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A LABORATORY STUDY OF STRUVITE PRECIPITATION FOR PHOSPHORUS
REMOVAL FROM CONCENTRATED ANIMAL FEEDING OPERATION
WASTEWATER

by

SUSHMITA DHAKAL

A THESIS

Presented to the Faculty of the Graduate School of the

UNIVERSITY OF MISSOURI-ROLLA

In Partial Fulfillment of the Requirements for the Degree

MASTER OF SCIENCE IN CIVIL ENGINEERING

2008

Approved by

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PUBLICATION THESIS OPTION

The body of this thesis has been prepared in the format in order to submit to Journal of Environmental Engineering as a journal article. Pages 14-39 have been submitted to Journal of Environmental Engineering for publication.

Page 1-13, 40-42 and appendices A, B, C, D, E, F, G, H, and I have been added for purposes normal to thesis writing.

ABSTRACT

Struvite precipitation occurs spontaneously in many wastewater treatment facilities as a nuisance. However, struvite precipitation is now being studied as a method to concurrently treat high phosphorus wastewaters and generate a valuable product. Many factors influence the precipitation of struvite such as component –ion molar ratios, pH, aeration, solubility, solids and mixing energy. In the present work, struvite precipitation in the actual swine wastewater was studied by strategically controlling aeration, pH, and mixing. Aeration alone was used to increase pH to initiate precipitation and decrease the necessary base addition. Laboratory experiments were conducted by varying pH values, to determine the optimal pH value at which maximum removal of phosphorus could be attained in real wastewater under expected conditions. The effect of organic solids in the wastewater has also been studied. Results show that there is no significant interference of solids in the precipitation of struvite and that aeration can be valuable in struvite precipitation in real wastewater. High concentrations of phosphorus observed in livestock wastewater lagoons can be treated to much lower levels, and phosphorus can be recovered.

KEYWORDS

Struvite, solubility, solids, mixing energy, aeration, phosphorus removal.

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TABLE OF CONTENTS

	Page
PUBLICATION THESIS OPTION.....	iii
ABSTRACT.....	iv
ACKNOWLEDGMENTS	v
LIST OF ILLUSTRATIONS.....	ix
LIST OF TABLES	x
 SECTION	
1. REVIEW OF LITERATURE	1
1.1. INTRODUCTION TO PHOSPHORUS IN THE ENVIRONMENT.....	1
1.1.1. Applications of phosphorus in agriculture.....	1
1.1.2. Applications of phosphorus in animal feeding.....	1
1.1.3. Sources of phosphorus in US streams.....	2
1.1.3.1. Industry.....	2
1.1.3.2. Livestock.....	3
1.1.3.3. Human source.....	4
1.1.3.4. Fertilizers.....	4
1.2. IMPACTS OF EXCESSIVE PHOSPHORUS IN WATER STREAMS.....	5
1.3. RECOVERY OF PHOSPHORUS.....	6
1.4 COMPARISON OF PHOSPHORUS REMOVAL TECHNIQUES	6
1.5. STRUVITE FORMATION	9
2. GOAL AND OBJECTIVES	12

PAPER

A LABORATORY STUDY OF STRUVITE PRECIPITATION FOR PHOSPHORUS REMOVAL FROM CAFO WASTEWATER.....	14
ABSTRACT.....	14
INTRODUCTION.....	15
Formation and use of struvite	16
Solids.....	20
MATERIALS AND METHODS.....	21
Lagoon characteristics and mixing	21
Wastewater collection, analysis and aeration	22
Struvite precipitation experiments	22
Organic solids impacts.....	24
Analytic methods	25
RESULTS AND DISCUSSIONS.....	26
Lagoon data and description	26
Mixing and aeration	28
Flow-Through struvite reactor.....	30
Effect of solids on struvite precipitation.....	32
Crystal formation of struvite.....	33
CONCLUSIONS.....	35
ACKNOWLEDGEMENTS.....	36
REFERENCES.....	38
SECTION	
3. CONCLUSIONS AND RECOMMENDATIONS	40

3.1. CONCLUSIONS.....	40
3.2. RECOMMENDATIONS.....	41
APPENDICES	
A. PHOSPHATE ANALYSIS USING HACH METHOD 8178.....	43
B. AMMONIA ANALYSIS USING HACH METHOD 10031	46
C. COD ANALYSIS USING HACH METHOD 8000	50
D. TS AND TSS ANALYSES	54
E. EFFLUENT PHOSPHATE CONCENTRATION AT DIFFERENT pH	57
F. PERCENT REMOVAL OF PHOSPHATE AT DIFFERENT pH.....	65
G. SCHEMATIC OF THE ANAEROBIC LAGOON AND SAMPLING STES.....	73
H. CHARACTERISTICS OF THE ANAEROBIC LAGOON.....	75
I. SEM IMAGE OF DEPOSIT AT DIFFERENT REACTOR CONDITIONS	77
BIBLIOGRAPHY.....	83
VITA.....	86

LIST OF ILLUSTRATIONS

Figure	Page
SECTION	
1.1. Sources of phosphorus in US streams.....	3
PAPER	
1. Component- ion concentration in effluent of solution.....	19
2. Mixing pattern and lagoon profile for the anaerobic swine waste lagoon.....	21
3. Schematics of struvite crystallization reactor.	23
4. Scanning electron microscopy image of deposit formed at the mixer installed in the anaerobic lagoon.....	27
5. Percent removal of phosphate from synthetic wastewater percentage at various operation times and mixing intensities in a Batch Reactor.....	28
6. Aeration impacts on pH of the swine wastewater versus times.....	29
7. Phosphate concentration of swine wastewater in the struvite reactor at various operation times and pH.....	30
8. Phosphate concentration of swine wastewater in the struvite reactor at different pH with standard errors.....	31
9. Phosphate concentration of synthetic wastewater at various solids in a batch reactor..	33
10. Scanning electron microscopy image of crystals of synthetic wastewater formed under G value of 76 s^{-1} in a batch reactor.....	34
11. Scanning electron microscopy image of crystals of swine wastewater formed in the struvite reactor at pH 8.7.....	35

LIST OF TABLES

Table	Page
SECTION	
1. Summary of phosphorus removal technologies.....	7
2. Summary of phosphorus recovery technologies.....	8
PAPER	
1. pH of minimum struvite solubility.....	18
2. Initial concentrations and molar ratios of four major ions in synthetic wastewater solution.....	25
3. pH and phosphate concentrations of the anaerobic lagoon.....	26

SECTION

1. REVIEW OF LITERATURE

1.1. INTRODUCTION TO PHOSPHORUS IN THE ENVIRONMENT

Phosphorus is problematic in many surface waters due to overuse and mismanagement in many areas of our society. To better understand these issues, the use of phosphorus and the pollution problems associated with this use are discussed.

1.1.1. Applications of phosphorus in agriculture. Agriculture is important to Missouri and to maintain the fertility of soil, phosphorus is applied as a fertilizer and sometimes in the form of manure (Burns, et al., 2002). Phosphorus is one of the three major plant nutrients in inorganic fertilizers; the other two are nitrogen and potassium (ICM, 2000). To maximize crop production, these elements are often applied in excess.

1.1.2. Applications of phosphorus in animal feeding. Phosphorus is one of the vital elements needed for animal growth and milk production. The functions include in metabolic activities in soft tissues, the maintenance of appetite, optimal growth, fertility, bone development and the prevention of bone diseases. The daily nutritional requirements for dairy cattle and beef cattle have been stated as 86-95 g/day and 35-40 g/day respectively (CEEP, 2003). The mechanisms of phosphorus digestion and metabolism differ substantially between ruminant and monogastric animals. In many cases excess phosphorus is used in order to maximize the production of livestock. However, feeding excess phosphorus increases phosphorus levels in animal waste streams. For example, common livestock feedstuffs (such as corn and soy meal) in a swine diet do not

offer high percentages of available phosphorus. Only 14 percent of phosphorus in corn and 31 percent of soybean meal phosphorus can be digested by swine. Because a large percentage of phosphorus is unavailable, much of it is excreted (ICM, 2000). To overcome the limited availability excess phosphorus is fed to animals. The waste stream is therefore very rich in phosphorus.

1.1.3. Sources of phosphorus in US streams. Phosphorus in municipal, industrial, and agricultural wastewater may come from a variety of sources listed below. The Southern Cooperative Series (1998) reports that phosphorus enters the soil solution by the following means: 1) dissolution of primary minerals, 2) dissolution of secondary minerals, 3) desorption of phosphorus from clays, oxides, and minerals, and 4) biological conversion of phosphorus by mineralization. In addition to these soil and livestock sources, other anthropogenic inputs to surface water are substantial and comprise the remaining balance of phosphorus inputs to surface waters. The percentage of each fraction is shown in Figure 1.1. While many sources have been decreased through managed use or treatment in past decades, livestock inputs have actually increased.

1.1.3.1. Industry. The application of phosphorus is wide in many aspects of industries. Phosphorus is used in some softened waters for stabilization of calcium carbonate to eliminate the need of recarbonation (Sawyer et al., 1994). Polyphosphates are also used in public water systems in order to control corrosion as well as in steam power plants to control scaling in the boilers. If complex phosphates are used, phosphates rapidly hydrolyze to orthophosphate at high temperatures involved (Sawyer et al., 1994).

Many industries release high phosphorus concentration wastewater, for example food and dairy processing, and other processes use phosphorus, phosphoric acid or phosphates also contribute.

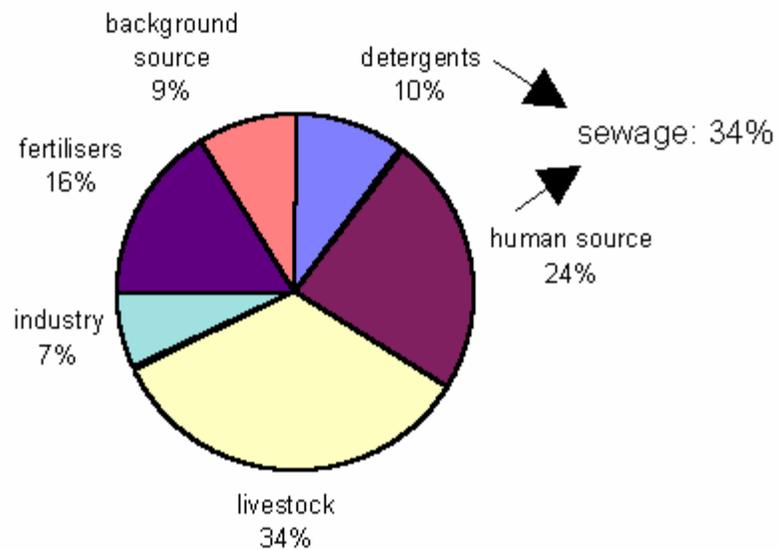


Figure 1.1. Sources of phosphorus in US streams (CEEP, 2003).

1.1.3.2. Livestock. Phosphorus is an essential element required for livestock. Animal feeding operations can provide a significant source of nutrients for crops through manure. The manure produced from the livestock is applied to the land, and often the ratio of nitrogen to phosphorus is unbalanced in a manure thus causing over-application of phosphorus to the land. However, supplying manure that is nutrient-balanced for nitrogen and phosphorus requires reducing the phosphorus content of manure, without

compromising the performance of the livestock (ICM, 2000). In the waters of Missouri, swine production facilities are the largest contributor of phosphorus amongst agricultural sources, which overall comprise the biggest source of fugitive phosphorus. The increasing productions of livestock, swine in particular in Missouri are problematic issues for the quality of water.

1.1.3.3. Human source. After elimination of phosphate – based detergents in the 1980s, much of the inorganic phosphorus is now contributed by human wastes as a result of the metabolic breakdown of proteins and elimination of the liberated phosphates in the urine. The amount of phosphorus released is a function of protein intake. An average person in United States releases 1.5 g/day of phosphorus (CEEP, 2003). The per capital contribution from human populations, after sewage treatment, was estimated at 0.62 kg total phosphorus/person/year in Morse et al., 1998, whereas, the report presented by CEEP 2007 estimated 0.43 kg total phosphorus/person/year. In a wastewater treatment plant at Metamorphosis, Greece, the average total phosphorus influent value is 30.6 mg/L (Sotirakou et al., 1999). In 1992, Point Loma Wastewater Treatment Plant, City of San Diego discharged 954 mt of total phosphorus (SCCWRP, 1992).

1.1.3.4. Fertilizers. Phosphorus is applied in the land as a fertilizer providing nutrient to the crops. Relative to crop needs, manure slurries contain higher levels of phosphorus than nitrogen, thus the phosphorus is over applied to meet crop nitrogen needs (Burns et al., 2002). Phosphate is extracted from rocks containing apatite. Phosphate fertilizers are produced by adding sulfuric acid to the phosphate rock which is

16 – 21 % as phosphorus pentoxide (Pollution Prevention and Abatement Handbook, 1998). Part of phosphorus applied to the land is taken up by the crops and is accumulated in them, whereas, the remaining fraction of phosphorus dissolves in the rain and can be transported to the nearby water body or infiltrates in to the groundwater (ICM, 2000).

1.2. IMPACTS OF EXCESSIVE PHOSPHORUS IN WATER STREAMS

The threat of livestock waste discharged to the streams is responsible for polluting 150 miles of Missouri's streams and killing hundreds of thousands of fish (American Fisheries Society, 1998). In 1995, spills from nine specific livestock facilities polluted over 56 miles of Missouri streams and killed over 302,000 organisms, including fish (Auckley, 2000). Manure spilled from animal confinement facilities when breaks down in water deplete the oxygen in the water, the ammonia in manure are also toxic to fish and other aquatic life. Phosphorus is also a prominent pollutant, degrading quality as an excess nutrient.

Studies show that eutrophication extends well beyond Missouri's borders, noted as the leading cause of the Gulf of Mexico hypoxia dead zone. The EPA recommends that total phosphorus should not exceed 0.1 mg/L in streams and that total phosphates (as phosphorus) should not exceed 0.05 mg/L in streams where they enter a lake or reservoir (USEPA, 1999). Many phosphorus sources have been attenuated, through the substitution of phosphorus in detergents, changing industrial uses. To further eliminate phosphorus sources to surface waters phosphorus is included on many municipalities' NPDES permits and modifications to wastewater plants have been expensive, running into the billions. The problem however still grows, as the projected 2007 Gulf hypoxic zone

covered the greatest area ever. This problem is also expected to grow, particularly with the increase in demand of corn production to produce ethanol, an alternative transportation fuel source. To increase crop production increases the fertilizer use is expected as more nutrient deficient and more sensitive, erodible land is pressed into corn production. With non-point source increases expected from fertilizer use, improved treatment from other sources is even more necessary.

1.3. RECOVERY OF PHOSPHORUS

Phosphorus is a non-renewal resource and is being mined at an increasing rate to meet the increasing demand of fertilizers necessary for crop production. Removal of phosphorus from wastewater can not only prevent nutrient enrichment of streams, but recovery from the wastewater streams can also lengthen the availability of a finite resource (CEEP, 2003). Precipitation of phosphorus minerals offers combined treatment and recovery of phosphorus, thereby serving dual purposes. First, precipitation efficiently removes high level of phosphorus from the swine wastewater; and second, it produces a recoverable and useful form of phosphorus, which can be further applied in the farm as a fertilizer in a form that requires little processing and expense. This recovery can also generate a sellable product and potentially revenue.

1.4. COMPARISON OF PHOSPHORUS REMOVAL TECHNIQUES

From 1950s, technologies started to develop for removal of phosphorus in response to the issue of eutrophication (Morse et al., 1998). A summary of phosphorus removal techniques is shown in Table 1, and a summary of phosphorus recovery techniques is shown in Table 2.

Table 1. Summary of phosphorus removal technologies adapted, from Morse et al. (1998).

Technology	Objective	Process Summary	Main Input	Auxiliary Inputs	Main Output	P Form/Content
Chemical Precipitation	P Removal	Addition of metal salt to precipitate metal phosphate removed in sludge.	Wastewater (primary, secondary, tertiary, or sidestream)	Fe, Al, Ca May require anionic polymer	Chemical Sludge	Mainly chemically bound as metal phosphate.
Biological Phosphorous Removal	P Removal (may also include N removal)	Luxury uptake of P by bacteria in aerobic stage following anaerobic stage.	Wastewater (primary effluent)	May require external carbon source (e.g. methanol)	Biological Sludge	Phosphorus biologically bound.
Crystallization (DHV Crystalactor™)	P Removal Recovery	Crystallization of calcium phosphate using sand as a seed material.	Wastewater (secondary effluent or sidestream)	Caustic soda/milk of lime, sand; may need sulfuric acid.	Calcium phosphate, sand	Calcium phosphate (40%-50%)
Advanced Chemical Precipitation (HYPRO)	P and N Removal	Crystallization of phosphorous/org anic matter and hydrolysis to give carbon source for N removal.	Wastewater (primary influent)	Poly-aluminum chloride (PAC)	Chemical sludge	Chemical sludge
Ion Exchange (RIM-NUT)	Fertilizer (struvite) Production	Ion exchange removes ammonium and phosphate which are precipitated.	Wastewater (secondary effluent)	H_3PO_4 , $MgCl_2$, $NaCl$, Na_2CO_3 , $NaOH$	Struvite	Phosphate slurry
Magnetic (Smit-Nymegen)	P Removal	Precipitation, magnetite attachment, separation and recovery	Wastewater (secondary effluent)	Lime, magnetite	Primarily calcium phosphate	Calcium phosphate
Phosphorus Adsorbents	P Removal	Adsorption and Separation	Wastewater	NA	No Information	Calcium Phosphate
Tertiary Filtration	Effluent polishing	Filtration	Secondary effluent	Media	Tertiary Sludge	Insoluble Phosphate
Sludge Treatment	Sludge Disposal	e.g. Sludge drying, reaction with cement dust	Sludge	Depends on process	Soil Conditioner	Dry granule, low in P
Recovery from sludge ash	P Recover	Extraction from sludge ash	Sludge ash from biological removal	NA	NA	NA

Table 2. Summary of phosphorus recovery technologies, adapted from Morse et al. (1998).

Technology	Industrial Recovery Value	Agriculture Recovery Value	Technology Advantages	Technology Disadvantages
Chemical Precipitation	Low – P binding to metals prohibits recycling.	Moderate – P availability variable.	Low technology, easy to install, & high P removal.	Chemicals required, variable P recycle ability, & increase in sludge production.
Biological Phosphorous Removal	Moderate – Biologically bound P is recyclable.	Moderate – Biologically bound P is more available.	Chemicals not necessary, removal possible of N & P, recyclable P, & established technology.	Requires more complex technology & difficulty in handling sludge.
Crystallization (DHV Crystalactor™)	Very High – Easily recycled.	Moderate – P availability variable.	Recyclable product and demonstrated technology.	Operation skills and chemicals required.
Advanced Chemical Precipitation (HYPRO)	Low – P binding to metals prohibits recycling.	Moderate – P availability variable.	P & N removal enhanced with part of a complete recycling concept.	Chemicals required & P may be inconvenient for recycling.
Ion Exchange (RIM-NUT)	Moderate – Requires modifications.	High – Struvite is a good slow-release fertilizer.	Removal of P high & struvite produced can be recycled for agricultural use.	Chemicals required and technology is complex.
Magnetic (Smit-Nymegen)	Moderate – Requires modifications.	Low – Unknown agricultural stability.	Removal of P high.	Chemicals required and technology is complex.
Phosphorus Adsorbents	Low	Low	Few chemicals involved & potential for P recovery.	Technology is unproven.
Tertiary Filtration	No potential.	No potential.	Technology is established and easy to use.	No useful product from recovery.
Sludge Treatment	Low – Recycling is difficult.	High – P reusable.	Sludge value is increased.	Chemicals required and technology is complex.
Recovery from sludge ash	High – P leached readily.	Moderate – Possible P reuse.	High concentrations result in potential for P recovery.	Technology is underdeveloped.

Technologies include chemical precipitation, crystallization, and biological phosphorus removal which are most common for phosphorus removal and recovery from wastewater. Studies show that an averaged 0.6 mg/L of total phosphorus in the effluent

can be attained by chemical precipitation that is alum at an average dose of 45 mg/L (Patoczka, 2005). In real wastewater, crystallization can remove 45 mg/L of phosphorus to 6 mg/L of phosphorus within a pH of 8.7 (Wang et al., 2003). Biological phosphorus removal technology can remove 6 mg/L of average influent total phosphorus concentration to 1.5 mg/L of total phosphorus (Park et al., 1997).

Waste stabilization and phosphorus removal may potentially be addressed with low-rate aeration and struvite precipitation in tandem. Struvite has numerous benefits; particularly it's highly stable crystal structure, providing three essential nutrients at sustained low release rates. A viable market value has not developed for struvite so far due to the limited amount produced, and the low cost of fertilizers produced from phosphorus rich mineral rock, which are finite. As resources dwindle and if a struvite generation stream exists, value will increase as struvite is a desired fertilizer. The "waste to product" potential is particularly attractive for struvite overall.

1.5. STRUVITE FORMATION

Struvite or magnesium ammonium phosphate hexahydrate (MAP) is a composition of equimolar concentrations of magnesium, ammonium and phosphate. Struvite precipitation is mostly found in areas of high turbulence, as turbulence releases carbon dioxide increasing the pH of the wastewater. Struvite in wastewater was first found in 1939 (Rawn et al., 1939) and since then struvite is well known for clogging pipes, fouling pumps, aerators, screens, and other equipment (Ohlinger et al., 1998). The formation of struvite scales in a wastewater treatment plants may require further maintenance, de-scaling and replacement of equipment (Benisch et al., 2000). One

promising method of preventing the accumulation of struvite in wastewater treatment plants is to precipitate struvite in a controlled manner to remove and recover high phosphorus concentration. Compared to other precipitates, struvite recovered from real wastewater has the following advantages:

- Low solubility of struvite releasing nutrients at a slower rate compared to other soluble fertilizers (von Münch and Barr, 2001),
- Struvite used as a fertilizer includes low metal content of the product when compared to phosphatic rocks that are mined and supplied to the fertilizer industry (Driver J et al., 1999).
- Application of other nutrients such as N and Mg simultaneously to the plants in ratios beneficial to plant growth.

Struvite is a white crystalline orthorhombic shaped crystal of magnesium, ammonium and phosphorus. The formation of struvite is according to the general reaction shown below



Precipitation of struvite can be influenced by physical and chemical attributes of the wastewater system. At the Los Angeles Hyperion Treatment Works, identified factors that contributed struvite precipitation on the walls of the digested sludge lines are as follows (Borgerding, 1972):

- High surface area to volume ratio from the digester to the sludge lines creating a large area for crystal growth,
- Pipeline roughness, especially at the joints,

- Increase in energy in the pipeline caused by vibration of the sludge screens.

Nucleation and crystal growth are the two chemical stages responsible for the occurrence and development of struvite crystals (Jones, 2002). The nucleation and growth stages are complex phenomenon involving factors including: thermodynamics of liquid-solid equilibrium, phenomena of matter transfer between solid and liquid phases (Jones, 2002), kinetics of reaction (Ohlinger, 1999), and interrelationship of many physico-chemical parameters: pH, mixing energy, supersaturation, and molar ion ratios. Studies have focused upon these phenomena individually in controlled laboratory studies or have evaluated nuisance struvite formation in wastewater facilities, but very little work has looked at promoting struvite in real livestock wastewater for phosphorus removal, and no work has looked at swine waste.

In this study, struvite precipitation in actual swine wastewater was studied by strategically controlling pH and mixing. Different experimental conditions were setup to run a struvite reactor and to find the optimal working parameters for efficient phosphorus removal and recovery. Struvite precipitation is dependent upon pH, mixing and component ions-molar ratio. To evaluate unknown interactions and efficient application aeration to achieve pH control prior to addition of chemicals for pH control, thereby reducing the addition of chemicals was studied as was chemical addition for pH control in a bench-scale reactor. Mixing strength and interference of solids present in the wastewater were also studied in batch experiments.

2. GOAL AND OBJECTIVES

The overall goal of this work was to evaluate efficient struvite precipitation from an anaerobic lagoon treating swine wastewater considering impacts of different factors on the struvite precipitation. To achieve this goal, specific objectives were developed for this research on the CAFO wastewater. These objectives are to:

1. Analyze the physical as well as chemical characteristics of the CAFO wastewater streams. The measures were COD, Total Nitrogen, Total Phosphorus, TS, and TSS.

Hypothesis: The wastewater of CAFO varies in compositions, but important parameters might fall within a practical range. These determined values can be used to create the composition of synthetic wastewater in the research and to design an efficient removal process.

2. Evaluate the effects of aeration on the removal of phosphorus from the wastewater.

Hypothesis: Aeration alone increases pH in the real wastewater by releasing CO₂ and volatile fatty acids, which may lead to removal of phosphorus from the wastewater.

3. Evaluate the impacts of pH on the precipitation of struvite in actual wastewater.

Hypothesis: With the increasing pH, solubility decreases which leads to an increase in precipitation potential from the wastewater, but factors such as competing ions, organic solids, and varying influent pH may impact results previously observed in 'clean solutions'.

4. Study the interference of organic solids and mixing strength in the removal of phosphorus from real and synthetic wastewater.

Hypothesis: Solids of different concentrations in the wastewater can interfere in the growth and settling of struvite precipitates. Optimal mixing strength can lead to higher removal of phosphorus from real and synthetic wastewater.

5. Evaluate the impacts of pH in the formation of crystals of struvite in active precipitation and removal from real wastewater in a bench- scale struvite reactor.

Hypothesis: The impact of pH might also effect induction time where increasing pH lead to a reduction in the induction time. Effectively, solids may still be formed, but if crystal growth is not adequate, removal by sedimentation may not be adequate.

Completing the objectives noted above will certainly lead to new knowledge of the struvite precipitation and phosphorus removal process. This knowledge may lead to achieving the overall goal and potentially to new phosphorus treatment processes at full scale livestock production facilities.

PAPER**A LABORATORY STUDY OF STRUVITE PRECIPITATION FOR
PHOSPHORUS REMOVAL FROM CAFO WASTEWATER**

By Sushmita Dhakal, Joel G. Burken¹

ABSTRACT: Struvite precipitation is being studied as a simple, cost efficient method to remove phosphorus in high-strength wastewater streams. Controlled struvite precipitate can quickly remove phosphorus and concurrently generate a valuable product for the fertilizer industry. Many factors influence the precipitation of struvite such as component-ion molar ratios, pH, temperature, solids, and mixing energy. In the present work, the impact of mixing, aeration and pH adjustment on the precipitation of struvite was studied in actual swine lagoon wastewater. Results show that just aeration and mixing can lead to some phosphorus removal, as was observed in the mixed anaerobic lagoon studied. Laboratory results revealed a wide pH range over which maximum removal of phosphorus could be attained. The effect of solids in the wastewater was also studied, and results show no significant interference of solids removal of phosphorus, but visual inspection raise concerns about crystal propagation to form easily-settled solids.

CE Database subject headings: Phosphorus, struvite, solids, mixing energy, phosphorus removal.

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INTRODUCTION

Livestock production, swine in particular, is a vital commerce for Missouri, ranking in the top five states nationally, and representing over \$7 billion in commerce per year. An unavoidable cost of this commerce is some detriment to the environment. In 1995, spills from nine specific livestock facilities polluted over 56 miles of Missouri streams and killed over 302,000 organisms, including fish (Auckley, 2000). Manure spilled from animal confinement facilities depletes the oxygen in the water, and ammonia in manure is toxic to fish and other aquatic life. In addition to acute problem, eutrophication is a leading water quality concern. Swine production facilities are also the largest contributors to eutrophication amongst agricultural sources, which overall comprise the biggest source of fugitive phosphorus.

Eutrophication extends well beyond Missouri's borders. Agricultural waste from the Midwest is, noted as the leading cause of the Gulf of Mexico hypoxia dead zone. In relation to the dead zone issues, the US EPA (1998) stated "harmful algal bloom may have been responsible for an estimated \$1,000,000,000 in economic losses during the past decade." The Federal Law of Hypoxia in the Gulf of Mexico (P.L 105-383) specifically targeted the cause and initiated investigative studies, which in turn contributed to EPA's Concentrated Animal Feeding Operation (CAFO) Final Rule, aimed at improving waste treatment for point sources. The EPA recommends that total phosphorus should not exceed 0.1 mg/L waste input to streams and that total phosphates (as phosphorus) should not exceed 0.05 mg/L in wastewater streams where they enter a

lake or reservoir (USEPA, 1999). Given the level of concern and scale of agriculture input, improved treatment options are needed.

In addition to being a pollutant, phosphorus is a limited resource and one of today's challenges is considering the increasing demand for food and correspondingly the growing nutrient requirement without depleting phosphate mineral resources. Phosphorus is a non-renewal resource and is being mined at an increasing rate to meet the demand of fertilizer needs in current agricultural practice. U.S phosphate rock production and use dropped to 40-year lows in 2006 owing to a combination of mine and fertilizer plant closures and lower export sales of phosphate fertilizers (U.S.G.S, 2007). The demand for phosphorus is expected to increase both in agriculture and industry. Combined treatment and recovery of phosphorus can be accomplished and serves dual purposes: one, it removes high level of phosphorus from the swine wastewater, and two, it recovers in the form of precipitate which can be used as a fertilizer in a form that requires little processing and effort. Thus, removal of phosphorus from wastewater as a precipitate is not only necessary to prevent nutrient enrichment of streams, but also lengthens the availability of a finite resource (CEEP, 2003).

One promising method of removing phosphorus and preventing the formation of struvite in wastewater treatment plants is to remove struvite by controlled precipitation from high strength waste streams allowing recovery of high level of phosphorus.

Formation and use of struvite

Struvite or magnesium ammonium phosphate hexahydrate (MAP) is a white crystalline orthorhombic shaped crystal of equimolar concentrations of magnesium, ammonium and phosphate. Struvite in wastewater was first found in 1939 (Rawn et al., 1939) and since

then struvite is well known for clogging pipes, fouling pumps, aerators, screens, and other equipment (Ohlinger et al., 1998). The formation stoichiometry of struvite is according to the general reaction shown in equation (1)



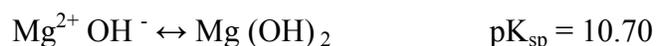
Waste stabilization and phosphorus removal may potentially be addressed with low-rate aeration and struvite precipitation in tandem. Low-rate aeration can aid in overall waste treatment and help to raise pH for struvite precipitation. Struvite has numerous benefits; particularly its highly stable crystal structure, providing three essential nutrients at sustained low release rates. A viable market value has not developed for struvite so far due to the limited amount produced, and the low cost of fertilizers produced from phosphorus rich mineral rock, which are finite. As resources dwindle and if a struvite generation stream exists, value will increase as struvite is a desired fertilizer. The “waste to product” potential is particularly attractive for struvite overall.

Nucleation and crystal growth are the two chemical stages responsible for the occurrence and development of struvite crystals (Jones, 2002). The nucleation and growth stages are complex phenomenon involving factors including: thermodynamics of liquid-solid equilibrium, phenomena of matter transfer between solid and liquid phases (Jones, 2002), kinetics of reaction (Ohlinger, 1999), and interrelationship of many physico-chemical parameters: pH, mixing energy, supersaturation, and molar ion ratios. Aeration of the wastewater can raise the pH and approach the pH values where struvite will form (Wang et al., 2003). The increase in pH by aeration may also reduce the chemical addition needed to reach optimal struvite precipitation. The presence of proper

component-ions is pH dependant and is necessary for struvite formation. The pK_A value for phosphoric acid and ammonium are present in the equations below (Benjamin, 2002):



Whereas, the solubility product for magnesium is present below:



Recent research shows that pH as low as 7.8 can lead to struvite precipitate (Wang et al., 2005). For struvite, number of researchers has published the pH of minimum solubility. It is well known that struvite solubility is a function of pH and a number of pH values have been suggested as the pH of minimum struvite solubility, Table1.

Table 1. pH of minimum struvite solubility, adapted from Doyle et al.(2002)

pH values	References
9.0	(Buchanan et al., 1994)
8.0-10.6	(Momberg and Oellermann, 1992)
9-9.4	(Booker et al., 1999)
10.3	(Booram et al., 1975)
10.3	(Ohlinger et al., 1998)
10.7	(Stumm and Morgan, 1970)
7.8	(Wang, 2005)

A solubility product may be calculated from the total molar concentrations of ions in solution, or can also take into account the ionic strength and the ion activity, which

will go on to form struvite from a specific solution (Doyle, et al., 2002). Numerous researchers have studied the solubility product. Published values range from 12.60 to 13.26 (Stumm and Morgan, 1970; Aage et al., 1997; and Ohlinger et al., 1998). The concentration at equilibrium can be calculated for different ion ratios in the real wastewater and the pH of reaction in a precipitation reaction. In recent work, this approach was used to model the equilibrium concentration of component- ions and also calcium a competing ion in precipitating hydroxyapatite, Figure 1.

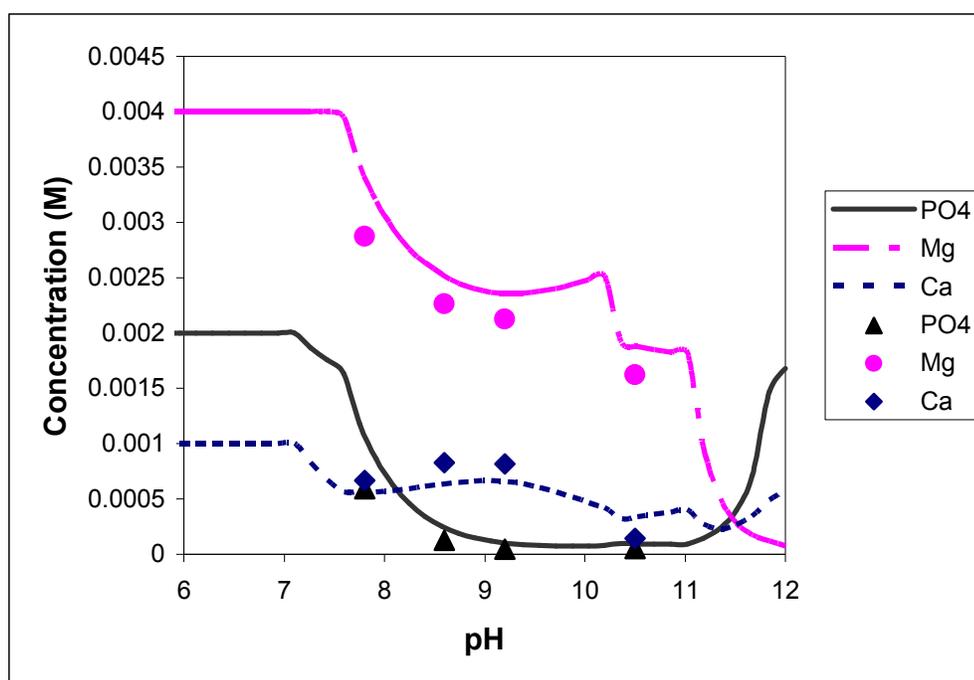


Figure1. Component-ion concentration in effluent of solution (Mg: Ca: PO₄: NH₄=2:0.5:1:20, points represent experimental results, lines represent model predictions) (Wang et al., 2005).

Four operational pH values of 7.8, 8.7, 9.2, and 10.5 were used to validate the equilibrium model. Figure 1 shows that pH as low as 7.8 can also lead to struvite precipitation, and at higher pH improved phosphate removal is achieved. While, the model results show that pH higher than 11 declines the phosphate removal efficiency, likely due to formation of $\text{Mg}(\text{OH})_2$ and its low solubility.

Mixing strength is also an important factor contributing struvite formation. Although pH and component ion molar ratios maybe appropriate, precipitation may cease before reaching equilibrium because poorly crystallized or amorphous precipitates forms initially, resulting in increased solubilities (Wang et al., 2003). Previous research conducted showed that larger crystals ($\sim 400\mu\text{m}$) require a considerable length of time to grow, generally in the order of days and weeks (Durrant et al., 1999). Other research revealed an optimal mixing strength where crystal growth was rapid and shearing of large crystals was low (Wang et al., 2005). Thus, mixing strength also governs the formation of crystals and efficient removable of phosphorus by sedimentation of the crystals.

Solids

Organic solids may interfere with the efficiency of crystal growth and also cause lower settling velocities and removal rates. Solids present in the wastewater solution have impacts as well as benefits on the growth of the struvite crystals. On one hand, suspended solids might provide an embryo- the first stage of formation of crystals and enhance the precipitation of struvite (Corre et al., 2005). On the other hand, solids present in the solution as impurities from which a compound precipitate might affect the growth rate of the struvite crystals by blocking the active growth sites inhibiting the increase of crystal size (Corre et al., 2005). The organic solids serving in nucleation or incorporating into the

crystals are generally of a much lower density and can settle much slower. Efficient removal of phosphorus by struvite precipitation is based largely on the ability to settle and collect the struvite crystals relatively free from degradable organic solids.

MATERIALS AND METHODS

Lagoon characteristics and mixing

A low rate mixer was installed on 8/20/2003 at a 0.75 acre anaerobic lagoon that receives raw swine waste in central Missouri. The low rate mixer is a two horse power mixer, Aerobisizer surface mixer/aerator (Lagoon Resolutions, Lexington, Nebraska), Figure 2. The mixer provides gently mixing, bringing lagoon slurry to the surface for passive aeration. Slurry is not mixed into the atmosphere for air entrainment.

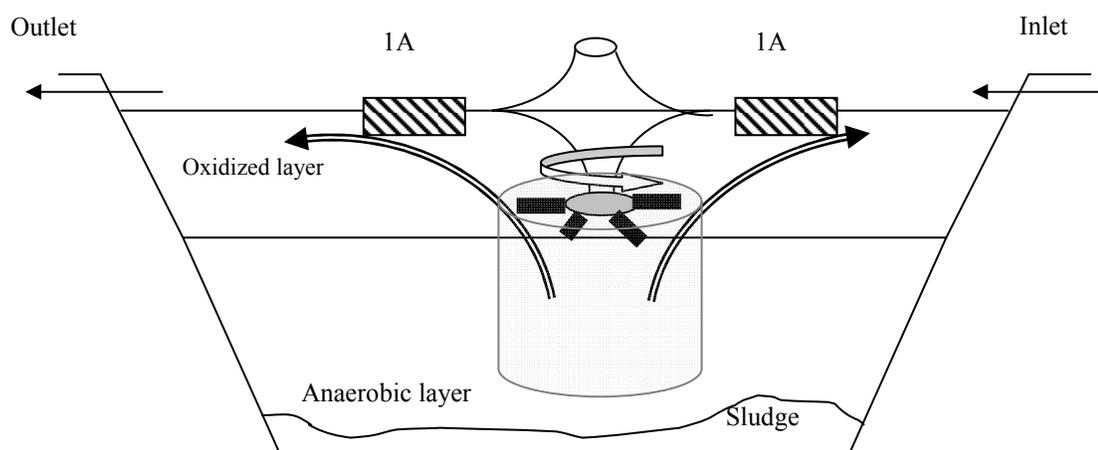


Figure 2. Mixing pattern and lagoon profile for the anaerobic swine waste lagoon.

Wastewater collection, analysis and aeration

Aqueous samples were collected from a 16' aluminum boat and direct measurements of pH, ORP, DO, and conductivity at several locations close to and at 6 m distant from the mixer and from the surface to a depth that ranges from 2.1 to 3.4 m were performed. A Water Analyzer (Cole Parmer, Vernon Hills, IL) equipped with sensors and probes were used to measure pH, ORP, DO, and conductivity. Following observation of crystals, suspected to be struvite, on the securing ropes and the mixer itself, materials of various compositions (PVC, aluminum, and galvanized iron) were placed on the securing ropes to measure any struvite further crystallization. Aqueous samples were collected and returned to the UMR laboratory on ice and analyzed for SCOD (soluble Chemical Oxygen Demand), ammonia-N, phosphate, and solid concentrations. Before analysis other than solids analysis, samples were filtered through a 0.45 μm syringe filter. SCOD was measured by using HACH Method 8000 (Hach, Loveland, CO). Ammonia-N and phosphate were analyzed using Method 10031 and Method 8178, respectively. Total solids (TS) and volatile solids (VS) were measured by using standard methods.

In laboratory studies, the initial concentration of phosphate was maintained at 2 mM for experimental purposes with ammonium phosphate monobasic by addition or dilution with DI water depending on the current concentration in the swine wastewater. To evaluate the pH effects of aeration, air was bubbled into 300 mL solution using a diffuser at 0.12 L/min, and pH was recorded over 60 minutes.

Struvite precipitation experiments

For each laboratory experiment, 38 liters of lagoon waste was collected from the anaerobic lagoon treating swine wastes, and aeration testing was completed as noted. The

struvite crystallization reactor is a clear PVC 0.9 m tall reactor with an effective volume of 5.75 L. A schematic of the reactor is shown in Figure 3. The phosphate levels in the reactor were maintained in the reactor as mentioned above. Reactions take place in the upflow reactor and form crystals. The crystals can collide with each other and grow to form larger particles. In the internal column, the larger particles can settle at a faster rate than the up flow velocity and do not remain in suspension. The settled particles are then collected from the bottom of the reactor.

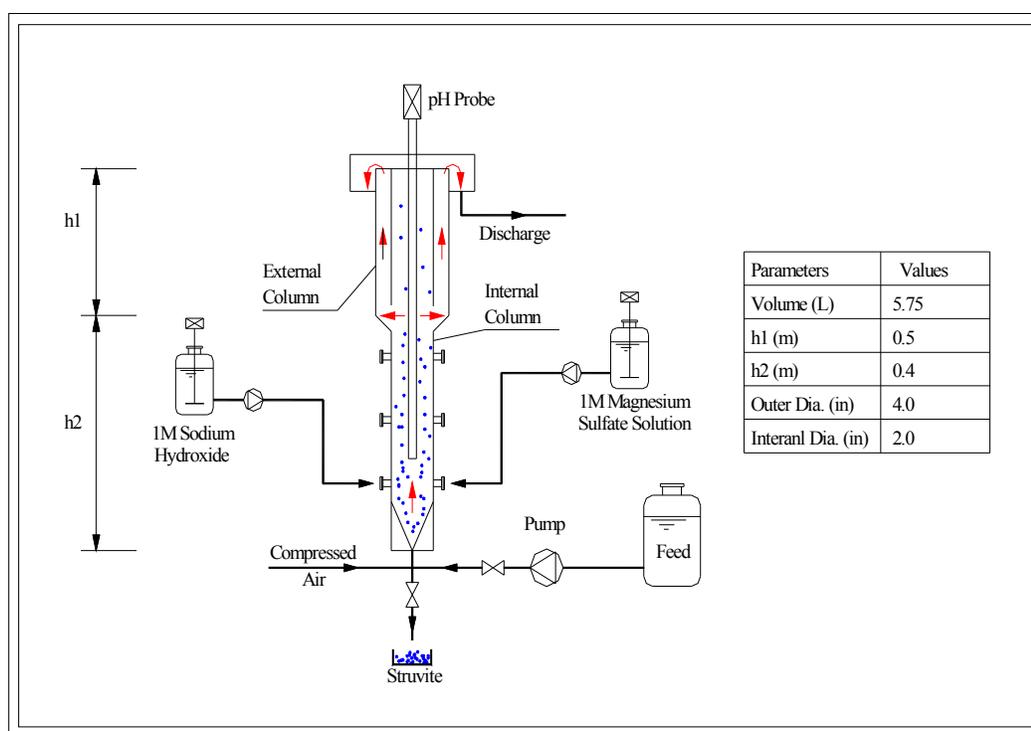


Figure. 3. Schematics of struvite crystallization reactor.

Swine wastewater is fed into the reactor from the bottom at 20 mL/min. A calibrated Orion 230 plus digital pH meter was placed from the top of the reactor to monitor the pH values of the wastewater. Magnesium sulfate was maintained at 4 mM concentration for uniform input and was fed in to the reactor. Compressed air was bubbled at 0.5 L/min in to the reactor to provide mixing. pH was controlled by NaOH addition. No other chemical addition was required. Phosphate removal and struvite generation was monitored for a minimum of 5 hours to ensure steady state was reached by analyzing the effluent collected from the top of the reactor. After running the reactor for 5 hours, solids were allowed to settle for one hour. Collected struvite crystals were washed with DI water, filtered with 47 mm Glass fiber filter, dried in a desiccator under room temperature for 24 hours, and then weighed and stored in capped 5 mL glass vials. Each precipitate sample was weighed with an analytical balance and stored for possible analysis with SEM.

Organic solids impacts

Digested solids were collected from the anaerobic lagoon and stored in glass bottles. The solids were then stirred in a magnetic stirrer and then total solids experiment was performed as mentioned in Appendix D. After measuring the total solids concentration, the solids were diluted with DI water to the desired concentrations. Experiments with solids of different concentrations: 50 mg/L, 250 mg/L, and 500 mg/L were conducted in a six-gang jar tester (Phipps and Bird PB-900) to investigate the impact of solids on struvite crystal size and phosphate removal. The initial concentrations and molar ratios of four major ions in two liters of synthetic wastewater solution are given in Table 2, and then the 2 liters of the prepared solution was transferred into each of four B Ker® mixing

jars. The solution was adjusted to pH 8.7 with 1.0 M NaOH (ACS grade, Fisher Scientific). Mixing strength was adjusted by controlling blade rotation rate. Initially the solution was mixed at high G value (240 s^{-1}) for 30 seconds. Then the mixing strength was lowered to 76 s^{-1} and the solutions were mixed for two hours. After two hours, the solution was filtered with 5 μm membrane filter paper (Millipore Corp.) and stored in plastic bottles for phosphate analysis.

Table 2. Initial concentrations and molar ratios of four major ions in synthetic wastewater solution (Wang et al., 2005 a)

Ions	Concentration (ppm)	Molar Conc. (mM)	Molar Ratio	Chemicals used
Mg^{2+}	96	4.0	2.0	$\text{MgSO}_4 \bullet 7\text{H}_2\text{O}$
NH_4^+	720	40.0	20.0	NH_4Cl
PO_4^{3-}	190	2.0	1.0	$(\text{NH}_4)\text{H}_2\text{PO}_4$
Ca^{2+}	40	1.0	0.5	CaCl_2

Analytic methods

Swine wastewater samples were collected from the anaerobic lagoon and stored in 125 mL Nalgene plastic bottles. The stored samples were then tested for phosphate, total suspended solids, chemical oxygen demand, and ammonium- N concentration using the methods stated above. For the crystalline phases of the precipitate samples obtained from the struvite reactor at different reactor conditions, Scanning Electron Microscopy (Hitachi S 570) with an accelerating voltage of 15 keV and working distance 12 mm in the Electron Microscopy Lab at the Missouri University of Science and Technology was

used to determine the shape of the crystal. The crystal precipitate was sputter coated with gold-palladium to obtain a conducting surface, and then micrographs were obtained of the struvite crystals.

RESULTS AND DISCUSSIONS

Lagoon data and description

The pH in the lagoon showed an increase over the first few months of mixing, and the phosphate levels dropped significantly, Table 3.

Table 3. pH and Phosphate concentrations of the anaerobic lagoon

Sampling date (installed 8/20/2003)	pH	Phosphate Mg/L
5/9/2003	7.3-8.0	54 ± 3
9/5/2003	6.8-7.9	40 ± 3
10/3/2003	6.9-8.1	15 ± 3
10/24/2003	6.9-8.2	9 ± 5
11/20/2003	7.0-8.2	29 ± 8
12/17/2003	7.2-8.4	13 ± 3
3/22/2004	7.1-7.9	122 ± 21
4/20/2004	6.9-7.9	106 ± 30
5/20/2004	6.9-7.7	34 ± 2
6/23/2004	6.9-8.0	56 ± 7
7/24/2004	7.1-7.9	84 ± 29
2/17/2005	8.0-8.2	47 ± 4
6/27/2006		52 ± 4
7/20/2006	6.8-7.3	46 ± 7
8/31/2006		30 ± 8
9/11/2006	8.0-8.3	26 ± 3
7/6/2007	6.9-8.4	66 ± 40
7/17/2007	6.8-7.9	63 ± 38

The increase in pH was due to the release of volatile fatty acids and CO₂ by mixing. Then mixer was removed for repairs in November 2003. Upon removal, visible inspection revealed much of the mixer and securing ropes were encrusted with crystals, which were proven to be struvite. The wastewater characteristics such as pH, conductivity, COD, NH₄-N, PO₄³⁻, temperature were recorded with the methods as explained above. The lagoon analysis results are shown in Table 3. Data obtained from the lagoon shows variable pH and phosphate values. At the time when the struvite crystals were observed the phosphate concentration had dropped to 9 mg/L and average pH was 8.1. Struvite crystals were observed at that pH and phosphate level. Molar ratios and SEM images taken of the struvite crystals obtained from the lagoon in Figure 4 show that the crystals are struvite.

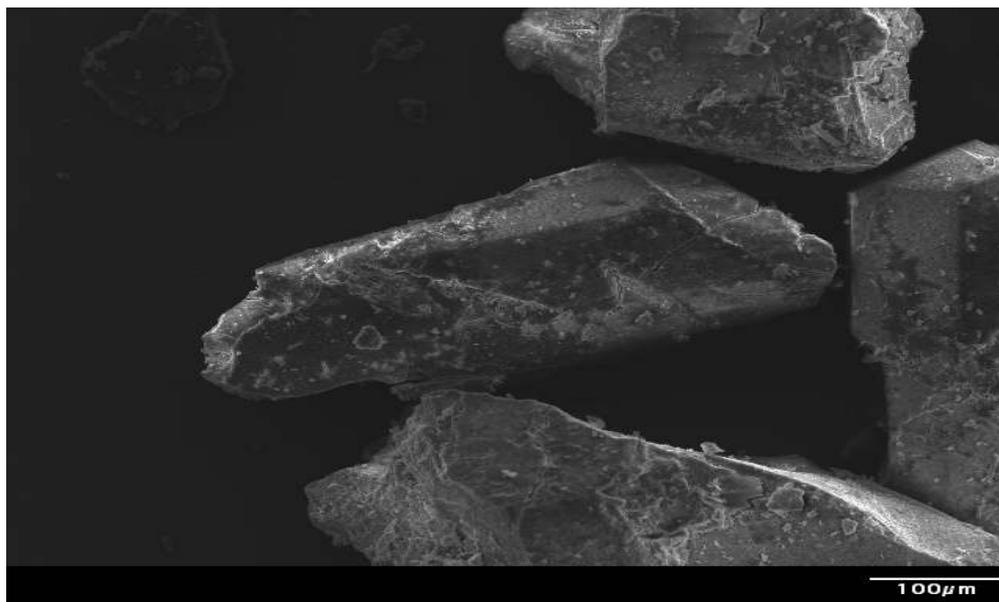


Figure. 4. Scanning electron microscopy image of deposit formed at the mixer installed in the anaerobic lagoon.

Later after the mixing had resumed, the phosphate level increased and pH level decreased. This could be due to dissolution of struvite and no significant precipitate was observed in the later periods of sampling on the mixer, securing ropes, or on the high surface area materials placed to enhance struvite precipitation. While precipitation was clearly observed, sustained precipitation and phosphate removal was not achieved through mixing and passive aeration of the 0.75 acre anaerobic lagoon.

Mixing and aeration

Results obtained from the batch tests shows that mechanical mixing had significant impact on phosphate removal efficiencies in the wastewater, Figure 5.

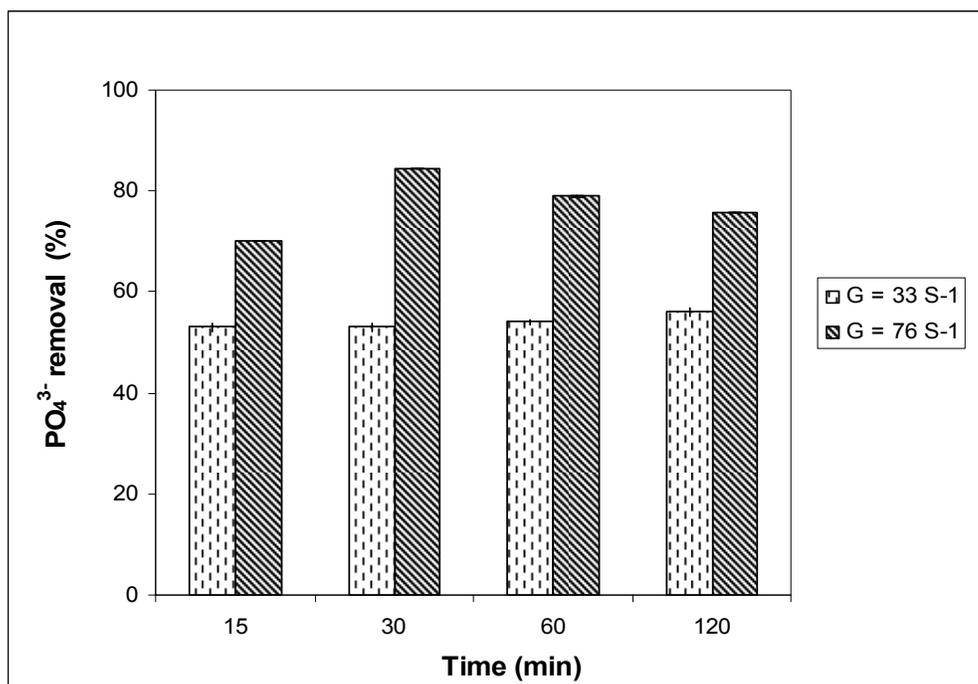


Figure. 5. Percent removal of phosphate from synthetic wastewater at various operation times and mixing intensities in a Batch Reactor.

After 30 minutes of reaction time, percentage removal of phosphate for 33 s^{-1} and 76 s^{-1} were 53% and 84%. Operation time beyond one hour has no major impact on phosphate removal. pH is one of the main driving forces behind the formation of struvite. Aerating the swine wastewater has the effect of stripping off CO_2 gas from the wastewater leading to localized increase in pH. Increasing turbulence leads to liberation of CO_2 , an increase in pH and hence an increase in struvite precipitation (Ohlinger et al., 1999). Here swine wastewater was aerated with an air diffuser and results showed that aerating led to a steady increase in pH from 7.73 ± 0.1 to 8.41 ± 0.06 within 60 minutes, Figure 6. The pH increase to 8.41 ± 0.06 by aeration is encouraging, as this can lead to struvite formation and phosphorus removal with no chemical pH adjustment.

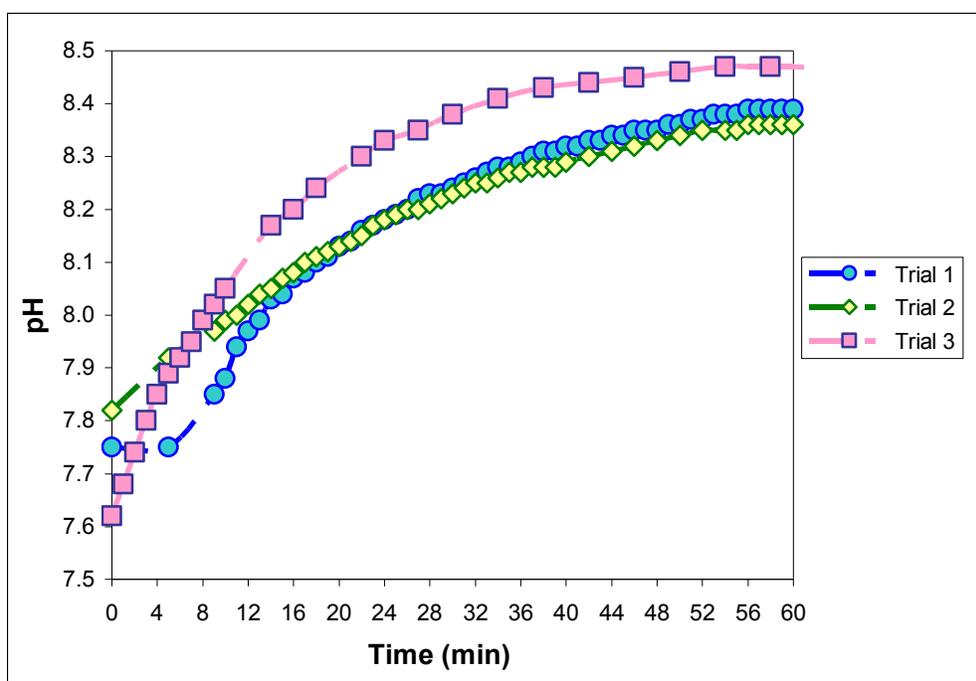


Figure. 6. Aeration impacts on pH of the swine wastewater versus times.

Flow - Through struvite reactor

Initially, the average pH of swine wastewater was 7.76 and the pH was increased by aerating at a rate of 0.5 L/min. This resulted in a pH of 8.4 for wastewater entering the flow-through the struvite reactor. After achieving a pH of 8.4 simply by aeration, minimal chemical addition was used to increase the pH in the real wastewater and evaluate for struvite precipitation. Figure 7 shows the phosphate concentrations at different pH and operation times.

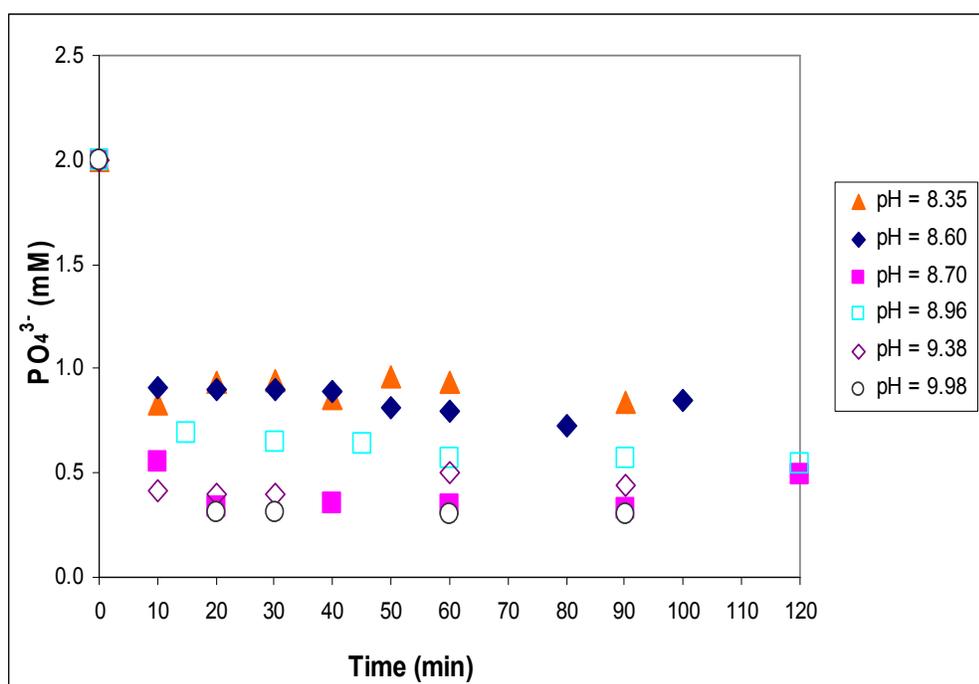


Figure. 7. Phosphate concentration of real wastewater in the struvite reactor at various operation times and pH.

As the pH increases, phosphate and magnesium are used up for potential struvite precipitation. Precipitation was consistent over the operational period. Potential struvite precipitation can be achieved at a pH range of 8.35 to 9.98, Figure 7. The efficiency of phosphate removal is approximately the same above pH 8.7, whereas, increase in cost of chemical addition as well as maintenance becomes an issue. While no testing was done above pH 10, recent research showed that beyond pH 10.5, struvite precipitation decreases due to unavailability of magnesium ions as they form $Mg(OH)_2$. Figure 8 shows the trends of phosphate concentrations at various operation times and pH.

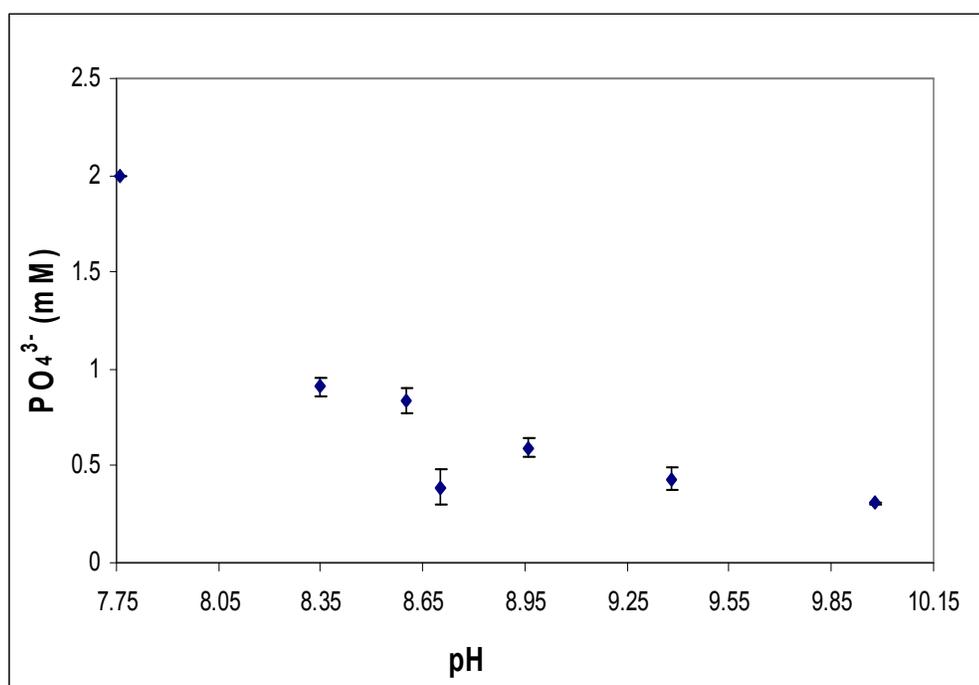


Figure. 8. Phosphate concentration of real wastewater in the struvite reactor at different pH with standard error bars.

Though in this experiment, concentration of calcium and ammonium were not measured, previous studies shows that at higher pH and relatively low calcium concentrations, most phosphate precipitates as struvite (CEEP, 2000). From previous field sampling and analysis of swine wastewater collected from the anaerobic lagoon showed higher concentration of ammonium and ammonium concentrations well above stoichiometry requirements for precipitation. As the magnesium concentration was adjusted above stoichiometric needs, a high phosphate precipitation was obtained at pH above 8.6. As the pH increased in the struvite reactor, the removal efficiency increased and the steady state effluent concentration decreased. Thus, as the pH increases, the removal of phosphate also increases.

Effect of solids on struvite precipitation

From the results of the jar test, organic solids had only slight impact on phosphate removal efficiencies in longer reaction times, Figure 9. The majority of the removal was also attained by sedimentation alleviating concerns about organic solids inhibiting sedimentation. Inorganic solids addition for seeding purposes have been shown to improve removal (Wang et al., 2005 a). The organic solids present in the wastewater may have helped in initial formation of the struvite crystal, and the increased solids concentrations did not negatively impact the removal for the settled and filtered samples after adequate mixing time of 10 minutes or greater. The mixing strength was maintained throughout the experiment at a G value of 76 s^{-1} . At the highest solids concentration tested, 500 mg/L, the settling removal was noticeably higher, Figure 9. This may be due to the dense solids settling, acting in a sweep-flocculation mode to enhance removal.

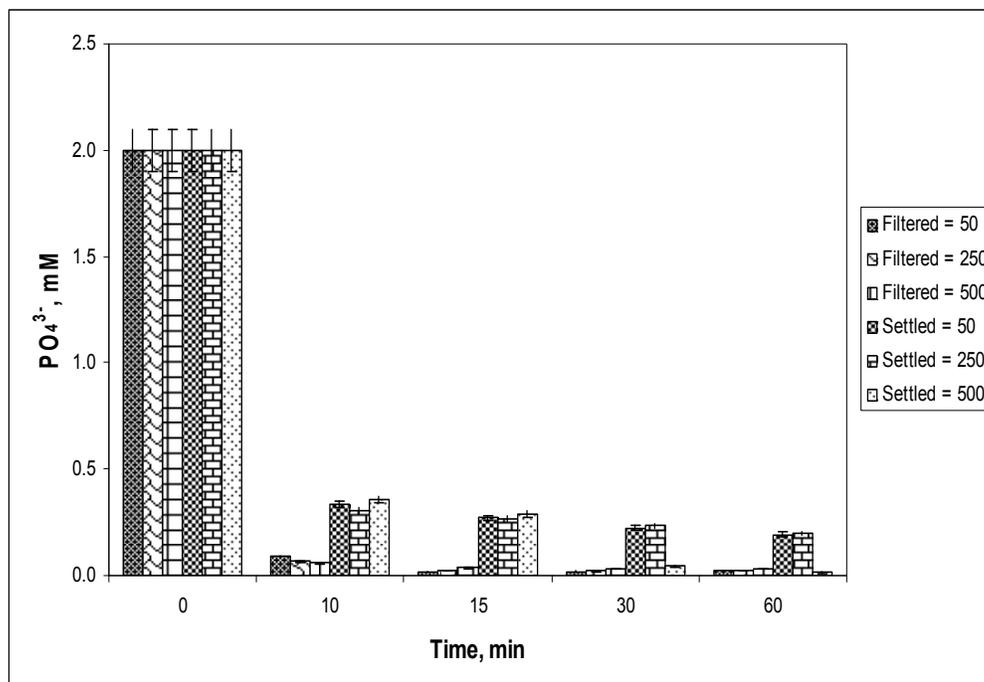


Figure. 9. Phosphate concentration of synthetic wastewater at various solids concentration in a batch reactor.

Crystal formation of struvite

To further investigate any impact on crystal formation or growth, the recovered struvite precipitate obtained from the batch reactor was analyzed by SEM. Figure 10 shows that the crystals formed under G value of 76 s^{-1} are considerably larger and have prominent orthorhombic shape, expected for pure struvite.

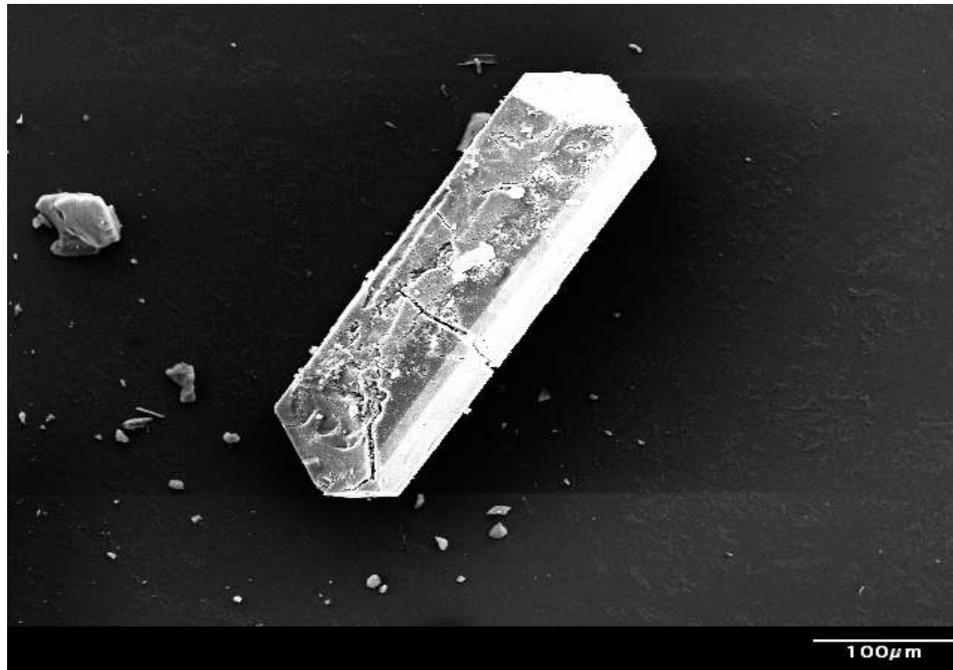


Figure 10. Scanning electron microscopy image of crystals of synthetic wastewater formed under G value of 76 s^{-1} in a batch reactor.

The crystals in the real swine wastewater did depict the shape of a struvite crystal though the shape orthorhombic shape was not as prominent. In general the crystals were much more irregular, with interruptions in the crystal propagation as is evident in Figure 11, but the crystals and the P removal data clearly show that phosphate precipitate can be efficiently achieved at pH levels less than 9. So while there is visual data to show crystal growth was inhibited, the combined impact of increased embryo growth an enhanced settling at high solids levels increased removal by sedimentation.

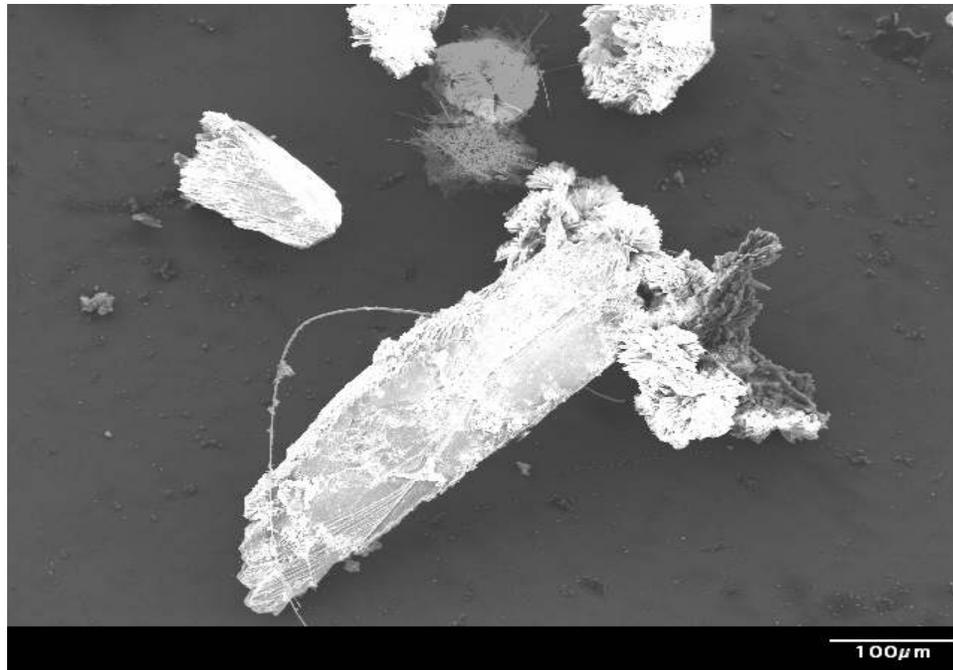


Figure. 11. Scanning electron microscopy image of crystals of real wastewater formed in the struvite reactor at pH 8.7.

CONCLUSIONS

Overall the experiments conducted did show that struvite precipitation can be used to treat high P concentration wastewaters. Aeration alone was shown to increase the pH of the swine wastewater and lead to approximately 60% removal of total phosphate from the wastewater without using chemical pH adjustment. At higher pH, removal of phosphate can be achieved at a higher rate but the cost of chemical addition and the operations and maintenance concerns of mechanical systems added to farming operations must be considered.

Mixing strength also has clear impact on struvite formation in real wastewater. Optimum mixing strength was observed at a G value of 76 s^{-1} was observed in synthetic

wastewater previously. High phosphate precipitation is obtained at pH 8.7 and above with minimal addition of chemical following aeration. The organic solids present in the wastewater were shown to have minimal impact in the removal of high phosphate concentration from the swine wastewater, but concerns on the crystal growth and subsequent settability were noted. Formation of struvite crystals from the batch reactor showed to be of orthorhombic shape, whereas the precipitate obtained from the struvite reactor formed similar structure that of pure struvite. In previous studies, inorganic solids were shown to increase the removal of P from synthetic wastewater, but when the organic waste solids in the real wastewater were present; the re-use of struvite precipitate as a seeding material did not appear to considerably enhance phosphate precipitation in the struvite reactor (data not shown). Perhaps further study in pilot testing is required to better understand the impacts of organic solids in wastewater on long-term treatment and removal by sedimentation.

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3. CONCLUSIONS AND RECOMMENDATIONS

3.1 CONCLUSIONS

This research investigated the positive potential of struvite crystallization process, mainly as a method to remove and recover high concentration of reactive phosphorus from CAFO wastewater. Results indicate that struvite precipitate can be used to recover phosphorus from real wastewater containing high concentration of phosphorus. Based on the experimental results, some distinct conclusions can be drawn:

1. pH could be increased by aeration and with no addition of a base chemical. Aeration releases CO_2 from the wastewater to raise pH and likely releases VFAs and decomposes ammonium bicarbonate, releasing more ammonium for struvite precipitation. Aeration alone lead to approximately 60% removal of phosphate from the wastewater without addition of chemical with an initial concentration of 2 mM of phosphate.
2. Mixing and passive aeration in the anaerobic lagoon lead to struvite precipitation, but precipitation was not sustained. Due to the orthorhombic shape of crystals obtained from the SEM analysis, shown in Appendix K, it proves that struvite crystals can be formed simply by mixing and aeration in the lagoon.
3. Mixing strength also has significant impact on struvite formation. For synthetic wastewater with and without organic solids, optimum mixing strength was at a G value of 76 s^{-1} . This removal was confirmed with organic solids present in the batch reactor at different concentrations.
4. Organic solids already present in the wastewater had minimal impact in the removal of high phosphate concentration from the swine wastewater. The re-use

of struvite precipitate obtained from the mixer installed in the anaerobic lagoon as a seeding material did not appear to significantly enhance phosphate precipitation in the struvite reactor, as had been observed with clean synthetic wastewater at high solids concentration there was a slight but clear improvement.

5. Formation of struvite crystals from the batch reactor showed to be of typical orthorhombic shape, and the precipitate obtained from the struvite reactor formed similar structure that of pure struvite, but crystal growth interruption was visibly observed causing concerns for using sedimentation as a removal process to recover clean struvite from a continuous-flow system.

Overall characteristics of the anaerobic lagoon were studied and determined the various compositions of CAFO wastewater. The impacts on the potential of struvite precipitation due to aeration and titration were studied and studies show that there are significant impacts on the real lagoon. From the experimental works performed on the real wastewater at different pH, results showed that as pH increased the removal of phosphate concentration increased.

3.2 RECOMMENDATIONS

The work reported in this thesis related mainly to the effects of aeration and pH on struvite precipitation and of mixing in a bench scale struvite reactor. Bench studies conducted in the struvite reactor with real CAFO wastewater of varied water quality were studied and optimal struvite precipitation process was better understood. On the basis of the study performed in the laboratory of Missouri University of Science and Technology,

Rolla, the swine wastewater as well as dairy wastewater from the anaerobic lagoon could be treated by installing pilot scale struvite reactors in the field. Operating costs of struvite recovery should be compared to operational savings such as: reduction in sludge handling, disposal costs and landfill. Thus, economic evaluation of phosphorus recovery as struvite from swine wastewater should be developed.

APPENDIX A.

PHOSPHATE ANALYSIS USING HACH METHOD 8178

(0 ~ 30.0 MG/L PO₄³⁻)

This method is developed based on HACH method to measure PO_4^{3-} concentrations in the experiment.

Materials and Apparatus:

1. Spectrophotometer DR 2010
2. Centrifuge
3. Centrifuge Vial
4. Cylinder, 25mL Graduated Mixing
5. Sample cells, 25mL, matched pair
6. 25 mL Pipette
7. Test Tube Rack
8. Pipet Tips
9. Amino Acid Reagent
10. Molybdate Reagent
11. Deionized Water

Procedure:

1. Transfer 20 mL of sample to a 50 mL centrifuge vial.
2. Centrifuge the sample for 15minutes at 10,000 RPM.
3. Pipet 1.0 mL of supernatant and transfer it into a 25 mL graduated mixing cylinder.
4. Pipet 24 mL of DI Water to the graduated mixing cylinder, mix it gently by hand.

5. Turn of the HACH Spectrophotometer, enter the program code 485 for the reactive phosphorus, amino acid method, and rotate the wavelength dial until 530 nm is shown on the display.
6. Add 1 mL of Molybdate Reagent using a 1-mL calibrated pipette.
7. Add 1mL of Amino Acid Reagent Solution using a 1-mL calibrated pipette and invert several times to mix.
8. Set timer to 10 minutes for reaction.
9. Clean the outside of the cells with a towel.
10. Pour 25 mL of sample (the blank) into a sample cell.
11. After 10 minutes, place the blank into the cell holder. Close the light shield.
12. Press ZERO for zeroing.
13. Pour the prepared sample into a sample cell. Place the prepared sample into the cell holder. Close the light shield.
14. Press READ and record the reading.

Calculation:

$$C_{PO_4^{3-}} = \text{Reading} * \left(\frac{25}{1} \right) (\text{mg}/L)$$

Note: Step 1 & 2 can be skipped if the samples are synthetic feed.

Reference:

HACH WATER ANALYSIS HANDBOOK, SEVENTH EDITION

APPENDIX B.

AMMONIA ANALYSIS USING HACH METHOD 10031

(0 ~ 50.0 MG/L NH₃-N)

This method is developed based on HACH method to measure $\text{NH}_3\text{-N}$ in the experiment.

Materials and Apparatus:

1. COD/TNT Adapter
2. Spectrophotometer DR 2010
3. Funnel
4. Centrifuge
5. Centrifuge Vial
6. pH Meter
7. 50 mL Erlenmeyer Flask
8. 10 mL Pipette
9. Test Tube Rack
10. Pipet Tips
11. AmVer Reagent Test 'N Tube Vials
12. Ammonia Salicylate Reagent Powder Pillows, 5 mL Sample
13. Ammonia Cyanurate Reagent Powder Pillows, 5 mL Sample
14. Deionized Water
15. 1.00 N Sulfuric Acid

Procedure:

1. Transfer 20 mL of sample to a 50 mL centrifuge vial.
2. Centrifuge the sample for 15minutes at 10,000 RPM.

3. Pipet 1.0 mL of supernatant and transfer it into a 50 mL Erlenmeyer flask.
4. Pipet 9 mL of DI Water to the flask, mix it gently by hand.
5. Add 1.00 N Sulfuric Acid to adjust the pH of the sample to about 7.0, record the volume of Sulfuric acid consumed.
6. Turn of the HACH Spectrophotometer, enter the program code 343 for High Range, Test 'N Tube Nitrogen, Ammonia, and rotate the wavelength dial until 655 nm is shown on the display.
7. Remove the caps from two AmVer Diluent Reagent High Range vials.
8. Add 0.1 mL of Deionized water to 1 vial as blank.
9. Add 0.1 mL of sample to the other vial.
10. Add the contents of 1 Ammonia Salicylate Reagent Powder Pillow for 5mL Sample to each vial.
11. Add the contents of 1 Ammonia Cyanurate Reagent Powder Pillow for 5mL Sample to each vial.
12. Cap the vials tightly and shake thoroughly to dissolve the powder.
13. Set timer to 20 minutes for reaction.
14. Clean the outside of the vials with a towel.
15. After 20 minutes, place the blank into the vial adapter with the Hach logo facing the front of the instrument.
16. Tightly cover the vial with the instrument cap.
17. Push straight down on the top of the vial until it seats solidly into the adapter.
18. Press ZERO for zeroing.

19. Place the prepared sample in the adapter with the Hach logo facing the front of the instrument.
20. Push straight down on the top of the vial until it seats solidly into the adapter.
21. Tightly cover the vial with the instrument cap.
22. Press READ and record the reading.

Calculation:

$$C_{NH_3-N} = \text{Reading} * (10 + V_{H_2SO_4}) (mg/L)$$

Note: Step 1 & 2 can be skipped if the samples are synthetic feed.

Reference:

HACH WATER ANALYSIS HANDBOOK, SEVENTH EDITION

APPENDIX C.
COD ANALYSIS USING HACH METHOD 8000
(0 ~ 15,000 MG/L COD)

This method is developed based on HACH method to measure COD in the experiment.

Materials and Apparatus:

1. COD Reactor, 120 V
2. COD Adapter
3. Spectrophotometer DR 2010
4. High Range, 0 to 15,000 mg/L COD
5. Centrifuge
6. Centrifuge Vial
7. 200 μ L Pipette
8. Test Tube Rack
9. Pipet Tips
10. Syringe Filter (0.45 μ m)
11. Syringe (10 mL)
12. Deionized Water

Procedure:

1. Turn on the COD reactor. Preheat at 150 °C.
2. Pipet 0.2 mL of supernatant into the high range COD vials.
3. Pipet 2 mL of DI Water for a blank into the high range COD vials. Use duplicate for each sample.
4. Rinse the outside of the COD vial with DI Water and wipe clean with a paper towel.

5. Invert gently several times to mix the contents and place the vials in the preheat COD Reactor.
6. Heat the high range COD vials for two hours.
7. Turn off the reactor and wait about 20 minutes for the vials to cool to 120 °C or less.
8. Invert each vial several times while still warm. Wait until the vials cool to room temperature.
9. Measure the COD using Colorimetric Method.
10. Turn of the HACH Spectrophotometer, enter the program code 435 for chemical oxygen demand, high range, and rotate the wavelength dial until 620 nm is shown on the display.
11. Place the COD Vial Adapter into the cell holder with the marker to the right.
12. Clean the outside of the blank with a towel.
13. Place the blank into the adapter with the Hach logo facing the front of the instrument.
Place the cover on the adapter.
14. Press ZERO for zeroing.
15. Clean the outside of the sample vial with a towel.
16. Place the sample vial in the adapter with the Hach logo facing the front of the instrument. Place the cover on the adapter.
17. Press READ and record the reading.

Filtered COD (soluble COD):

Prior to the measurement samples are centrifuged 10,000 rpm for 15 minutes.

Filter the samples with 0.45 μm nylon syringe filter.

Note: If any dilutions made, the results shall be multiplied with the dilution factor.

Reference:

HACH WATER ANALYSIS HANDBOOK, SEVENTH EDITION

APPENDIX D.
TS AND TSS ANALYSES

This method is developed to measure TS and TSS in the experiment.

Materials and Apparatus:

1. Porcelain dish
2. Whatman Glass Micro- fiber Filter (2.5 cm)
3. Vacuum Flask
4. Rubber Tube
5. Pipet (25mL)
6. Pipet (10 mL)
7. Dryer
8. Desiccator
9. Waste Water Sample

Procedure:

TS:

1. Mark each dish and weigh the dish as 0 time (a).
2. Mix slurry samples using a stirrer to homogenize the samples.
3. Pipet 25 mL of mixed slurry samples to the dish.
4. Put in the oven 105 ° C until dry and the weight is constant. It should take one day.
5. Put all dishes in the desiccator to cool them down.
6. Weigh the dish and the solid. Record as after 105 ° C (b).

Calculation:

$$\text{TS} = (b-a) \text{ g/ mL of sample} * 1000 \text{ mL/L} * 1000 \text{ mg/g} = \text{mg/L}$$

TSS:

1. Mark each dish and weigh the dish + filter as 0 time (a).
2. Mix slurry samples using a stirrer to homogenize the samples.
3. Place the filter on to the filter apparatus.
4. Pipet 10 mL of mixed slurry samples to the filter apparatus and filter the samples.
5. Put in the oven 105 ° C until dry and the weight is constant. It should take one day.
6. Put all dishes in the desiccator to cool them down.
7. Weigh the dish and the solid. Record as after 105 ° C (b).

Calculation:

$$\text{TSS} = (b-a) \text{ g/ mL of sample} * 1000 \text{ mL/L} * 1000 \text{ mg/g} = \text{mg/L}$$

APPENDIX E.

EFFLUENT PHOSPHATE CONCENTRATION AT DIFFERENT pH

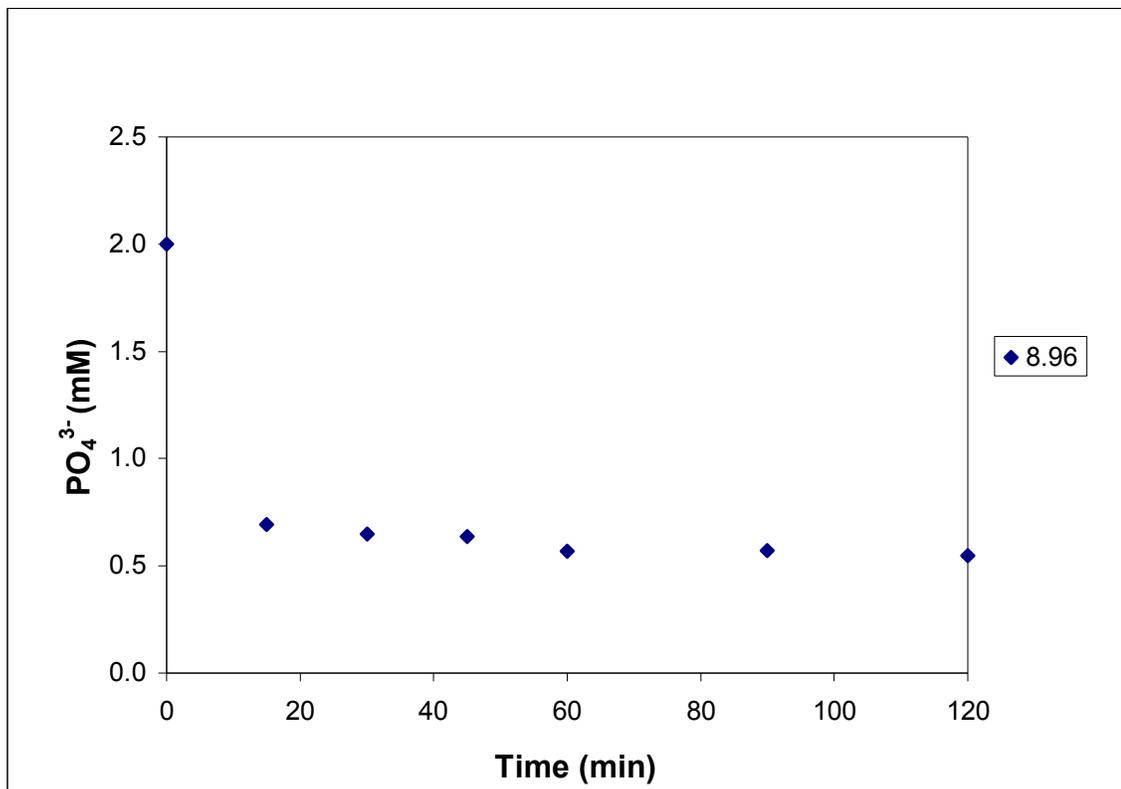


Figure 1. Effluent phosphate concentration at pH 8.96.

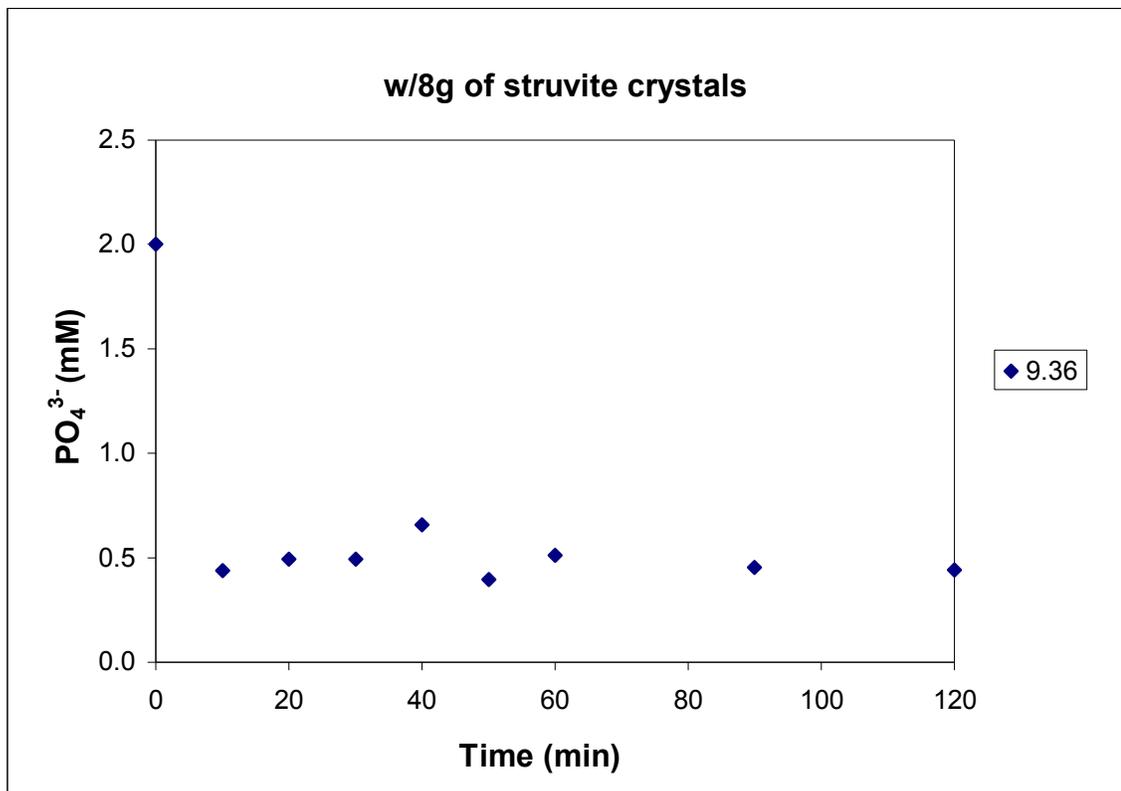


Figure 2. Effluent phosphate concentration at pH 9.36 with 8 grams of struvite crystals.

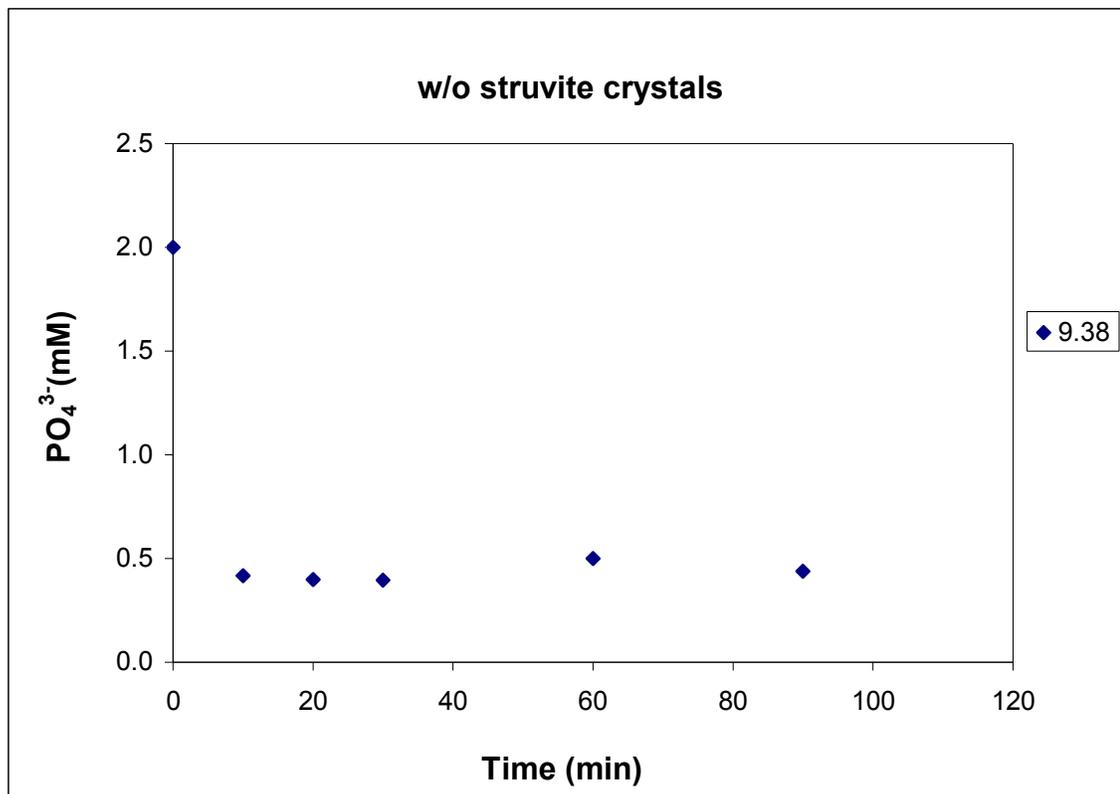


Figure 3. Effluent phosphate concentration at pH 9.38 without struvite crystals.

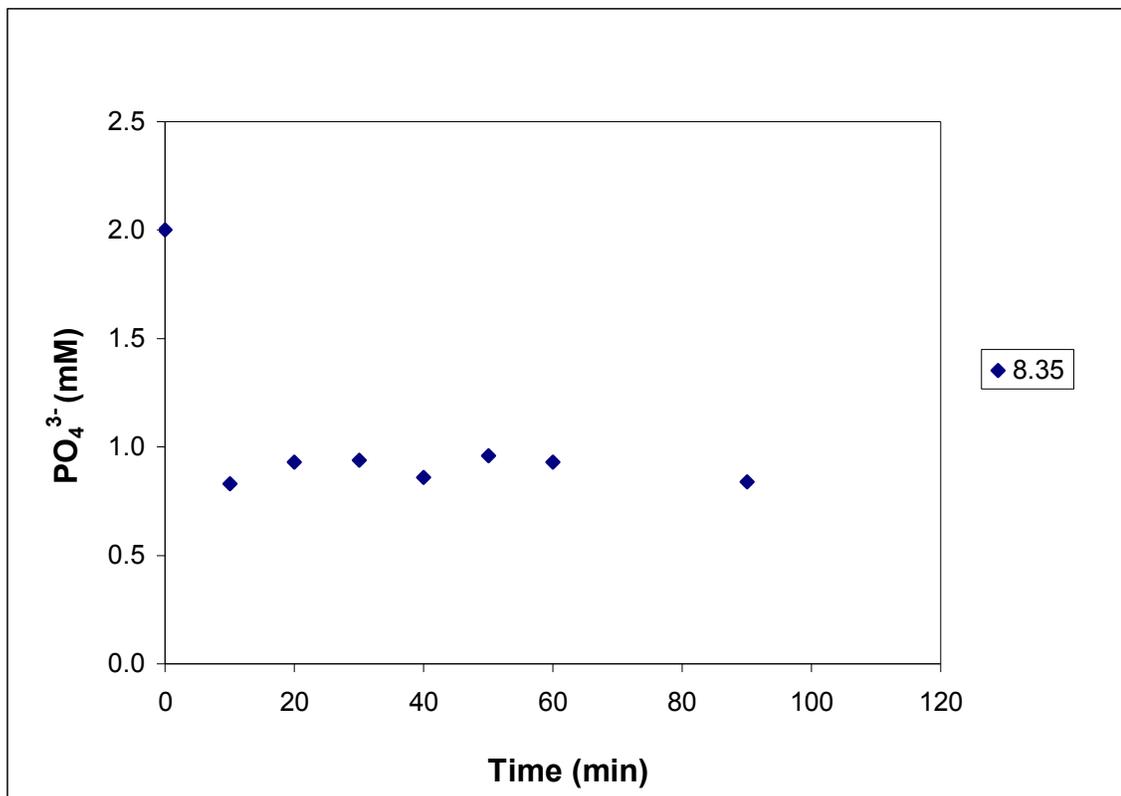


Figure 4. Effluent phosphate concentration at pH 8.35.

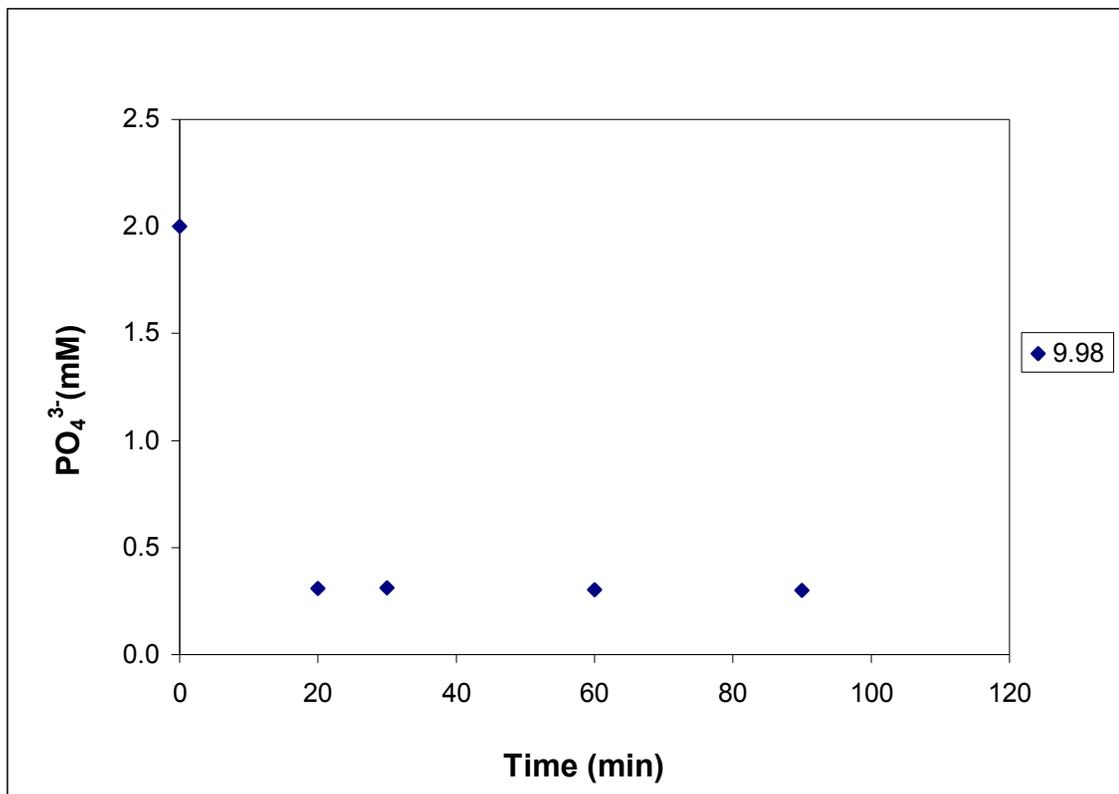


Figure 5. Effluent phosphate concentration at pH 9.98.

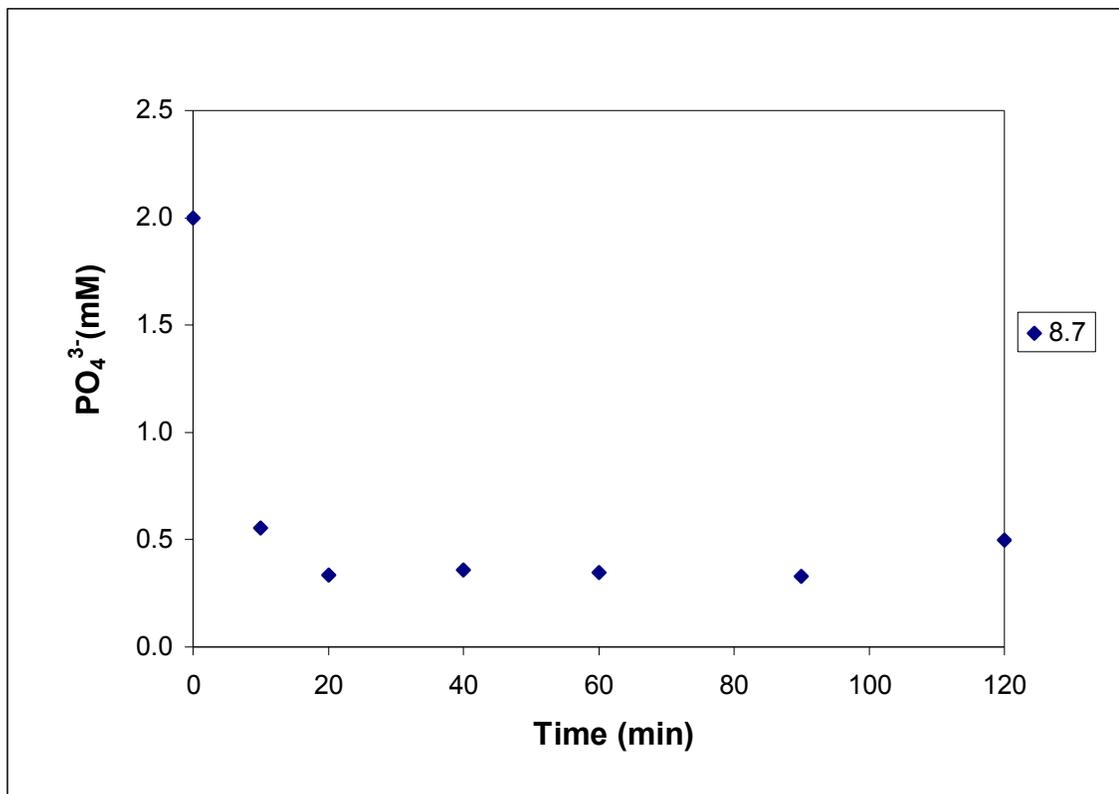


Figure 6. Effluent phosphate concentration at pH 8.7.

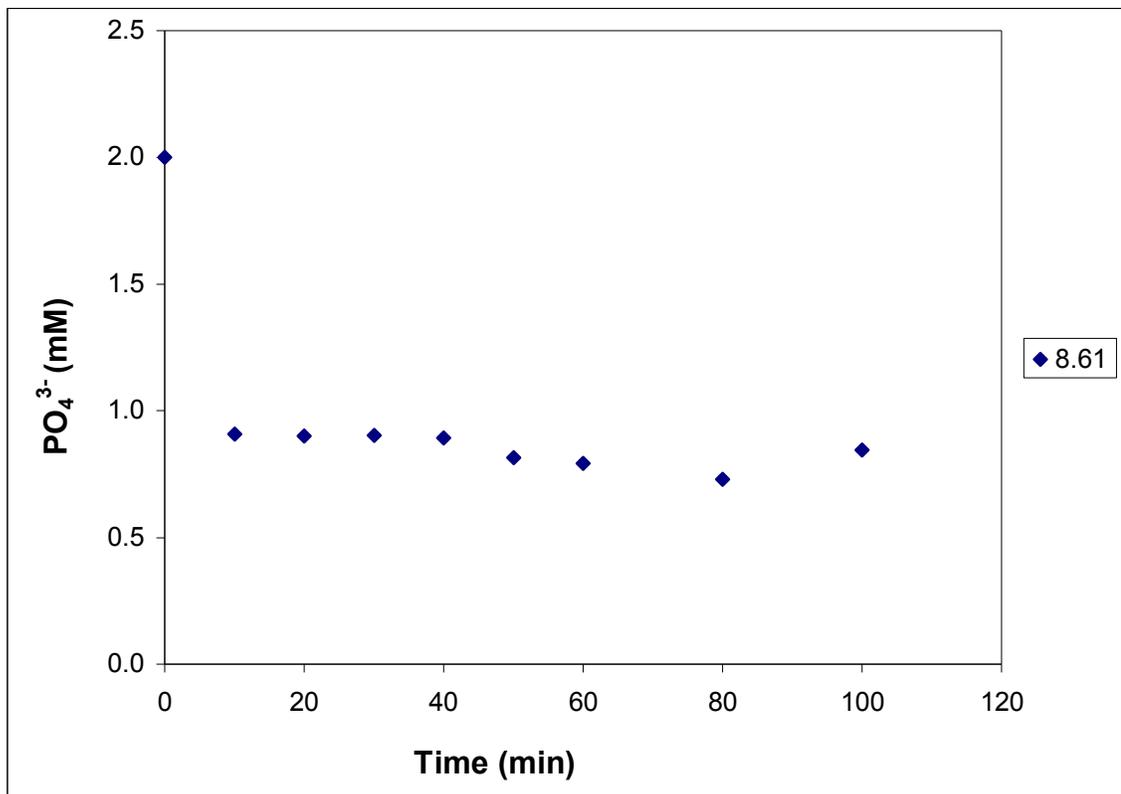


Figure 7. Effluent phosphate concentration at pH 8.61.

APPENDIX F.

% REMOVAL OF PHOSPHATE AT DIFFERENT pH

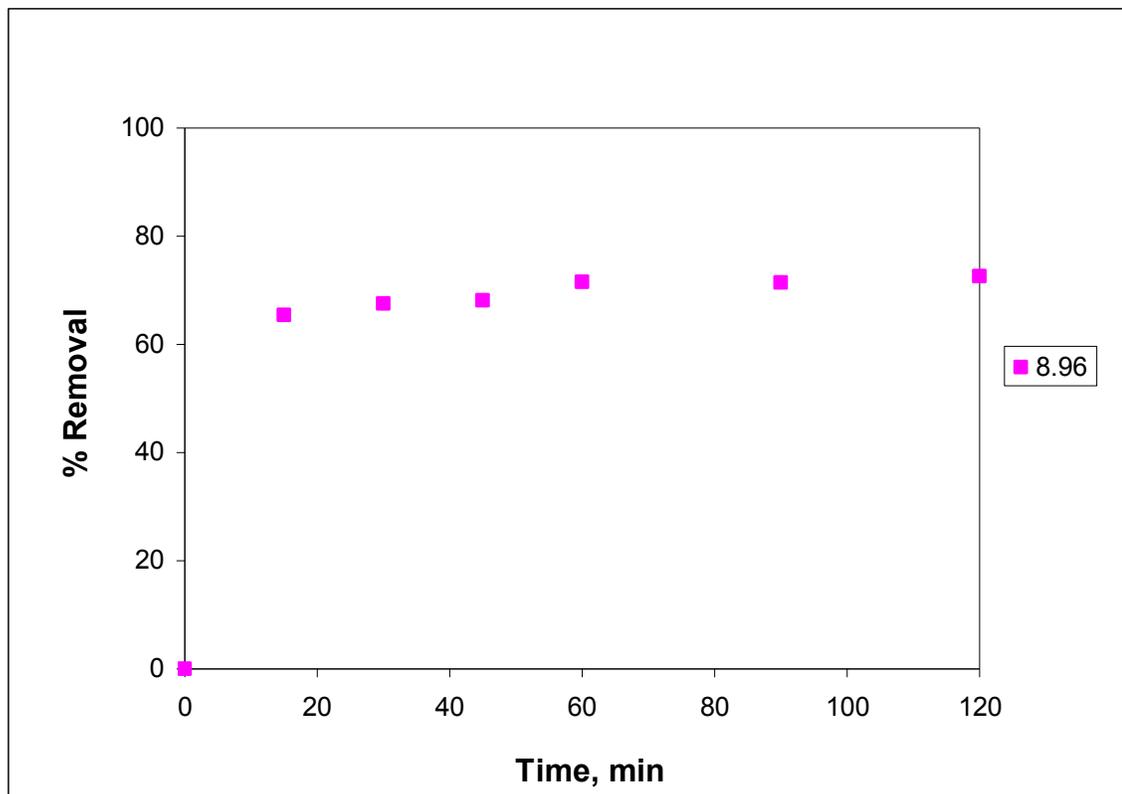


Figure 1. % Removal of phosphate at pH 8.96.

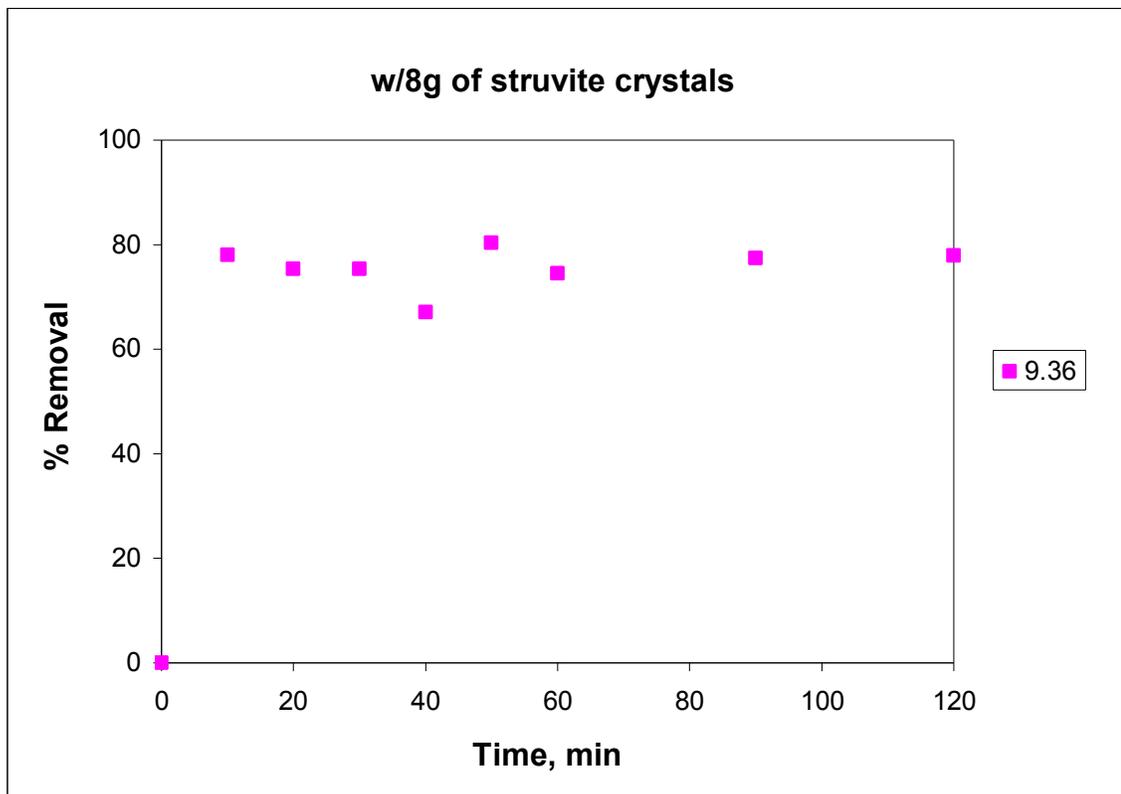


Figure 2. % Removal of phosphate at pH 9.36 with 8 grams of struvite crystals.

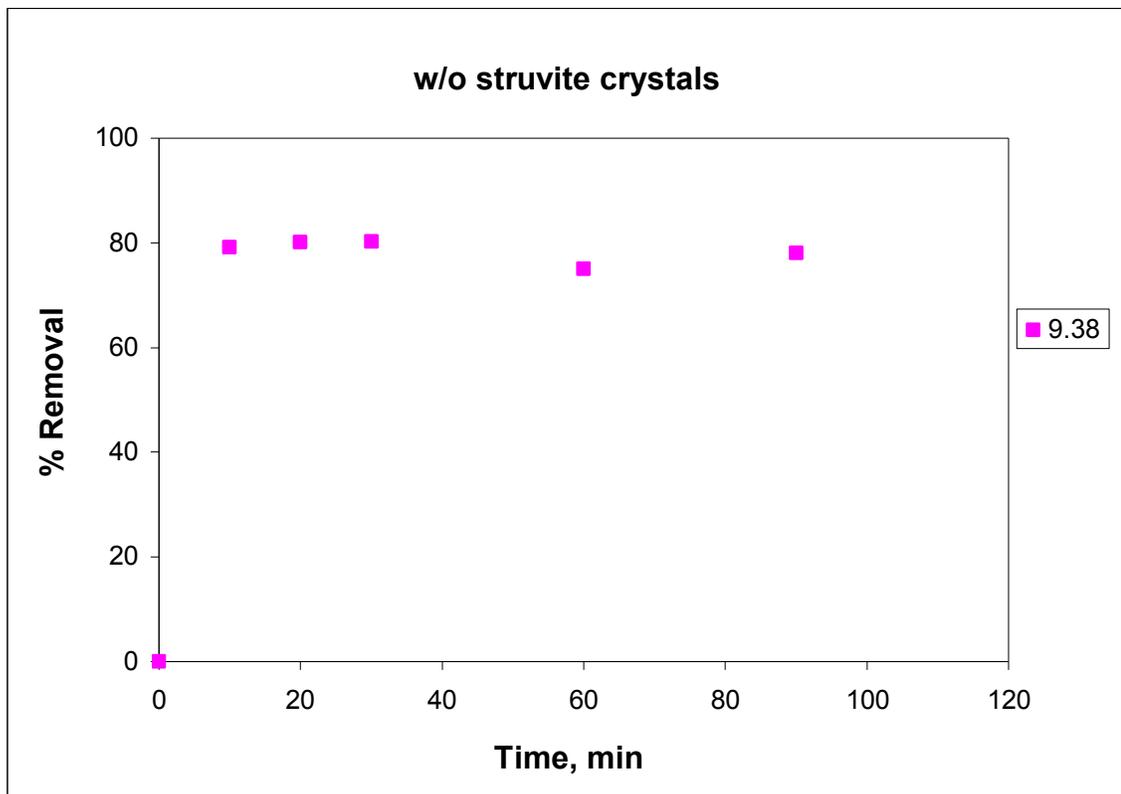


Figure 3. % Removal of phosphate at pH 9.38 without struvite crystals.

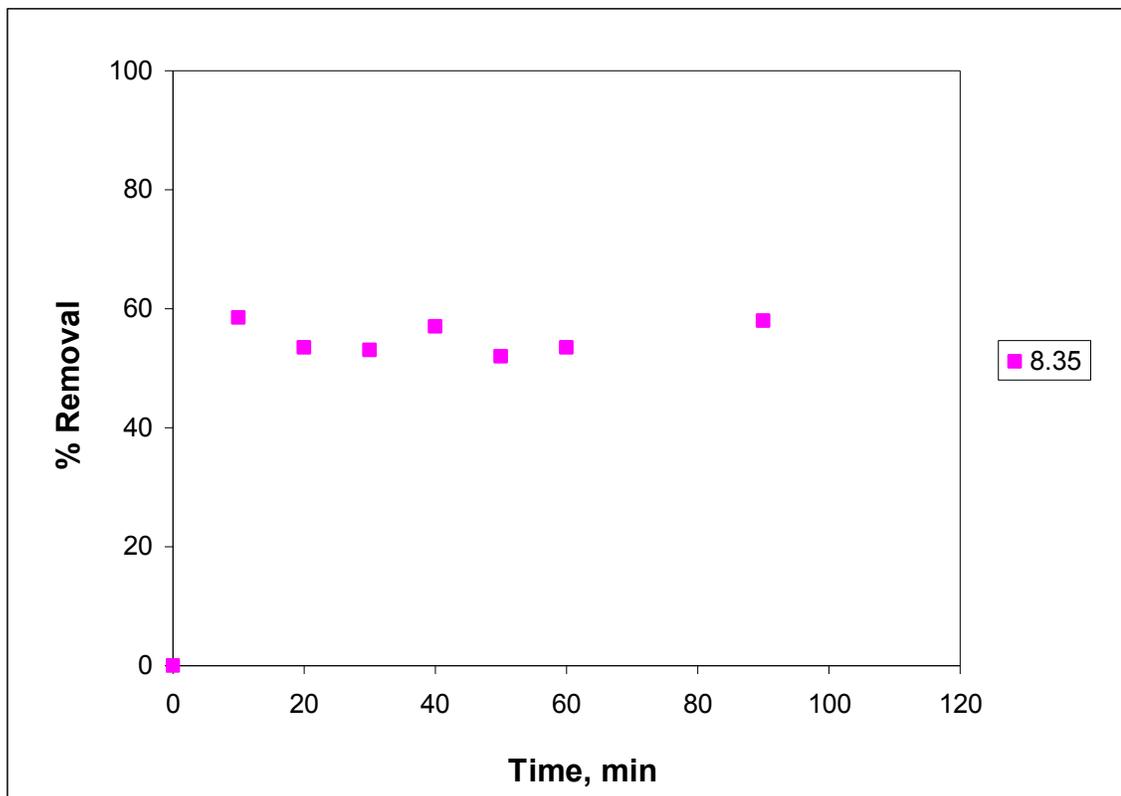


Figure 4. % Removal of phosphate at pH 8.35.

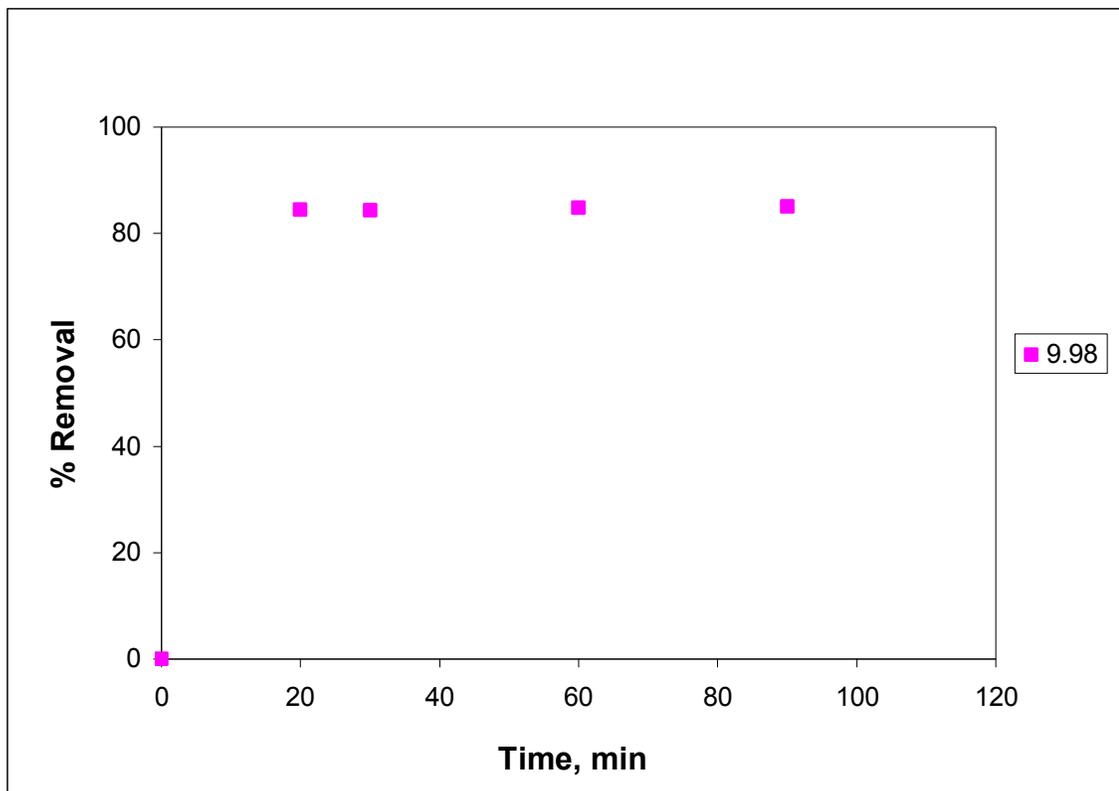


Figure 5. % Removal of phosphate at pH 9.98.

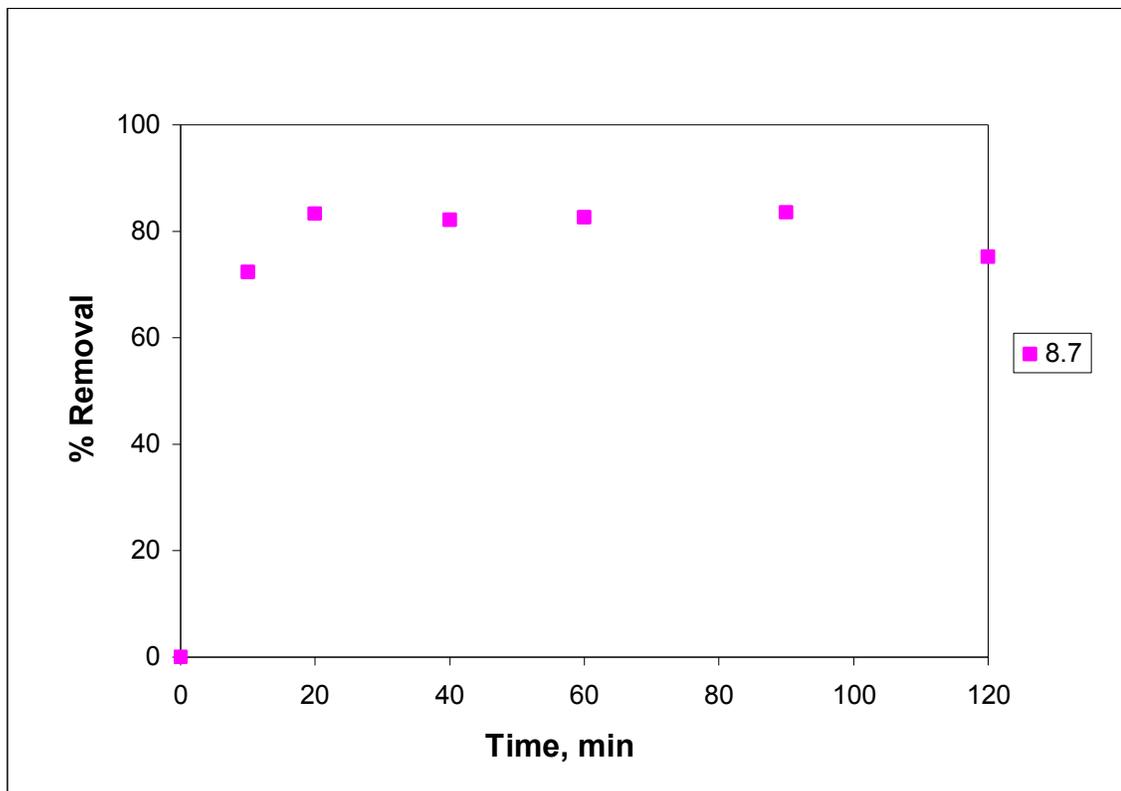


Figure 6. % Removal of phosphate at pH 8.7.

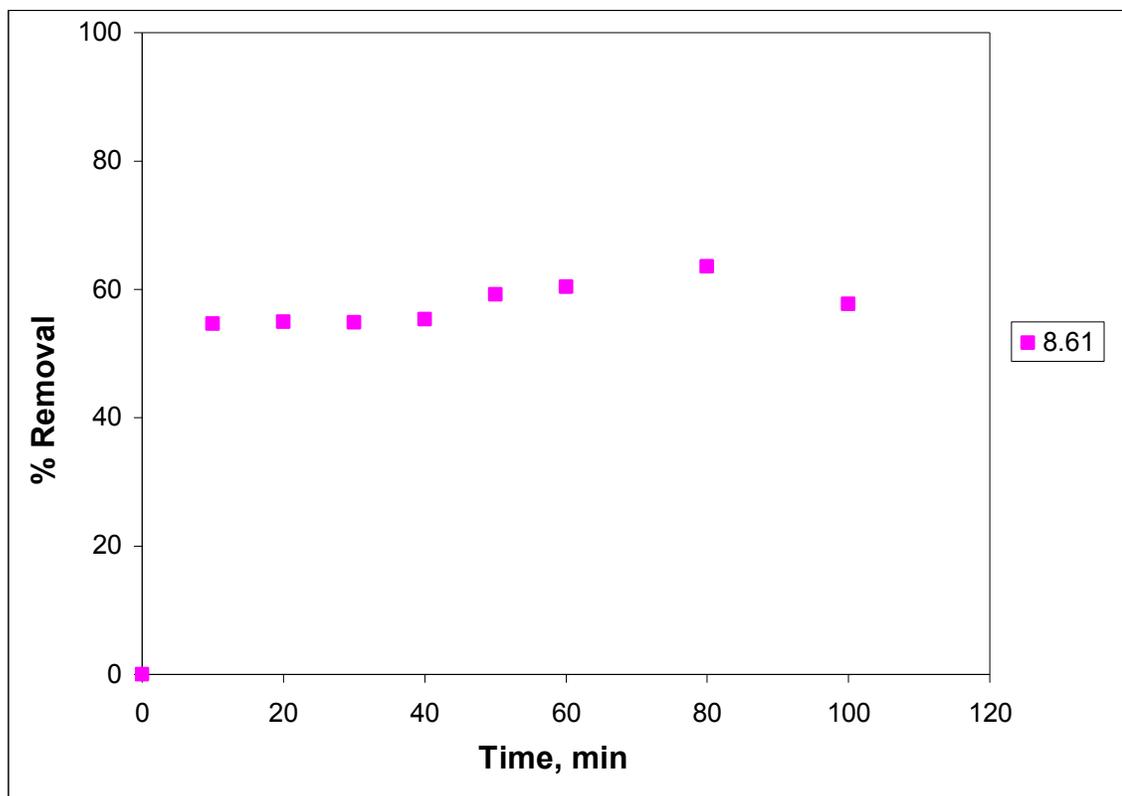


Figure 7. % Removal of phosphate at pH 8.61.

APPENDIX G.

SCHEMATIC OF THE ANAEROBIC LAGOON AND SAMPLING SITES.

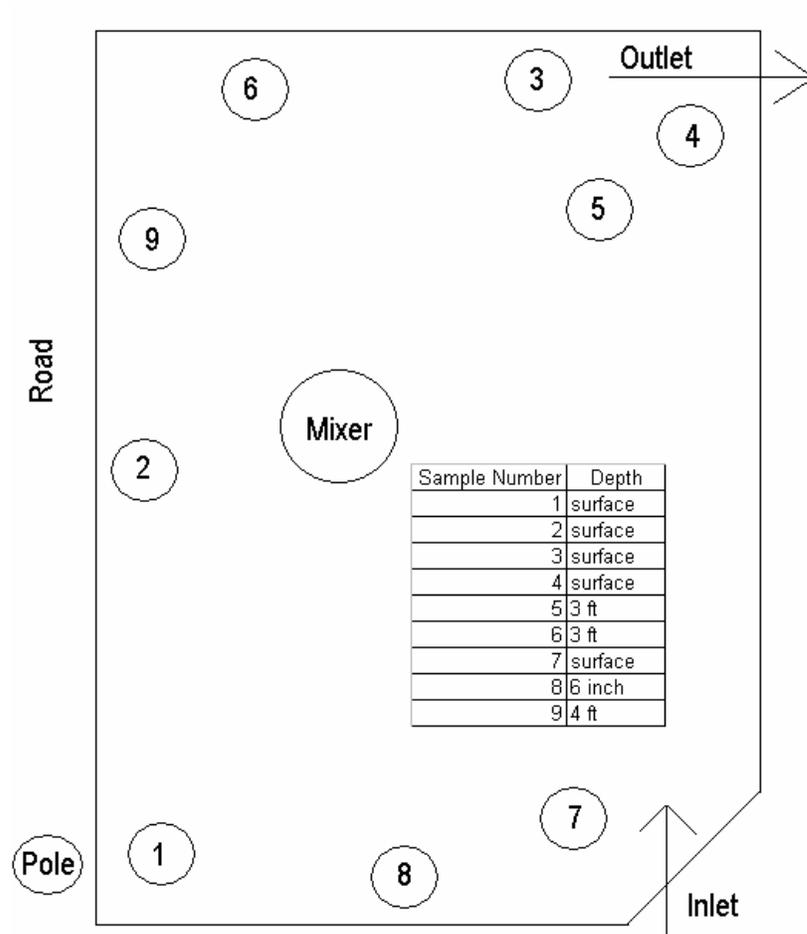


Figure 1. Schematic of the anaerobic lagoon and sampling sites.

APPENDIX H.

CHARACTERISTICS OF THE ANAEROBIC LAGOON.

Table 1. Characteristics of the anaerobic lagoon.

Table/Plot	Depth	pH	Temperature °C	DO mg/L	Conductivity us	ORP mV	PO ₄ ³⁻ mg/L	NH ₃ -N mg/L	COD mg/L	
Sample 1	Surface	7.72	39.6	0.0	1.23	109	30.50	53.9	110	
Sample 2	Surface	7.75	36.1	0.0	1.28	112	25.25	51.7	120	
Sample 3	Surface	8.03	37.0	0.0	1.25	111	35.25	64.9	40	
Sample 4	Surface	8.15	37.4	30.0			31.25	53.9	220	
	3 inch	8.40	39.3	24.0						
	6 inch			0.8						
	8 inch	7.98	36.0	0.2		105				
Sample 5	3 ft	7.10	35.0	0.0		-250	98.25	83.6	40	
Sample 6	3 ft	7.03	34.5	0.0		-260	106.75	74.8	230	
Sample 7	Surface	Only sample was taken, no readings taken at this plot						62.75	73.7	360
Sample 8	6 inch	7.60	36.9	0.0		24	48.75	55.0	250	
Sample 9	4 ft	6.95	34.8	0.0	1.93	-280	126.75	94.6	570	

APPENDIX I.

SEM IMAGE OF DEPOSIT AT DIFFERENT REACTOR CONDITIONS.

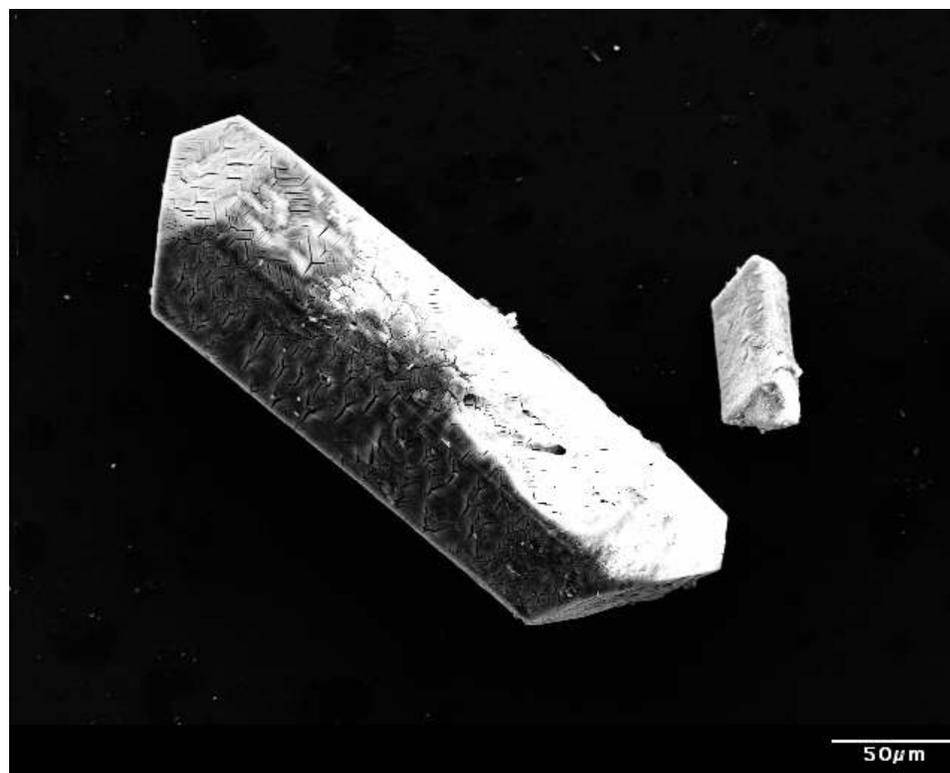


Figure 1. Struvite crystals from batch tests_ 300X.

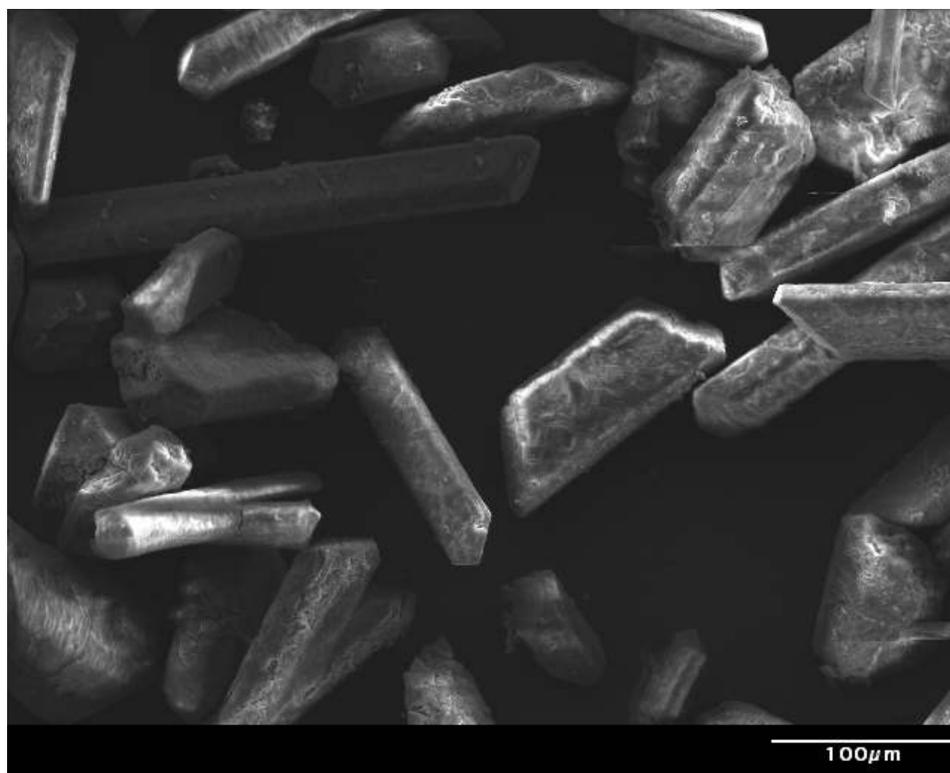


Figure 2. Struvite crystals from batch tests_220X.

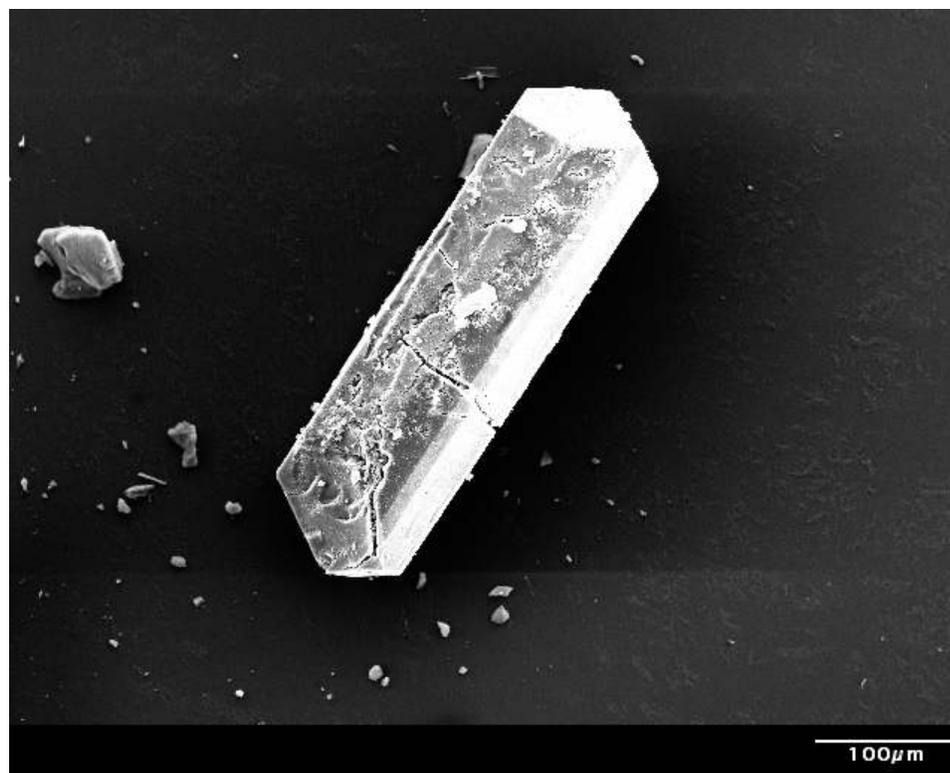


Figure 3. Struvite crystals from batch tests_ 170 X.

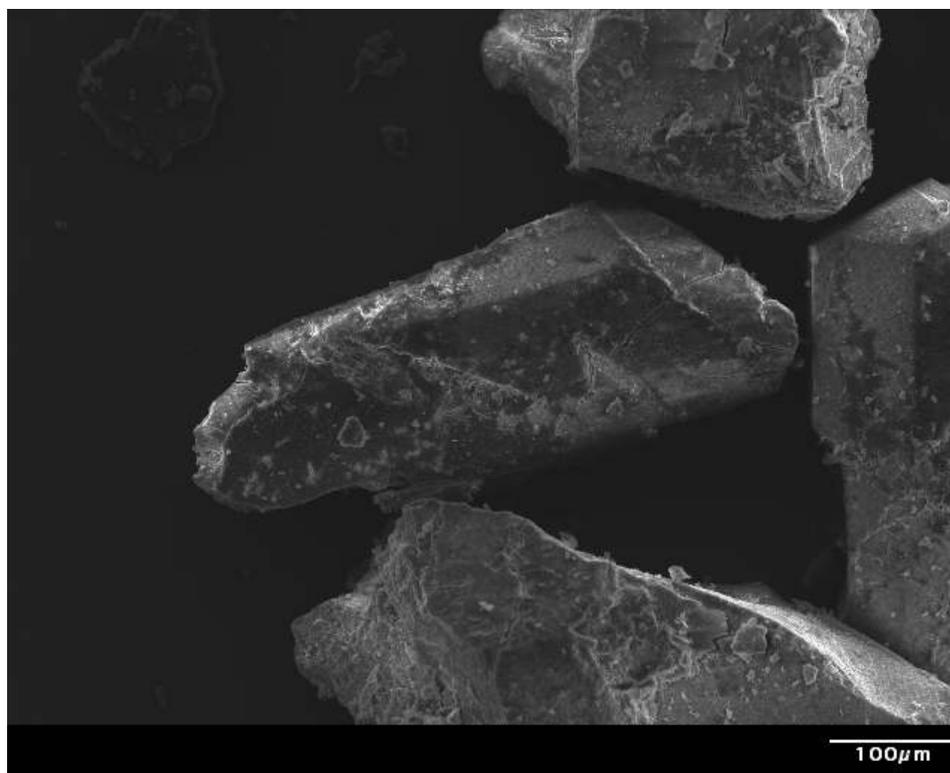


Figure 4. Struvite crystals formed on the surface of the mixer_ 150 X.

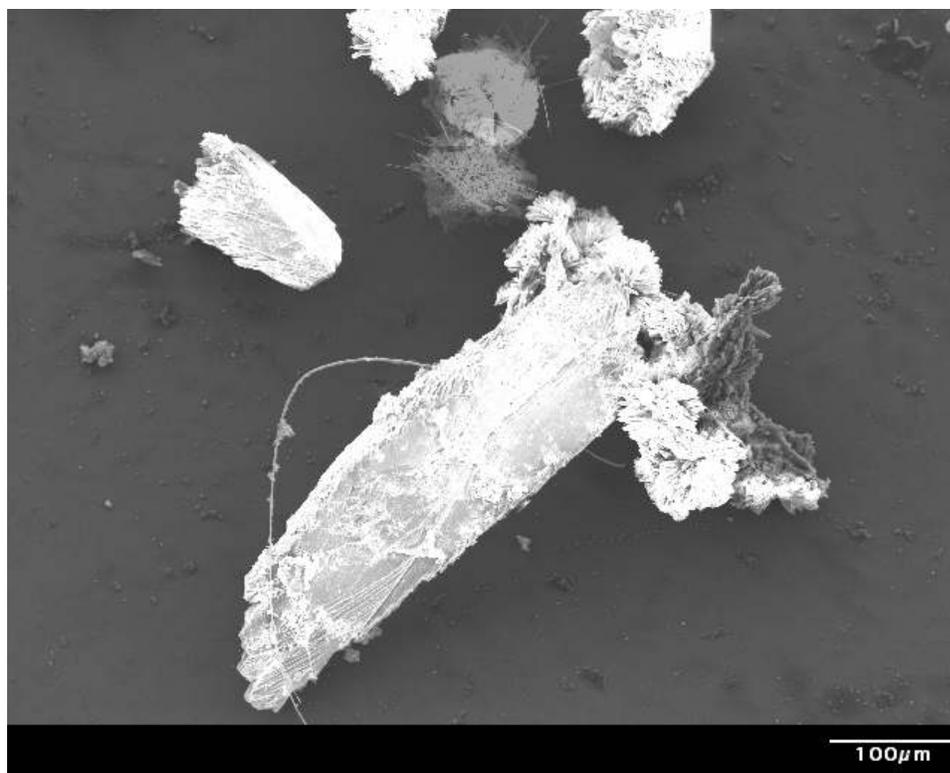


Figure 5. Struvite crystals at pH 8.7_ 150 X.

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