<td>6</td>
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<td>1</td>
</tr>
<tr>
<td>Ca</td>
<td>5</td>
<td>1</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td><strong>Trace elements (µM)</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
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<td>909</td>
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<td>2.85</td>
</tr>
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<td>Fe</td>
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<td>3</td>
<td>0.00</td>
<td>0.18</td>
</tr>
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<td>Al</td>
<td>12</td>
<td>3</td>
<td>1.11</td>
<td>1.11</td>
</tr>
<tr>
<td>Ba</td>
<td>8</td>
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<td>5</td>
<td>DL(^d)</td>
<td>DL(^d)</td>
</tr>
<tr>
<td>Zn</td>
<td>4</td>
<td>1</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>Cu</td>
<td>2</td>
<td>DL(^d)</td>
<td>DL(^d)</td>
<td>DL(^d)</td>
</tr>
<tr>
<td>Ni</td>
<td>1</td>
<td>DL(^d)</td>
<td>DL(^d)</td>
<td>DL(^d)</td>
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<tr>
<td><strong>Organics (mg/L)</strong></td>
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<td></td>
</tr>
<tr>
<td>DOC</td>
<td>800</td>
<td>200</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Total organics</td>
<td>1500</td>
<td>230</td>
<td>0</td>
<td>0</td>
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<tr>
<td><strong>Other chemical properties</strong></td>
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<tr>
<td>pH(^b)</td>
<td>7.9</td>
<td>6.8</td>
<td>8</td>
<td>8</td>
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<tr>
<td>I(^c) (mM)</td>
<td>45</td>
<td>107</td>
<td>62</td>
<td>106</td>
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<tr>
<td>Struvite SI at pH 9(^c)</td>
<td>1.40</td>
<td>1.72</td>
<td>1.40</td>
<td>1.65</td>
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<tr>
<td>Calcite SI at pH 9(^c)</td>
<td>2.52</td>
<td>1.59</td>
<td>2.51</td>
<td>1.54</td>
</tr>
</tbody>
</table>

\(^a\)as TOC mg/L, \(^b\)initial pH, \(^c\)calculated using Visual MINTEQ \(^d\)below detection limit (DL).
Composition of aerated-FBR Solids

Approximately 12-24% of solids collected from DW were in the insoluble fraction, consisting of wastewater suspended solids, compared to 2% of SW solids (Table 2.2). In the soluble fraction, DW solids had higher DOC content (7-29% w/w) while SW solids had negligible DOC concentration (2-5% w/w), this is in accordance with the higher DOC content in DW (Table 2.2). The P content of the aerated-FBR solids follows the trends of P removal, where highest P removal and struvite formation was observed for SW and S-model. The potassium (K) content was used as an indicator for K-struvite formation, with significant K only observed in DW solids due to higher wastewater K concentrations. Similarly, higher carbonate concentration yielded higher calcite content for DW solids. The presence of trace elements in solids is attributed to their build up through cation sorption by struvite \(^{159-161}\) and / or calcite. This increased the trace element concentrations of the
solids, even from the model solutions which had initial concentrations below ICP-OES detection limits.

Table 1.2. Composition of aerated-FBR solids

<table>
<thead>
<tr>
<th>Elements (mM/kg)</th>
<th>DW 35</th>
<th>DW 68</th>
<th>D-model 35</th>
<th>D-model 68</th>
<th>SW 15</th>
<th>SW 35</th>
<th>S-model 15</th>
<th>S-model 35</th>
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<tbody>
<tr>
<td>Ca</td>
<td>1900</td>
<td>3067</td>
<td>4275</td>
<td>3703</td>
<td>69</td>
<td>57</td>
<td>443</td>
<td>56</td>
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<tr>
<td>K</td>
<td>177</td>
<td>105</td>
<td>41</td>
<td>26</td>
<td>84</td>
<td>86</td>
<td>51</td>
<td>80</td>
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<tr>
<td>Mg</td>
<td>897</td>
<td>1021</td>
<td>2113</td>
<td>1106</td>
<td>3815</td>
<td>3872</td>
<td>3888</td>
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<tr>
<td>P</td>
<td>819</td>
<td>927</td>
<td>2186</td>
<td>1343</td>
<td>3519</td>
<td>3615</td>
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<td>Al</td>
<td>389</td>
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<tr>
<td>Fe</td>
<td>392</td>
<td>336</td>
<td>97</td>
<td>31</td>
<td>32</td>
<td>24</td>
<td>6</td>
<td>25</td>
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<tr>
<td>Mn</td>
<td>136</td>
<td>142</td>
<td>11</td>
<td>10</td>
<td>57</td>
<td>74</td>
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<td>2</td>
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<tr>
<td>Zn</td>
<td>90</td>
<td>59</td>
<td>47</td>
<td>15</td>
<td>17</td>
<td>10</td>
<td>14</td>
<td>13</td>
</tr>
</tbody>
</table>

Insoluble (% w/w) | 24 | 12 | 2 | 2 |

DOC (% w/w) | 7 | 29 | 5 | 2 |

Mineralogy and crystallinity of aerated-FBR solids

The XRD patterns of aerated-FBR solids were used to confirm the mineralogy and determine crystallinity (Figure 2.3, Appendix A Table A.3). The mineral phase distributions, as calculated by minerology analysis of the XRD diffraction patterns (Appendix A, Figure A.4), were compared to results from the solid elemental analysis. Results showed a poor match between struvite and K-struvite estimates from the minerology analysis and measured K content in solids. This occurs due to significant overlap between the XRD patterns of struvite and K-struvite. The K-struvite content was therefore estimated from the K:P molar ratio in solid samples. Calcite and arcsine cannot be distinguished based on the total Ca content, however their XRD diffraction patterns are distinct, resulting in good minerology predictions.
Results of the semi-quantitative analysis show differences in precipitated minerals contingent upon wastewater type. The SW and S-model solids yielded almost pure struvite (93-98%), consistent with the highest P removal and lower influent Ca concentration. The -S-model-15 solid had the lowest fraction of struvite (78%), also in keeping with the P removal trend. This solid also had the highest fraction of calcite (21%), correlated with the highest elemental Ca concentration. Therefore, the presence of Ca lowers the rate of struvite formation, through precipitation of Ca-bearing minerals.

Figure 2.3. Mineral phase analysis of aerated-FBR solids: a. weight percent of each mineral phase based on mineralogy analysis of XRD patterns, and elemental analysis of solids (Appendix A, Table A.3). b. Statistical output of analysis, where Rwp is the cumulative model error estimate and GOF is the ratio between calculated Rwp and an estimated minimum cumulative error for each solid sample.
The DW solids were a mixture of struvite (28-33%), K-struvite (3-8%), calcite (17-55%) and monohydrocalcite (13-42%). The low fraction of struvite correlates with less effective P removal compared to SW samples. The D-model solids had higher struvite content (50-58%) and a lower fraction of Ca-bearing minerals (41-44%) though the initial Ca content in DW and DWM influents were the same. This result confirms that the high Ca content of DW and D-model inhibits struvite formation, but also that Ca alone cannot account for reduced struvite precipitation from DW solutions. As DOC is also present in the DW solutions, and is known to impact struvite formation, this likely accounts for a further reduction in the fraction of struvite. Thus, when both influent Ca and DOC concentrations are high, conditions for struvite precipitation are most unfavorable.

The crystallinity evaluation showed that SW and S-model were highly crystalline (94%), while DW solids were less crystalline (75-87%) and D-model solids most amorphous (43-60% crystallinity; Appendix A, Figure A.5). In comparing SW to DW it is clear that the higher DOC and Ca concentrations promote poor mineral structure. The lower crystallinity of D-model solids suggests that higher Ca concentration may have a greater impact on mineralization from these solutions. Better P removal for D-model compared to DW, even though its solids are poorly crystalline, is due to rapid precipitation of amorphous P polymers, a known problem for struvite recovery.39

Speciation of IR sensitive functional groups

Qualitative evaluation of FTIR spectra of aerated-FBR solids (Figure 2.4) supports findings from P removal experiments and XRD analysis. Struvite has characteristic vibrations centered at 992 and 1432 cm⁻¹ associated with the ν₃ PO₄³⁻, and ν₄ NH₄⁺
Figure 2.4. FTIR absorption spectra of aerated-FBR solids, struvite and calcite standards. Dashed lines indicate absorbance at bandwidths associated with different functional groups present in struvite and calcite. In order of decreasing wavenumber: a. H₂O ν₂, 1600 cm⁻¹; b. NH₄ν₄,1432 cm⁻¹ c. CO₃ν₃, 1382 cm⁻¹; d. PO₄ν₃+ν₁, 992 cm⁻¹; e. CO₃ ν₂, 875 cm⁻¹; f. CO₃ ν₄, 712 cm⁻¹.

Calcite bands are located at 712, 875 and 1382 cm⁻¹, for the ν₄, ν₂ and ν₃ CO₃²⁻ vibrations. The SW and S-model-35 FTIR spectra were similar to the struvite standard spectrum, consistent with the >90% struvite content detected by XRD. The S-model-15 solid with 78% struvite and 21% calcite has spectral features dominated by struvite, but calcite peaks for the ν₂ and ν₄ CO₃²⁻ bands are also evident. The DW and D-model solids are primarily a mixture of struvite, calcite and monohydrocalcite, with all spectra exhibiting ν₂ CO₃²⁻, ν₃ CO₃²⁻ and ν₃ PO₄³⁻ vibrations. The struvite ν₄ NH₄⁺ band overlaps with the ν₃ CO₃²⁻ band for these samples, so is not distinguishable. The DW solids with
lowest struvite content (28-33%) of all the solids are dominated by the carbonate minerals (59-68%), and therefore exhibit the sharpest carbonate features. The DW-35 solid with the highest monohydrocalcite content (42%) also exhibits a distinct split in the $\nu_3$ CO$_3^{2-}$ peak at 1300-1500 cm$^{-1}$, in addition to the appearance of a structural $\nu_2$ H$_2$O peak at 1600-1700 cm$^{-1}$. The D-model solids have higher struvite content (50-58%), and are also the least crystalline (43-60%), which may account for broadening of all bands in the spectra. The D-model-68 solid has no detected calcite, but does exhibit the $\nu_2$ CO$_3^{2-}$ peak at 875 cm$^{-1}$, splitting in the $\nu_3$ CO$_3^{2-}$ band, and a broad $\nu_2$ H$_2$O band at 1600 cm$^{-1}$ due to the presence of 41% monohydrocalcite. The D-model-35 and DW-68 solids with lower monohydrocalcite content (5-13%) also have these features present in their spectra to some extent.

For all dairy solids there is an observed shift in the $\nu_3$ PO$_4^{3-}$ band from 992 cm$^{-1}$ for the struvite standard to 1002 cm$^{-1}$ for DW, and to 1041 cm$^{-1}$ for D-model solids. This shift in the $\nu_3$ PO$_4^{3-}$ band is likely a result of structural deformation of the PO$_4^{3-}$ tetrahedron due to sorption of Ca and/or metal cations, such as Ni and Mn, present in these wastewaters (Table 2.1). Such deformation is caused by changes in symmetry of the PO$_4^{3-}$ tetrahedron through elongation or compression of the P-O bond, resulting in a change of the IR vibration absorption energy. Shifts in the $\nu_3$ PO$_4^{3-}$ band has been observed when various cations sorb to struvite, though this has not been observed for Ca$^{2+}$. There is an increase in the $\nu_3$ PO$_4^{3-}$ bandwidth shift for D-model solids, with no DOC, compared to DW. The shift to higher wavenumber for the $\nu_3$ PO$_4^{3-}$ band in the absence of DOC suggests that DOC may reduce interactions between Ca$^{2+}$ and struvite PO$_4^{3-}$ groups due to Ca-DOC complexation. Though the effect of Ca on the struvite structure is evident for D-model
solids, the impact on both the percent P removed from solution and the struvite percent detected in the solids is less pronounced than that of DOC, as observed for DW.

**Thermal analysis**

The thermal stability of the aerated-FBR solids measured by STA-EGA (Appendix A, Figure A.6) was consistent with the mineral compositions. For all of solids, the TG mass loss was associated with the evolution of NH$_3$(g), H$_2$O(g) and/or CO$_2$(g). Solids that were mostly struvite had a single mass loss step at 50-400 °C, and a maximum NH$_3$(g) emission at 140-160 °C. Samples with high calcite or monohydrocalcite content displayed a mass loss step at 500-600 °C associated with CO$_2$(g) and H$_2$O(g), typical for calcite minerals. The SW and S-model solids had a TG mass loss typical for struvite, except for S-model-15 that displayed the additional mass loss step for calcite (Figure 2.5.a, Appendix A; Figure A.7). The DW and D-model solids have a two-step mass loss at 120-180 °C and 250-500 °C. The first mass loss is associated with evolution of NH$_3$(g) and H$_2$O(g) from struvite, and the second is due to release of CO$_2$(g) and H$_2$O(g) from carbonate minerals. The DW solids also release CO$_2$(g) from organic material in the first, and additional NH$_3$(g) in the second mass loss step. The release of NH$_3$(g) at two distinct temperatures, is evidenced by two peaks of maximum intensity in the GS curve at 140 °C and at 320 °C (Figure 2.5.b). This indicates a higher fraction of NH$_4$-N in the DW struvite structure that is more thermodynamically stable compared to other solids (Figure 2.5.c). Total enthalpy of mass loss was calculated for all solid samples within the NH$_3$(g) release temperature range of 50-400°C (Figure 2.5.d). Both SW treatments and S-model-35, which were mostly pure struvite, had the highest enthalpies of 1400-1600 J g$^{-1}$. The S-model-15 solid, with 78%
struvite had an enthalpy of 1000 J g\(^{-1}\). For dairy samples, DW-35 and D-model-35 had 720 J g\(^{-1}\) enthalpy (33-50% struvite), while both DW-68 and D-model-68 had 350-420 J g\(^{-1}\) enthalpy (28-58% struvite). For dairy samples, there was no difference between model and wastewater solids, and the sole difference seems to be the struvite content. Overall, higher struvite content resulted in higher enthalpy, as NH\(_3(g)\) release has a relatively high heat capacity compared to release of H\(_2\)O\(_(g)\) and CO\(_2(g)\) from organic matter. When comparing dairy samples, a slight decrease in enthalpy to struvite content is observed, but overall there is a linear relation between higher struvite content and higher enthalpy (Appendix A; Figure A.8).

Figure 2.5. STA-EGA analysis of aerated-FBR solids: a. TG % mass (Table S4); b. GS curve for total absorbance in the IR; c. intensity of NH\(_3(g)\) IR absorption at 966 cm\(^{-1}\) bandwidth; d. integrated enthalpy (J/g) over the 50-400 °C temperature range at which NH\(_3(g)\) is released.
**Implications for nutrient reclamation from livestock wastewater**

The aerated-FBR treatment is an efficient method to reclalm P nutrients from dairy and swine wastewater, as was recognized for other methods from phosphate recovery from livestock wastewater and manure.\textsuperscript{167} The use of aeration in aerated-FBR treatment effectively raises the pH, and lowers the operation costs associated with lye (NaOH) addition.\textsuperscript{168} The price of lye is \$330 per ton,\textsuperscript{169} making it the most expensive component in FB treatments compared to Mg\textsuperscript{2+} addition and energy costs. Treatment to remove P was most effective for SW (93–94\%) and slightly less effective for DW (46–63\%). Comparison of solids from treated livestock wastewater to model solutions showed that higher concentrations of either DOC or Ca hinder struvite formation. The minerals collected from DW and SW were mostly struvite or a mixture of struvite, calcite and monohydrocalcite. Higher struvite content was observed for SW (95–98\%) compared to DW (28–33\%) solids. The application of carbonate minerals together with struvite fertilizer has no known negative impact for soils, and struvite fertilizer is effective both in alkaline and acidic soils.\textsuperscript{170} Thermal analysis showed a slight benefit for DW solids, with higher maximum release temperatures (320 °C) for some of its NH\textsubscript{4}-N, and maximum release temperatures that are similar to pure struvite (130-160 °C) for other volatiles. Higher thermal stability of struvite from DW fertilizer may reduce NH\textsubscript{3}(g) emissions, posing a great environmental and economic benefit. The aerated-FBR process is thus a viable means of nutrient recovery from livestock wastewater, for reuse and controlled application.
Acknowledgments Support was provided by National Science Foundation Grants EAR-1506653, EAR-1337450 (XRD), EAR-1530582 (ICP-OES). Special thanks to Clint Burgher, Rutgers New Brunswick New Jersey Agricultural Experiment Station and Robert Fulper, Fulper Farm, for technical support, and to E.J. Elzinga for use of the FTIR.

Effluent: A Pilot Scale Evaluation

3.1 Introduction

Concentrated animal feed operations (CAFO) store wastewater effluents in lagoons or tanks to prevent the contamination of surface and groundwater. Under current regulations in effect for most United States (U.S.) localities, the best management practice for dairy wastewater (DW) treatment is to discard these effluents onto topsoil as part of a nutrient management plan. While this practice is cost-effective and widely implemented, it has shortcomings with respect to nutrient deposition, the spread of microbial antibiotic resistivity traits, and odor nuisance. In the Northeast and Mid-Atlantic regions of the U.S. this is becoming an issue to producers, as a growing number of counties have limited DW soil application to control phosphorus (P) deposition and prevent development of harmful algal blooms (HAB). Alternative DW treatment methods are focused on P recovery, since often it is the limiting factor for HAB growth and it is a key nutrient resource for agriculture with diminishing reserves worldwide.

In recent years, the production of struvite (MgNH₄PO₄·6H₂O) fertilizer (7-29-0 N-P-K, Mg-10) has become popular as a means to harvest P and other nutrients from livestock waste. Review of current commercially available methods to treat DW showed that most nutrient recovery is conducted by producing struvite, and contaminant removal is achieved by several methods including digestion, filtration and constructed wetland treatment (CWT). Pretreatment is used to improve P recovery from DW by reducing hinderances to struvite precipitation from dissolved organic matter (DOM) and calcium (Ca); and freeing complexed nutrients (e.g. Ca-P complexes) for precipitation. This
can also function as a primary treatment for wastewater and help meet treatment goals of removing total suspended solids (TSS) and biochemical oxygen demand (BOD). Commercial struvite producers use effluent acidification as a pretreatment to improve struvite production in DW. This method applies acidification to decouple P complexed with Ca, allowing P to re-precipitate as struvite in pre-set reaction conditions. Enzyme or aerobic microbial application is an additional treatment to free organic phosphates (Org-P) such as phytate, hydrolyzing it into orthophosphate (PO$_4$-P) for struvite precipitation. Other approaches such as belt press, large scale geotechnical bags, rotating disc solid separation and polymer flocculation to settle TSS and DOM are used to clarify and treat DW. The recovered concentrated sludge can then be pretreated by anaerobic digestion for struvite precipitation.

Treatment of DW by struvite recovery is implemented by large dairy farm operations, or as a regional treatment shared by multiple farms. Most cattle farms (per integer units; beef, dairy) in the U.S. (68%) are small-scale farm operations (1-49 animal-year, a-y). For these operations, the assimilation of current DW treatment methods is hindered by the high ratio of investment per a-y for small farm operations; lack of flexibility of mass produced equipment apparatus to fit into various farm setups (fluid consistency, wide range of custom equipment, etc.); lack of integration with other farm operations, requiring an investment in a specially designed control system; and relatively low nutrient recovery rate (20-70% P recovery) compared to other livestock waste. There is therefore a need to provide a sustainable DW treatment method, incorporating struvite recovery, suitable for use on a small-scale cattle farm CAFOs.
In this study, a concept pilot test was used to determine if a compact reactor design\textsuperscript{186} with open source automation control could mitigate problems associated with nutrient recovery from DW on small-scale cattle farms. The objective was to evaluate the feasibility of a coupled aerated-FBR and CWT system to recover nutrients from DW, treat these effluents to meet 30 mg L\textsuperscript{-1} TSS and 30 mg L\textsuperscript{-1} BOD (60 mg L\textsuperscript{-1} chemical oxygen demand, COD) discharge requirements,\textsuperscript{3} and evaluate the use of open source automation to facilitate effluent treatment. The aerated-fluidized bed reactor (aerated-FBR) for nutrient recovery method is a compact setup geared for small farm operations.\textsuperscript{186} It uses a dual chamber reactor, combining a continuous stirred tank reactor (CSTR) with a plug flow reactor (PFR) for minimal instrument footprint. The use of aeration to raise DW pH minimizes the need for investing in costly reagents to reach alkaline pH for P recovery.\textsuperscript{186} A newer generation of single board computers such as Raspberry Pi \textsuperscript{187} and open source automation software (Mycodo)\textsuperscript{188} are used to facilitate farm automation assimilation in small farm operations. This is coupled with CWT, the goal of which is to remove TSS, BOD and excess nutrients from wastewater. In contrast to nutrient recovery, CWT does not directly generate nutrients and therefore is proposed as a supplementary treatment for DW. The use of CWT can be potentially modified to generate feed crops, as CWT plants such as cattail (Typha) contain high nutrition value similar to grain seeds.\textsuperscript{100} Overall, the aerated-FBR process coupled with CWT addresses the need for combined nutrient recovery and contaminant reduction from DW in small-scale dairy operations as an alternative to current treatment and disposal practices.
3.2 Materials and Methods

Experiment design

A field pilot site evaluating the combined aerated-FBR and CWT method to treat DW was placed at Fulper Farm, a 100 milking cow dairy located at Hunterdon county NJ. The treatment facility was placed in proximity to the farm lagoon, an earthen pool holding 2840 m$^3$. The site lagoon is used to collect all milking parlor and animal yard waste effluents after a solid separation process done with a screw press.

Based on preliminary lab and field work (Season one of pilot trial, 2018), two consecutive treatment stages assessed the cumulative benefits for nutrient recovery and water treatment goals. As a baseline treatment, DW was channeled through the CWT pools without any additional treatments. The second treatment applied aerated-FBR prior to CWT treatment. Response parameters from four aerated-FBR-CWT treatments were sampled biweekly over a two-week period (n=4) with a two-week pre-run (~2-3 hydraulic retention time, HRT) for each treatment. Parameters evaluated were total and dissolved P removal, TSS and BOD measured as COD. Samples were collected at the point of entry to the aerated-FBR, and exits of three CWT pools (P1, P2, P3) (Appendix B, Figure B.1).

Aerated-FBR setup

In-order to scale up an aerated-FBR from lab-scale to pilot field-scale, a 40 L aerated-FBR reactor was constructed. This method for P recovery uses wet chemistry and pH manipulation for salt harvesting of struvite (MgNH$_4$PO$_4$·6H$_2$O) mixed with potassium struvite (K-struvite; MgKPO$_4$·6H$_2$O) fertilizer. Struvite and K-struvite become supersaturated if potassium (K$^{+\text{aq}}$), magnesium (Mg$^{2+\text{aq}}$), ammonium (NH$_4$-N, NH$_4^+$) and
PO₄-P as PO₄³⁻aq are available, and pH is within the range of 7-11 where its component ions are primarily uncomplexed, facilitating precipitation (at lower pH PO₄³⁻ is complexed, while at higher pH NH₄⁺ and Mg²⁺ become unavailable). The rate of struvite or K-struvite precipitation is maximized at pH 9-10 when mineral supersaturation is highest. However, the presence of either Ca²⁺aq or DOM can hinder struvite precipitation. The mixture of struvite and K-struvite is composed of equimolar ratios of PO₄³⁻aq, Mg²⁺aq, and monovalent cations (i.e. NH₄⁺aq + K⁺aq) with formula \([\text{NH}_4]^x[\text{K}]_{1-x}\text{PO}_4\text{Mg} \cdot 6\text{H}_2\text{O} (0 < x < 1)\). The reactor design, as described in length elsewhere, coupled a CSTR with a vertical PFR, and aeration is used to raise DW pH. Precipitation of struvite in DW occurs spontaneously within a pH range of 8-10, however a one-time initial addition of struvite seeding at 0.1 g L⁻¹ reactor volume reduces the agglomeration time and hinders the formation of competing P minerals such as hydroxyapatite (Ca₅(PO₄)₃OH). Previous work showed that adding Mg to the wastewater suppressed the formation of undesired P minerals (e.g. hydroxyapatite) and the treatment of 0-20 mM Mg addition is achieved by applying a 0.2 M MgCl₂·6H₂O solution at appropriate flow rates for dilution with DW influent.

For the pilot field-scale study, the aerated-FBR (Figure 3.1; Appendix B, Figure B.2,3) was placed in a protective enclosure adjacent to DW lagoon. Pilot Reactor operation required a reliable continuous low-flow influent feed that was achieved with a two-step pump. The first step used a submergible sewage pump (Everbuilt) placed in the lagoon to push wastewater through a crushed rock filter into a 220 L primary container. The second stage used a chemically resistant auger pump (PVC, custom built) to feed the aerated-FBR reactor (Appendix B, Table B.1, Figure B.4, B.5). Air was applied to the reactor with an
air linear-diaphragm pump with a 0-50 L min\(^{-1}\) regulator. Chemical solutions of caustic soda (NaOH), and Mg were applied with peristaltic pumps (Catalyst, FH100). Measurements of pH were taken continuously using a submersible pH probe with a self-cleaning flat tip (Cole-Parmer).

Figure 3.1. Schematic of aerated-FBR setup showing reactor components: a. float switch, b. seep pump, c. one-way valve, d. float switch, e. crushed rock filter, f. auger, g. gear and gear motor, h. FBR reactor with mixer and air diffuser, i. titration pumps, j. Raspberry controller, k. foam vent, l. DW effluent exit.

A microcontroller single board computer (Raspberry pi, 3B+) was used to operate the aerated-FBR system (Appendix B, Figure B.6, Table B.2) using an open source farm
management software (Mycodo). The reactor was able to maintain the pH between 9-9.3 with a simple logical condition of turning the pump on if pH<9 and running the pump for 30 seconds. More advanced control options as well as a proportional–integral–derivative controllers (PID controller) are now built into the Mycodo program. The microcontroller acquired effluent pH measurements, generated datalogging and governed power relays supply for the reactor components: air pump, auger pump, chemical metering pumps and overhead mixers agitator.

The initial pH of DW ranged from 7.6-8.2 and needed to be raised to ~pH 9 to improve the rate of struvite formation and mineral crystallinity. Poor precipitation rate makes the HRT requirements longer thus reducing the treatment method efficiency, while poor crystallinity results in polymerized phosphate filaments that have too high buoyancy for FB separation. For the pilot scale aerated-FBR with 40 L volume, a HRT of 60 min. was applied using a total flow rate (titration solutions+ lagoon effluent) of 0.66-0.7 L min⁻¹. Titration of DW to pH 9 was accomplished by aeration that strips carbonic acid as carbon dioxide gas (CO₂(g)), and supplemental NaOH application. Aeration at 0.75 volume air per volume reactor-minute (VVM) was applied, and DW pH was raised from 7.6-8 to pH 8.3-8.5 at 60 min. HRT.

**CWT for DW treatment**

In the process of DW flow through CWT, surface interaction with microbial biofilms and soil/root surface area removes TSS and BOD. This is improved by transitioning from aerobic to mildly anaerobic conditions between CWT pools that promote microbial and chemical reactions of TSS sorption and BOD decomposition. The use of CWT for DW is
applied commercially as free water surface (FWS) or vegetated submerged bed (VSB) systems (Figure 3.2). Three such pools with a ~3100 L volume each, were constructed in series near to the aerated-FBR enclosure. Each of the three pools (P1, P2, P3) was 1.2 m wide, 0.6 m deep and 4 m long, made of wood frame and a 45 mil. EPDM liner (1.14 mm). The first pool to receive DW effluent from the aerated-FBR was a VSB pool (P1), followed by two FWS pools (P2, P3 respectively). The HRT in the pools depended on the effluent flow rate out of the aerated-FBR and each pool’s pore volume, yielding ~3 d HRT in the VSB and ~6 d HRT in the FWS pools. The VSB pool floor was covered with 7-15 cm of sand, filled with 7-13 cm of river rock pebbles and covered with 7-15 cm of sand and crushed rocks that support vegetation cover. The vegetation cover was a mixture of wetlands and alkaline soils plants: swamp rose mallow, sweet-flag, cordgrass, milkweed, bulrush, soft stem bulrush, saltgrass, common reed. Plants were distributed across the flow path to evaluate their ability to establish in different aerated-FBR and CWT settings.

![Diagram of VSB (P1) to FWS (P2) to FWS (P3)](image)

Figure 3.2. Aerated-FBR treated, or untreated DW effluent enters the VSB (P1) canal then overflows from to FWS (P2) and to FWS (P3) by gravity.

From the VSB pool, effluent overflows into the first FWS pool that was populated with more hardy plants, narrow leaf cattail, sweet-flag and common reed. From this pool,
effluent overflowed to the second FWS pool populated with narrow and broad leaf cattail and sweet-flag. In the first season of pilot run (2018), the second FWS pool (P2) was populated with submerged plants that did not successfully establish in DW effluent. Following this, for the second season experiment (2019) FWS P2 was converted to a second emerging plants CWT to assess if extending FWS residence would improve the treatment outcome. Both FWS pools were filled with 7-15 cm of sand and 12 mm crushed rock bedding for emerging wetland plants. CWT pools were covered with a 2.6 m clear greenhouse liner tunnel to prevent rainfall from diluting the effluent and affecting the collected results.

**Analytical methods**

Samples of DW collected from the field site were analyzed for elemental composition, TSS and BOD as COD. Samples were collected in 50 mL vials and refrigerated prior to processing. Both the dissolved phase and total composition were analyzed. Dissolved phase samples were centrifuged at 6000 rpm for 30 min., then filtered with a 0.4 µm syringe filter (Advantech GF140). Samples for elemental analysis were acid digested with 35% HNO₃ (2.5 mL sample: 2.5 mL 70% HNO₃) at 150 ºC for 6 h in 50 mL Pyrex vials, then 1 mL 36% HCl was added and the sample was heated for 45 min. Prior to analysis, samples were diluted to 25 mL with deionized water. Elemental analysis was done using inductively coupled plasma optical emission spectroscopy (ICP-OES, Agilent 5110 SVDV) and ultraviolet-visible spectroscopy (UV-Vis, Hach DR 3900). Mineralogical analysis was done using X-ray diffraction (XRD; Brucker Advance D8) at 0.1 s step-1 in 0.011 °2θ increments from 5-60 °2θ. Patterns for relevant reference minerals were also collected from
mineral standards or generated from the american mineralogist crystal structure database\textsuperscript{190} using Crystal Diffract 4.2 software.

3.3 Results and Discussion

Design of pilot-scale nutrient recovery system

Evaluation of scaling up the aerated-FBR system (Figure 3.1) from lab-scale to pilot-scale resulted in several operational problems. These included excessive foaming due to aeration for the first 24-48 h of continuous operation, and intake of DW into the FBR needed to overcome repeated clogging from large particles, while still maintaining a low-flow rate.

To deal with excessive foam formation, a 50.8 mm vent was added to the reactor lid, a 45 mil (1.4 mm) PVC liner was added as a seal, and a seal bearing (Cowie) was installed with the overhead mixer shaft. This prevented damage to instruments from foam expansion due to positive pressure in the aerated-FBR reactor. A 38 mm PVC pipe vent carried the foam overflow from the top of the reactor head to the CWT by open canal flow. To overcome the issue of delivering DW into the aerated-FBR at low flow, an auger pump was installed. Commercially available manure auger pumps cost ~$4,500 and upwards, deliver a high flow rate (102-104 L h\textsuperscript{-1}) and do not offer much chemical resistivity. As an appropriate cost-effective alternative, a simple PVC auger design that is compatible with the Raspberry Pi microcontroller was tested. An in-depth analysis of the auger pump design is described elsewhere.\textsuperscript{191} The key parameters considered for the aerated-FBR auger were using standard size whole saws for auger helix fabrication, and readily available PVC materials that offer chemical resistivity. For compact placement, a maximum auger slope of 45\textdegree{} was used and a single helix auger was found to be sufficient. A ratio of 1.5 between auger radius and auger helix span, with an inner diameter of 32 mm and an outer diameter of 76.2
mm gave the best outcome with regards to constant DW flow of 0.05-4 L min\(^{-1}\). at 20-220 rpm (Appendix B figure B.7 table B.3). A 24 VDC gear motor (Dyton) with 1.9 Kg-meter torque at 54 rpm was coupled to the auger via a 1.44 kg-m disc clutch and a 25.4 mm steel shaft to rotate the auger. While it is much more cost effective to use shear bolts, it was observed that at such low rpm/torque the shear-bolts tend to underperform. A 1:4 gear ratio was set with 15 teeth sprockets on the motor and 60 teeth sprockets on the auger shaft. The operation of the reactor and auger was controlled by a single board computer (Raspberry Pi 3 B+) with Mycodo software. The auger rpm was set with a motor speed/direction controller (Cytron MD30C) coupled to system microcontroller, where 35-38% power output yielded 0.6-0.65 L min\(^{-1}\) flow.

The microcontroller collected pH input from the reactor using an analog to digital signal processor (pH EZO, Atlas Scientific) over Inter-Integrated Circuit (I2C) wiring with a signal isolator mount (T3, Whitebox). Using a simple logical condition in input for function operation, pH was kept constant at pH 9 by turning on titration with 2.5 N NaOH when the pH fell below the desired value. Application of Mg, NaOH and auger rpm was set with Mycodo software. The recorded measurements and application of titration were exported to a datasheet file (csv) format for further analysis.

To optimize the recovery of nutrients from DW, the effect of adding Mg to DW at concentrations of 0-20 mM and pH 9-10 were evaluated. Treatment parameters for aerated-FBR operation were HRT (DW flow rate), pH as a function of aeration rate (VVM), and NaOH and Mg application rates. Preliminary tests showed that aeration at 0, 1, 2 and 24 h HRT durations with 0.75 VVM air flow, raised DW pH to 7.6-8, 8.2, 8.5 and 9 respectively, lowering the titration demand for NaOH application in the aerated-FBR. From the range of
previously tested HRT, 60 min HRT was chosen since prior work showed it is sufficient for P recovery.\(^{186}\) When application rates of 0-20 mM Mg (0-4 g L\(^{-1}\) (MgCl\(_2\)·6H\(_2\)O) were evaluated, NaOH titration demand for DW to reach the target pH 9 in the aerated-FBR at HRT 60 min were 0.61-2.13 g L\(^{-1}\) DW (Table 3.1) with a quadratic relationship (R\(^2\)=0.98; p 0.012, \(\alpha=0.05\); Appendix B, Figure B.8), where:

\[
\text{[NaOH]} \text{ g L}^{-1} = 0.0038 \text{ [Mg]}^2 \text{ mM} + 0.61 \quad \text{(eq. 3.1)}
\]

<table>
<thead>
<tr>
<th>Mg Mm</th>
<th>Dissolved P removal (%)</th>
<th>n</th>
<th>Std Error</th>
<th>Comparison of means</th>
<th>Total P removal (%)</th>
<th>N</th>
<th>Std Error</th>
<th>Comparison of means</th>
<th>Average titration requirements (g NaOH L(^{-1}) DW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>60.5</td>
<td>4</td>
<td>7.7</td>
<td>A B</td>
<td>2.4</td>
<td>4</td>
<td>26.8</td>
<td>A</td>
<td>0.61</td>
</tr>
<tr>
<td>5</td>
<td>49.3</td>
<td>4</td>
<td>4.9</td>
<td>A B</td>
<td>-3.4</td>
<td>4</td>
<td>21.3</td>
<td>B</td>
<td>0.83</td>
</tr>
<tr>
<td>10</td>
<td>50.3</td>
<td>3</td>
<td>3.4</td>
<td>A B</td>
<td>33.0</td>
<td>3</td>
<td>24.0</td>
<td>A</td>
<td>0.85</td>
</tr>
<tr>
<td>20</td>
<td>76.3</td>
<td>4</td>
<td>10.8</td>
<td>A</td>
<td>20.7</td>
<td>4</td>
<td>24.9</td>
<td>A</td>
<td>2.16</td>
</tr>
</tbody>
</table>

\(^a\) Levels with the same letter are not significantly different (Tukey-Kramer, JMP-15; \(\alpha=0.05\)).

The reactor operated at a continuous flow of 0.66 L min\(^{-1}\) that yielded a 60 min HRT (after Mg addition at 16 mL min\(^{-1}\)). To reach an approximated steady state, the reactor ran for three hours (3-HRT) then four consecutive samples were collected from the aerated-FBR inlet and outlet at 1 h (1-HRT) intervals for a total of four samples (n=4). For estimated P recovery rates, the composition of DW Influent (I\(_{1-4}\)) was compared to DW Effluent (E\(_{1-4}\)). Comparison of means was done by arcsine transformation of P removal % into a non-binary mode and using Tukey-Kramer method with JMP 15 software. While the composition of DW varied over the experiment period the averaged composition from the total experimental database, over a two-month period is presented as an overall DW baseline for the pilot site in Table 3.2.
Table 3.2. Average DW composition

<table>
<thead>
<tr>
<th>Element</th>
<th>Al (mg L(^{-1}))</th>
<th>Ca (mg L(^{-1}))</th>
<th>Fe (mg L(^{-1}))</th>
<th>K (mg L(^{-1}))</th>
<th>Mg (mg L(^{-1}))</th>
<th>Mn (mg L(^{-1}))</th>
<th>Na (mg L(^{-1}))</th>
<th>P (mg L(^{-1}))</th>
<th>S (mg L(^{-1}))</th>
<th>Zn (mg L(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>mg L(^{-1})</td>
<td>10</td>
<td>344</td>
<td>16</td>
<td>1001</td>
<td>207</td>
<td>2</td>
<td>332</td>
<td>98</td>
<td>62</td>
<td>2</td>
</tr>
<tr>
<td>SD (n=16)</td>
<td>6</td>
<td>73</td>
<td>6</td>
<td>229</td>
<td>40</td>
<td>1</td>
<td>105</td>
<td>23</td>
<td>12</td>
<td>1</td>
</tr>
</tbody>
</table>

Results from Mg application rate trial indicated 45-61% recovery of dissolved P and up to 33 ± 24 % removal of total P (Table 3.1), with no significant difference for dissolved P removal for lower application rates, or total P for all treatments. Following Mg application rates trial, the optimal Mg application was set for 5 mM. This was done since no significant difference in P recovery was observed for total P recovery, and similar results were observed for dissolved P removal at lower Mg (5-10 mM). Applying Mg at a minimal rate of 5mM Mg L\(^{-1}\) DW was used to ensure the formation of struvite if and when DW composition varied over time during the continuous aerated-FBR trial. This was done with consideration that this will be the most economically sound approach with regards to the amount of P recovered, minimizing the need for NaOH application (higher for high Mg application) will improve cost effectiveness, and some Mg should be applied to ensure high struvite content in the recovered solids when the lagoon became diluted (high summer rain falls periods) and existing Mg concentrations in DW influent dropped.

Analysis of solids recovered from aerated-FBR with 0-20 mM Mg application and continuous run with 5 mM Mg was done with XRD for mineral phase identification, and ICP-OES or UV-Vis for elemental composition. The XRD patterns (Figure 3.3) and the elemental composition (Table 3.3) showed that the minerals formed were mostly struvite, calcite, monohydrocalcite, and at highest Mg concentrations, magnesite (MgCO\(_3\)) and nesquehonite (MgCO\(_3\)·3H\(_2\)O). Findings from elemental composition (high Ca, Mg, P, K
content) were consistent with XRD mineral phase evaluation that identified mostly struvite and calcium carbonate minerals. For these minerals it was observed that Ca and Mg content increased when higher Mg application rate was applied, while P content plateaued at 5 mM Mg application. This is likely since higher Mg content increased calcite and monohydrocalcite precipitation and promoted the formation of magnesite and nesquehonite, resulting in a decrease of the overall fraction of struvite (main P mineral phase observed).

Table 3.3. Elemental composition of solids collected from aerated-FBR treatment with 0-20 mM Mg

<table>
<thead>
<tr>
<th>Treatment</th>
<th>g kg⁻¹</th>
<th>mg Kg⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg (mM)</td>
<td>Al</td>
<td>Ca</td>
</tr>
<tr>
<td>0</td>
<td>3</td>
<td>45</td>
</tr>
<tr>
<td>5</td>
<td>4</td>
<td>58</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
<td>68</td>
</tr>
<tr>
<td>20</td>
<td>2</td>
<td>81</td>
</tr>
<tr>
<td>4 w run with 5 mM Mg</td>
<td>1</td>
<td>140</td>
</tr>
</tbody>
</table>

Solids collected from aerated-FBR during a four-week continuous run with 5 mM Mg addition and reaction pH 9 were analyzed and had similar composition to Mg application rates trial. The collected fertilizer had an approximated 1-2-1 N-P-K (N was measured as NH₄-N using a Hach colorimetry kit) while recovered solids from the Mg trial had a 1-3-1 composition, most probably due to the higher Ca:P (15.5:1 versus 3.75:1) ratio in the continuous run solids which indicated a much higher calcite content or higher content of amorphous Ca-P compounds, which are not detected by XRD. Accumulation of carbonates for longer aerated-FBR runs was also observed at the CWT entry area (VSB entry). This may indicate that as the concentration of carbonates in the aerated-FBR reactor
increased over time, their precipitation rate increased. Another reason for the variation in solids composition may be due to a weather pattern of record high precipitation in July-Aug 2019. This activity altered the DW composition where frequent lagoon emptying to prevent over fill resulted in higher TSS content in the recently emptied lagoon.

Figure 3.3. XRD diffraction patterns of solids collected from aerated-FBR treatment (Brown) with 0-20 mM Mg application rates, and patterns for reference minerals (Black).
Performance of Aerated-FBR+CWT for treating DW effluent

Over a two-month period, the pilot system design was evaluated by operating continuously, allowing sufficient time for a 2-HRT flush of CWT followed by a 2-HRT period of approximately bi-weekly sampling the DW effluent (HRT of CWT was estimated at 6-7 d). Pilot site operation was first performed in CWT mode where DW was pumped directly into the CWT without prior treatment (1st Run, August 2019). Operation was then switched to aerated-FBR + CWT mode where DW was first pumped into the aerated-FBR and titrated to pH 9 with 5mM Mg addition, then the effluent overflowed into the CWT for further treatment (2nd run, September 2019), recorded pilot operation data for 1st and 2nd runs are presented in Figure 3.4.

Continuous running of the pilot site showed that the DW lagoon pH remained constant at ~pH 8 during the 1st run and the auger feed system for pumping DW operated well. Applying the aerated-FBR in continuous mode worked as well, aside from a down period at the end of August that resulted from a failure of the submerged seep pump. This is visible in Figure 3.4 where a period of no oscillation between 0-1 is shown as white background on the NaOH titration y-axis (left). As seen from Figure 3.4.b, the rate of NaOH application duration oscillated somewhat during the continuous experiment period resulting in a calculated application rate between 0.2-0.7 g NaOH L⁻¹ DW, and the average NaOH application was 0.4 g L⁻¹ DW. This indicated that the titration needs are somewhat affected by periodic changes in lagoon composition, but not to an extent that significantly affects the operation or treatment costs.
Figure 3.4. Datalogger records of CWT and aerated-FBR+CWT treatments over time during CWT treatment (a) and aerated-FBR (b) continuous pilot site treatment. Values of DW pH measured continuously in-line (Black), microcontroller NaOH titration pump on/off status read (every 15 s as 0;1, light blue) and duration of titration pump operation (seconds, dark blue) were plotted for continuous CWT and aerated-FBR+CWT treatments.

Several potential wetland plants were evaluated to assess suitability for use in the combined aerated-FBR+CWT setup. Such a setup was somewhat of a hindrance for plant growth due to high salinity, pH and COD of the effluent leaving the aerated-FBR. Plants for CWT were placed in March-May 2018 for a first trial run of the pilot site and replanted in March-May of 2019. From the population of CWT plants tested (Table 3.4), the most well-established plant was Wide-leaf Cattail (*typha latifolia*), followed by Narrow-leaf...
Table 3.4. Results for CWT plants in VSB, FWS1, FWS2 pools
Results for CWT plants in VSB, FWS1, FWS2 pools treated with DW and aerated-FBR+CWT effluents. Qualitative observed establishment of plants was rated from none (-) to high (+++); stressed or dwarfish plants observation recorded as yes (Y) or no (N).

<table>
<thead>
<tr>
<th>CWT VSB</th>
<th>Established</th>
<th>Stressed Dwarfish</th>
</tr>
</thead>
<tbody>
<tr>
<td>CWT plant</td>
<td>Common plant name</td>
<td>DW</td>
</tr>
<tr>
<td>spartina alterniflora</td>
<td>Smooth-cordgrass</td>
<td>+++</td>
</tr>
<tr>
<td>hibiscus moscheutos</td>
<td>Swamp rose mallow</td>
<td>++</td>
</tr>
<tr>
<td>acorus americanus</td>
<td>Sweet-flag</td>
<td>++</td>
</tr>
<tr>
<td>phragmites australis</td>
<td>Common-reed</td>
<td>++++</td>
</tr>
<tr>
<td>scirpus Validus</td>
<td>Soft-stem Bulrush</td>
<td>-</td>
</tr>
<tr>
<td>Juncus effuses</td>
<td>Soft-rush</td>
<td>-</td>
</tr>
<tr>
<td>FWS1</td>
<td>DW</td>
<td>DW+aerated FBR</td>
</tr>
<tr>
<td>spartina alterniflora</td>
<td>Smooth-cordgrass</td>
<td>+</td>
</tr>
<tr>
<td>lemna major</td>
<td>Duckweed</td>
<td>++++</td>
</tr>
<tr>
<td>phragmites australis</td>
<td>Common-reed</td>
<td>++++</td>
</tr>
<tr>
<td>typha latifolia</td>
<td>Wide-leaf Cattail</td>
<td>++++</td>
</tr>
<tr>
<td>typha angustifolia</td>
<td>Narrow-leaf Cattail</td>
<td>+++</td>
</tr>
<tr>
<td>acorus americanus</td>
<td>Sweet-flag</td>
<td>+++</td>
</tr>
<tr>
<td>FWS2</td>
<td>DW</td>
<td>DW+aerated FBR</td>
</tr>
<tr>
<td>Ceratophyllum demersum</td>
<td>Hornwort</td>
<td>-</td>
</tr>
<tr>
<td>vallisneria americana</td>
<td>Wild celery</td>
<td>++</td>
</tr>
<tr>
<td>potamogeton nodosus</td>
<td>Long-leaf Pondweed</td>
<td>-</td>
</tr>
<tr>
<td>elodea canadensis</td>
<td>Canadian Pondweed</td>
<td>-</td>
</tr>
<tr>
<td>typha latifolia</td>
<td>Wide-leaf Cattail</td>
<td>++++</td>
</tr>
<tr>
<td>typha angustifolia</td>
<td>Narrow-leaf-Cattail</td>
<td>+++</td>
</tr>
<tr>
<td>pontederia cordata</td>
<td>Pickerel Weed</td>
<td>+++</td>
</tr>
</tbody>
</table>

Cattail (*typha angustifolia*), Smooth-cordgrass (*spartina alterniflora*), Common-reed (*phragmites australis*) and Sweet-flag (*acorus americanos*). From the plant establishment trials results it was clear that none of the submerged plants were suitable for use in the current FWS setup, and that some of the emerging plants such as Duckweed (*lemna*) or
Pickerel-weed (*Pontederia cordata*) are suitable for CWT but not for aerated-FBR+CWT treatment. The severe stress and dwarfish growth of many plants prevented maturity and/or flowering, and no such symptoms were observed for Cattail (*typha*) plants. Therefore, the setup for the pilot CWT + aerated-FBR run was mostly cattail (*typha*) and Common-reed (*phragmites*) plants.

During the continuous run trial at the pilot site, an initial approximated 2-HRT flush period for the CWT (2 w), effluent samples were collected along the DW pathway. Results for TSS, COD and total P concentrations are presented in figure 3.5. It is apparent from COD and TSS that while a significant reduction in these contaminants was observed, the goal of reaching 30 mg L\(^{-1}\) TSS and 60 mg L\(^{-1}\) COD were not met. Removal of TSS outcome was similar (60-70% removal) for CWT and aerated-FBR+CWT where for the latter, maximum removal occurred after VSB treatment (P1) while for CWT it occurred later after the first FWS pool (P2). Removal of COD was less effective for both treatments (20-30% removal), where the rate for COD reduction for aerated-FBR+CWT treatment (320 mg L\(^{-1}\) COD d\(^{-1}\)) was higher than COD removal by CWT treatment (244 mg L\(^{-1}\) COD d\(^{-1}\)). For COD results, the continuous reduction in concentration indicated that extrapolating the treatment length will improve the removal results, in contrary to TSS where the addition of a second FWS pool (P3) did not improve the outcome. For total P removal, both CWT and aerated-FBR+CWT treatments have similar outcomes with ~50% removal, and no further P removal occurred after the first FWS pool (P2). Aerated-FBR had a limited impact on total P recovered since the majority of P in DW was complexed in the suspended solids phase and did not precipitate into struvite.
Figure 3.5. TSS, COD and P removed by CWT and aerated-FBR+CWT treatments during continuous runs. Each dashed line represents an individual sampling period and each dot (blue) represents the average TSS, COD or P concentration with SD error (n=4). Samples analysis for TSS, COD and P concentrations are shown for untreated DW at entry (labeled DW), treated DW at aerated-FBR exit (labeled FBR), VSB exit (labeled P1), FWS 1 (labeled P2) and FWS2 (labeled P2). Note: for P values of P1 pool with CWT treatment (c), the value of sample taken on 8.7 was excluded as an outlier based on analysis of variance (α 0.05).

**Economic assessment of aerated-FBR+CWT system**

While the aerated-FBR+CWT system is still in the early stages of trial and a longer evaluation of this method is needed to establish best management practice
recommendations, the following observations were made about its cost effectiveness, based on a list of key parameters for aerated-FBR+CWT operation (Table 3.5). In addition, the cost of aerated-FBR operation were estimated based on electricity cost of $0.09 kW h-1 rates, and $17 per h farm labor (Table 3.6).

Table 3.5. Key parameters for aerated-FBR+CWT operation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dairy farm</td>
<td></td>
</tr>
<tr>
<td>Herd size (a-y)</td>
<td>100</td>
</tr>
<tr>
<td>DW (m³ year⁻¹)</td>
<td>2840</td>
</tr>
<tr>
<td>Operating days (d y⁻¹)</td>
<td>270</td>
</tr>
<tr>
<td>Treatment flow rate (L h⁻¹)</td>
<td>130</td>
</tr>
<tr>
<td>Treatment operation (h d⁻¹)</td>
<td>22</td>
</tr>
<tr>
<td>FBR</td>
<td></td>
</tr>
<tr>
<td>HRT (min)</td>
<td>60</td>
</tr>
<tr>
<td>Reactor size (L)</td>
<td>492</td>
</tr>
<tr>
<td>Mg application (g L⁻¹)</td>
<td>1</td>
</tr>
<tr>
<td>NaOH application (g L⁻¹)</td>
<td>0.85</td>
</tr>
<tr>
<td>VVM aeration</td>
<td>0.75</td>
</tr>
<tr>
<td>CWT</td>
<td></td>
</tr>
<tr>
<td>Average porosity</td>
<td>0.5</td>
</tr>
<tr>
<td>HRT (days)</td>
<td>14</td>
</tr>
<tr>
<td>Depth (m)</td>
<td>0.6</td>
</tr>
<tr>
<td>Area (m²)</td>
<td>536</td>
</tr>
</tbody>
</table>

Table 3.6. Initial and continuous cost estimate of FBR components for DW treatment. (Values of cost were estimated from the manufacturer rated power consumption).

<table>
<thead>
<tr>
<th>Component</th>
<th>Installation $</th>
<th>Operation</th>
<th>$ cost</th>
<th>$ L⁻¹ DW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerated-FBR</td>
<td>3,500</td>
<td>NaOH (Kg)</td>
<td>0.57</td>
<td>0.0024</td>
</tr>
<tr>
<td>DW auger</td>
<td>1,200</td>
<td>Mg (Kg)</td>
<td>0.38</td>
<td>0.002</td>
</tr>
<tr>
<td>Aerator</td>
<td>1,200</td>
<td>Aeration (Kw h⁻¹)</td>
<td>0.0050</td>
<td>0.0005</td>
</tr>
<tr>
<td>Overhead mixer</td>
<td>2,500</td>
<td>Mixer (Kw h⁻¹)</td>
<td>0.0050</td>
<td>0.0005</td>
</tr>
<tr>
<td>DW prefiltration</td>
<td>800</td>
<td>Seep pump (Kw h⁻¹)</td>
<td>0.0012</td>
<td>0.0002</td>
</tr>
<tr>
<td>Seep pump</td>
<td>400</td>
<td>Auger (Kw h⁻¹)</td>
<td>0.0065</td>
<td>0.0006</td>
</tr>
<tr>
<td>CWT</td>
<td>10,000</td>
<td>Labor (2h day⁻¹)</td>
<td>34.0000</td>
<td>0.0119</td>
</tr>
<tr>
<td>Total installation</td>
<td>$20,000</td>
<td>Running cost $ L⁻¹ DW</td>
<td>0.008</td>
<td></td>
</tr>
</tbody>
</table>

Using input from these cost components, the cost of treatment for the 2840 m² DW is $135 a-y⁻¹ for a 100-animal herd. The implementation of automation software can lower the cost of installation and labor, and being open source, it can be fitted to individual farm needs and compiled with several farm operations (feed, waste management, irrigation, etc.)
in one interface. The estimated assimilation effort for this open source system by cattle farmers is approximately 3-10 h of training based on the background user knowledge. The cost of key aerated-FBR+CWT components is $20,000. While such costs are not economically sound under the current state of operation in the U.S. for most dairy farms, this may not be so if increased HAB damage or change in public opinions impose stricter environmental regulations. In such regions (e.g. European Union) where stricter discharge regulations have imposed DW treatment and banned most topsoil spraying for raw DW, the estimated cost of DW handling for dairy was as high as $150a-y-1 when current practices ranging from aerobic digestion to landfill solids disposal were applied.

3.4 Conclusion

An aerated-FBR-CWT system was designed to determine P recovery rates, TSS/BOD removal, and adaptation of open source automation. The cost effectiveness, ease and potential of system assimilation into farm operation, and value of using recovered nutrients as fertilizer was also evaluated. Overall, the pilot site aerated-FBR operated well in continuous mode without much labor input (was visited 2-3 times per week). The auger design allowed for DW input without clogging and maintained constant application, as apparent from a steady state NaOH titration application. The application of 5-10 mM Mg was found to be sufficient to promote P recovery as struvite. The content of N-P-K in recovered solids collected from continuous aerated-FBR run with DW was 1-3-1, due to high calcite content. This is on par with many organic fertilizers but lower in N-P than many mineral fertilizers and pure struvite (7-29-0). The use of Mycodo software for operating the reactor was very effective and met all the needs of operation (pH control,
timer, various motors control, datalogging). The Raspberry Pi microcontroller used in the experiment was suitable for field application, operating at maximum ambient air temperature of 49 °C and minimum of -15 °C over a prolonged period. The operation of CWT in VSB and FWS modes managed to remove a significant amount of TSS and COD from DW, but failed to meet (or get near) the 30/60 mg L\(^{-1}\) TSS/COD target. Extending of the FWS residence time by doubling the number of FWS pools had no effect, indicating that the issue is not with lack of reaction time. Future work will explore further modifications for CWT application to establish a best management practice, as the treatment system has promise for improved nutrient recovery and contaminant reduction on small-scale dairy farms.
4. Magnesium Supplementation for Improved Struvite Recovery from Dairy Lagoon

Abstract

Recovery of phosphate (PO₄-P) as struvite (MgNH₄PO₄·6H₂O) from dairy lagoon wastewater (DW) limits contamination of surface water arising from application of DW to crop fields. Magnesium (Mg) addition to DW during PO₄-P recovery is used to promote struvite precipitation and suppress formation of undesired PO₄-P mineral products. A pilot-scale aerated fluidized-bed reactor was used to treat DW for PO₄-P recovery. The effect of Mg concentration (0-20 mM) and reaction pH (9-10) on mineralogy, thermal stability and micronutrient content of collected solids was evaluated. Elemental analysis, scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDX), X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy confirmed that the major PO₄-P and NH₄-N mineral recovered from DW was struvite (20-30 % w/w). Simultaneous thermal analysis with evolved gas analysis (STA-EGA) showed that ammonium (NH₄-N) in recovered struvite had two thermal maximums of decomposition into ammonia gas (NH₃(g)): low temperature (LT-NH₃) at 100-109 °C, and high temperature (HT-NH₃) at 295-318 °C. Increasing Mg concentration did not improve PO₄-P recovery as struvite and reduced the fraction of HT-NH₃ in solids from 50% to 14%. Higher Mg concentrations also decreased the sorption of micronutrients such as zinc and iron with recovered solids. These observations indicate a potential benefit to application of lower Mg concentrations during PO₄-P recovery that will increase the content of micronutrients and reduce thermal losses of NH₄-N in the produced struvite fertilizer.

4.1 Introduction

Reclamation of phosphate (PO₄-P) and ammonium nitrogen (NH₄-N) out of dairy lagoon wastewater (DW) is a viable approach to limit the growth of harmful algal blooms resulting from nutrient contamination of surface waters, while implementing farming practices that will secure a supply of nutrients for future crops. In the United States (U.S.), current best management practice recommendations for cattle growers is to discharge DW onto crop fields as part of a crop nutrition management plan. This practice, while agronomically sound, is prone to cause PO₄-P deposition into surface and groundwater, as well as groundwater contamination with nitrates (NO₃-N) and nitrous oxide (N₂O) greenhouse gas emissions. A sustainable alternative to direct soil application of DW is pretreatment for PO₄-P and NH₄-N recovery as struvite (MgNH₄PO₄·6H₂O) through wet chemistry precipitation using an aerated-fluidized bed reactor (aerated-FBR). In this process, the saturation index (SI) of struvite is pH dependent whereby struvite becomes supersaturated at pH 7-11, and undergoes a precipitation reaction (Eq 4.1).

\[
\text{Mg}^{2+} (\text{aq}) + \text{HPO}_4^{2-} (\text{aq}) + \text{NH}_4^+ (\text{aq}) \leftrightarrow \text{MgNH}_4\text{PO}_4\cdot6\text{H}_2\text{O(s)} + \text{H}^+ (\text{aq}) \quad (\text{Eq. 4.1})
\]

Dissolved organic matter (DOM) and calcium (Ca) are generally known to hinder struvite precipitation from DW, however interaction between these two components mitigate the overall hinderance effect. While the dissolved PO₄-P content in DW is often the limiting factor for struvite precipitation, addition of surplus of magnesium (Mg) can promote struvite precipitation and suppress the formation of hydroxyapatite (HAP; Ca₁₀(PO₄)₆(OH)₂) and other undesired or more amorphous PO₄-P minerals such as beta tricalcium metaphosphate (β-TCP; Ca₃(PO₄)₂) or monetite (CaHPO₄). Formation of struvite at alkaline pH of 8-11 coincides with the coagulation-flocculation of DOM in high
turbidity wastewater such as DW (2-10 g L\(^{-1}\) suspended solids), as well as the co-precipitation of potassium struvite (K-struvite, KMgPO\(_4\)·6H\(_2\)O), monetite, β-TCP, halite (NaCl), sylvite (KCl), niter (KNO\(_3\)) and carbonates. The formation of HAP is undesirable since its insolubility makes it an ineffective fertilizer source. In contrast, β-TCP, monetite and other more amorphous PO\(_4\)-P solids are viable fertilizer, however these tend to form flaky aggregates with high buoyancy, making them harder to recover from DW by the process of fluidized bed separation.

The recovered solid product from DW treated with aerated-FBR is a mixed phase mineral with high struvite, and monohydrocalcite (CaCO\(_3\)·H\(_2\)O) content that can be used as a slow release fertilizer (N-P-K; ~1-3-1). When struvite undergoes thermal decomposition its structural water and NH\(_4\)-N are released as water vapor (H\(_2\)O\(_g\)) and ammonia gas (NH\(_3\)\(_g\)) respectively between 40-400\(^\circ\) C. Previous work has demonstrated that a significant amount of the NH\(_4\)-N in this mixed fertilizer has higher thermal stability as indicated by thermal decomposition into NH\(_3\)\(_g\). Struvite NH\(_4\)-N either from synthetic, swine, municipal wastewater or an organic free DW model, had a maximum release of NH\(_3\)\(_g\) only as low thermal stability NH\(_3\)\(_g\) (LT-NH\(_3\)) between 100-160\(^\circ\) C. In contrast, the mixed phase solid from treated DW released NH\(_3\)\(_g\) as both LT-NH\(_3\) and high thermal stability NH\(_3\)\(_g\) (HT-NH\(_3\)) at 280-330 °C. While there are several thermally stable NH\(_3\)-N mineral sources such as ammonium sulphate ((NH\(_4\))\(_2\)SO\(_4\)) or ammonium nitrate (NH\(_4\)NO\(_3\)) (HT-NH\(_3\) 307 °C, 280 °C respectively), for nutrient recovery mineral products this thermal stability behavior has so far been unique to the struvite-calcite mix produced from DW. Higher thermal stability of NH\(_4\)-N improves soil N
nutrients conversion, where the volatility of such nutrients can result in as much as 50% w/w loss due to the combination of biochemical and thermal processes.\textsuperscript{204}

The reclamation of micronutrients is another area of interest in nutrients recovery research. The polyvalent transition metal cations zinc (Zn), iron (Fe), cobalt (Co) and molybdenum (Mo) are essential micronutrients for most crop production and are regularly applied as part of a nutrition plan.\textsuperscript{205} Therefore, reclaiming these elements improves nutrient security and offsets rising costs for farmers due to competing industrial demand.\textsuperscript{206}

The role of micronutrients in preventing plant infections also has implications for use of recovered Zn, Mo, and Cu in this capacity.\textsuperscript{62} The high affinity of struvite for polyvalent ion sorption \textsuperscript{144,145,160-162,186} makes struvite production from wastewater an effective approach for micronutrients reclamation.\textsuperscript{207}

This work evaluates the effect of 0-20 mM Mg concentrations and pH 9-10 treatments, applied using an aerated-FBR method, on the recovery of PO\textsubscript{4}-P as struvite fertilizer from DW at a dairy farm pilot site. The impact of Mg concentration and pH on co-precipitating minerals, micronutrient sorption and the thermal stability of NH\textsubscript{4}-N was determined for recovered solids. Expanding the understanding of geochemical processes involved in Mg and pH applications during struvite recovery treatments has significance to a wide range of crop yield considerations. Increasing the struvite content in the recovered solids applied as fertilizer improves the availability of PO\textsubscript{4}-P in the soil solution as compared to HAP and other less soluble minerals, while the intermediate solubility of struvite makes it a more effective slow release fertilizer.\textsuperscript{208} Improved control of the types and concentrations of micronutrients sorbed with struvite enables targeting their content to meet the crop producer nutrition needs, increasing yields and preventing phytotoxicity.
commonly occurring when present in excess. Finally, there is a need for increasing the thermal stability of NH$_4$-N salt fertilizers to improve plant nutrients conversion and reduce excess production of NH$_4$-N that is both costly and environmentally harmful. Thus, exploring the means in which thermally stable NH$_4$-N is formed in DW will pose both environmental and economic benefits. Overall, findings are valuable for assessing the efficacy of DW recovered struvite, contingent upon Mg and pH treatment conditions, as a soil PO$_4$-P, NH$_4$-N and micronutrient source.

4.2 Materials and Methods

4.2.1 Dairy farm wastewater lagoon and pilot aerated-FBR reactor.

A pilot study for struvite production was conducted using an aerated-FBR placed at a 100 milking cows dairy farm located in Hunterdon County, New Jersey, USA. During the treatment process, continuous DW flow from a 750,000 gallon earthen lagoon into a 40 L aerated-FBR was achieved with an auger pump (custom built) at 0.66 L min$^{-1}$ yielding a 60 min hydraulic retention time (HRT). This pilot site reactor is described in detail elsewhere, where an open source farming microcontroller software was used to control DW inflow, meter chemical solutions, record pH readings and apply caustic soda (NaOH) titration. Solutions of NaOH and magnesium chloride (MgCl$_2$·6H$_2$O) were applied with peristaltic pumps (Catalyst FH100). Magnesium chloride was applied at variable rates (0-70 mL min$^{-1}$) from a 0.2 M stock solution for a final concentration of 0-20 mM Mg. The aerated-FBR was aerated for carbon dioxide (CO$_2$(g)) purge at 0.75 L volume air per volume reactor min$^{-1}$ (VVM) raising DW pH from pH 7.6-8 to pH 8.3-8.5, and supplementary NaOH was applied from a 2.5 M stock solution to reach treatment pH of 9 or 10. For
each Mg application rate and pH treatment, the aerated-FBR was operated continuously for 6 hours (6-HRT) treating ~240 L of DW. All reagent solutions for the treatments (MgCl₂·6H₂O, NaOH) were prepared on-site from technical grade materials certified for low contamination by the supplier (Seidler Chem) and stored in 30 gallon HDPE flasks.

Figure 4.1. Pilot site aerated-FBR was composed of: a. agitator for circular motion in a reaction cell and upward flow in a fluidized bed cell using an overhead mixer (Arrow 1200); b. submersible pH probe insert and influent application tubes for DW, MgCl₂·6H₂O and NaOH solutions; c. air frit for carbon dioxide stripping; d. mount of sealed stirrer guide (Cowie) for continuous overhead mixer operation; e. sealed PVC reactor cover; f. struvite precipitation reactor; g. fluidized bed reactor for solids separation; h. effluent outlet.

4.2.2 Collection of DW and solid precipitates

Wastewater samples for evaluation of DW characteristics and nutrient recovery were collected from the lagoon and the aerated-FBR (reactor inflow and outflow tubes respectively). Liquid samples were collected at an approximate steady state after 3 h of
operation (3-HRT) at 1 h frequency (n = 4, except for pH 10 treatment where n = 3). All samples were collected in 50 mL HDPE flasks and kept on ice for refrigeration prior to analysis within 1-2 days. Samples were collected either as unmodified for determining the total components and dissolved phase composition, or acidified to 2% w/w HCl on-site for acid-soluble components (in addition to the dissolved phase). All samples, except for total composition samples, were centrifuged at 6000 rpm for 30 min and filtered with a 0.45 µm PES filter prior to analysis. At the end of each treatment of 6 h operation, solids in the aerated-FBR were left to settle for approximately 1-2 h in a plastic pan, then solid samples were collected and air dried.

4.2.3 Chemical composition analysis of DW and solids recovered from aerated-FBR

Collected DW and recovered solids were analyzed for elemental phosphorus (P) and micronutrient content. For solid NH₄-N content, a mass of 50 mg of solid was digested by sonication with 10 mL 2% HCl and the digestate analyzed by colorimetry using NH₃-N kits (TNT 832, Hach) and a spectrophotometer (Hach DR 3900). Inductively coupled plasma optical emission spectrometry (ICP-OES; Agilent SVDV 5110) was used for elemental P and micronutrients analysis of all solid and liquid samples. Both solid samples at 80 g L⁻¹ acid (~200 mg) and 2.5 mL liquid DW samples, were digested with 2.5 mL trace metal grade 70% nitric acid (HNO₃) followed by 1 mL 36% trace metal grade hydrochloric acid (HCl) at 150º C, then diluted 1:100 (solids final concentration 0.8 g L⁻¹). Statistical analysis of datasets for analyses of variance (ANOVA) and comparison of means were done using JMP 15 (SAS) software.
4.2.4 Structural analysis of recovered solids

X-ray diffraction (XRD, Bruker Advance D8, LynxEye XE detector) scans were collected for recovered solid samples, from 5-90° 2θ at 0.0025° 2θ resolution at a step rate of 1s using a Cu light source, Ge-monochromator, 2.5° soller slit and 0.075 mm detector slit. The data was evaluated for mineral phase distribution using Profex-4 software at a refinement confidence for statistical evaluation of $\chi^2 \leq 1.5$. Structural deformation of the collected solids was observed using attenuated total reflectance Fourier transform infra-red (ATR-FTIR) spectroscopy (Spectrum 100, Perkin Elmer). Scans were recorded 21 times between 4000-650 cm$^{-1}$ at 8 cm$^{-1}$ resolution using a deuterated-triglycine sulfate (DTGS) detector. Scanning electron microscopy (SEM) imaging coupled with an energy dispersive X-Ray (EDX) analyzer, was done at 5-10 kV; 5-10 mA (Hitachi S4800; EDAX). Samples for SEM were mounted on carbon tape and coated twice with iridium (~9 nm). Thermal stability was evaluated by simultaneous thermal analysis coupled with evolved gas analysis (STA-EGA; Netsch Perseus 449 Jupiter-Brucker Alpha). A mass of 20-35 mg of sample was heated between 25-1200 °C at 10 K min$^{-1}$ under 50 mL min$^{-1}$ nitrogen purge. Evolved gases were determined by FTIR analysis of an average of 16 scans collected between 4000-650 cm$^{-1}$ at 4 cm$^{-1}$ resolution. Regression analysis for EGA IR absorption was done using JMP 15 (SAS) software.

4.3 Results and discussion

4.3.1 Liquid phase DW composition

The concentration of major elements in three phases of DW influent samples, dissolved, acidified and total was analyzed (Figure 4.2, Appendix C, Figure C.1). For P, aluminum (Al), Ca, iron (Fe), Mg and Mn nutrient elements, average concentrations in acidified
samples were higher than in the dissolved phase, indicating that a significant portion was
complexed to acid-soluble or other colloidal suspended solids < 0.45 µm. Of these
elements, P, Al and Fe as well as S, had higher total concentrations relative to dissolved
and acidified, indicating some association with suspended solids > 0.45 µm. This is likely
since prior work found high suspended solids content (2-7 g L⁻¹) in DW.¹⁸⁶,¹⁹⁸ For Ca, Mg
and Mn, similar total and acidified concentrations suggests that dissolved plus acid-soluble
colloids only contribute to the total metal concentration. In contrast to the other elements,
potassium (K), sodium (Na) and Zn had similar average concentrations between dissolved
and total samples indicating limited association with suspended solids of any size.

The effect of Mg dosing (0-20 mM Mg) and higher alkalinity (pH 10) treatments
on the mass balance of major DW components in the dissolved phase was calculated by
comparing the dissolved phase of DW before and after aerated-FBR treatments (Figure 4.3;
Appendix C, Figure C.2). It is noticeable that while the average for the 5 mM Mg treatment
showed a release of all nutrients other than P and Ca, this was not statistically significant
compared to 0 mM Mg. When higher pH was applied at 10 mM Mg, only the removal of
Fe improved. Accumulation of Na occurred due to NaOH titration, and Mg accumulation
increased only at higher dosing of 10-20 mM Mg. Applying higher Mg dosing (up to 20
mM Mg) or higher pH treatments (pH 10) did not improve the removal of P from DW,
indicating that for the purpose of P recovery there was no added benefit for these
treatments. As for the recovery of other nutrients, increased Mg dosing did not improve
removal of these elements.
Figure 4.2. DW influent elemental composition. Average DW influent elemental composition (n=19) and standard deviation in dissolved (0.45 µm filtered), acidified (extractable by 2% HCl) and total liquid phases. Results for dissolved, acidified or total with the same alphabetic symbol for a given element are not significantly different (Tukey Kramer, α=0.05).

Figure 4.3. Change in mass balance of DW components (n=4; n=3 for pH 10 treatment) in the dissolved phase after aerated-FBR treatments of 0-20 mM Mg (pH 9) and pH 10 (10 mM Mg). Comparison of means (Tukey-Kramer, α 0.05) is shown, where for each element, results with the same alphabetic label in other DW treatments are not significantly different.
4.3.2 Bulk compositional analysis of recovered solids

4.3.2.1 Elemental composition of solids

While no significant removal was observed in DW mass balance, slight changes in treated DW over time resulted in a significant effect on the composition of the recovered solids. Elemental composition analysis of solids collected from the aerated-FBR (Figure 4.4; Appendix C Figure C.3) showed that 5-20 mM Mg dosing resulted in a constant P concentration of ~16 g kg⁻¹ compared to no Mg application (12 g kg⁻¹) or higher alkalinity at pH 10 and 10 mM Mg (7 g kg⁻¹). For K, higher Mg dosing did not improve K uptake (13-18 g kg⁻¹) other than for the 10 mM Mg, pH 9 treatment, which may be due to a spike of K in lagoon DW (+300 mg L⁻¹). Highest concentrations of the micronutrients Fe, S, Mn and Zn were observed at 0-5 mM Mg dosing, with the concentrations decreasing at higher Mg dosing or alkalinity. There is an apparent discrepancy between higher Fe removal from the dissolved phase of DW at higher pH or Mg application dosing (Figure 4.3) and lower accumulation in collected solids. This may indicate that the majority of removed Fe at higher pH or Mg application is complexed to suspended solids rather than aggregated into the newly formed and larger minerals, and as such leave the aerated-FBR and are not retained in the fluidized bed.²⁸,⁵¹,⁵² The concentration of Al, an element that is not generally considered a micronutrient but may promote growth when present at low concentrations, also decreased for higher Mg dosing and pH. Conversely, the Ca concentration increased with Mg dosing, but was lower at higher pH. While the increase in Na concentration for solids from the pH 10 treatment can be explained by higher NaOH application, lower Na content at 20 mM Mg is not explained by the experimental setup and might be due to periodical variation in DW composition. As expected, the Mg concentration of the solids
increased with dosing and pH. These observations confirmed that for the purposes of the aerated-FBR treatment of DW there was no additional benefit of the higher pH application. Since increased pH did not improve P recovery or significantly impact micronutrient recovery, this was not further investigated as NaOH treatment is costly and therefore will not likely be justified for DW treatment applications.

Figure 4.4. Elemental composition of solids recovered from DW treated with aerated-FBR at 0-20 mM Mg (pH 9) and pH 10 (10 mM Mg).

4.3.2.2 Morphology and composition of individual solid aggregates

The SEM images of recovered solids (Figure 4.5) showed that the morphology of individual aggregates did not change significantly with higher Mg dosing or pH. Comparing the elemental composition of aggregates from EDX spectroscopy (Figure 4.5), and the predicted elemental content based on thermodynamically favorable mineral phases calculated from DW composition (Appendix C, Table C.1) showed that aggregates did not
match one mineral but formed mixed phases. This is supported by the overall morphology, whereby calcite typically forms cubic aggregates and struvite forms dendritic or elongated needles that often appear with macropores,\textsuperscript{186,214} while the aggregates observed mostly lacked a single distinguished form. It is apparent that where higher Ca content was observed by EDX, aggregates tended to form a less dense and more flaky structure. When higher Mg dosing or pH was applied, the abundance of aggregates larger than ~100 \( \mu \)m particle size increased, indicating a lower buoyancy potential. This was visible empirically in the increase of overall mass of the solids trapped in the fluidized bed\textsuperscript{57,186} of the aerated-FBR.

The micronutrients (Co), nickel (Ni), Selenium (Se), Silicon (Si), Fe, Zn, S and Mn were detected in various amounts (\( \leq 3\% \) atomic) in the sampled aggregates (Appendix C, Figure C.4), and due to the mixed composition of samples cannot be attributed to a single estimated mineral phase. The presence of micronutrients was detected for all Mg dosing treatments, while the only clear effect for the pH 10 treatment was an increase in Mn sorption. This is in contrast to the bulk elemental composition analyses that showed significantly higher micronutrient uptake for lower Mg dosing treatments. This observation suggests there is variable distribution of micronutrients associated with mineral aggregates on the micron-scale and reveals a potential limitation of the SEM EDX approach when dealing with very heterogeneous samples.
Figure 4.5. SEM EDX imaging and analysis of solid aggregates recovered from the aerated-FBR for 0-20 mM Mg (pH 9) and pH 10 (10 mM Mg) treatments. Letters A-T and corresponding individual aggregates represented characteristic mineral forms in each sample selected for polygon area EDX scan (pie chart of samples A-T and reference minerals). The micronutrient content within the Other element composition label in the pie charts is depicted in Appendix C Figure C.4.
4.3.3 Mineralogy and structural properties of recovered solids

4.3.3.1 Mineral phase distribution

The overall mineral composition of recovered solids was calculated semi-quantitatively from powder XRD scans (Figure 4.6, Appendix C Figure C.5). These analyses found that the dominant mineral phase for PO₄-P in solids recovered from DW was struvite (19-31% w/w) when 0-20 mM Mg dosing was applied. At lower Mg treatments (0-5 mM) the additional PO₄-P minerals monetite (2-10% w/w) TCP (2% w/w) and TCP-Mg (2.5% w/w) also precipitated. The estimated fraction of struvite decreased from 30% (w/w) to 20% (w/w) with higher Mg dosing, which is in slight contrast to elemental analyses showing that PO₄-P content increased from 12 g kg⁻¹ for 0 mM Mg to 16 g kg⁻¹ for 5-20 mM Mg. This is most likely due to a combined circumstance of slight over estimation of struvite phases with lower degree of crystallinity (Mg 0 mM), increase in carbonate precipitation, and flocculation of suspended P solids out of DW when Mg was applied. The related broadening of the XRD diffraction patterns for PO₄-P minerals that is indicative of a more amorphous phase in the 18.5-26 2Θ range (d=3.48-4.75 Å) decreased with higher Mg dosing and disappeared at 10 and 20 mM Mg treatments (Appendix C, Figure C.5). The Mg treatment did not affect the well-crystalline mineral phases calcite, monohydrocalcite, magnesite, quartz (SiO₂) and nesquehonite that appeared at higher diffraction counts with less 2Θ broadening. In contrast, XRD analyses eliminated the formation of thermodynamically favorable Mg-P minerals such as trimagnesium phosphate (TMP, Mg₃(PO₄)₂) or newberyite (MgHPO₄.3H₂O) for higher Mg dosing as a cause for discrepancy with elemental composition results. A significant reduction in calcite content and an overall transition from Ca carbonates (calcite, monohydrocalcite) to Mg carbonates
occurred at higher Mg dosing (10-20 mM), with ~50 % w/w of carbonates forming as nesquehonite.

Figure 4.6. Mineral phases (% w/w) in solids collected from DW treated with aerated-FBR. Fundamental parameter analysis was derived from XRD scans of DW solids using Profex 4 software.

4.3.3.2 Structure of mineral functional groups

Recovered solids were analyzed by FTIR spectroscopy (Figure 4.7) to determine which mineral functional groups were most affected by Mg addition. At 0-5 mM Mg dosing, bands at 2850 and 2920 cm⁻¹, possibly due to sorption of phenolic organics present in DW, were observed but were eliminated at 10-20 mM Mg dosing. A similar trend was observed for the hydrated phosphate (PO₄-H₂O H-bond) detected at a bandwidth of 2280 cm⁻¹ that disappeared when higher Mg dosing was applied. This is likely due to the
elimination of amorphous phosphate phases such as monetite which is often recovered in hydrous form.\textsuperscript{26} The evolution of a split peak at 1400 cm\-1 with increased Mg dosing is attributed to transition of the CO$_3$ v3 IR vibration from mixed calcite-monohydrocalcite to monohydrocalcite-nesquehonite.\textsuperscript{218} Broadening of the 900-1150 cm\-1 band can be a result of the effect of Ca coprecipitation on the PO$_4$ v1+3 IR vibration,\textsuperscript{162} or mixed sulphate mineral IR absorption from precipitated gypsum at 0-5 mM Mg treatment.\textsuperscript{163,219}

Figure 4.7. FTIR absorption of solids collected from DW treated with aerated-FBR with highlighted bands a. C-OH 2850 cm\-1, 2920 cm\-1; b. P-H$_2$O 2280, 2180 cm\-1; c. H$_2$O v2 1640 cm\-1; d. CO$_3$ v3, KNO$_3$ v3 1484 cm\-1, 1410 cm\-1; e. PO$_4$ 938-1015 cm\-1, SO$_4$ v1+3 983-1105 cm\-1; f. CO$_3$ v2 873 cm\-1; g. H$_2$O-H$_2$O H-bond 765 cm\-1; h. CO$_3$ v4, KNO$_3$ v4, H$_2$O-H$_2$O H-bond 696 cm\-1.\textsuperscript{163,165,218}
4.3.4 Thermal properties and stability of recovered solids

The STA-EGA analyses of recovered solids (Figure 4.7, Appendix C Figure C.6) were used to further confirm the mineral composition and evaluate the stability of recovered NH$_4$-N for soil nutrition applications. Differential scanning colorimetry (DSC) and mass thermal gravimetric (TG) changes over the 25-1200 °C temperature range were compared with IR signals from EGA readings to determine the relation between individual functional groups (NH$_4$; CO$_3$; H$_2$O) in solids emitted as evolved gas and their thermal stability. While a typical struvite TG plot includes a single mass loss step between 75-400 °C with a maximum rate at 140-160 °C, a multiple step mass loss was observed in the recovered solids. Dual TG step-wise mass losses that are larger in proportion (75-180 °C; 180-360 °C) occurred for the 0 mM Mg treatment. As Mg dosing increased up to 20 mM, the TG curve exhibited multiple step-wise (3-4) mass losses, with a smaller proportion of individual mass losses, forming a more linear TG curve. An opposite TG trend is observed for the higher temperature range of 500-1000 °C (Appendix C, Figure C.6) which is associated mostly with carbonate decomposition, where higher Mg dosing of 10 and 20 mM resulted in a more step-wise TG mass loss and overall TG steps increased from 1 to 3. Results demonstrated that lower application of 0-5 mM Mg increased the number of TG mass loss steps at the lower temperature range (75-400 °C) associated with carbonates, NH$_4$-N, H$_2$O and organic thermal decomposition.

To determine if these TG behaviors were related to a change in individual mineral structure or to a change in overall mineral composition, results were compared both with the DSC and EGA outputs (Figure 4.8, 4.9; Appendix C, figure C.6) and with overall mineralogy findings from XRD and elemental analyses (Figure 4.4, 4.6). Analysis of EGA
results relies on the fingerprint IR vibration of gases where unique IR absorption bandwidths of H2O(g) (1505 cm\(^{-1}\)), CO\(_2\)(g) (2336 cm\(^{-1}\)) and NH\(_3\)(g) (996 cm\(^{-1}\)) are compared with the overall EGA signal in the Gram Schmidt (GS) curve. An evaluation of the EGA IR absorption at 25-450 °C was used to quantify the thermal stability of NH\(_4\)-N, where at higher temperatures it is effectively eliminated as NH\(_3\)(g). At the lower temperature range (≤ 200 °C), release of carbon dioxide gas (CO\(_2\)(g)) from 10-20 mM Mg samples could be associated with nesquehonite at 150-200 °C\(^{216}\) as well as breaking of organic compounds through pyrolysis (0-20 mM Mg solid samples). Such pyrolysis due to the presence of organic content is in line with likely increased flocculation and coagulation of DOC from DW at higher Mg dosing. Higher temperature CO\(_2\)(g) release at 400-800°C was associated with nesquehonite as well as other carbonates, as apparent in the IR signal at the 2336 cm\(^{-1}\) bandwidth.\(^{162,186,220,221}\) Variation in the stability of CO\(_3\) between the above minerals accounted for the additional TG mass loss steps at higher temperatures as apparent from the corresponding IR absorption at 2336 cm\(^{-1}\) (Appendix C, Figure C.6). Since the only major NH\(_4\)-N mineral formed was struvite, the NH\(_3\)(g) 966 cm\(^{-1}\) vibration bandwidth can be reliably associated with struvite thermal stability. Release of NH\(_3\)(g) from NH\(_4\) in solids is summarized in Table 4.1, with integrated values for IR absorption for NH\(_3\)(g) and the corresponding temperature of the IR signal peak. From this data it is clear that higher Mg dosing decreased the thermal stability of NH\(_4\) in solids.
Figure 4.8. STA EGA analyses of solids recovered from DW treated with aerated-FBR at 0-20 mM Mg (pH 9), depicting the thermally active range of NH$_4$(s) (25-450 °C). a. TG mass loss (%); b. DSC; c. GS conversion for total EGA IR absorption.

Figure 4.9 EGA analysis of recovered solids. Comparison of the normalized EGA IR absorption of the major functional groups being emitted H$_2$O, CO$_2$, NH$_3$ over the thermally active range of NH$_4$-N (25-450 °C).
A reciprocal relation was fitted (Appendix C, Figure C.7) between Mg addition and NH₄ stability ($R^2 0.95$, $p=0.025$):

$$\frac{1}{HT-\text{NH}_3 \text{ (\% w/w)}} = 0.0163 + 0.0028 \times [\text{Mg}] \text{ (mM)} \quad \text{(Eq. 2)}$$

Higher HT-\text{NH}_3 content at lower Mg dosing suggested that the formation of HT-\text{NH}_3 is likely to be associated with the mixed phase of struvite-Ca-carbonate minerals rather than Mg-carbonates or accumulation of DOM in the solids due to flocculation.

Table 4.1 Thermal distribution for ammonia release based on integrated IR absorption from EGA analyses

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<th>Mg (mM)</th>
<th>LT-\text{NH}_3 (s⁻¹)</th>
<th>LT-\text{NH}_3 (ºC)</th>
<th>HT-\text{NH}_3 (s⁻¹)</th>
<th>HT-\text{NH}_3 (ºC)</th>
<th>HT \text{NH}_3%</th>
</tr>
</thead>
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<td>0</td>
<td>2.969</td>
<td>103.6</td>
<td>2.904</td>
<td>310.6</td>
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<td>2.299</td>
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<td>20.8 %</td>
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<tr>
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<td>108.8</td>
<td>0.645</td>
<td>306.6</td>
<td>13.9 %</td>
</tr>
</tbody>
</table>

$a$Appendix C, Figure C.6

4.4 Conclusions

Applying higher Mg dosing (20 mM) and alkalinity (pH 10) to DW treatment by aerated-FBR, did not significantly improve the recovery of dissolved PO₄-P with 2.7-9.4 mg P L⁻¹ removal. In contrast, higher Mg dosing transformed the carbonate liming agent in the recovered solids from calcite to monohydrocalcite and nesquehonite respectively, and resulted in less sorption of micronutrients (Zn, Fe) in the recovered solids. A potentially beneficial outcome for higher Mg application was the higher abundance of larger
aggregated particles (>100 µm) for 10-20 mM Mg treatments as observed in SEM images of the recovered solids. An EDX analysis of the elemental composition of representative individual aggregated minerals confirmed that the majority of recovered solids were a mixed mineral phase aggregate, with atomic (%) composition that fit mostly mixed struvite and carbonates.

Thermal analysis of the solids recovered from treated DW found a significant correlation between low Mg application and improved thermal stability of NH$_4$-N(s), whereby the fraction of HT-NH$_4$ decreased from 50% to 13% for 0 mM and 20 mM Mg applications respectively. In addition, TG and DSC analyses confirmed the mineralogy findings for carbonate composition where an increase in step-wise TG mass loss corroborates the formation of nesquehonite and other magnesium carbonates for 10-20 mM Mg treatments. Observations of the thermal properties of volatile N nutrients and composition of liming agents in recovered DW solids also demonstrated the potential benefit of using STA-EGA to evaluate the soil nutrition potential of such recovered nutrients. This work indicates that for DW there is little benefit to Mg addition in the aerated-FBR process, and that addition of as little as 5 mM Mg can be used to promote PO$_4$-P recovery as struvite. The application of excess Mg is not only costly but can result in a less stable NH$_4$ in the recovered fertilizer, as well as less micronutrient uptake.

**Acknowledgment** Special thanks to Fulper Farm LLC for their support in facilitating this study. Thanks to Dr. Evert Elzinga for the use of XRD and FTIR instruments. This study was supported by USDA SARE GNE 17-158 grant.
5. Effect of Phenolic Organics in Simulated Dairy Wastewater on Struvite Precipitation

Abstract:
The production of struvite (MgNH₄PO₄·6H₂O) from dairy lagoon wastewater (DW) improves phosphorus (P) resource sustainability and reduces the rate of deposition of P into surface waters. Struvite formation can be hindered by dissolved organic matter (DOM) and calcium (Ca), but the prevalence of the phenolic functional group (R-OH) in DW DOM may counteract any limiting effects. A constant composition reactor was used to determine the effect of R-OH on the precipitation of struvite from simulated DW in the presence of Ca, with phenol (Ph) as a model R-OH. The presence of Ph increased the struvite precipitation rate relative to those of Ca, Ph, blank (no Ca or Ph), and Ca treatments (51.3, 30.5, 5.8, and 2.7 μmol of struvite min⁻¹, respectively). Solid analysis showed that Ph limited the struvite morphology deformation caused by Ca and Ca mineral coprecipitation. Coprecipitation with Ca–P minerals with or without Ph did not significantly change the thermal properties of struvite, with the thermogravimetric mass loss associated with ammonia gas and water vapor emissions occurring at 80–160 °C. The observed effects of Ph on struvite formation suggest a beneficial contribution of dissolved low-molecular weight organics such as R-OH to improved recovery of struvite from DW.

This chapter is published under:
5.1 Introduction

Dairy wastewater (DW) contains high concentrations of phosphorus (P), a key nutrient for crop production, but also a key contributor to growth of undesired harmful algal blooms (HAB). A sustainable approach to recover P from DW is to precipitate it as struvite (MgNH₄PO₄·6H₂O), for use as a slow release fertilizer (N-P-K: 7-29-0; Ksp 10⁻¹³.26) or in some cases dittmarite (MgNH₄PO₄·H₂O). The majority of struvite production processes use wet chemistry to precipitate P out of DW, followed by solids separation. One such method is to use a continuous stirred reactor and fluidized bed separation for chemical precipitation of struvite from DW under alkaline conditions. Struvite becomes saturated at pH 7-11 with maximum precipitation normally occurring at pH 9-10, but lower pH values of 7.5-8.5 can be applied in the recovery process or in some cases dittmarite (MgNH₄PO₄·H₂O). The majority of struvite production processes use wet chemistry to precipitate P out of DW, followed by solids separation. One such method is to use a continuous stirred reactor and fluidized bed separation for chemical precipitation of struvite from DW under alkaline conditions. Struvite becomes saturated at pH 7-11 with maximum precipitation normally occurring at pH 9-10, but lower pH values of 7.5-8.5 can be applied in the recovery process.

Due to the high calcium (Ca) content in DW, struvite crystallization often coincides with formation of hydroxyapatite (Ca₅(PO₄)₃OH; HAP). The mineral HAP is a less desirable fertilizer product as it is practically insoluble (Ksp 10⁻¹¹⁶.8) making it a relatively poor P source for agricultural applications without further treatment such as processing into nanoparticles with high surface area. Other commonly occurring Ca-P minerals in treated DW are beta tri-calcium phosphate (Ca₃(PO₄)₂; β-TCP), octacalcium
phosphate \( (\text{Ca}_8\text{H}_2\text{(PO}_4\text{)}_6\cdot5\text{H}_2\text{O}; \text{OCP}) \) and dicalcium phosphate (hydrated: \( \text{CaHPO}_4\cdot2\text{H}_2\text{O}; \text{DCPD} \); anhydrous: \( \text{CaHPO}_4; \text{DCPA} \)).\(^{26,231,232}\) When abundant magnesium (Mg) is present in DW or applied as part of the treatment process, an isomorph of \( \beta \)-TCP, magnesium phosphate (\( \text{Mg}_3(\text{PO}_4)_2; \text{TMP} \)) or its hydrated form bobierrite (\( \text{Mg}_3(\text{PO}_4)_2\cdot8\text{H}_2\text{O} \))\(^{233-235}\) may form. The presence of Ca can also significantly inhibit P precipitation and reduce the crystallinity struvite,\(^{39,186,236}\) while the presence of Mg inhibits the formation of HAP, DAP and polyphosphates such as \( \beta \)-TCP.\(^{19,26}\)

Dissolved organic matter (DOM) is also known to hinder struvite formation in most wastewaters, where it is found to decrease the rate of crystal growth, requiring longer hydraulic retention time to meet P recovery goals.\(^{77,79,153,237}\) In contrast, it was previously observed that when DW was compared to a DOM-free model solution of similar ionic composition, rates of both P recovery and precipitation were improved in DOM-bearing DW.\(^{186}\) This observation alluded to a synergic Ca-DOM interaction that shielded the Ca hindrance for struvite precipitation. For DOM interactions with Ca and P in dairy manure, it has been suggested that DOM simultaneously adsorbs to colloidal P minerals and complexes with Ca, hindering the formation of stable Ca-P minerals such as HAP.\(^{238}\) An experimental electrochemical reactor for P recovery showed that under increased polarity in DW there was an increase in DOM coprecipitation, suggesting that pH manipulation during wet chemistry may similarly affect DOM-Ca-P interactions as a result of an increase in surface potential.\(^{239}\) The composition of DOM is heterogeneous and complex, however in both DW and fresh cattle manure, phenolic (R-OH) functional groups were identified as abundantly present by Fourier transform infra-red (FTIR) spectroscopy.\(^{70,156}\) Therefore the
R-OH group may play an important role in the interaction between DOM, Ca and struvite in DW.

The current study aims to identify the effect of R-OH groups on struvite crystal nucleation, growth, and thermal stability in the presence and absence of Ca. A constant composition approach\textsuperscript{240} is used to model struvite formation during P recovery from DW\textsuperscript{4} using phenol (Ph; C\textsubscript{6}H\textsubscript{5}OH) in simulated wastewater (SW) as a proxy for dissolved R-OH in DW. The constant composition approach keeps the dissolved constituents of struvite at a constant concentration or struvite saturation, by countering precipitation with an equimolar titration of struvite components. The rate of titration with and without Ph in turn describes the effect of R-OH on struvite formation. In addition, it is of interest to evaluate the effect of polyvalent cations on struvite formation in SW\textsuperscript{1864,26,162} as they can affect the struvite structure.\textsuperscript{146} Since the dominant polyvalent cation in DW is Ca\textsuperscript{2+},\textsuperscript{26} introducing Ca will evaluate the effects of both Ca and Ca+Ph on struvite precipitation. Identifying the possible components in DW that reduce the overall hinderances to P recovery as struvite\textsuperscript{4} can improve the prospect of sustainable nutrient recovery from wastewaters.

5.2 Materials and Methods

Constant Composition Model for Struvite Growth

To model struvite growth in simulated wastewater (SW) under steady state conditions, a constant composition approach was used,\textsuperscript{48,77,240} keeping the molarity of dissolved struvite components: Mg\textsuperscript{2+}\textsuperscript{(aq)}, H\textsubscript{2}PO\textsubscript{4}\textsuperscript{−}\textsuperscript{(aq)} and NH\textsubscript{4}\textsuperscript{+}\textsuperscript{(aq)} constant throughout the struvite precipitation reaction (Eq. 5.1).

\[
\text{Mg}^{2+}_{(aq)} + \text{H}_{2}\text{PO}_{4}^{-}_{(aq)} + \text{NH}_{4}^{+}_{(aq)} \leftrightarrow \text{MgNH}_{4}\text{PO}_{4} \cdot 6\text{H}_{2}\text{O} + 2\text{H}^{+}_{(aq)} \quad \text{(Eq. 5.1)}
\]
This follows that the growth rate of struvite is proportional to the decrease in pH due to the deprotonation of $\text{H}_2\text{PO}_4^{-}\text{aq}$, where C is an empirical constant for a given x molarity of struvite components in solution, m is struvite solids molarity and V is the reaction volume (Eq. 5.2).

$$\frac{dpH}{dV} = \frac{dm}{dV} = Cx \quad \text{(Eq. 5.2)}$$

Using Eq. 5.2, an empirical unitless constant (C) of 35 was found to suffice as a mass balance parameter for struvite precipitation with an initial concentration of $x = 4$ (mM). This was validated by testing other values, and $C = 35$ was found to perform well for the blank. The constant C was evaluated for struvite in the absence of Ph or Ca, accounting for the loss of precipitated mass over volume change in the constant composition solution. At pH 8.5 and an estimated saturation index (SI) of 1 calculated using Visual Minteq 3.1 software (Appendix D, Table D.1), the concentration of struvite components is 4 mM. Such a mass balance solution was put into a constant composition solution77. A three titration pump system (Eq. 5.3-6, see supporting information).

Pump 1: 0.1 M NaOH \quad \text{(Eq. 5.3)}

Pump 2: $(2x + Cx) \text{ M MgCl}_2 \cdot 6\text{H}_2\text{O} + (2x + Cx) \text{ M NH}_4\text{H}_2\text{PO}_4 + y \text{ M CaCl}_2 \quad \text{(Eq. 5.4)}$

Pump 3: 0.2 M NaCl + $(2Cx - 2x) \text{ M NaOH} + z \text{ M C}_6\text{H}_5\text{OH} \quad \text{(Eq. 5.5)}$

$x = [\text{Mg}] = [\text{PO}_4] = [\text{NH}_4]; y = [\text{Ca}] \text{ treatment}; z = [\text{Ph}] \text{ treatment} \quad \text{(Eq. 5.6)}$

These equations were used to determine the constant composition molarity experimental requirements for SW treatments.

**Constant Composition Experiments**

Four SW model treatments, Blank (no Ph or Ca), Phenol (Ph$_{sw}$), Calcium (Ca$_{sw}$), Phenol and Calcium (Ph+Ca$_{sw}$), were used to evaluate the combined effect of dissolved R-OH
functional groups and Ca on struvite precipitation (Table 1). The use of Ph minimizes the potential for reactions competing with struvite precipitation as very little coprecipitation or adsorption of Ph with struvite occurs as the lower molecular weight limits stacking through van der Waals interactions. Constant composition was achieved using a batch reactor (Appendix D Figure D.1-2) where a 1000 mL start solution with 4 mM Mg\(^{2+}\)\(_{(aq)}\), PO\(_4^{3-}\)\(_{(aq)}\) and NH\(_4^+\)\(_{(aq)}\) in 0.1 M NaCl, was used to supersaturate struvite with an estimated SI =1 at pH 8.5. A pH of 8.5 was chosen as it is acceptable for both struvite precipitation and generation of a reasonable amount of solids for recovery. All reagents used were ACS grade, mixed in deionized water (DI). All solutions were filtered through a 0.45 µm filter prior to use and titration solutions were made fresh daily. All experiments were carried out in triplicate (n=3).

The constant composition reactor was assembled in a 2000 mL HDPE flask, equipped with a double junction pH probe (Orion) and 2-inch PTFE magnetic stirrer. The experiment was done under gas purge (~50 mbar) using ultrapure nitrogen gas (N\(_2\)(g), Airgas) to eliminate carbonate pH drift. The SW solution (Table 5.1) was added to the reactor and purged under N\(_2\)(g) until the pH reading stabilized at pH 4.6-4.7 (5-10 min). For initial titration, a 0.1 M NaOH solution (T1) was pumped into the reactor at a 5 mL min\(^{-1}\) rate, delivering 40-60 mL of base. When the pH reading reached 8.5, a single board computer (Raspberry Pi 4 B+) stopped T1 and activated continuous titration with solutions T2 and T3 (Table 1). Continuous titration (T2, T3) was done at 0.5, 1 and 2 mL min\(^{-1}\) rates using peristaltic pumps (Catalyst FH100). Since C (Eq. 5.2) was kept constant throughout the experiment, higher flow rates were applied when struvite precipitation rate (dm dt\(^{-1}\)) exceeded the empirical rate of application (C= 35) set for the struvite Blank
treatment, and a pH drift downward occurred. Although T2 and T3 titration rates varied between treatments, for the duration of each treatment and for each replicate (R1-3) flow rates were constant. Effluent samples were collected prior to initial titration (after N\textsubscript{2(g)} purge) and at 60 and 120 min. Samples were filtered (0.45 µm PES) and acidified to a final concentration of 2% nitric acid (HNO\textsubscript{3}). Solid samples were collected by filtration (0.45 µm cellulose acetate) at the end of each run, followed by rinsing with 60 mL of filtrate from 1 g L\textsuperscript{-1} equilibrated struvite and air drying for 48 h at 38-40 ºC.

Table 5.1. Composition of simulated wastewater (SWW) (Eq. 5.6) start solution and initial (Init.) and continuous (Cont.) titration solutions for constant composition experiments with different treatments (TMT).

<table>
<thead>
<tr>
<th>TMT</th>
<th>Start Solution</th>
<th>Init. Titration</th>
<th>Cont. Titration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SWW</td>
<td>T1</td>
<td>T2</td>
</tr>
<tr>
<td></td>
<td>Ph mM</td>
<td>CaCl\textsubscript{2} mM</td>
<td>Struvite Reagents</td>
</tr>
<tr>
<td>Blank</td>
<td>0</td>
<td>0</td>
<td>100 mM NaCl; 4 mM NH\textsubscript{4}H\textsubscript{2}PO\textsubscript{4}; 4 mM MgCl\textsubscript{2}·6H\textsubscript{2}O</td>
</tr>
<tr>
<td>Ph&lt;sub&gt;sw&lt;/sub&gt;</td>
<td>0</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Ca&lt;sub&gt;sw&lt;/sub&gt;</td>
<td>2</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Ph+Ca&lt;sub&gt;sw&lt;/sub&gt;</td>
<td>2</td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>

**Analytical Methods**

Elemental composition of digested solid and liquid phases was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES; Agilent 5110 SVDV). Ammonium concentrations were measured using a spectrophotometer (Hach DR3900). Solid mineralogy was determined by X-ray diffraction (XRD, Brucker D8 Advance, LynxEye XE) using 0.1 s scans at 0.018 ° 2θ steps from 5-90 ° 2θ. Mineral phase distribution was evaluated with Profex 4.1 software\textsuperscript{212} at a refinement acceptance value of χ\textsuperscript{2} ≤ 1.5.\textsuperscript{243}
Crystal morphology evaluation was done by scanning electron microscope (SEM) coupled with an energy dispersive X-ray analyzer (EDX) at 5-10 keV (Hitachi S4800). Samples for SEM were mounted on carbon tape and coated with iridium (~9 nm). Structural deformation of struvite was observed using Fourier transform infra-red (FTIR) spectroscopy (Perkin Elmer, spectrum 100) using attenuated total reflectance (ATR) with DTGS. Thermal stability of the solids was evaluated by simultaneous thermal analysis coupled with evolved gas analysis (STA-EGA, Netzsch 449 F3 with Bruker Alpha FTIR). Samples were heated from 25-600 °C under 50 mbar N₂(g) at 10-K min⁻¹, and IR scans of evolved gases were taken at 4 cm⁻¹ resolution between 4000-650 cm⁻¹. Statistical analyses were done with OriginPro (OriginLab) and Jmp 15 (SAS) software. Thermodynamic predictions of mineral phase saturation were calculated using Visual Minteq 3.1 (KTH).

5.3 Results and Discussion

Validating Constant Composition

Elemental analysis of Mg, P and Ca dissolved content in SW treatments is shown in Figure-5.1. Comparison of average Mg concentration over time showed that for Ca₅w and Ph+Ca₅w treatments changes in Mg concentration were not significantly different from the application goal of ~4 mM. Comparison of mean P concentration over time showed that for all treatments aside from Ph₅w, the P concentration was similar. For all treatments, the composition of Mg and P remained constant through steady state titration (60, 120 min). The average Mg:P molar ratio of ~1:1 was maintained for all treatments at each sampled time point, indicating that the titration solutions were applied equally and mostly equimolar precipitation occurred. This showed that the solutions remained at a similar saturation with respect to potential struvite precipitation, with SI values within the same order of
These observations confirmed that although the average Mg, P and NH$_4$ decreased over time for all treatments, the potential for struvite precipitation as estimated from SI did not significantly change during steady state.

Figure 5.1. Evaluation of constant composition. Comparison of means (n=3) for the estimated struvite SI and Ca, Mg, P concentrations in the dissolved phase with time for Blank, Ph$_{sw}$, Ca$_{sw}$ and Ph$_{sw}$+Ca$_{sw}$ constant composition experiments. The standard deviation (error bar) and comparison of means (labels) are given for each component, with similar letters indicating that values are not significantly different (Tukey-Kramer, $\alpha 0.05$).

Initial Ca concentration in Ca$_{sw}$ and Ph+Ca$_{sw}$ solutions was slightly lower than the applied 2 mM for most samples, likely due to some precipitation occurring during preparation of the start solutions. While the average decrease in concentration of Ca over
time was greater for Ca$_{sw}$ (-1.22 mM) than Ph+Ca$_{sw}$, (-0.88 mM) and occurred within a shorter time-frame (between 0-60 min), comparison of means showed that Ca concentration in both treatments was similar. Based on the thermodynamic prediction for a near complete removal of Ca by precipitation at equilibrium (calculated final dissolved Ca concentration = 0.002 mM; Visual Minteq) for both Ca$_{sw}$ and Ph+Ca$_{sw}$, the experimental result of ~0.5 mM Ca in both treatments at steady state (60-120 min) indicated that a constant composition condition was maintained. Precipitation inhibition of Ca-P minerals such as HAP, β-TCP, OCP, etc. (Table S1) in the presence of Ph$_4$ may account for the slightly lower rate of Ca removal in the Ph+Ca$_{sw}$ treatment.

Analysis of Solid Phases

To attribute the observed nucleation and precipitation rates in SW under constant composition to struvite formation, collected solids were analyzed. The elemental composition of solids collected from SW treatments is shown in Figure 5.2.a. The presence of Ph alone (Ph$_{sw}$) did not alter the ~1:1:1 molar ratio of Mg:P:N as observed for the Blank. The mole fraction value of ~4 mol kg$^{-1}$ in Blank and Ph$_{sw}$ treatments suggests that struvite (mineral molar density 4.081 mole kg$^{-1}$) is likely to be the primary mineral in these recovered solids (Ph$_{sw}$ 99.1%; Blank 98.8%). When Ca was present in the solution (Ca$_{sw}$, Ph+Ca$_{sw}$) there was a decrease in struvite content with a Ca:Mg:P:N molar ratio of 2:2:3:1 and 1:4:4:3 respectively, indicating coprecipitation of Ca-P minerals. Based on the estimated Ca$_{sw}$ and Ca+Ph$_{sw}$ equilibrium saturation (Appendix D Table D.1), struvite is the most likely N mineral formed. For Ca$_{sw}$ treatment this indicated that 32-44 %w/w of recovered solids is struvite based on the confidence interval of N molarity in the recovered
solids (Figure 5.2a), and that any additional P mol fraction (~3 mol kg^{-1}) is either in newberyite (MgHPO_{4}·3H_{2}O) or Ca-P mineral form. For the Ph+Ca_{sw} treatment, the impact of Ca on solid molar ratio was nearly cancelled where precipitation of Ca as Ca-P minerals is reduced by 50%, and a molar ratio closer to 1:1:1 is observed for Mg:N:P, with 81% struvite. This confirmed that Ca-P minerals coprecipitated with struvite in the Ca_{sw} treatment and that such coprecipitation decreased in the presence of Ph for Ph+Ca_{sw}.

Figure 5.2. solids composition: a. concentration of Ca, Mg, P and N in solids collected from constant composition experiments; b. semi-quantitative estimate of mineral phase distributions in solid samples (n=3), powder XRD analysis was used to confirm the overall mineral composition of solids recovered from SW treatments and estimate the mineral phases distribution (Appendix D Table D.2, Figure D.3-4).

At the first stage of evaluation, diffraction patterns of solid samples from the first replicate (R1) of Blank, Ph_{sw}, Ca_{sw} and Ph+Ca_{sw} treatments, were compared to XRD patterns for struvite and other probable mineral phases (Appendix D, Table D.1, Figure D.3). Results showed that struvite is the dominant mineral phase for all treatments with lower observed counts for other Mg-P and Ca-P minerals. Also apparent is the decrease in crystallinity when Ca is present, shown as broadening of peaks between 20-40 °2θ, and
improved crystallinity when Ph is present. Powder diffraction patterns of all solid samples (R 1-3) for Blank, Phsw, Castr and Ph+Castr were evaluated (Appendix D. Figure D.3) for pre-identified mineral phase distribution (% w/w) using the mineral structure library within the Rietveld refinement program BGMN\textsuperscript{212,243} in Profex software and supplementary structure files.\textsuperscript{190} For Phsw and Blank treatments where no Ca was present struvite formed an estimated 90-95 %w/w of the mineral phase, with lesser amounts of newberyite and magnesium phosphate (Mg\textsubscript{3}(PO\textsubscript{4})\textsubscript{2}). The formation of newberyite in SW was explained by the high concentration of Mg in T2 solution, that generated a temporary localized formation when introduced to an elevated pH in the constant composition reactor.\textsuperscript{244} Struvite content in the Castr treatment averaged 58% w/w, while other mineral phases formed were mostly newberyite, OCP and HAP (averaged 9-11% w/w each). This estimate for struvite content is slightly higher than predicted by elemental analyses (Figure 5.2a) and is likely due to an overestimation of the amorphous phase in the fundamental parameters refinement process. Such an overestimate occurs when the amorphous phase results in a broadening of the diffraction counts plot and an excess weight in the refinement output.\textsuperscript{243} In the Ph+Castr treatment, struvite formation increased to an average estimated 76% w/w which was in line with the probable range predicted from solids analysis (72-90% w/w), with lesser amounts and more variations of Ca minerals formed (1-3 %w/w averaged).

All R1 samples were evaluated for crystal morphology and representative single minerals were analyzed for elemental distribution using SEM/EDX (Figure 5.3). Images from SEM scans of Blank and Phsw solids did not display much morphological difference, with both showing the distinct rod-like form characteristic of struvite formed at lower pH 7-8.5, alongside with increased vee-shaped macro-porosity (~0.2-4 µm) along the crystal
Blank and Phsw solids morphology differed in that solids from Phsw formed dendritic crystals\textsuperscript{246} in addition to the rod-shaped form, and generally were thicker and less elongated. Polygon area EDX analysis of several crystals in Phsw and Blank samples were consistent with struvite elemental composition (a1, b1) with mass distribution of 5-7\% N, 40-60\% O, 14-20\% Mg, 17-22\% P (struvite Mg-N-P-O \%w/w, 10-6-12-65 respectively). When Ph+Ca_{sw} solids were examined, a mixed mineral phase was observed (d1), where a smaller cubic crystal was budding on top of a struvite rod-like mineral. The EDX scan of the cubic mineral showed localized high Ca content of 21\% together with struvite, indicating that a Ca-P mineral was formed on top of struvite. This stood in contrast to scans of solids collected from the Ca_{sw} treatment that displayed larger, round and orthorhombic forms for Ca-P minerals detached from struvite (c1).

**Mineral Nucleation and Growth Rates**

A qualitative comparison of titration rates was done by comparing the frequency of titration pump application for T2+T3 solutions (logged On = 0) and pH oscillation (Figure 5.4). This showed that following an initial nucleation stage, a nearly constant titration rate was kept at constant pH, further confirming that constant precipitation occurred in all four SW treatments. It is apparent from the frequency of titration that Ca free treatments (Blank, Phsw) had less variability in precipitation rates between replicates (R1-3) (Appendix D Figure D.5). A precipitation hinderance effect in Ca_{sw} compared to Blank was apparent from lower frequencies of titration, while very high frequencies of titration when Ph is present clearly indicated that accelerated precipitation occurred in Phsw and Ca+Phsw treatments. Transition from an initial low frequency of titration to high frequency for Ph+Ca_{sw} treatment compared to Ca_{sw} suggested that as Ca concentration decreased, the
effect of Ph (accelerated precipitation) became dominant, confirming the synergic nature of Ca and Ph on struvite precipitation.

Figure 5.3. SEM images of representative samples of the solids were collected at a similar magnification scale (~50 µm) from treatments: a. Blank, b. Phsw, c. Casmw, d. Ph+Casmw. Representative morphologies for each are treatment are marked in subscripts: a1,b1,c1,d1. For each of these, a polygon area analysis of elemental composition was done with EDX and compared to elemental composition of identified mineral phases (Appendix D, Table D.1, Table D.3).

Logged titration data for each treatment was used to determine the synergic effect of Ph and Ca on struvite nucleation time and growth rates (Table 5.2). For determination of the nucleation state, 1st and 2nd derivative of pH (Appendix D, Figure D.6) was calculated for identifying the point where struvite formation generated a significant pH reduction. The
time between the end of initial titration and nucleation was then calculated using logged
time stamps. For growth rate, the total titration time was averaged for the span of treatment
time after nucleation and converted to \( \mu \text{mol min}^{-1} \) values based on mass balance of T2 and
T3 flow rate times and the molarity of struvite components (Appendix D, Table D.4).

![Figure 5.4. constant composition titration log for each treatment: Blank, Ph\textsubscript{sw}, Ca\textsubscript{sw}, Ph+Ca\textsubscript{sw}, pH (left y-axis, black) and T2+T3 on/off state (right y-axis, red) were plotted over time for 1\textsuperscript{st} replicate (R1). The full database is displayed in Appendix D, Figure D.5](image)

Table 5.2. Effect of different treatments (matrix effect) on struvite time of nucleation
and average growth rate in SWW (Standard deviation is included in italics)

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Nucleation Time (min : s)</th>
<th>Approximated Growth Rate (( \mu \text{mol struvite min}^{-1} \text{ L}^{-1} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>4:23 ± 0:51</td>
<td>5.8 ± 4.0</td>
</tr>
<tr>
<td>Ph\textsubscript{sw}</td>
<td>2:44 ± 0:51</td>
<td>51.3 ± 24.0</td>
</tr>
<tr>
<td>Ca\textsubscript{sw}</td>
<td>0:43 ± 0:07</td>
<td>2.7 ± 1.8</td>
</tr>
<tr>
<td>Ph\textsubscript{sw}+Ca\textsubscript{sw}</td>
<td>1:33 ± 0:24</td>
<td>30.5 ± 16.9</td>
</tr>
</tbody>
</table>
It is clearly evident from these observations that Ph addition both accelerates nucleation and growth of struvite for Phsw compared to the Blank treatment and shielded the hinderance effect of Ca on struvite growth rate in Ph+Ca~sw compared to Ca~sw treatment. Shortest nucleation times occurred in the order Ca~sw < Ph+Ca~sw < Ph~sw < Blank. In contrast, the rate of struvite growth is slower when Ca is present and faster when Ph is present. Preliminary analysis of struvite coprecipitation with Ca and Ph at higher Ca concentration (5 mM), evaluated with high performance liquid chromatography (HPLC) coupled with UV-vis analysis did not observe Ph sorption when struvite precipitated (Appendix D, Figure D.7). This indicates that a different sort of interaction between struvite and Ph takes place, where the exact mechanism is unclear and requires further study. The effect of Ca on shortening the estimated struvite nucleation time cannot be completely explained with this experimental setup, as it could be a result of either a change of struvite nucleation time or the formation of Ca-P minerals that act as seeding surfaces for struvite and other mineral phases.

**Effects on Struvite Structure**

To determine the effect of Ca and Ph on struvite PO_4^{3-}, NH_4^+ and water functional groups, solid powder IR vibration was measured with ATR-FTIR (Figure 5.8). The average IR bandwidth of PO_4v1+ v3 (900-1150 cm^{-1}) showed an asymmetric broadening in Ca~sw and Ca+Ph~sw treatments toward higher wavenumbers and a maximum shift from 980 cm^{-1}, characteristic for struvite formed at pH 9,\textsuperscript{186} to 1020 cm^{-1} for Ca~sw. For Ph~sw there was no shift in PO_4v1+3 bandwidth, and when Ph+Ca was present the IR shift was the same as Ca but reduced broadening occurred. This is likely due to coprecipitation of Ca-P minerals.
that resulted in IR absorption at higher bandwidth for the portion of PO₄³⁻ complexed with Ca-P structures such as OCP (1055 cm⁻¹), DCPA, DCPD (1100 cm⁻¹) and other Ca-P phases previously discussed. For water-water hydrogen bond bandwidths (700-800 cm⁻¹, 850 cm⁻¹) there was no effect of Ca and Ph treatments. For P-water and water ν₁-ν₃ symmetric-antisymmetric stretch, the presence of Ca or Ph had a significant effect. When Ca was present without Ph, increased bandwidth broadening indicated a less homogeneous structure and shift to higher wavenumber indicated a distorted PO₄³⁻ water coordination or mixed mineral structure.

![Figure 5.5. Structural analysis of solids: a. averaged normalized ATR-FTIR scans of collected solids, Blank, Phsw, Cašw and Ph+Cašw, showing absorption bands of PO₄, NH₄ and H₂O functional groups of struvite or mixed mineral phases in solids collected from SW treatments. The shaded blue regions are the estimated standard deviation margin (n=3). Identified functional groups IR bandwidths were: a. water ν₁ + ν₃, b. water-PO₄, c. water ν₂, d. NH₄ ν₄, e. PO₄ ν₁+ ν₃. b. Thermogravimetric (TG) mass loss over analysis temperature range 25-600 °C.](image)

The impact on structural stability was evaluated by thermal analysis using STA-EGA. The effect of Ca and Ph on the temperature of maximum mass loss, signal from
evolved gas FTIR and the enthalpy were compared (Appendix D, Figure D.7). Highest mass loss was observed for Ph (56.9%) followed by Blank (50.8%), Ph+Ca_{sw} (45.2%) and Ca_{sw} (34.9%) (Figure 5.7; Appendix D, Figure D.8). This trend is consistent with the struvite content, whereby the increase in mass loss is due volatilization of NH$_4$(s) and H$_2$O(s), which occur in struvite in higher molar quantities compared to other identified phases.$^{166,249}$ The evolution of NH$_3$(g) and H$_2$O(g) is confirmed by EGA using FTIR. For Ph$_{sw}$ and Ph+Ca$_{sw}$ solids the EGA did not show IR vibrations at 3100-3200 cm$^{-1}$ or 1100-1200 cm$^{-1}$ that indicates the release of sorbed phenol.$^{250}$

5.4 Conclusion

The constant composition setup for precipitation of struvite in SW produced up to 99% struvite product in a reproducible manner (n=3). Analysis of mineral phases in recovered solids using open source software Profex 4.1 was corroborated with supplementary elemental composition analysis both of the whole sample by ICP-OES and individual minerals using SEM/EDX. Results indicate that in contrary to the widely accepted hindrance effect of DOM in DW on struvite formation, individual functional groups such as R-OH organics may accelerate struvite growth. The rate of estimated struvite precipitation increased by an order of magnitude compared to a Blank from 5.8 to 51.3 µmol struvite min$^{-1}$ L$^{-1}$ when Ph was present and decreased by half to 2.7 µmol struvite min$^{-1}$ L$^{-1}$ when Ca was present. The effect of Ca and Ph on nucleation times is less conclusive with regards to Ca$_{sw}$ and Ph+Ca$_{sw}$ treatments, because nucleation was determined by pH decreases that may be due to the precipitation of other minerals. In both treatments the newberyite and OCP content was 7-10% w/w, and their formation dissociates 1 and 4 moles H$^+$(aq) respectively (Appendix D, Table D.1-2). While struvite
was the most abundant mineral phase in both, there is no way to differentiate from the current experimental setup the sequence of formation of struvite, OCP, or newberyite. When comparing Blank and Phsw treatments, the nucleation time of Phsw was 62% shorter than the Blank, while the content of newberyite in solids recovered dropped from 8.1 to 2.6 %w/w. This observation indicated that the presence of Ph did accelerate struvite nucleation rather than newberyite, but the exact mechanism of Ph interaction with struvite cannot be determined based on the experimental setup. Results also demonstrated that the presence of Ph shielded the hinderance effect of Ca on struvite formation and prevented the formation of Ca-P minerals. This is most evident in the observation for Ph+Casw, where an overall decrease in Ca concentration over time coincided with accelerated overall precipitation rate and the majority of mineral recovered was struvite. The higher precipitation rate also predicts a lower pH requirement to reach the P removal goals. This is because an order of magnitude increase in precipitation rate when Ph is present is more than equivalent to the effect of optimizing the reaction pH from pH 8.5 to pH 9-9.5 which multiplied struvite precipitation rate by \( \sim 2-6 \). These two parameters of struvite production significantly reduce the cost of operation, where reactor size and reagents for pH titration are major components of the recovery process. Moreover, lowering the pH of reaction from pH 9-10 to 8.5 enables the application of cost effective and more sustainable approaches to raise the wastewater pH such as carbon dioxide stripping. This is of key significance for P recovery from DW where high carbonates and other dissolved components greatly increase the potential titration input for P recovery.
Acknowledgments. This study was supported by USDA SARE grant GNE-17-158. Preliminary results were supported by a Rutgers University Newark Chancellor’s Seed Grant. Special thanks to Dr. Evert Elzinga for assistance with FTIR analysis, Dr. Kyle Gabriel for support with MyCodo open source software and Dr. Lee Blaney for HPLC analysis.
6. Formation of Struvite in the Presence of Low Molecular Weight Organics

6.1 Introduction

Recovery of phosphate (PO$_4$-P) from wastewater through struvite (MgNH$_4$PO$_4$·6H$_2$O) precipitation is a widely accepted geochemical approach to mitigate the harmful effect of algal bloom (HAB), formed from surface water contamination with nutrients from livestock wastewaters effluents (LWE). The key nutrients in LWE that promote water fouling algal growth are nitrogen (N), mainly as nitrate (NO$_3$-N) and ammonium (NH$_4$-N), and phosphorous (P) mostly as PO$_4$-P. The concentration of PO$_4$-P in wastewaters is often the growth limiting nutrients because the concentration of N $>>$ PO$_4$-P at most effluent sources (Agricultural, Domestic). A wet chemistry approach to recover P, N out of wastewater effluent (WWE) is through struvite (MgNH$_4$PO$_4$·6H$_2$O) precipitation, where the recovered product can be re-used as a slow-release fertilizer. The process of struvite production is effective due to the relatively low solubility product (Ksp, $10^{-13.26}$) that make the recovery process fairly irreversible. Struvite is precipitated out of LWE in alkaline conditions (pH 8-11), where its maximum saturation, which can be described by saturation index (SI) often occur at pH 9-10.

The kinetics of struvite formation in LWE can be modeled as a two-stage growth starting with nucleation and transitioning into growth. While both nucleation and growth rates are governed by the supersaturation (i.e. SI) of the solution with respect to the struvite mineral phase, the growth stage of the mineral is faster as a result of surface interactions that lower the overall free energy barrier ($G_n$). This occurs because of solids surfaces that were formed during an induction time out of short molecular polymers organized into struvite, and acts as a stabilizing catalyst for bond formation.
The presence of both calcium (Ca) and non-discrete overall dissolved organic matter (DOM) in LWE is known to hinder the nucleation and growth rates of struvite, even when considerable high SI (> 1) is induced by modifying pH to pH 9-10 or supplementing struvite components with PO₄-P dosing.

Several approaches have been applied to mitigate the hinderance effect of DOM on struvite recovery from LWE, mostly through removal from the dissolved phase of LWE. Removal of DOM was applied through flocculation, osmosis/filtration and digestion. In the flocculation process the DOM substance is polymerize out of liquid by forming covalent bonds either with itself or with short chained polymers. Filtration apply mass separation where molecules of higher dalton (Da) size are removed while nutrients remain in solution. Digestion of DOM was done with microwave, microbial anerobic or combustion, where supplement organic phosphorus (Org-P) nutrients incorporated in organic form can also be recovered as an inorganic PO₄-P.

Recent work has shown that in contrast to hinderance from non-descript DOM such as humic substance to struvite growth, negatively charged low molecular weight organics may promote nucleation and growth of struvite in LWE. A study outlined in chapter 5 part of this dissertation, evaluated the effect of phenol (pKa 10) on struvite precipitation under constant composition in simulated wastewater (SWW) at pH 8.5 found that it accelerated struvite growth rate from 5 µ mol min⁻¹ to 51 µ mol min⁻¹, or to 30 µ mol min⁻¹ when Ca was present. Similarly, prior research work modeling struvite precipitation in the presence of a negatively charged short peptide labeled shADP5 (short human-derived amelogenin-derived peptide 5) showed it increased both the nucleation and growth rated for struvite in SWW.
This work is therefore evaluating the relation between the charge of a low molecular weight (LMW) DOM and the rate of struvite nucleation and growth in SWW. The LMW of interest were: a negatively charged carboxyl, positively charged amine and non-polar methyl. These functional groups were found to be abundantly present in LWE through IR analyses, and previous work done with struvite recovery from LWE indicated that lower concentration (200 mg L$^{-1}$ organic carbon) of DOM could promote struvite precipitation.

![Chemical structures of benzoate, benzylamine, and toluene](image1)

Figure 6.1. LMW treatments, benzoate ($C_6H_5COO^-$; pKa 4.3), benzylamine ($C_6H_5NH_3^+$; pKa 9.3) and toluene ($C_7H_8$; pKa 41) were compared to an organic free SWW Blank treatment at an approximated SI = 1 at pH 8.5 that is occurring in struvite recovery process for LWE.

### 6.2 Materials and methods

#### 6.2.1 Constant composition experiment

A constant composition experiment was used to model struvite formation in LWE using a simplified SWW with three LMW with a singular functional group treatment (TMT) as described in table 6.1. The setting and geochemical principles of the applied constant composition approach were described in depth elsewhere and in chapter 5 of this dissertation, where titration of struvite components in equimolar proportion to pH change maintain a steady state of struvite precipitation (eq 6.1).

$$\text{Mg}^{2+}_{(aq)} + \text{H}_2\text{PO}_4^{-}_{(aq)} + \text{NH}_4^+_{(aq)} \leftrightarrow \text{MgNH}_4\text{PO}_4\cdot6\text{H}_2\text{O}_{s} + 2\text{H}^+_{(aq)} \quad (\text{Eq. 6.1})$$
To keep the titration proportional to pH change while preventing the titration solution components from self-interacting, a three-titration solution system was applied as described in eq. 6.2-5 for titrants (T1-3) added to a start solution volume.

\[
T1: 0.1 \text{ M NaOH} \quad \text{(Eq. 6.2)}
\]

\[
T2: (2x + Cx) \text{ M MgCl}_2 \cdot 6\text{H}_2\text{O} + (2x + Cx) \text{ M NH}_4\text{H}_2\text{PO}_4 + y \text{ [LMW] M} \quad \text{(Eq. 6.3)}
\]

\[
T3: 0.2 \text{ M NaCl} + (2Cx - 2x) \text{ M NaOH} + z \text{ M C}_6\text{H}_5\text{OH} \quad \text{(Eq. 6.4)}
\]

\[x = [\text{Mg}] = [\text{PO}_4] = [\text{NH}_4]; \quad y = [\text{LMW}] \text{ treatment} \quad \text{(Eq. 6.5)}
\]

This mass balance approach to constant composition incorporate the ratio of change in struvite mass (\(\Delta m\)) and volume change (\(\Delta V\)) for a given struvite constant composition of x M.\(^{48,68,257}\)

---

**Table 6.1. LMW treatments for SWW constant composition model**

### 6.1.a. Start solution + initial titration (T1)

<table>
<thead>
<tr>
<th>TMT</th>
<th>Struvite reagents</th>
<th>T1 (Q, 5 mL min(^{-1}))</th>
<th>LMW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>4 mM NH(_4)H(_2)PO(_4) + MgCl(_2) \cdot 6\text{H}_2\text{O}</td>
<td>NaOH 100 mM</td>
<td>0 mM</td>
</tr>
<tr>
<td>LMW</td>
<td>100 mM NaCl</td>
<td>NaOH 100 mM</td>
<td>2 mM</td>
</tr>
</tbody>
</table>

### 6.1.b constant composition titration (T2 + T3)

<table>
<thead>
<tr>
<th>TMT</th>
<th>C</th>
<th>T1</th>
<th>T2</th>
<th>Q (mL min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>35</td>
<td>148 mM NH(_4)H(_2)PO(_4); 148 mM MgCl(_2) \cdot 6\text{H}_2\text{O}</td>
<td>200 mM NaCl; 272 mM NaOH</td>
<td>0.5</td>
</tr>
<tr>
<td>Benzyamine</td>
<td>70</td>
<td>288 mM NH(_4)H(_2)PO(_4); 288 mM MgCl(_2) \cdot 6\text{H}_2\text{O}</td>
<td>200 mM NaCl; 552 mM NaOH</td>
<td>2</td>
</tr>
<tr>
<td>Toluene</td>
<td></td>
<td>4 mM LMW</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzoate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Empirical assessment demonstrated that for blank, benzylamine and toluene treatments a C constant value of 35 was sufficient for \( x = 4 \text{ mM} \) at pH 8.5, a \( C = 70 \) was needed for a steady state of benzoate model system. A summary of treatments was outlined in Table 6.1. Determination if \( C \) satisfy the constant composition requirements for the SWW system was decided ad hoc where if increase of \( \Delta V \) to maintain a constant \( x \) (in effect, constant pH), then \( C \) was increased from 35 to 70, however all replicate-treatment triplicates were done using the same \( C \) and/or \( Q \) flow rates.

All reagents used for the preparation of start and T1-3 solutions were ACS grade >99.9% w/w, mixed with triple deionized water. All flask used for processing and analyses were HDPE except for NaOH application that used borosilicate, all solutions were sonicated at 37 MHz for 20 min and prefiltered with 0.45 µm membrane (Nylon or PES) shortly prior to application within the constant composition system. In order to initiate the constant composition model solution reaction, titration solution T1 (40-60 mL) was applied to 1000 mL start solution with peristaltic pump at 5 mL min\(^{-1}\) and T2+T3 were applied with a variable rate dual syringe pump. Two 140 mL luer lock syringe were filled with either T2 or T3 solutions, mounted with 0.45 µm PES prefilter and connected to the reactor with 1/16 in. teflon tube. The reactor utilized a 2000 mL screw cap flask with a submerged double junction probe, 2 inch PTFE magnetic stirrer and a 1000-2000 mL working volume. All pH reading were logged at 2 s intervals and titration of T2 +T3 from syringe pump was recorded at 1 s intervals using raspberry pi single board processor with MyCodo\textsuperscript{188} software (Appendix E, Figure E.1). A \( N_2 \) atmosphere was maintained using constant gas flux through the effluent at \( \sim 50 \text{ mbar} \), starting with pre-application flux of the start solution until pH was stabilized (5-10 min) and throughout the experiment. Effluent samples were
collected at 0, 60, 90, 120 min of continuous reaction duration, and solids from 60,90 min samples were collected with 25 mm 22 µm membrane. Final total solids were collected with 45 mm 0.45 µm membrane. All solutions were acidified to 2 % w/w HNO₃ for stabilization.

6.2.1 Analytical methods
Elemental composition analysis was done with Inductively coupled plasma - optical emission spectrometry (ICP-OES; Agilent, 5110). Scanning electron microscopy (SEM) was done (Hitachi, 4800 EDAX) using aluminum stubs with carbon adhesive and 9 nm zirconium coating. SEM scans analyses were done at 8-9 mm focal, 15-20 kV and 5-7 mA. For each treatment replicate; reaction duration, a 100 µm by 100 µm area was marked out of a x500 magnification scan and the length and width of 25 single crystals (µm) were recorded with graphical software by converting measured image size (in.) to scale (µm). The roundness of a crystal was determined as the ratio of length over width (L/W), with a maximum roundness of one. X-ray diffraction (XRD) spectroscopy (Bruker, D8) was done at 5-90 2θ scan with 0.1 s steps of 0.022 2θ, using Cu cathode light source, 2.5 o Ge monochromator soller, 0.075 mm slit and lynxeyeXE detector. Fourier transform infrared spectroscopy (FTIR) was done (spectrum 100, Perkin Elmer) with deuterated triglycine sulfate (DTGS) detector between 4000-650 cm⁻¹ at 16 scans of 4 cm⁻¹ resolution. Mineral phase verification was done using Profex 4.1 software, statistical analyses of variance and comparison of means were done using Jmp 15 software (SAS), graphical and regression analyses of datalogger data from constant composition reactor were done using origin-pro software (Origin lab 2020).
6.3 Results and discussion

6.3.1 Validation of constant composition

In order to evaluate the steady state and constant composition of the model SWW solutions (labeled after their LMW treatment) Blank, Toluene, Benzylamine and Benzoate, the concentration of elemental Mg and P were measured at 0-120 min (Figure 6.1). Result showed that for Blank SWW the molarity of solution remained constant at ~4 mM and the applied struvite components concentration (Mg, P) did not significantly differ over time. For Toluene, Benzylamine and Benzoate, the averaged solution molarity in SWW decreases somewhat between 0 min and 120 min, but did not significantly changed between 0-120 min for Blank and Toluene, between 90-120 min for Benzoate and benzylamine. These observations indicated that that a constant composition state was maintained and that the titration resulting in constant pH 8.5 was satisfying the experimental design for supplementing struvite components precipitation (Appendix E, figure E.2).

Figure 6.2. elemental composition of SWW treatment showing the average concentration (n=3; standard deviation error bar) over time (min.) of Mg, P (mM). Averaged measurements of Mg or P over time with the same alphabetic label are not significantly different (Tukey Kramer, α=0.05).
Figure 6.3. elemental composition of recovered solids from SWW, showing the average composition of Mg, P (mole kg\(^{-1}\), standard deviation error bars) at 120 min. Composition of Mg or P with similar alphabetic letter are not significantly different between treatments.

Figure 6.4. spectroscopy analysis of recovered solids: a. XRD diffraction spectrum showing a mostly struvite samples composition for replicates (R1-3; bottom-up respectively) of the recovered solid from Blank (red), Benzoate (green), Benzylamine (cyan), Toluene (purple) and struvite standard (Arcos organics, 99.99 % w/w). Diffraction is reported at 10-35 \(2\theta\) which is of interest since struvite was the major mineral formed, however no other mineral phase was observed at 5-90 \(2\theta\) scans. b. normalized absorption FTIR scans of recovered solids with identical labels as outlined in 6.4.a between 650-3600 cm\(^{-1}\) bandwidth.
6.3.2 Analyses of recovered solids bulk composition

Elemental composition analysis of the recovered solids (Figure 6.2) showed an equimolar concentration of Mg:P for all solid samples recovered from the constant composition reactor. A molar ratio of ~4 mol kg\(^{-1}\) is in line with struvite molar density (formal weight 245 g mol\(^{-1}\); 4.08 mol kg\(^{-1}\)) or trimagnesium phosphate (TMP; 262 g mol\(^{-1}\); 3.82 mol kg\(^{-1}\)) rather than other thermodynamically favorable phases (Appendix E, Table E.1) such as dittmarite (155 g mol; 6.45 mol kg\(^{-1}\)), newberyite (174 g mol\(^{-1}\); 5.75 mol kg\(^{-1}\)) or bobbierrite (408 g mol\(^{-1}\); 2.45 mol kg\(^{-1}\)). A supplementary XRD analysis for mineral phase (Figure 6.3.a, Appendix E, Figure E.3) confirmed high struvite content (> 90 %) with low (≤ 6 % w/w) concentrations of newberyite or bobbierrite, for all recovered solids except for the 1\(^{st}\) replicate of Blank treatment (R1) where an estimated 11 % w/w was newberyite and 4 % bobbierrite (Appendix E, figure E.3). This was further corroborated through FTIR spectroscopy (Figure 6.3.b) showing a partial IR shift in the \(\nu_3\) vibration of PO\(_4\) from 1000 cm\(^{-1}\) bandwidth to 1100 cm\(^{-1}\). No other significant IR bandwidth vibrational shifts or significant IR absorption from uptake of organic functional groups were observed in the collected IR spectrums. This is in line with previous work that found very little coprecipitation of or LMW with struvite.\(^{214}\)

6.3.3 Analysis of crystal morphology

The morphology of recovered struvite minerals in the process of PO\(_4\) recovery is significant for the ease of retaining them in wet chemistry reactor and separating them from the treated effluent discharge. Solid separation is most commonly done through utilizing a form of fluidized bed (FB), where higher density equal lesser buoyancy and better retention. A simplified approach to compare buoyancy between minerals is the ratio of
Figure 6.5. SEM imaging showing R1 solids samples (yellow scale bars) collected from the constant composition reactor at 60, 120 min for Blank, Benzoate, Benzylamine and Toluene SWW treatments. Comparison of single crystal morphology for recovered solids in larger scale scan (100 µm) and smaller scale (10, 20 µm) scan.
their length to width (L/W) as a measure of their roundness. An estimated L/W and crystal size for the single crystal qualitative assessment of 60 min retention time in the constant composition reactor is shown for R1 replicates (Figure 6.4), and analyses of overall crystal size and roundness were described for SWW treatments over time (Figure 6.5 -6).

A qualitative evaluation of crystal morphology at 60 and 120 min reaction time (Figure 6.5) showed visible differences at the macro scale (100 µm; x500) and micro scale (10-20 µm x2,200). It is apparent that both at 60 min and 120 min residence time the overall size of crystal for all LMW treatments was larger than Blank treatment, more nonlinear acicular forms were observed with more frequent kink sites258 (Appendix E, Figure E.4). Formation of X-shape (hopper) twin structure259,260 was observed in LMW treatment, and not in the blank treatment. All twin statures observed were parallel (along the length) and not adjunct from a crystal base connection, no fully dendritic forms were observed.261 In addition, more frequent and larger macropores were observed for LMW treatments. While there was no apparent difference in crystal kink sites and twin splitting between LMW treatments over time, the presence of benzylamine and toluene formed more frequent bent crystal habits262 along the crystal length comparing to benzoate, these were less apparent for 120 min than 60 min.

An quantitate evaluation of mineral size (Figure 6.6) and roundness as L/W ratio (Figure 6.7) for R 1-3 of SWW treatments also confirmed a significant effect from LMW presence on size and shape. While sampled struvite crystals from LMW treatments Benzoate, Benzylamine and Toluene were on average significantly larger than Blank treatment, average size of Benzoate treatment was significantly larger than Benzylamine and Toluene treatments between 60-90 min residence time. The roundness of crystals
(L/W) was on average similar for all treatments at 60-90 min, followed by a significantly rounder mineral forms for Blank and Benzoate treatments comparing to average Benzylamine and Toluene at 120 min. Additional evaluation of the size and roundness of struvite crystals looked at the densities diagrams outlining the variance histograms. While the outline of both size and L/W density plot for Blank treatment remained similar between 60-120 residence time, apparent changes in distribution histogram occurred for Benzoate, Benzylamine and Toluene treatments. Benzoate crystal size density plot outlined an asymmetric increase of size frequency towards larger size at 60-120 min residence time, and no increase in roundness distribution over time (60-120 min). In contrast, Benzylamine and Toluene treatments size and roundness (L/W) density plots became more asymmetric towards higher values (larger mineral size, high L/W) with longer residence time. Overall, these morphology traits indicate that Benzoate LMW had a beneficial effect on the recoverability of struvite, forming a less buoyant solid, while toluene and benzylamine formed a more buoyant solid. This is because a rounder mineral with larger mineral size will be positioned lower at a fluidized bed. The increase in surface roughness apparent from megaspores, kink sites and twin structure can contribute to the application of struvite as fertilizer. This is because roughness of surface is associated with an increase in surface area and in turn with improved solubility.
Figure 6.6. Changes in the mean crystal length (µm) were compared (outer, mid and center bars indicate for SD, CI and mean respectively) for LMW treatments for SWW, Blank, Benzoate, Benzylamine and Toluene treatments at 60, 90 and 120 min of residence time in the constant composition reactor (left). The corresponding density distribution (right) of sampled minerals (n=75) length (µm) was shown as fraction of total normalized population (0-1). Treatments with similar alphabetic label are not significantly different (Tukey Kramer α 0.05)
Figure 6.7. changes in mean crystal length as length to width (L/W) ratio were compared (outer, mid and center bars indicators for SD, CI and mean respectively) for LMW treatments for SWW, blank, benzoate, benzylamine and toluene at 60, 90 and 120 min residence time in the constant composition reactor (left). Change in density distribution (right) of sampled minerals (n=75) roundness was shown as fraction of total normalized population (0-1). Treatments with similar alphabetic label are not significantly different (Tukey Kramer α 0.05)
6.3.4 Estimated growth rate of struvite in SWW

Figure 6.8. Effect of LMW in SWW on struvite precipitation rate is plotted as change in cumulative titration of struvite components over time (\(\mu\) mol s\(^{-1}\)). Average precipitation (red) with standard deviation (shaded) was plotted for R1-3 of constant composition SWW treatments. Linear regression was fitted to approximate the changes in average precipitation rates over time, presented as \(\mu\) mol min\(^{-1}\).

The data from constant composition reactor of logged pH and titration application (Appendix E, Figure E.5) was used to derive the estimated rate of struvite precipitation over time and to confirm that a constant composition precipitation occurred at a constant pH. The rate of crystal growth over residence time in the reactor was outlined for Blank, Benzoate, Benzylamine and Toluene treatments in figure 6.7. These results clearly showed increased of average struvite precipitation for Benzoate SWW treatment (33,000 \(\mu\) mol), and a decreased precipitation for Benzylamine SWW (1,700 \(\mu\) mol) and Toluene SWW (3070 \(\mu\) mol) treatments comparing to Blank SWW (3,900 \(\mu\) mol). Linear regression fit (Appendix E, Figure E.5; \(\alpha = 0.05\)) of the precipitation rate over time found a constant
linear struvite precipitation rate ($R^2 > 0.99$) for Benzoate (389.32 µ mol min$^{-1}$) and Blank (38.52 µ mol min$^{-1}$) SWW treatments. A dual linear struvite precipitation rate ($R^2 > 0.95$) was observed for Benzylamine and Toluene SWW with an initial higher average rate (25.82, 45.44 µ mol min$^{-1}$ respectively) followed by a transition to slower struvite precipitation at ~60 min residence time (7.19, 16.23 µ mol min$^{-1}$ respectively).

6.4 Conclusions
The constant composition approach to model struvite precipitation in SWW using LMW as a model for functional groups in DOM present in LWE, was able to reach a steady state condition that is needed to promote continuous mineral growth. While the average concentration measured for Mg and P in the reactor solution decreased from an initial 3.5-4 mM concentration to 2 mM for all LMW treatments (Benzoate, Benzylamine, Toluene), it remained constant through 60-120, and comparison of means was not significantly different for toluene. This indicated that sufficient titration of struvite components occurred to maintain a constant composition, which was corroborated by maintaining a constant pH and similar molar ratio of Mg:P in the solution over time. Analyses of the recovered solids elemental composition found an equimolar Mg:P content for all solids and XRD spectroscopy confirmed that struvite was the primary mineral phase.

The effect of LWE on struvite growth rate was evaluated by comparing the rate of struvite components titration over time. While the control treatment without LMW application (Blank) had a constant precipitation rate of 38 µ mol min$^{-1}$, it increased to 389 µ mol s$^{-1}$ (Also constant) when negatively charged benzoate LMW was present. In contrast when positively charged benzylamine LMW or neutral and nonpolar toluene LMW were
present, the rate of precipitation both deceased overall (7, 16 µ mol min⁻¹ respectively) and was not constant with a somewhat faster initial growth (26, 45 µ mol min⁻¹ respectively) comparing to their steady state growth (90-120 min). This indicated that a negatively charged organic functional groups may promote a higher struvite precipitation rate, although the experimental design in this study does not determine the mechanism of this interaction. The presence of LMW organics also changed the morphology of struvite crystals, both in overall roundness as the ratio between the longest dimension and its adjunct length, and overall size of the crystal formed. The largest crystal formed for SWW with benzoate and those were rounder than Toluene and benzylamine treatments. This finding indicate that negatively charged organic functional groups such as carboxylic acids may have a beneficial role both in increasing struvite precipitation rate and promoting a denser morphology that is associated with better solids recovery through nutrients recovery treatments with fluidized bed separation.
7. Enhanced Phosphorus Recovery as Struvite from Cattle Manure with Aerobic *Bacillus* sp. Mineralization Pretreatment

7.1 Introduction

Recovery of phosphates (P) from cattle manure (CM) has a significant impact on reducing the formation of water fouling algal blooms in major watersheds in the U.S.,\(^{267,268}\) which is associated with negative public health and higher water treatment cost outcomes.\(^{269-271}\) According to best management practice recommendations, topsoil application of manure in the U.S is agronomically sound at most cases,\(^ {174}\) however it increases the risk of P contamination for surface when farms are placed in proximity of vulnerable watersheds.\(^ {272}\) In such areas processes of deposition, erosion and leaching have been shown to transfer significant amounts of P from crop soils to surface water by either surface or sub-surface transport.\(^ {25,273-275}\)

The content of total P in CM ranges from 1-5 g kg\(^{-1}\), primarily as a result of the applied feed composition, where lower grain content tends to improve P conversion by animals and reduce its excretion.\(^ {105,276,277}\) Efforts to improve P conversion by livestock are mostly directed at metabolizing the organic phosphate (Org-P) myo-inositol hexaphosphate (C\(_6\)H\(_{18}\)O\(_{24}\)P\(_6\); IP\(_6\)) in animal guts, or lowering its content in the feed. Digestion of IP\(_6\) requires the expression of the enzyme phytase (Phy) that is naturally occurring in microorganisms and plants but not in higher animals.\(^ {278}\) In the gut of ruminants there is some Phy activity on feed due to its expression by gut microbiome, but the effect on total Org-P intake by cattle is limited with ≤ 60% conversion.\(^ {276}\) A far lower percent of P uptake from IP\(_6\) was observed with an increase of soy grain content in feed serving and lowering of forage portion, which is a typical condition for most AFO’s.\(^ {277}\) As a result, the
content of IP\(_6\) out of the total PO\(_4\)-P in livestock manures range between 10-70\%, where the lowest IP\(_6\) content was observed for cattle and the highest for poultry.\(^{279}\) Other approaches to reduce IP\(_6\) excrement in LM are plants breeding modifications that suppress IP\(_6\) genes to lower its content in the feed which is beyond the scope of this work,\(^{280}\) or by supplementing Phy in animal feed mixture.\(^{281,282}\)

While understanding of the Phy enzymes is ever growing due to their industrial significance, three major enzyme classes (E.C.): 3.1.3.8, 3.1.3.26 and 3.1.3.72 are generally in use.\(^{283}\) This classification system also refers to 3-phytase, 4-phytase, 5-phytase respectively with EC. 3.1.3.8-72, as the position on the myo-inositol C\(_1\)-C\(_6\) carbon inositol ring where the initial ligand bond with the enzyme is formed and PO\(_4\)-P is being hydrolyzed (Figure 7.1). The first two E.C. 3.1.3.8 and E.C. 3.1.3.26 are most active in acidic pH and therefore suitable for gut application, while E.C. 3.1.3.72 is alkaline Phy with limited current industry applications and is not currently used for livestock feed or readily available commercially.

![Figure 7.1. Ligand site on the IP\(_6\) inositol ring (C\(_1\)-C\(_6\)), where Phy initial bond is formed for three Phy enzyme (E.C. 3.1.3.8, E.C. 3.1.3.26, E.C. 3.1.3.72) and the nature of polyvalence cation cofactor for E.C. 3.1.3.8. Serial operation by enzymatic Phy hydrolysis transform IP\(_6\) into IP\(_5\)…IP\(_1\) and eventually into myo-inositol and six PO\(_4\)-P.](image)
When considering the efficacy of Phy enzymes in the LWE solution, the presence of excess polyvalence cation cofactors, especially calcium (Ca) aluminum (Al) and iron (Fe) suppress the operation of E.C. 3.1.3.8 Phy use for experimental nutrient recovery. While Ca$^{2+}$ act as a co-enzyme that is crucial to some Phy enzymes in the E.C. 3.1.3.8 group, excess concentration in the LWE suppress the enzyme activity. Naturally occurring Phy enzymes in LWE are expressed by microorganisms, where many of the identified Phy’s were sequenced from bacteria belonging to *bacillus sp.* Out of these, the species *b. subtills, b. amyloliquefacien* and *b. licheniformis* showed tendency for high exocellular Phy enzyme units (EU) expression rates (3-200 EU mL$^{-1}$). A key driving signal for bacterial Phy expression is the ratio of P to carbon (C) from TSS or DOM, and nitrogen (N) from urea excretions (i.e. P:N:C molar ratio). In LM and LWE the low P and high C,N results in high concentrations of naturally occurring Phy expression by the LWE microbiome and a near complete elimination of Org-P over the ≤ 6 month residence time in lagoon / storage tank. However, due to the high stability of IP$_6$ in soils, it tends to accumulate as LWE is discharged by soil application and its fraction out of the total P increases from ~1 % in LWE to ≤ 20 % in soils. This discrepancy in IP$_6$ stability (lower stability in aqueous systems) is one of the key contributor factors to the high eutrophication risk of particulate P deposition from soils where LWE or LM is applied.

Recovery of phosphates (P) from cattle manure (CM) has a significant impact on reducing the formation of water fouling algal blooms in major watersheds in the U.S., which is associated with negative public health and higher water treatment cost outcomes. While local environmental regulations allows CM discharge onto crop soil as part of a nutrition plan, deposition through aeolian, wash-off and subsurface transport carries
significant amounts of CM-P. The content of total P in CM ranges from 1-5 g kg\(^{-1}\), primarily as a result of the applied feed composition, where lower grain content tends to improve P conversion by animals and reduce its excretion. According to best management practice recommendations, topsoil application of manure in the U.S is at most cases agronomically sound, however it increases the risk of surface water contamination when farms are placed in proximity of vulnerable watersheds. In such areas processes of deposition, erosion and leaching have been shown to transfer significant amounts of P from crop soils to surface water by either surface or sub-surface transport. When P is introduced to surface water, it is often the limiting nutrient factor for algal bloom growth, resulting in rapid increase of algal water fouling and toxin release. In light of CM-P negative impact on water quality there is a growing need for mitigation treatments to reduce P content in CM.

Production of struvite (MgNH\(_4\)PO\(_4\)·6H\(_2\)O) is a widely applied approach for P recovery from wastewater in general, and LWE in particular. Some of the currently applied methods to recover P include phytoextraction, milling, and precipitation by wet chemistry. The most common approach for P recovery CM wastewater via wet chemistry is harvesting it from storage lagoons, these are mostly mildly-highly anaerobic with pH 7-8 and high total suspended solids (TSS) content (\(\leq 10\) g L\(^{-1}\)) and high calcium (Ca) content (\(\leq 500\) mg L\(^{-1}\)). Under these conditions and due to long residence time (\(\leq 6\) months), the majority of P to be recovered from CM is in mineralized as an inorganic PO\(_4\)-P complexed either in a Ca-P or colloid-P forms and only a fraction (\(\leq 30\) %) is readily available for precipitation. A variety of methods evaluated freeing complexed P including acidification, chelation with Ethylenediaminetetraacetic acid (EDTA) and
An additional hinderance to P recovery is high dissolved organic matter (DOM) content (≤ 2 g L\(^{-1}\)) that slows struvite growth rate\(^{39}\). The use of anaerobic digestion pretreatment can remediate this by metabolizing these DOM and improving P recovery.

Another approach to P recovery targets the organic phosphate (Org-P) of CM-P. This consists mostly of inositol hexaphosphate (IP\(_6\)) from seeds and plant material in animal feed. Although animals cannot digest IP\(_6\), some of it is hydrolyzed into PO\(_4\)-P by microbial enzymes in cattle ruminant gut, but the majority is excreted. Application of the enzyme phytase (Phy) was used to mineralize Org-P for struvite production, and \textit{bacillus sp.} bacteria that express Phy were used to mineralize IP\(_6\) in soils where high legacy P was present.\(^{24}\)

One of the traits of these bacteria making them suitable for IP\(_6\) mineralization is the expression of exocellular phosphatases such as the Phy enzymes.\(^{122,286,293}\) Previous studies of the species of \textit{b. licheniformis}, \textit{b. subtills} and \textit{b. amyloliquefaciens} express exocellular Phy enzymes when phosphate deficiency as a low P:N:C ratio occur.\(^{294-296}\)

This study evaluated aerobic pre-digestion of Org-P in CM as an alternative approach to increase the availability of PO\(_4\)-P in LWE for recovery as struvite. It was hypothesized that induced mineralization of Org-P to PO\(_4\)-P in CM slurry followed shortly after by recovery as struvite will improve P recovery. Such pretreatment was expected to promote struvite formation without the need for pre-acidification to free complexed PO\(_4\)_P.

To the best of our knowledge this approach has not yet been applied to livestock manure in general and CM in particular. Previous research have described the use of aerobic pretreatment for CM to mitigate odor\(^{297}\) and greenhouse gas emission that result from the
anaerobic microbial activity that release the metabolites methane (CH₄), nitrous oxide (N₂O) hydrogen sulfide (H₂S).²⁹⁸⁻³⁰⁰ It is also used to remediate high alkalinity of groundwater polluted with high pH wastewater from landfill or mines leachate by utilizing aerobic respiration to carbonate the effluent and neutralize its pH from 10-11 to ~7.³⁰¹,³⁰² One of the major disadvantages of struvite wet chemistry recovery treatment is the high alkalinity (pH 9-10) of the effluent and high sodium (Na) or Mg that may harm soil fertility if discharged untreated to crop soil. In order to address this problem, a supplement post treatment to the aerated-FBR P recovery process used aeration flux to neutralize the pH of LM slurry following struvite recovery process by promoting aerobic microbial respiration.

7.2 Materials and methods

Preparation of CM and bacillus sp slurry

Samples of CM were collected from a dairy farm cattle yard into sealed 5-gallon HDPE flasks and kept in -20°C prior to analysis. Homogenized Slurry of CM was made by processing through a dual stage waste processor and mixing with water. Three bacillus sp. (b. licheniformis, b. subtilis, b. amyloliquefaciens) are compared to microbiome from fresh manure, phytase (Phy) enzyme and blank (autoclave manure, no inoculation). Dried spores of bacillus sp. were acquired (BIO-CAT Microbials), revived and grown in sterile Tris 0.1 M pH 7 with 10 g L⁻¹ ammonium sulphate ((NH₄)₂SO₄) and 20 g L⁻¹ yeast extract and incubated at 37 ºC. Immobilized bacillus sp. (Encapsulated 1-3) treatments were prepared by soaking a 2 inch sterile tryptic soy agar bar in bacillus sp. suspension and enclosing withing a folded 100 mm 0.45 µ cellulose acetate filter paper (Figure 7.2). These were then sealed and mounted onto a zinc alloy coated steel bar with silicone glue (190 ºC).
**Batch reactors**

All batch reactors (Appendix F Figure F.1) were carried in 1000 mL reaction volume, using open top flasks placed in 30-37 °C heat bath placed at a constant flow fume hood. Batches were agitated with 2 inch PTFE magnetic stirrer (125 rpm) and aerated with fritted silica mounted onto a PVC tube equipped with flow regulator (0-1.5 L min⁻¹). For fresh CM treatment, 250 mL of recently made homogenized CM was mixed with water to 1:3 v/v in a 1000 mL HDPE flask. For and all treatments (Blank, Bacillus 1-3, Encapsulated 1-3, Phytase), a 250 mL of homogenized CM was transferred into 1000 mL Pyrex jars and mixed with 250 mL water, then autoclaved at 121 °C for 30 min cycle and kept in 4-6 °C prior to treatment. All batch jars were diluted to a final 1:3 concentration with 100 mL of 1M Tris base and water. The final batch concentration was 25% v/v CM, 0.1 M Tris at pH 7. Samples of CM slurry were collected at time 0, 60, 1500, 3000, 3060 min and liquid phase was collected shortly after. Following aeration of 0-3000 min, the pH of the batch reactor was adjusted to pH 9 with NaOH 1 M and a final sample was collected after 60 minutes (3060 min). Experiment was done in duplicates and each slurry sample was immediately centrifuged for 30 min at 6000 rpm; 5°C, then filtered with 0.45um PES membrane, acid digested and analyzed for elemental composition with ICP-OES.

**Treatment of aerated-FBR effluent for pH neutralization**

Sample of effluent from CM slurry treated for phosphorous recovery using aerated fluidized bed reactor (aerated-FBR) in flow through mode (Figure 7.3) were generated by scaling up the batch experiment to 200 L. To this end 12.5 gallon of CM slurry were mixed with water to 200 L volume, inoculated with 2.5 L *b. subtilis slurry* and agitated for 24 h with 0.01 VVM aeration. Following the microbial pretreatment, the liquid phase was
collected with geotextile filtration (200 µm) and treated for P recovery at pH 9. Following an approximated 1 h of residence time in the aerated-FBR, 50 L of aerated-FBR effluent were collected in HDPE flask and aerated with 0.1 VVM for 80 h. Submerged pH and oxidation-reduction probe (ORP) readers were logged continuously using datalogger.

Figure 7.2. Fabrication of SBP capsules: agar bar is soaked in bacillus sp. solution, then filter is folded over (I.-II.), placed inside a 25 micron (Whatman, P 20) protective layer (III.) and its rim is sealed with hot silicon glue to form a SBP setup. After glue solidified, SBP is placed within the reactor (IV.).

Figure 7.3. Flow through apparatus was fabricated as a scale up of the batch experiment (Appendix F, Figure F.2): a. slurry prepped in 200 L HDPE drum and agitated under air for 24 h, b-c. geotextile separation of liquid phase, d. treatment with aerated-FBR to pH 9 at 60 min retention time, e. effluent sample was aerated for pH neutralization.
Analytical methods

For elemental composition analyses, samples of effluent or solids were digested in nitric acid (70% w/w HNO$_3$) at 1:1 ration in 150 °C for six hours and organic remnants were oxidized with hydrogen peroxide (H$_2$O$_2$ 30% w/w). Elemental composition analysis was done using Inductively coupled plasma - optical emission spectrometry (ICP-OES; Agilent, 5110).

7.3 Results and discussion

Batch reactor

The change in concentration of elemental P in the liquid phase was measured over time between 0-3060 min (figure 7.3.) using ICP-OES elemental analysis of the dissolved phase. The average concentration of dissolved elemental P species increased for all dosing microbial treatments and raw (naturally occurring microbiome) compared to blank treatment between 0-3000 min, while a null improvement in average dissolved P was observed for Phy treatment. The maximum of normalized increase (% w/w) in dissolved P was recovered for *b. subtills* and *b. amyloliquefaciens* (90-92 %) at 3000 min time and *b. subtills* also had the best averaged impact on encapsulated bacteria together with *b. licheinformis* (60 %, 49% respectively). The difference in maximum response time between encapsulated and dosing *bacillus sp.* application is not definitively explained by this experimental setting, however it may be speculated that either membrane fouling occur overtime that blocks the exocellular enzyme, or that insufficient inoculation mass or protection of capsuled resulted in suppression of microbial treatment after 1500 min. Simulation of nutrient recovery treatment for CM slurry at pH 9 undergoing a 60 min of retention time (3000-3060 min) showed a similar final average concentration of dissolved...
P for all treatments (~30 mg L\(^{-1}\)) except for *b. subtillis* SBP capsule treatment (53 mg L\(^{-1}\)). This simulation indicated that the recoverability potential for PO\(_4\)-P, the dominant form in the dissolved P occurring in CM wastewater,\(^{123,303}\) is independent of its concentration elevation prior to the pH increase and subsequent precipitation.

![Graph showing dissolved P concentrations](image)

**Figure 7.4.** Results from the batch experiment for averaged (n=2) Org-P mineralization are shown as dissolved P concentrations for Blank, Phy, and three *bacillus sp.* (standard deviation error bar). In figure 6.a the inoculation treatments were compared with encapsulated bacteria (slotted pattern) Phy enzyme and blank control between 0-3000 min and following 60 min at pH 9 (3060 min). This was presented as a normalized percent in solution P over time in figure 6.b.
The effect of Phy enzyme on dissolved P concentration was lesser than expected, in light of literature from previous research, since the chosen Phy from an E.C. 3.1.3.26 was expected to be less susceptible to hinderances from polyvalence cations in the CM slurry. There are several likely reasons for this observation: a. that the Phy expressed by bacillus sp. or naturally occurring microbiome in raw treatment is more effective in mineralizing IP6 at the high ionic strength of CM slurry; b. Supplemental phosphate solubilizing enzymes (e.g. phosphatases) increased the release of PO4-P into the solution comparing to the direct Phy enzyme. To assert the nature of difference in these preliminary finding between microbial activity and direct Phy application there is a need for an expanded experimental design.

**pH neutralization post-treatment**

![Graph showing changes in pH and ORP over time](image)

Figure 7.5 Aerobic post treatment for pH neutralization. A 50 L sample of CM: water 1:3 v/v slurry from a *b. subtilis* inoculation pretreatment and an aerated-FBR nutrient recovery treatment at pH 9 with 1 h HRT, was aerated continuously at 0.05 VVM for 80 h showing changes in pH (Red) and ORP (mV, Black) over time.
Results from aeration trial shows the potential for pH neutralization for aerated-FBR effluents, which is likely to greatly improve the outcome of the CWT post treatment approach for nutrients recovery from LM and LWE. Evaluation of the pH neutralization of CM slurry effluent from aerated-FBR showed it was effective, transforming the pH 9 sample into pH 7.6 with a near linear decrease between pH 9 and 7.8, followed by pH plateau at pH 7.6 between 70-80 h aeration. Comparison of ORP values showed than increase in ORP coincided with decrease in pH, indicating that a more oxygenated environment was occurring.

**Conclusions**

Results from batch experiment showed that aerobic pretreatment for LM may in fact improve the availability of recoverable PO₄-P in LM slurry with a maximum increase (averaged 90-92 %) for LM inoculated with *b. subtilis* and *b. amyloliquefaciens* after 24-48 h of aeration. These results imply that applying aeration with microbial pretreatment in an environment similar to the manure collection chamber used in AFO for solid separation prior to LWE transfer could improve PO₄-P availability for recovery. To further validate these finding, trials for optimization of the batch experiment condition (VVM rates, Temperature of incubation and pH of reaction) are needed in order to establish the conditions for upscaling this approach to pilot scale. The moderate increase for SBP treatment comparing to inoculation treatment might be a result of the experimental setting where fouling of the outer protective layer may hinder the diffusion transfer between the inner volume of SBP and slurry solution. In addition, it might be that a longer introduction time is needed for the SBP to get establish as indicated from similar experiment to treat
wastewaters with immobilized bacteria. The result of testing microbial dosing at flow through mode were not complete at the time of this thesis conclusion, however aeration of effluent leaving the aerated-FBR at pH 9, was successful at neutralizing its pH with a minimum of pH 7.6 at 72-80 h. This indicate that low-rate aeration may improve the performance of constructed wetlands by reducing the alkalinity stress that hinder vegetative growth.
8. Discussion and conclusions

This thesis work evaluated the recovery of phosphate from livestock manure and livestock wastewater effluent through the wet chemistry process of struvite precipitation by using an aerated-FBR method. The recovery process utilized pretreatment of livestock manure to improve phosphate recovery through organic phosphorous mineralization into phosphate, and an aeration or constructed wetland post treatments to supplement effluent water quality mitigation. Current state of the art review has demonstrated that fluidized bed reactor method is a well-established approach to recover phosphate as well as ammonium from most type of wastewaters (Agricultural, Municipal, Industrial), and to mitigate nutrients deposition into surface waters in order to decrease the formation of water fouling harmful algal bloom. The utilization of fluidized bed reactor as a mean to recover phosphate is also growing globally due to limited supply that justify the cost of nutrient recovery treatments. However, this process is hindered by the presence of calcium and non-descript dissolved organic matter in livestock wastewater effluent that require an expensive pretreatment to improve recovery rates. In addition, there are concerns related to the uptake of excess micronutrients, disposal of the alkaline (pH > 9) effluent and N nutrient loss through emission from using struvite as an ammonium fertilizer.

Therefore, this work focused on the following hypotheses:

a. The use of aerated fluidized bed reactor can effectively recover phosphate from livestock wastewater effluent.

b. In livestock manure where a large portion of phosphorous is unavailable for recovery as organic phosphorous, microbial mineralization pretreatment can improve its recovery
c. A combined aeration and constructed wetland post treatment can address the high pH, total suspended solids, and other nutrients content of fluidized bed reactor effluent
d. Enhanced struvite formation in some livestock wastewater effluent might be occurring due to specific functional groups of dissolved organics
e. Optimization of magnesium dosing application may improve the thermal stability and micronutrients uptake in fertilizers recovered from livestock wastewater effluent using the aerated fluidized bed reactor.

8.1 Overview of the geochemical research outcomes

Treatment of LWE with aerated-FBR

An initial study compared the recovery of phosphate from dairy wastewater and swine wastewater in bench scale, and then a follow up study evaluated treatment of dairy wastewater at a pilot scale. At the bench scale study nutrients recovery from livestock wastewater effluent was compared with an organics-free model solution (dairy-model, swine-model) to assess the hinderance effect of calcium and dissolved organic matter. Recovery rates of orthophosphate from swine wastewater and dairy wastewater (94%, 64% dissolved orthophosphate respectively) were comparable with current recovery rates reported for livestock wastewater effluent treatment through wet chemistry struvite precipitation. The effect of aeration on the pH of fluidized bed reactor was more significant for dairy wastewater treatment, where longer hydraulic retention time requirement for struvite precipitation allowed for a more significant pH manipulation (+0.5 pH). While for treated swine wastewater the recovered solids were nearly pure struvite (≤95 % w/w), for treated dairy wastewater mixture of struvite, k-struvite (~40% w/w) and
carbonates (~60 % w/w) was recovered. Comparison of mineral formed in the organic free
swine-model and dairy-model treated with aerated fluidized bed reactor showed that at
higher concentrations of dissolved organic matter and calcium present in dairy wastewater
there was an overall suppression of struvite formation, while at lower dissolved organic
matter and calcium concentration present in swine wastewater samples struvite
precipitation rate improved.

Following the evaluation of the aerated fluidized bed reactor design, treatment
conditions of pH and supplement magnesium dosing were tested for treating dairy
wastewater at a pilot scale. When 0-20 mM magnesium dosing was applied to dairy
wastewater treated for struvite recovery at pH 9-10, there was no significant increase in
dissolved orthophosphate recovery (49 ±5 - 76 ±10 %) or total phosphorous (-2.4 ±21 - 33
±25 %) for higher Mg dosing (10-20 mM) or higher pH (pH 10). On the other hand,
evaluation of the recovered solids composition found an increase in phosphorous content
for 5 mM Mg (16 g kg⁻¹) comparing to 0 mM Mg (12 g kg⁻¹) and no improvement in
phosphorous content for either higher magnesium dosing or reaction pH (pH 10).

**Thermal analyses and thermal stability of NH₄-N in solids recovered from treated DW**

The thermal stability of ammonium recovered as struvite from livestock wastewater
effluent was evaluated using simultaneous thermal analysis with evolved gas analysis.
Samples of solids recovered from the aerated fluidized bed reactor were analyzed for
thermogravimetry and differential scanning calorimetry between 25-1200 °C under inert
nitrogen environment, and the infra-red signal from the corresponding evolved gas analysis
was recorded. For the evaluation of ammonium stability, solids samples were compared to struvite standard since it was determined struvite was the near sole ammonium mineral form in recovered solids (> 95% w/w) by mineral phase analysis (x-ray diffraction, elemental, scanning electron microscopy). While the thermal stability of solids recovered from SW was similar to struvite standard with a maximum ammonium solid breaking into ammonia gas only as low temperature ammonium at 140-160 ºC, solids recovered from treated dairy wastewater had both a low temperature ammonium and high temperature ammonium with a variable fraction of ammonium solids breaking into ammonia gas as high temperature ammonium at 280-320 ºC. Result showed that lower magnesium dosing rates (0-5 mM magnesium) result in higher high temperature ammonium content (44-50 % w/w) comparing to high magnesium dosing (20 mM ,14 % w/w). In addition, it was determined that simultaneous thermal analysis with evolved gas analysis at a wide range temperature apparatus (100-900 ºC) is an effective approach to determine the carbonate composition of mixed mineral phase such as recovered from treated dairy wastewater. These resulted demonstrated that its ability to differentiate between liming components such as calcite, monohydrocalcite and nesquehonite.

**Effect of DOM and Ca on struvite formation in LWE**

The effect of calcium and dissolved organic matter on struvite growth rate and on the overall minerology of recovered solids was evaluated both in real livestock wastewater or simulated wastewater, treated with either aerated fluidized bed reactor flow through setting or constant composition batch model. Results from swine wastewater and dairy wastewater treated with aerated fluidized bed reactor showed an opposite effect for dissolved organic
matter and calcium on struvite precipitation rates and phosphate minerals structure. In swine wastewater where lower calcium (1 mM) and dissolved organic matter (200 mg L\(^{-1}\) as total organic carbon) were present there was a synergic effect whereby the presence of dissolved organic matter mitigated the hinderance from calcium on struvite growth rate. This resulted in no effect to longer hydraulic retention time in aerated fluidized bed reactor on struvite growth (15-35 min hydraulic retention time) and maximum recovery at 15 min hydraulic retention time (< 90%). When a dissolved organic matter free swine model solution was tested the presence of unmitigated calcium decreased struvite precipitation rate and longer hydraulic retention time (< 35 min) was needed to reach maximum phosphate recovery. In contrast, for dairy wastewater where high calcium (5 mM) and dissolved organic matter (800 mg L\(^{-1}\) as total organic carbon) were present, high dissolved organic matter or the difference in dissolved organic matter composition resulted in a suppressed struvite growth rather facilitating a beneficial synergic effect with calcium that promote struvite growth. As a result, longer hydraulic retention time was needed (< 68 min) to reach maximum phosphate recovery from dairy wastewater comparing to dissolved organic matter free dairy -model (35 min hydraulic retention time).

In order to evaluate the synergic relation between dissolved organic matter, calcium and struvite growth rate, a constant composition approach was applied to model continuous struvite growth conditions in livestock wastewater effluent treated with aerated fluidized bed reactor. This method applied a constant saturation index for struvite with respect to livestock wastewater constituents, so that the effect of calcium, dissolved organics or synergic calcium-dissolved organics presence on struvite growth can by isolated as an independent rate determining factor. This was measured as the rate of pH change in the
solution and corresponding titration of struvite components that maintained a mass balance of the dissolved phase. This work used phenol or benzoate, a negatively charged dissociated low molecular weight organics (pKa 10, 8.5 respectively) in simulated wastewater (pH 8.5) to model negatively charged dissolved organic matter in livestock wastewater effluent. It was found that when these anionic organics were present in simulated wastewater, the rate of precipitation increased by 1-2 orders of magnitude (51, 345 µmole min\(^{-1}\) L\(^{-1}\) respectively) comparing to control Blank (5, 40 µmole min\(^{-1}\) L\(^{-1}\) respectively). When calcium was present with phenol, an overall hinderance to struvite precipitation occurred compare phenol treatment, but struvite precipitated at a higher rate than blank or calcium treatments. In contrast to negatively charged low molecular weight organics, when non polar toluene modeling nonionic organics or positively charged benzylamine (pKa 9.33) modeling cationic dissolved organics were present the rate of precipitation decreased over time by ~50%.

**Microbial pretreatment for enhanced struvite recovery**

A pretreatment to mineralize the organic phosphate inositol hexaphosphate in cattle manure into phosphate was used as a mean to enhance struvite recovery by aerated-fluidized bed reactor method. Mineralization pretreatment compared aerobic application of dosing or immobilized *bacillus sp.* with direct phytase enzyme application. The dosing approach used inoculation while immobilized treatment used small bioreactor process encapsulation to promote the microbial expression of phytase enzymes. Results from batch experiment showed that highest normalized increase in dissolved phosphorous concentration was observed for *b. subtilis* and *b. amyloliquefaciens* (+90-92 %) after 3000 min aeration, while
best small bioreactor process results (48-60 %) were achieved by *b. licheniformis* and *b. subtilis* at 1500 min aeration. Raw treatment (no bacillus sp.) promoted 30% increase at 1500 min aeration while Phy application had no significant impact comparing to blank treatment. All treatments had a similar minimal concentration dissolved P (~30 mg L⁻¹) following a simulation of nutrients recovery process at pH 9 with 60 min reaction time, demonstrating that the removal of dissolved phosphorous is independent of its availability prior to alkaline pH modification from pH 7 to pH 9. This indicated that there is a potential benefit to microbial pretreatment as a mean to improve phosphate recovery from livestock wastewater effluent.

### 8.2 Agrotechnical applications of finding

While this work focused primarily on the geochemical aspects of struvite formation in livestock wastewater effluent treated for phosphate recovery, it concluded several agrotechnical insights related to sustainability application for small scale animal feed operations and livestock wastewater effluents management. Among the recognized barriers to assimilation of nutrients recovery practices by small animal feed operation are the cost of system adoption and the increase in labor or professional training input requirements. The novel approach outlined in this thesis evaluated a flexible and low input treatment system that rely mostly on an existing farm infostructure. The agrotechnical considerations for this series of studies were: a. the use of aeration can reduce operation costs associated with caustic soda application; b. open-source automation can be applied to reduce labor cost of treatment. A survey of the livestock manure to soil pathway within animal feed operation system (Figure 1.1) shows an overlap between the nutrient recovery with aerated
fluidized bed reactor setting at the cattle manure collection point prior to solids separation and the lagoon effluent storage prior to soil application. This allows to integrate the pretreatment microbial mineralization of organic phosphate at an existing cattle manure slurry pool and apply aerobic constructed wetland post treatment on top of an existing earthen lagoon. As a result, the estimated cost of installation can by kept considerably lower, where the main input is in installing the aerated fluidized bed reactor system. Our cost assessment analyses has found that an approximated $135 per animal-year operation cost and $20,000 per farm installation costs for a 100 cattle head AFO. A key mitigator in operation cost is the proposed assimilation of open-source automation solutions. Through informal inquiries as well as a farmer survey conducted in the course of this thesis work it was recognized that although there is a relatively high interest in farm automation (>50% describe it as of high significance), there is a lack in available training resources.

Other agrotechnical conclusions of significance are the effects of magnesium dosing on the thermal stability of ammonium and micronutrients uptake. The potential implication of a more thermally stable struvite is an improved nitrogen conversion for crops, as up to 50% w/w of applied ammonium can be lost to ammonia gas emission. While the biotic effect of soil microbiome as well as a more in-depth soil model analyses are needed to determine the actual impact on overall nitrogen loss, a significant increase (≤ 34% w/w) in high temperature ammonium was observed for solids recovered from cattle livestock wastewater effluent treated with aerated fluidized bed reactor. Optimizing the operation setting (pH, Mg dosing) also modified the uptake of micronutrients (zinc, iron, manganese) and potentially phytotoxic Al. This implies that supplementing a low-cost Mg dosing treatment ($ 0.01-2 m^{-3} livestock wastewater effluent) at a maximum dosing of 20 mM
magnesium (cost range depend on the reagent grade of applied magnesium), will reduce the uptake of micronutrients if needed and prevent toxicity buildup in sensitive soils.

8.3 Future research

In conclusion to the thesis research of phosphorus recovery as struvite from livestock manure and livestock wastewater effluent, future work will expand on some of the finding related to struvite thermal stability, application of struvite for soil fertility and the upscaling of the aerobic treatment approach to pilot scale.

This will include the following planned research projects:

1. Use of solids recovered from aerated fluidized bed reactor for soil fertility. This study will look into the nitrogen and phosphate response of struvite recovered from LWE compared to various nutrients sources in a corn, soy, rye crop cycle.

2. Ammonia and greenhouse gas emission from livestock wastewater effluent struvite soil application. This study will look into evaluating ammonia gas emission from soils treated with struvite from dairy wastewater using simultaneous thermal-evolved gas analyses of model soil.

3. Improvements to the aerobic contracted wetland and microbial treatments for livestock wastewater. This research will look into post-treatment aeration for improved wetland performance on a pilot scale. In addition, scaling up of the microbial pretreatment for organic phosphate mineralization is also in plans for pilot scale evaluation.
Appendices

Appendix A: Supporting information for chapter 2

Estimating the struvite saturation index

Struvite formation in the aerated-FBR is based on the saturation index (SI) of struvite. The dissociation equation for struvite is

$$\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O} \leftrightarrow \text{Mg}^{2+} + \text{NH}_4^+ + \text{PO}_4^{3-} + 6\text{H}_2\text{O} \quad (\text{eq. A.1})$$

The ion activity product (IAP) of dissolved ions and the struvite solubility product ($K_{\text{sp}}$) are used to determine the SI:

$$\text{SI} = \log_{10} \left( \frac{\text{IAP}}{K_{\text{sp}}} \right) \quad (\text{eq. A.2})$$

For wastewater and model solutions, the SI is calculated by Visual MINTEQ using the relevant solution composition and the default thermodynamic database. With respect to struvite saturation, dairy (DW) and swine wastewaters (SW) are undersaturated (SI<0) at the initial wastewater pH (6.8-7.9), but are sufficiently oversaturated (SI>0) at pH 9 to facilitate struvite precipitation during aerated-FBR treatment (Figure A.1).
Figure A.1 Estimated struvite saturation index as a function of pH for a) DW and b) SW wastewater, calculated using Visual MINTEQ.

**Modeling complexation of calcium (Ca) and dissolved organic carbon (DOC)**

For metal ligand complexation, there is a higher affinity for polyvalent cations compared to monovalent cations such as Na\(^{+}\). Based on the wastewater solution composition (Table 2.1), the dominant polyvalent cations are Mg\(^{2+}\) and Ca\(^{2+}\). In order to get an estimate to the extent of interactions between these cations and DOC, a Gaussian complexation model for multiple ligands was used. The applications of this model are described at length elsewhere. This model assumes that the population of DOC ligands is distributed normally over their deprotonating equilibrium constants (K\(_a\)), and therefore solves for metal ligand complexation as a function of dissolved constituent concentration for a given pH. Although this model is considered somewhat less reliable that other models, such as the non-ideal competitive adsorption model (NICA) or the Stockholm humic model (SHM), it is less dependent on specific ligand parameters. This makes it more applicable for use in wastewaters that have high ligand variability. The concentration of
DOC sites may be given as a function of the mass of DOC in Dalton (Da) mass units. In order to estimate the ratio of dissolved Ca that is in the Ca-DOC form, the median mass of DOC was estimated at 1500 Da based on a 1-3000 Da range from published work reporting on DOC properties in DW.\(^ {156}\) Data from SW and DW samples (Table A.1) was used to model the percent Ca-DOC/Ca total at pH 9 as a function of DOC concentration using a multi-step analysis (Figure A.2).

Table A.1. Visual MINTEQ prediction of Ca-DOC complexation and Ca speciation in SW and DW using a Gaussian model at 1500 Da and 50% w/w C content in DOC

<table>
<thead>
<tr>
<th>Component</th>
<th>% of total concentration</th>
<th>Species name</th>
<th>Component</th>
<th>% of total concentration</th>
<th>Species name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(^{2+})</td>
<td>50.0</td>
<td>Ca(^{2+})</td>
<td>Ca(^{2+})</td>
<td>34.8</td>
<td>Ca(^{2+})</td>
</tr>
<tr>
<td></td>
<td>17.4</td>
<td>Ca DOM1</td>
<td></td>
<td>34.5</td>
<td>Ca DOM1</td>
</tr>
<tr>
<td></td>
<td>1.4</td>
<td>CaCl(^+)</td>
<td></td>
<td>1.6</td>
<td>CaCl(^+)</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>CaNH(_3)(^+)</td>
<td></td>
<td>0.7</td>
<td>CaNH(_3)(^+)</td>
</tr>
<tr>
<td></td>
<td>0.0</td>
<td>CaNO(_3)(^+)</td>
<td></td>
<td>0.1</td>
<td>CaNO(_3)(^+)</td>
</tr>
<tr>
<td></td>
<td>1.1</td>
<td>CaHPO(_4) (aq)</td>
<td></td>
<td>0.3</td>
<td>CaHPO(_4) (aq)</td>
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<tr>
<td></td>
<td>5.6</td>
<td>CaPO(_4)(^-)</td>
<td></td>
<td>1.1</td>
<td>CaPO(_4)(^-)</td>
</tr>
<tr>
<td></td>
<td>2.7</td>
<td>CaHCO(_3)(^+)</td>
<td></td>
<td>4.6</td>
<td>CaHCO(_3)(^+)</td>
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<tr>
<td></td>
<td>20.5</td>
<td>CaCO(_3) (aq)</td>
<td></td>
<td>21.8</td>
<td>CaCO(_3) (aq)</td>
</tr>
<tr>
<td>DOC (Gaussian DOM)</td>
<td>100</td>
<td>DOC (Gaussian DOM)</td>
<td>DOM1</td>
<td>100</td>
<td>DOC (Gaussian DOM)</td>
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<tr>
<td>DOM1</td>
<td>68.5</td>
<td>DOM1</td>
<td></td>
<td>83.9</td>
<td>DOM1</td>
</tr>
<tr>
<td></td>
<td>0.02</td>
<td>Ba DOM1</td>
<td></td>
<td>0.0</td>
<td>Ba DOM1</td>
</tr>
<tr>
<td></td>
<td>12.1</td>
<td>Ca DOM1</td>
<td></td>
<td>0.1</td>
<td>Ca DOM1</td>
</tr>
<tr>
<td></td>
<td>19.2</td>
<td>Mg DOM1</td>
<td></td>
<td>15.8</td>
<td>Mg DOM1</td>
</tr>
</tbody>
</table>
Effect of aeration on struvite saturation and pH in aerated-FBR

Aeration, including the effect of vacuum and aeration on NH$_3$(g) volatilization, and pH were tested by comparing S$_{0a}$ and S$_1$-S$_4$ with S$_0$ samples for all eight treatments (Figure A.3). Ammonium losses were minimal (<10%) (Figure A.3a), and did not affect struvite SI. Aeration increased the pH of DW and SW to 8.5 and 8, respectively (Figure A.3b). Titration with NaOH was used to further increase the pH to 9.
Figure A.3 a.

Effect of vacuum and aeration on ammonia gas (NH\textsubscript{3}(g)) volatilization

Figure A.3 b.

pH changes over aeration time in aerated-FBR for DW and SW

Figure A.3. Effect of aeration on ammonia emission and pH

**Experimental design and statistical analysis for dissolved phosphate recovery:**

The evaluation of dissolved phosphate (P) removal from livestock wastewater and model solutions was done using comparison of means for P removal. The application of Tukey-Kramer method for comparing means allow us to compare multiple treatments. The treatments evaluated were two wastewater types: dairy, swine; two retention times: long, short; and actual wastewater, organic free model solution (Table A.2).
Table A.1. Experimental design for statistical analysis

<table>
<thead>
<tr>
<th>Reaction time (min.)</th>
<th>Dairy Wastewater with high DOC+Calcium</th>
<th>Swine Wastewater with low DOC+Calcium</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wastewater sample</td>
<td>Organic wastewater model solution</td>
</tr>
<tr>
<td>15</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>35</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>68</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

In this experimental setting, each one of the four repeats for eight treatments is a nominal value with binomial parameter distribution, as it represent the fraction of P recovered within the zero to one range. Since the study aims to compare multiple means, one-way analysis of variance (ANOVA) followed by the application of Tukey-Kramer comparison for multiple means are being used. However, since Tukey-Kramer analysis assumes a normal distribution of parameters, a transformation from binomial to normal distribution is needed. For fractural parameters, an arcsine transformation is appropriate when some of the results parameter values are lower than 0.3 or over 0.7 in the zero to one range. The transformed values are then used to compare the parameter means for statistical significance of difference.\(^{310}\) To perform the arcsine transformation, the following computation was applied for each parameter:

\[
\text{Transformed parameter} = \arcsine(\sqrt{\text{fractional parameter}}) \quad (\text{eq. A.3.a})
\]

or

\[
T(y) = \arcsine\sqrt{\frac{8u-51}{80}}. \quad (\text{eq. A.3.b})
\]
Applying TOPAS 4.2 software for a fundamental parameter approach for mineral phase distribution

The TOPAS 4.2 software (Bruker) was used to estimate the distribution of mineral phases in the solids by semi-quantitative analysis. The analysis model uses general nonlinear least squares fitting to estimate the fraction of each detected mineral out of the total sample diffraction. This is done using convolution based profile fitting-fundamental parameters approach (CPF-FPA), combined with phase analysis of samples with EVA software (Bruker). The calculated model fit to each sample is described as goodness of fit (GOF), which is the ratio between a hypothetical minimum fit error to a calculated fit error value: Rwp. The closer the GOF value is to 1, the higher the confidence in the accuracy of the model. In order to improve the phase model fit, the following constraints were applied, based on the Bruker Advance D8 XRD mechanical properties: monochromator angle, 26.6°; fixed divergence slit (FDS) shape angle, 2.2°; receiving slit, 0.075 mm; radius, 280 mm. The computational initial conditions were Chebychev polynomial order of 3-5; 1/x background of 100; and appropriate preferred orientations were applied. Structure data files were built from published CIF files for struvite, K-struvite, calcite and monohydrocalcite. For aerated-FBR solids XRD scans (Figure A.4a), a 0.016 °2θ step over 5-60 °a span was used to allow a sufficiently high ratio of data points per degrees of freedom in the model. For aerated-FBR solids XRD scans (Figure A.4a), a 0.016 °2θ step over 5-60 °a span was used to allow a sufficiently high ratio of data points per degrees of freedom in the model.

In order to validate the sensitivity of the percent phase estimate for calcite and struvite, homogenized samples with 25, 50 and 75% w/w ratios of struvite/calcite were
analyzed (Figure A.4b). In the model fit results, a plot of counts over $^\circ \theta$ for actual sample diffraction (black) is compared to each phase structure file (blue). This is used to calculate the mass percent of each phase as a function of total peak area and intensity. The lower plot indicates the total residual diffraction counts between the modeled phase and measured diffraction. The distinguished peaks of each mineral phase are marked in bold below the residual counts plot. Comparison of estimate ratios with actual w/w ratios found that both phases had good results, where the calcite estimate was slightly better (~1% error) than struvite (~7% error). This is mostly because the CPF-FPA model resolves better for broader XRD peaks, such as are typical for calcite crystals.

Results from CPF-FPA analysis (Figure A.4c) shows model output/counts over the $^\circ \theta$ span. The upper plot in each output shows the XRD diffraction count (black) and calculated model (red) with residual counts below. The assigned modeled peaks and corresponding mineral structure parameters are shown below. When comparing CPF-FPA output for K-struvite with the elemental analysis of the solids, there is a significant deviation from measured K. Since K-struvite is the only K mineral phase evident in the XRD pattern, it is reasonable to assume the source of error is due to overlapping struvite and K-struvite diffractions. The actual semi-quantitative mineral phase output (Table A.3) used for Figure 2.3 adjusted K-struvite values by applying the molar ratios of K:Mg in aerated-FBR solids based on elemental analysis, to the total struvite + K-struvite estimate in the CPF-FPA output. The use of the K:Mg ratio as an indicator for distribution of K-struvite and struvite phases in the solid sample is applicable since no significant amount of other Mg mineral was detected in the XRD diffraction. Similar validation for
monohydrocalcite bears a computation limit as there is no elemental marker to separate calcite from monohydrocalcite.

Figure A.4.a Diffraction data from XRD scans and mineral standards: A.4 a. Diffraction data from XRD scans and mineral standards. Monohydrocalcite and K-struvite diffractions are calculated using Crystal Diffract 1.2.3 software.
Figure A.4 b. Convolution based profile fitting- fundamental parameters approach (CPF-FPA) for known calcite-struvite mixtures.
Figure A.4 c. CPF-FPA analysis of aerated-FBR solids.
Table A.2. Data input for figure 2.3

<table>
<thead>
<tr>
<th>Sample</th>
<th>struvite</th>
<th>K-struvite</th>
<th>Calcite</th>
<th>MHC</th>
<th>Crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>DW-35</td>
<td>33</td>
<td>8</td>
<td>17</td>
<td>42</td>
<td>75</td>
</tr>
<tr>
<td>DW-68</td>
<td>28</td>
<td>3</td>
<td>55</td>
<td>13</td>
<td>87</td>
</tr>
<tr>
<td>D-model-35</td>
<td>50</td>
<td>1</td>
<td>44</td>
<td>5</td>
<td>60</td>
</tr>
<tr>
<td>D-model-68</td>
<td>58</td>
<td>1</td>
<td>-</td>
<td>41</td>
<td>43</td>
</tr>
<tr>
<td>SW-15</td>
<td>98</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>94</td>
</tr>
<tr>
<td>SW-35</td>
<td>95</td>
<td>2</td>
<td>2</td>
<td>-</td>
<td>94</td>
</tr>
<tr>
<td>S-model-15</td>
<td>78</td>
<td>1</td>
<td>21</td>
<td>-</td>
<td>94</td>
</tr>
<tr>
<td>S-model-35</td>
<td>93</td>
<td>2</td>
<td>7</td>
<td>-</td>
<td>94</td>
</tr>
</tbody>
</table>

**Scanning Electron Microscopy (SEM)**

Scanning electron microscopy (Hitachi S-4800 SEM) images were collected for all recovered solids. The solids were mounted on copper adhesive tape and prepared with 1.5 nm iridium coating. Images were collected at 3-5 keV beam intensity. Images generated by SEM were used to compare the morphology and particle size of the aerated-FBR solids collected from different wastewaters, and with struvite and calcite standards (Figure A.6). The estimated particle size for solids derived from swine influents, ranged from ~20-100 µm, and were generally larger and less aggregated than the solids from the dairy influents which had a size range of 5-50 µm. For the dairy solids, the minerals cannot be easily distinguished based on shape, and grow as flaky structures mixed with colloids from the wastewater influent (Figure A.6 c-f). The struvite crystals in the SW and S-model solids maintain their porous needle-like structure, with the exception of the SW-15 solids that contained some pyramid-shaped crystals (Figure A.6 g-j). The difference in overall morphology of the solid particles between DW and SW corresponds with the struvite
content, where higher struvite content resulted in less flaky structures. These trends are also consistent with the calculated crystallinity, with the dairy solids having poor particle morphology and low crystallinity, and the swine solids showing well-defined crystals and higher crystallinity.

Figure A.5. SEM images of aerated-FBR solids and standards, a. calcite; b. struvite; c. DW-35; d. DW-68; e. D-model-35; f. D-model-68; g. SW-15; h. SW-35; i. S-model-15; j. S-model-35. The dashed line is the approximate scale for each of the images, ranging from 5-50 µm.
Simultaneous Thermal Analysis (STA)

The method was developed to allow maximum gas evolution and sufficient time for IR analysis of evolved gases. The temperature span of 28-1068°C is sufficient to analyze the detected mineral phases: struvite, calcite, monohydrocalcite and K-struvite, and for analysis of organic and water content. STA-EGA output for a mixed struvite-calcite standard (Figure A.6) and for the aerated-FBR solids (Figure A.7) was used to compare the thermal stability of the solids collected from the wastewaters and model solutions (Figure 2.5). The final TG % mass loss is reported in Table A.4. For DSC results, enthalpy is positively correlated with struvite content crystallinity (Figure A.8).

![Graph](image)

Figure A.6. STA-EGA data for a struvite+calcite standard which was 60% w/w struvite and 40% w/w calcite.
Figure A.7. STA-EGA data for aerated-FBR solids
Table A.3. Final TG % mass loss of aerated-FBR solids.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SW 15</th>
<th>SW 35</th>
<th>S-model 15</th>
<th>S-model 35</th>
<th>DW 35</th>
<th>DW 68</th>
<th>D-model 35</th>
<th>D-model 68</th>
</tr>
</thead>
<tbody>
<tr>
<td>TG mass loss (%)</td>
<td>39.5</td>
<td>42.3</td>
<td>48.7</td>
<td>45.4</td>
<td>36.4</td>
<td>41.8</td>
<td>49.6</td>
<td>67.3</td>
</tr>
</tbody>
</table>

Figure A.8. Correlation between integrated enthalpy (J/g) and struvite content or crystallinity for aerated-FBR solids.
Figure B.1. Pilot site details: 1. Pilot site at Dairy lagoon, with aerated-FBR enclosure and CWT with cover 2. Seep pump. 3. Aerated-FBR placement. 4 FBR foam vent and VSB inlet 5. Construction of VSB 6. CWT canal 7. FWS pools 8. Protective cover for CWT
Figure B.2 aerated-FBR schematics: 1. Arrow 1200 Overhead mixer with 10 mm chuck. 2. 10 mm mixer shaft (stainless still) 100 cm with 50 mm left turn propeller blade. 3. 3-inch PVC pipe serve as stand for overhead mixer. 4. Sealed 10 mm bearing (Cowie) with 19 mm NPT base 5. 7.6 cm PVC hole-saw cutout with centered ¾ NPT threaded centered hole for shaft bearing. 6. Inserts for pH probe, air diffuser. For ease of maintenance a slide-in set-up of 19 mm NPT probe /diffuser connected to 1-inch PVC tube inserted into a short 3.17 cm PVC tube that form a sealed fitted contact. A 2.54 cm PVC pipe cup hold the probe in place. 7. Open in lower part of reactor head to vent foam 8. Entry of DW from auger. 9. Flange in reactor head to bolt/clump and seal the reactor head and reactor top 10. Open in top of reactor to vent foam 11. Top of aerated FBR 12. 3.17 cm PVC vent for aerated-FBR 13. PFR chamber 14. Separating wall with ¾-inch slit passage at its base 15. FBR chamber 16. DW effluent exit 17. Ball valve for solids collection.
Material: 10 mm clear PVC. Manufacturer: Glasplex LLC NJ

Figure B.3. aerate-FBR fabrication schematics
A 40 L aerated-FBR fabrication schematics. overall dimensions (a) and fabrication steps (b-c):
Table B.1. solution to single helix auger design: An approximated solution to single helix screw auger fabrication design with commonly available tools and materials:

**Sizing table for one helix auger at 45 degrees (units in inch)**

<table>
<thead>
<tr>
<th>Inner PVC pipe size</th>
<th>½</th>
<th>¾</th>
<th>1</th>
<th>1¼</th>
<th>1½</th>
<th>2</th>
<th>2¼</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Actual inner diameter</td>
<td>0.84</td>
<td>1.05</td>
<td>1.31</td>
<td>1.66</td>
<td>1.9</td>
<td>2.37</td>
<td>2.87</td>
<td>3.5</td>
<td>4.5</td>
</tr>
<tr>
<td>Optimal outer diameter</td>
<td>1.53</td>
<td>1.91</td>
<td>2.39</td>
<td>3.02</td>
<td>3.45</td>
<td>4.32</td>
<td>5.23</td>
<td>6.36</td>
<td>8.18</td>
</tr>
<tr>
<td>Nearest saw diameter</td>
<td>1.5</td>
<td>2</td>
<td>2.5</td>
<td>3</td>
<td>4</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>8</td>
</tr>
<tr>
<td>Helix pitch</td>
<td>0.76</td>
<td>0.95</td>
<td>1.20</td>
<td>1.51</td>
<td>1.73</td>
<td>2.16</td>
<td>2.61</td>
<td>3.18</td>
<td>4.09</td>
</tr>
<tr>
<td>Target hole saw in</td>
<td>0.87</td>
<td>1.09</td>
<td>1.37</td>
<td>1.70</td>
<td>1.98</td>
<td>2.47</td>
<td>2.99</td>
<td>3.64</td>
<td>4.68</td>
</tr>
<tr>
<td>Target hole saw out</td>
<td>1.52</td>
<td>2.02</td>
<td>2.53</td>
<td>3.02</td>
<td>4.04</td>
<td>4.06</td>
<td>5.07</td>
<td>6.08</td>
<td>8.11</td>
</tr>
</tbody>
</table>

For hole saw add ~1/8 inch to hole saw size

The 3-inch auger design with 1-1/4 in. helix shaft (Yellow shade in above table) was used at the pilot site.

Figure B.4 auger helix fabrication: 1. Hole saw outer and inner dimension of the PVC sheet (see above table for hole saw sizing), cut all sheet discs at a single radius line. 2. Stack and glue-weld the sheets with a 10-25 mm overlap, cure dry for 24 h. 3. Test helix structure for faults. 4. Bolt screw the helix to inner PVC shaft, extend and bolt to the other end. Cement glue along helix and cure dry for 24 h.
Figure B.5. Auger design: 1. screen cover of auger entry, 19 mm wire-mesh screen with screw tie band. 2. Auger tube. 3. Centering bearing (Lubrication-free plastic flanged ball bearing, chemical resistant), fitted into a 7.6 cm to 3.81 cm PVC tube reducer. 4. 1.44 Kk-m. torque-limiting flexible shaft couplings with alarm. 5. 15 teeth 2.54 cm bore steel sprocket. 6. Flanged ball bearing. 7. Self-adjusting tensioner (Fenner drives FS0072). 8. Gear motor with (Dyton 1.9 Kg-m 24VDC). 9. 60-teeth sprocket with 15.8 mm bore.

Table B.2. Raspberry GPIO list

<table>
<thead>
<tr>
<th>Use</th>
<th>PWR</th>
<th>GPIO PIN</th>
<th>PIN 1-40</th>
<th>GPIO PIN</th>
<th>PWR</th>
<th>Use</th>
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<td>1 2</td>
<td>5VDC</td>
<td></td>
<td></td>
<td>external PWR</td>
</tr>
<tr>
<td>pH RX</td>
<td>5VDC</td>
<td>2 3 4</td>
<td>5VDC</td>
<td></td>
<td></td>
<td>Relay for Mixer Outlet</td>
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<tr>
<td>pH TX</td>
<td>5VDC</td>
<td>3 5 6  GND</td>
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<td></td>
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<td>Relay for Air pump Outlet</td>
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<tr>
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<td></td>
<td>4 7 8</td>
<td></td>
<td></td>
<td></td>
<td>Relay for Mg pump outlet</td>
</tr>
<tr>
<td>17</td>
<td></td>
<td>9 10 15</td>
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<td></td>
<td></td>
<td>GND Catalyst FH 100 control</td>
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<tr>
<td>27</td>
<td></td>
<td>13 14  GND</td>
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<td></td>
<td></td>
<td>GND Gear motor controller GND</td>
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<tr>
<td>22</td>
<td></td>
<td>15 16  23</td>
<td></td>
<td></td>
<td></td>
<td>GND Gear motor CW/CCW</td>
</tr>
<tr>
<td>27</td>
<td></td>
<td>17 18  24</td>
<td></td>
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<td></td>
<td>19 20  GND</td>
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<td>21 22  25</td>
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<td></td>
<td>Peristaltic CW/CCW remote</td>
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<tr>
<td>11</td>
<td></td>
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<td></td>
<td></td>
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<tr>
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<td>27 28  1</td>
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<td></td>
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</tr>
<tr>
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<td></td>
<td>29 30  GND</td>
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</tr>
<tr>
<td>6</td>
<td></td>
<td>31 32  12</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>13</td>
<td></td>
<td>33 34  GND</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td></td>
<td>35 36  16</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>26</td>
<td></td>
<td>37 38  20</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Remote</td>
<td></td>
<td>39 40  21</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Catalyst FH100 DB9 external controller pinout
1. speed 0-10V (+) input
2. speed 4-20mA (+) input
3. speed ref com
4. JumperA local/remote speed
5. JumperA local/remote speed ref
6. JumperB start / stop and cw/ccw ref
7. JumperB start/stop (+) control
8. cw/ccw
9. ground

For raspberry pi 40-GPIO pins, the above setting was applied at pilot site
Figure B.7. Effect of Mg addition on NaOH application rate

**Bivariate Fit of OH (g/L DW) By Mg (mM)**

<table>
<thead>
<tr>
<th>OH (g/L DW)</th>
<th>0.5</th>
<th>1</th>
<th>1.5</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg (mM)</td>
<td>0</td>
<td>5</td>
<td>10</td>
<td>15</td>
</tr>
</tbody>
</table>

**Transformed Fit to Square**

\[
\text{OH (g/L DW)} = 0.6148387 + 0.0037917 \times \text{Square(Mg (mM))}
\]

**Summary of Fit**

- RSquare: 0.975934
- RSquare Adj: 0.963902
- Root Mean Square Error: 0.134279
- Mean of Response: 1.1125
- Observations (or Sum Wgts): 4

**Analysis of Variance**

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>Sum of Squares</th>
<th>Mean Square</th>
<th>F Ratio</th>
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<td>1.4624132</td>
<td>1.46241</td>
<td>81.1061</td>
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<td>Error</td>
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<td>0.01803</td>
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<tr>
<td>C. Total</td>
<td>3</td>
<td>1.4984750</td>
<td>0.1664816</td>
<td>0.12161*</td>
</tr>
</tbody>
</table>

**Parameter Estimates**

| Term                  | Estimate | Std Error | t Ratio | Prob > |t| |
|-----------------------|----------|-----------|---------|---------|---|
| Intercept             | 0.6148387| 0.086956  | 7.07    | 0.0194* |
| Square(Mg (mM))       | 0.0037917| 0.000421  | 9.01    | 0.0121* |

Appendix C: Supporting information for chapter 4

Figure C.1. Composition of DW in dissolved, acidified and total phase samples, ANOVA (diamond green) at α=0.05 and Tukey Kramer comparison of mean where levels with similar letters are not significantly different.
Figure C.2. Mass balance of major components in dissolved phase of DW, showing results (black), analysis of variance (green; diamond 95% confidence interval span) and Tukey-Kramer comparison of means values (Table, $\alpha = 0.05$).
Figure C.3. Detailed depiction of nutrients composition in recovered solids from DW treated with 0-20 mM Mg, showing linear reduction of Fe and increase of Ca for higher Mg dosing, decrease in Zn, S between 0-10 mM Mg, and no effect for Mg treatment on Al, K, Mn, Na and P.
Table C.1. Common carbonate and phosphate mineral phases occurring in DW

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formation</th>
<th>Ksp</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Phosphates</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Struvite ³⁸</td>
<td>( \text{Mg}^{2+} + \text{H}_2\text{PO}_4^- + \text{NH}_4^+ \leftrightarrow \text{MgNH}_4\text{PO}_4\cdot 6\text{H}_2\text{O} + 2\text{H}^+ )</td>
<td>(10^{-13.26})</td>
</tr>
<tr>
<td>K-struvite ⁴⁰</td>
<td>( \text{Mg}^{2+} + \text{H}_2\text{PO}_4^- + \text{K}^+ \leftrightarrow \text{MgNH}_4\text{PO}_4\cdot 6\text{H}_2\text{O} + 2\text{H}^+ )</td>
<td>(10^{-11})</td>
</tr>
<tr>
<td>HAP ⁵⁹</td>
<td>(5\text{Ca}^{2+} + 3\text{PO}_4^{3-} + \text{OH}^- \leftrightarrow \text{Ca}_5(\text{PO}_4)_3\text{OH})</td>
<td>(10^{-58.62})</td>
</tr>
<tr>
<td>β-TCP ²⁶</td>
<td>(3\text{Ca}^{2+} + 2\text{PO}_4^{3-} \leftrightarrow \text{Ca}_3(\text{PO}_4)_2)</td>
<td>(10^{-28})</td>
</tr>
<tr>
<td>Monetite ²⁶</td>
<td>(\text{Ca}^{2+} + \text{HPO}_4^{2-} \leftrightarrow \text{CaHPO}_4)</td>
<td>(10^{-6.9})</td>
</tr>
<tr>
<td><strong>Carbonates</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcite ³¹³</td>
<td>(\text{Ca}^{2+} + \text{CO}_3^{2-} \leftrightarrow \text{CaCO}_3)</td>
<td>(10^{-8.48})</td>
</tr>
<tr>
<td>Monohydrocalcite ³¹³</td>
<td>(\text{Ca}^{2+} + \text{CO}_3^{2-} + \text{H}_2\text{O} \leftrightarrow \text{CaCO}_3\cdot \text{H}_2\text{O})</td>
<td>(10^{-7.54})</td>
</tr>
<tr>
<td>Nesquehonite ³¹³</td>
<td>(\text{Mg}^{2+} + 3\text{CO}_3^{2-} + 3\text{H}_2\text{O} \leftrightarrow \text{CaCO}_3\cdot 3\text{H}_2\text{O})</td>
<td>(10^{-4.67})</td>
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<tr>
<td><strong>Others and evaporites</strong></td>
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<td></td>
</tr>
<tr>
<td>Gypsum ³¹⁴</td>
<td>(\text{Ca}^{2+} + \text{SO}_4^{2-} + \text{H}_2\text{O} \leftrightarrow \text{CaSO}_4\cdot 3\text{H}_2\text{O})</td>
<td>(10^{-4.65})</td>
</tr>
<tr>
<td>Niter ³¹⁵</td>
<td>(\text{K}^+ + \text{NO}_3^- \leftrightarrow \text{KNO}_3)</td>
<td>(10^{1.15}) (evaporite)</td>
</tr>
<tr>
<td>Sylvite ³¹⁵</td>
<td>(\text{K}^+ + \text{Cl}^- \leftrightarrow \text{KCl})</td>
<td>(10^{0.35}) (evaporite)</td>
</tr>
<tr>
<td>Halite ³¹⁵</td>
<td>(\text{Na}^+ + \text{Cl}^- \leftrightarrow \text{NaCl})</td>
<td>(10^{1.58}) (evaporite)</td>
</tr>
</tbody>
</table>
Figure C.4. Solids EDX analysis for micronutrients composition (element %) for representative mineral samples (A-T) within the “Other” elements pie chart section of aerated-FBR solids from treated DW depicted in Figure 5.
Figure C.5. XRD diffraction pattern and mineral phase distribution of solids recovered from DW.
Figure C.6. STA-EGA analysis of solids collected from aerated-FBR treated with 0-20mM Mg. For each 0-20 mM Mg DW treatment, measured TG; Gram-Schmidt (GS) conversion of total EGA IR signal; actual IR of NH$_3$, H$_2$O and CO$_2$; DSC were plotted over 25-1200 °C. For TG (black), thermal steps are indicated with mass change (% w/w) and inflection point (maximum loss rate temperature). Plot of GS (orange) is compared with individual IR EGA signal of NH$_3$(g) (pink), water-vapor (blue) and CO$_2$(g) (red) over temperature (°C). Integrated IR signal from NH$_3$ over temperature (°C) was used to determine the fraction of high temperature (HT) NH$_3$ release of total NH$_3$ release. DSC for measured TG is plotted (green) where exothermic heat transfer is negative.
Figure C.7. Model fit for NH4s thermal stability
### Appendix D: Supporting information for chapter 5

Table D.1. Results from calculations using Visual Minteq software to determine the most thermodynamically feasible mineral precipitates

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formation</th>
<th>Ksp $\times 10^n$</th>
<th>Blank $\text{SI}^*$</th>
<th>Ph$\text{sw}$ $\text{SI}^*$</th>
<th>Ca$\text{sw}$ $\text{SI}^*$</th>
<th>Ph+Ca$\text{sw}$ $\text{SI}^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Struvite</td>
<td>$\text{Mg}^{2+} + \text{H}_2\text{PO}_4^- + \text{NH}_4^+ + 6\text{H}_2\text{O} \leftrightarrow \text{MgNH}_4\text{PO}_4\cdot6\text{H}_2\text{O} + 2\text{H}^+$</td>
<td>$10^{-13.26}$</td>
<td>0.769</td>
<td>0.769</td>
<td>0.727</td>
<td>0.727</td>
</tr>
<tr>
<td>Dittmarite</td>
<td>$\text{Mg}^{2+} + \text{H}_2\text{PO}_4^- + \text{NH}_4^+ + 2\text{H}_2\text{O} \leftrightarrow \text{MgNH}_4\text{PO}_4\cdot\text{H}_2\text{O} + 2\text{H}^+$</td>
<td>$10^{-13.3}$</td>
<td>0.818</td>
<td>0.818</td>
<td>0.775</td>
<td>0.775</td>
</tr>
<tr>
<td>Newberyite</td>
<td>$\text{Mg}^{2+} + \text{H}_2\text{PO}_4^- + 3\text{H}_2\text{O} \leftrightarrow \text{MgHPO}_4\cdot3\text{H}_2\text{O} + \text{H}^+$</td>
<td>$10^{-5.51}$</td>
<td>-0.246</td>
<td>-0.246</td>
<td>-0.288</td>
<td>-0.288</td>
</tr>
<tr>
<td>TMP</td>
<td>$3\text{Mg}^{2+} + 2\text{PO}_4^{3-} \leftrightarrow \text{Mg}_3(\text{PO}_4)_2\cdot8\text{H}_2\text{O}$</td>
<td>$10^{-23.1}$</td>
<td>0.478</td>
<td>0.478</td>
<td>0.399</td>
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<tr>
<td>Bobierrite</td>
<td>$3\text{Mg}^{2+} + 2\text{PO}_4^{3-} + 8\text{H}_2\text{O} \leftrightarrow \text{Mg}_3(\text{PO}_4)_2\cdot8\text{H}_2\text{O}$</td>
<td>$10^{-25.2}$</td>
<td>N/A</td>
<td>N/A</td>
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<td>N/A</td>
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<td>HAP</td>
<td>$5\text{Ca}^{2+} + 3\text{PO}_4^{3-} + \text{OH}^- \leftrightarrow \text{Ca}_5(\text{PO}_4)_3\text{OH}$</td>
<td>$10^{-116.8}$</td>
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<td>-</td>
<td>15.466</td>
<td>15.466</td>
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<tr>
<td>β-TCP</td>
<td>$3\text{Ca}^{2+} + 2\text{PO}_4^{3-} \leftrightarrow \text{Ca}_3(\text{PO}_4)_2$</td>
<td>$10^{-28.9}$</td>
<td>-</td>
<td>-</td>
<td>5.103</td>
<td>5.103</td>
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<tr>
<td>OCP</td>
<td>$8\text{Ca}^{2+} + 6\text{HPO}_4^{2-} + 5\text{H}_2\text{O} \leftrightarrow \text{Ca}_8\text{H}_2(\text{PO}_4)_6\cdot5\text{H}_2\text{O} + 4\text{H}^+$</td>
<td>$10^{-96}$</td>
<td>-</td>
<td>-</td>
<td>5.358</td>
<td>5.358</td>
</tr>
<tr>
<td>DCPD</td>
<td>$\text{Ca}^{2+} + \text{HPO}_4^{2-} + 2\text{H}_2\text{O} \leftrightarrow \text{CaHPO}_4\cdot2\text{H}_2\text{O}$</td>
<td>$10^{-5.9}$</td>
<td>-</td>
<td>-</td>
<td>0.222</td>
<td>0.222</td>
</tr>
<tr>
<td>DCPA</td>
<td>$\text{Ca}^{2+} + \text{HPO}_4^{2-} \leftrightarrow \text{CaHPO}_4$</td>
<td>$10^{-5.59}$</td>
<td>-</td>
<td>-</td>
<td>0.506</td>
<td>0.506</td>
</tr>
</tbody>
</table>

$^*$SI = log (IAP/Ksp) was estimated using Visual Minteq where IAP is ion activity product
Theoretical expansion on the development of the constant composition approach

A constant composition approach to model struvite formation Eq. 1) is depicted below, according to work published by Wei L. et al.\textsuperscript{77}, Kofina, A. et al.\textsuperscript{240} and Tomson M. B. et al.\textsuperscript{257}

\begin{equation}
\text{Mg}^{2+} (aq) + \text{H}_2\text{PO}_4^{-} (aq) + \text{NH}_4^{+} (aq) \leftrightarrow \text{MgNH}_4\text{PO}_4\cdot6\text{H}_2\text{O} + 2\text{H}^{+} (aq) \quad (\text{Eq. 5.1})
\end{equation}

At a constant composition the change in pH is proportional to the change in struvite solid being formed ($dm$) and the change in batch solution volume as the titration solutions are applied ($dV$) as shown in Eq. 2. Solving this differential relation yield a constant (C) for mass of struvite formed as a linear function of struvite components concentration (x), therefore $C \cdot x$ is in effect a proportion constant requirement for the titration solutions.

\begin{equation}
\frac{dpH}{dV} = \frac{dm}{dV} = C \cdot x \quad (\text{Eq. 5.2})
\end{equation}

For mass balance description (eq. 5.3-6), let:

\begin{align*}
\text{Start solutions (x$_i$)} & \quad \text{Titration solutions (y$_i$)} \\
x_1 &= \text{mole L}^{-1} \text{MgCl}_2 & y_1 &= \text{mole L}^{-1} \text{MgCl}_2 \\
x_2 &= \text{mole L}^{-1} \text{NH}_4\text{H}_2\text{PO}_4 & y_2 &= \text{mole L}^{-1} \text{NH}_4\text{H}_2\text{PO}_4 \\
x_3 &= \text{mole L}^{-1} \text{NaOH} & y_3 &= \text{mole L}^{-1} \text{NaOH}
\end{align*}

Solving $y_1$ for $x_1$ will show that at a constant composition ($x_1$ is constant) when only two titration lines with equal application rates are applied:

\begin{equation}
x_1 = \frac{x_1V+y_1dV-dm}{V+2dV} \quad \text{or when rearranged: } y_1 = 2x_1 + \frac{dm}{dV} \rightarrow y_1 = 2x_1 + C \cdot x_1.
\end{equation}

Similarly, $y_2 = 2x_2 + C \cdot x_2$ ; $y_3 = 2C \cdot x_3 - 2x_3$ and the only other constrain is matrix mass balance achieved by supplementing it in double proportions to the NaOH titration solution.

For struvite formation $x_1 = x_2 = x_3$ hence a single x variable is needed,

Titrant 1:
\[ y_1 + y_2 = (2x + C \cdot x) \text{ M MgCl}_2 \cdot 6\text{H}_2\text{O} + (2x + C \cdot x) \text{ M NH}_4\text{H}_2\text{PO}_4 + y \text{ M CaCl}_2 \quad (\text{Eq. 4}) \]

Titrant 2:

\[ y_3 + \text{matrix} = 0.2 \text{ M NaCl} + (2C \cdot x - 2x) \text{ M NaOH} + z \text{ M C}_6\text{H}_5\text{OH} \quad (\text{Eq. 5.5}) \]

Finally, matrix considerations for the constant composition system are defined:

\[ x = [\text{Mg}] = [\text{PO}_4] = [\text{NH}_4]; \ y = [\text{Ca}] \text{ treatment}; \ z = [\text{Ph}] \text{ treatment} \quad (\text{Eq. 5.6}) \]

**Figure D.1.** Constant composition reactor components: a. titration pump inlets; b. sample exit tube to 60 mL syringe; c. N\(_2\) submergence inlet and overhead exhaust tube; d. SW under N\(_2\)\(_{(g)}\) atmosphere; e. pH probe; f. PTFE magnetic stirrer.
Figure D.2. Tutorial for constant composition apparatus: D.2.a Apparatus of open source constant composition apparatus. Detailed in figure are the components experimental setup: microcontroller (Top) and pumps + reactor (bottom). The wirings of Raspberry Pi controller function GPIO pins are depicted in details below. For raspberry pi 40-GPIO pins, the above setting was applied. Components of microcontroller were: Atlas Scientific EZO pH; Whitebox Tentacle T3 (signal isolator); DB9 terminal port; CAT-5 wire; MyCodo Software (Open source).

Figure D.2.b Raspberry Pi pinout
Figure D.3. Normalized XRD diffraction (with baseline subtraction) of solid samples collected from constant composition treatments
Figure D.4. Results from XRD collection and analysis a) normalized XRD diffraction patterns for solids collected from 1st replicate (R1) of Blank, Ph_sw, Ca_sw and Ph+Ca_sw treatments and standard minerals diffraction (derived from AMCSD using crystal diffract software) between 5-90 2θ and b) average mineral phase distribution estimated from fundamental parameter refinement of powder XRD scans for replicates R1-3.
Table D.2. Profex software fundamental parameter analysis output

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<tr>
<th>Blank R1</th>
<th>% w/w</th>
<th>ESD</th>
<th>Phθ, R1</th>
<th>% w/w</th>
<th>ESD</th>
<th>Caθ, R1</th>
<th>% w/w</th>
<th>ESD</th>
<th>Ph+Ca, R1</th>
<th>% w/w</th>
<th>ESD</th>
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<td>GoF = 1.05</td>
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<td>GoF = 1.3622</td>
<td>Rwp = 18.92</td>
<td>χ² = 1.30</td>
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<td>Rwp = 15.37</td>
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<table>
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<th>Phθ, R2</th>
<th>% w/w</th>
<th>ESD</th>
<th>Caθ, R2</th>
<th>% w/w</th>
<th>ESD</th>
<th>Ph+Ca, R2</th>
<th>% w/w</th>
<th>ESD</th>
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<td>0.8</td>
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<td></td>
<td></td>
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<td></td>
<td></td>
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<td>4.7</td>
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<td>DCPA</td>
<td>3.9</td>
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</tr>
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<td>DCPD</td>
<td></td>
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<td>DCPD</td>
<td></td>
<td></td>
<td>DCPD</td>
<td>1.2</td>
<td>0.6</td>
<td>DCPD</td>
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<td>0.2</td>
</tr>
<tr>
<td>Rwp = 13.27</td>
<td>χ² = 1.11</td>
<td>GoF = 1.05</td>
<td>Rwp = 19.80</td>
<td>χ² = 2.06</td>
<td>GoF = 1.43</td>
<td>Rwp = 9.89</td>
<td>χ² = 0.37</td>
<td>GoF = 0.61</td>
<td>Rwp = 19.38</td>
<td>χ² = 1.74</td>
<td>GoF = 1.32</td>
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<tr>
<th>Blank R3</th>
<th>% w/w</th>
<th>ESD</th>
<th>Phθ, R3</th>
<th>% w/w</th>
<th>ESD</th>
<th>Caθ, R3</th>
<th>% w/w</th>
<th>ESD</th>
<th>Ph+Ca, R3</th>
<th>% w/w</th>
<th>ESD</th>
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</thead>
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<td>Struvite</td>
<td>5</td>
<td>1</td>
<td>Struvite</td>
<td>2.3</td>
<td>0.5</td>
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<td>Newberyite</td>
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<td>Newberyite</td>
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<td>0.4</td>
<td>Bobierrite</td>
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<td>0.2</td>
<td>Bobierrite</td>
<td>4</td>
<td>0.7</td>
<td>Bobierrite</td>
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<td>0.2</td>
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<td>HAP</td>
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<td>16</td>
<td>2</td>
<td>HAP</td>
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</tr>
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<td>β-TCP</td>
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<td>β-TCP</td>
<td></td>
<td></td>
<td>β-TCP</td>
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<td>0.9</td>
<td>β-TCP</td>
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<td>0.2</td>
</tr>
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<td>OCP</td>
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<td>OCP</td>
<td></td>
<td></td>
<td>OCP</td>
<td>16</td>
<td>2</td>
<td>OCP</td>
<td>1.8</td>
<td>0.4</td>
</tr>
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<td>DCPA</td>
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<td>DCPA</td>
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<td>DCPD</td>
<td></td>
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<td>DCPD</td>
<td>2.8</td>
<td>0.7</td>
<td>DCPD</td>
<td>0.9</td>
<td>0.2</td>
</tr>
<tr>
<td>Rwp = 15.75</td>
<td>χ² = 1.47</td>
<td>GoF = 1.21</td>
<td>Rwp = 17.08</td>
<td>χ² = 1.4326</td>
<td>GoF = 1.196</td>
<td>Rwp = 8.29</td>
<td>χ² = 0.27</td>
<td>GoF = 0.52</td>
<td>Rwp = 12.64</td>
<td>χ² = 0.72</td>
<td>GoF = 0.85</td>
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</table>
Table D.3. Elemental composition for minerals found in solid samples

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>Element (% w/w)</th>
<th>Mg</th>
<th>N</th>
<th>H</th>
<th>P</th>
<th>O</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>Struvite</td>
<td>MgNH₄PO₄·6H₂O</td>
<td></td>
<td>9.9</td>
<td>5.7</td>
<td>6.6</td>
<td>12.6</td>
<td>65.2</td>
<td></td>
</tr>
<tr>
<td>Newberyite</td>
<td>MgHPO₄·3H₂O</td>
<td></td>
<td>13.9</td>
<td>4</td>
<td>17.8</td>
<td>64.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TMP</td>
<td>Mg₃(PO₄)₂</td>
<td></td>
<td>27.7</td>
<td></td>
<td></td>
<td>23.6</td>
<td>48.6</td>
<td></td>
</tr>
<tr>
<td>Bobierrite</td>
<td>Mg₃(PO₄)₂·8H₂O</td>
<td></td>
<td>17.9</td>
<td>4</td>
<td>62.9</td>
<td>15.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HAP</td>
<td>Ca₅(PO₄)₃·OH</td>
<td></td>
<td>18.5</td>
<td></td>
<td></td>
<td>41.4</td>
<td>39.9</td>
<td></td>
</tr>
<tr>
<td>β-TCP</td>
<td>Ca₃(PO₄)₂</td>
<td></td>
<td>20</td>
<td></td>
<td></td>
<td>41.3</td>
<td>38.8</td>
<td></td>
</tr>
<tr>
<td>OCP</td>
<td>Ca₈H₂(PO₄)₆·5H₂O</td>
<td></td>
<td>18.9</td>
<td></td>
<td></td>
<td>47.2</td>
<td>32.6</td>
<td></td>
</tr>
<tr>
<td>DCPA</td>
<td>CaHPO₄·2H₂O</td>
<td></td>
<td>22.8</td>
<td></td>
<td></td>
<td>47</td>
<td>29.5</td>
<td></td>
</tr>
<tr>
<td>DCPD</td>
<td>CaHPO₄·2H₂O</td>
<td></td>
<td>31</td>
<td>16</td>
<td></td>
<td>40.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure D.5. Logged titration ‘On’ time and pH for constant composition treatments
Logged titration ‘On’ time and pH for constant composition treatments. Titration data for constant composition showing the frequency of titration pumps 2+’On’ period applying solution T2, T3 for replicates R1-3 for SW treatments with corresponding pH change over time (0-120 min).
Figure D.6. Derived time of nucleation for constant composition treatments
### Table D.4. Estimated time of nucleation and growth rate calculation

<table>
<thead>
<tr>
<th>Treatment</th>
<th>N</th>
<th>Nucleation duration time (h: min: s)</th>
<th>Average titration rate (mL min(^{-1}))</th>
<th>average titration rate (mL min(^{-1})) (standard deviation)</th>
<th>Applied titration (10^6 µM)</th>
<th>Struvite precipitation (µmol struvite min(^{-1}) L(^{-1})) (standard deviation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>R1</td>
<td>0:05:10</td>
<td>0.0081</td>
<td>0.039 (0.027)</td>
<td></td>
<td>5.8 (4.0)</td>
</tr>
<tr>
<td></td>
<td>R2</td>
<td>0:03:28</td>
<td>0.0509</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>R3</td>
<td>0:04:31</td>
<td>0.0585</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ph(_{sw})</td>
<td>R1</td>
<td>0:01:49</td>
<td>0.2012</td>
<td>0.346 (0.162)</td>
<td>0.148</td>
<td>51.3 (24.0)</td>
</tr>
<tr>
<td></td>
<td>R2</td>
<td>0:02:54</td>
<td>0.3165</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>R3</td>
<td>0:03:29</td>
<td>0.5217</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca(_{sw})</td>
<td>R1</td>
<td>0:00:45</td>
<td>0.0139</td>
<td>0.018 (0.012)</td>
<td></td>
<td>2.7 (1.8)</td>
</tr>
<tr>
<td></td>
<td>R2</td>
<td>0:00:48</td>
<td>0.0320</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>R3</td>
<td>0:00:35</td>
<td>0.0096</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ph+Ca(_{sw})</td>
<td>R1</td>
<td>0:01:06</td>
<td>0.1456</td>
<td>0.206 (0.114)</td>
<td></td>
<td>30.5 (16.9)</td>
</tr>
<tr>
<td></td>
<td>R2</td>
<td>0:01:53</td>
<td>0.1348</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>R3</td>
<td>0:01:39</td>
<td>0.3382</td>
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<td></td>
</tr>
</tbody>
</table>

Average precipitation (µmol-struvite min\(^{-1}\) L\(^{-1}\)) was calculated as the average titration rate (mL min\(^{-1}\)) x molarity of applied Mg\(^{2+}\); NH\(_{4}^{+}\); PO\(_{4}^{3-}\)\(_{aq}\) = 0.148 x10\(^{6}\) µM.
b: Methodology example
Average rate of titration was derived from datalogger output, as listed below in calculation example for Blank treatment R2:

- Total count of titration T2+T3 pump Off signals = 1
- Total count of overall titration T2+T3 pumps signals = 8351
- Total count of titration T2+T3 pump Off signals: 8351-7494 = 857
- Frequency of titration T2+T3 pump Off signals (s⁻¹) = 1
- Total seconds of titration T2 +T3 solutions = 857
- Total min T3+T2 On = 14.283
- mL T3 ; T2 (Flow rate titration was 0.5 mL min⁻¹) = 7.142
- Duration of Blank R1 replicate constant composition treatment from end of nucleation to end of run (min) = 140.25
- Average titration rate for Blank R2 (mL T3; T2 min⁻¹) = 0.0509

Figure D.7. Experimental results for Ph and other low molecular weight (LMW) organics sorption by struvite. Struvite was either precipitating (CoP) or equilibrated as sorbent (Ads) for 24 h at 15 mM struvite components (3 g L⁻¹; SI ~2.5) in SW of 0.1 M NaCl, 5 mM Ca and 0.1 mM LMW (7-15 ppm). No significant removal from solution was observed for all LMW comparing to a sorbent free control. For each LMW type (Benzensulfonamine, Phenol, Benzoate, Benzylamine) treatment R (SW with struvite) was compared to C (struvite free control), n=3. Analysis was done with HPLC (UVvis or MS)
Figure D.8 STA-EGA analysis are shown as: a. Thermogravimetric (TG) mass loss over analysis temperature range 25-600 °C, b. Overall IR absorbance signal as Gram-Schmidt orthogonalization curve, c. differential scanning calorimetry (DSC) as mW mg\(^{-1}\) over temperature
Figure E.1 Constant composition apparatus: a. syringe pump (HarvardApparatus) connected to SBC was used to apply titration solutions (T2, T3) using two 140 mL HDPE syringes with 0.45 µm PES filters. b. sampling tube for SWW solution. c. Inflow of N₂ flux. d. 1000-2000 mL operation SWW volume in constant composition reactor. f. PTFE magnetic stirrer. e. pH probe

Table E.1 Thermodynamically favorable mineral phases for SWW model solution

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formation</th>
<th>Ksp</th>
<th>SI*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Struvite</td>
<td>( \text{Mg}^{2+} + \text{H}_2\text{PO}_4^- + \text{NH}_4^+ + 6\text{H}_2\text{O} \leftrightarrow \text{MgNH}_4\text{PO}_4\cdot6\text{H}_2\text{O} + 2\text{H}^+ )</td>
<td>10^{-13.26}</td>
<td>0.769</td>
</tr>
<tr>
<td>Dittmarite</td>
<td>( \text{Mg}^{2+} + \text{H}_2\text{PO}_4^- + \text{NH}_4^+ + \text{H}_2\text{O} \leftrightarrow \text{MgNH}_4\text{PO}_4\cdot\text{H}_2\text{O} + 2\text{H}^+ )</td>
<td>10^{-13.3}</td>
<td>0.818</td>
</tr>
<tr>
<td>Newberyite</td>
<td>( \text{Mg}^{2+} + \text{H}_2\text{PO}_4^- + 3\text{H}_2\text{O} \leftrightarrow \text{MgHPO}_4\cdot3\text{H}_2\text{O} + \text{H}^+ )</td>
<td>10^{-5.51}</td>
<td>-0.246</td>
</tr>
<tr>
<td>TMP</td>
<td>( 3\text{Mg}^{2+} + 2\text{PO}_4^{3-} \leftrightarrow \text{Mg}_3(\text{PO}_4)_2 )</td>
<td>10^{-23.1}</td>
<td>0.478</td>
</tr>
<tr>
<td>Bobierrite</td>
<td>( 3\text{Mg}^{2+} + 2\text{PO}_4^{3-} + 8\text{H}_2\text{O} \leftrightarrow \text{Mg}_3(\text{PO}_4)_2\cdot8\text{H}_2\text{O} )</td>
<td>10^{-25.2}</td>
<td>N/A</td>
</tr>
</tbody>
</table>

*estimated SI calculated using visual minteq 3.1 software
Figure E.2. constant composition reactor titration log of pH and titration (GPIO on =1) duration over time (s) for replicates (R1-3) of SWW LMW treatments done in constant composition reactor.
Figure E.3 mineral phase analyses
Figure E.4. Characteristics of crystal deformation occurring in SWW with LWE
Figure E.5. Evaluation of precipitation rate via linear regression fit (Origin-lab pro)
Appendix F: Supporting information to chapter 7

Figure F.1. Batch reactor apparatus for CM pretreatment used a 1000 mL borosilicate reactor was placed in a 2000 mL water bath set at 65 ºC yielding a constant 30-38 ºC reactor temperature. Each reactor had a 0-1.5 L min\(^{-1}\) air flow regulator and air frit. A 2 inch magnetic stirrer was used to agitate the slurry at 125 rpm.

Figure F.2. Flow through apparatus for microbial treatment components: A. Homogenized CM was passed through a dual action waste processor (A.1) then placed within a 220 L HDPE drum with a geotextile liner (A.2), B. Press for effluent collection from CM slurry, C. Flow through reactor apparatus with peristaltic pump transfer from CM slurry collector (C.1) by application of experiment microcontroller (C.2) into a 14-L bench scale aerated-FBR (C.3)
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