University of Alberta

Phosphorus Removal/Recovery from Swine Manure

By

Kevin Zheng Zhang

A thesis submitted to the Faculty of Graduate Studies and Research
in partial fulfillment of the requirements of the degree of
Master of Science in Environmental Engineering

Department of Civil and Environmental Engineering
University of Alberta

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This manuscript is dedicated to Sunny, my dear fiancee, who greatly helped me with her love, understanding and encouragement,

to my family and friends who have always encouraged and supported me in my academic and life pursuits.

Abstract

Lab and pilot experiments were conducted to develop an efficient, easy-operation process to remove phosphorous from swim manure, while enable simultaneously recovery of the phosphorous, via struvite precipitation. The characteristic of the diluted and pre-settled swine manure were also investigated in this research. The performance of two different reactors was investigated, one was cone-shaped fluidized bed crystallizer (CFB), and another was enhanced struvite crystallizer (ESC). The study results showed that CFB can be applied to treat diluted swine manure, which supposed to have similar characteristic with swine waste lagoon effluent, while ESC can be applied for both pre-settled and diluted swine manure. Up to 64% and 70% total phosphorous removal were reached by CFB and ESC, respectively. Higher Mg dose (up to 2.0) or higher pH value in range of 7.7 ~ 8.8, would increase the phosphorus removal, while the treatment flow rate would not affect the phosphorus removal significantly in the design range.

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ACRONYMS

ASAE	American Sociaty of Agriculture Engineer
Counts/mL	Number of particles measured by Particle Counter per milliliter of sample
mg/L	Milligram per liter
mL	Milliliter
mm	Millimeter
um	Micrometer (10^{-6})
min	Minute
m^3/s	Cubic meter per second
psi	Pound per square inch
BOD_5	5-day Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
N	Nitrogen
P	Phosphorus
TP	Total Phosphorus
DP/OP	Dissolved Phosphorus
TKN	Total Kjeldahl Nitrogen
TSS	Total Suspended Solids
TDS	Total Dissolved Solids
SBR	Sequencing Batch Reactor
ASBR	Anaerobic Sequencing Batch Reactor
UASB	Upflow Anaerobic Sludge Blanket Reactor
EPC	Enhanced Phosphorus Crystallizer
FBC	Fluidized Bed Crystallizer
CSTR	Continuous Stirred Tank reactor
WWTP	Waste Water Treatment Plant

1 Introduction

1.1 Background

Swine manure treatment and disposal has become a major environmental concern since the last decade, as the operation has become more and more centralized (Gronauer and Neser 2003). The common method for dealing with swine manure in North America was to store and treat the animal manure in the stabilization ponds and use the effluent for land application periodically. By this way, the nutrients present in swine manure can be recycled through plants by land application. However, there have been growing environmental concerns with this practice (Cheng & Liu 2001), because the overloaded phosphorus may penetrate the soil layer and pollute the groundwater or cause eutrophication in the surface water by run-off. Several investigations indicated that nutrients concentration was in groundwater due to the unproper land application of swine manure. (Goss et al. 1998; Mikkelsen 1995; Stone et al. 1998).

Conventional treatment processes are hardly to be satisfied for treating the swine manure in terms of cost efficiency, easy operation and high quality efflutent, because of the high concentration of organic, nutrients and solids. Although organic and solids removal are still the major concern for swine manure treatment, nutrients management has become much more important, to avoid the nutrient pollution of surface or ground water, and to reuse the precious nutrients in environmental friendly way. Innovative technologies are required for the efficient and environmentally safe swine manure management.

This project was planned to provide an overall solution for effective swine manure management, through the application of several physical, chemical and biological treatment processes and their combinations. From previous studies, the plain settling was proved to be an effective pretreatment of swine manure to remove most of the suspended solids and to improve the efficiency of the following treatment (Zhu 2002). Alum coagulation and flocculation followed by inclined plate settling was evaluated as an effective method to further remove solids, organic and nutrients; while ultraviolet (UV) disinfection was successfully tested to remove total and fecal coliforms (TC and FC) (Zhu 2002; Singh 2004). At this stage of the overall project, three sub-projects were divided and conducted parallelly to investigate several alternatives for effective swine manue treatment and management. The three sub-projects were: (1) to investigate the soil treatment and land application of the chemically treated swine manure with soil columns; (2) to evalualte the performance of a combined reactor for coagulation, flocculation, sludge blanket settling, and submerged filter; and (3) to investigate the phosphorus removal and/or recovery from the swine manure through struvite crystallization, which is the purpose of this study.

Struvite crystal has been recognized as a good strategy to recover phosphorus, because it could be easily seperated from the waste water stream, and it could be directly applied as a slow-released fertilizer. Many lab or pilot scale experiments have been conducted to generate struvite from swine manure (Bowers and Westerman 2003; Kim et al. 2004a), because of the high concentration of phosphorus, ammonia and the presence of magnesium in swine manure. However, no full scale operation has been reported in North America, because of the operational difficulty and high concentration of organic matter and solids in swine manure. But with a better understanding of the process chemistry and effective reactor design, there is great possibility to produce a cost-effective way for phosphorus removal/recovery from swine manure.

The effluent of the struvite process could be further treated by the Upflow floc blanket clarifier (UFFBC), or treated by soil column or untilized for land application, which were the other parts of the whole project. Then the chemical dose and the amount of generated sludge would be highly reduced for UFFBC, and the land area required would be highly reduced for the reduced concentraion of phosphorus. The separated struvite mixtures could be utilized as phosphorus rich fertilizer on barren areas or for land reclamation.

1.2 Research Objectives

In this research, laboratory and pilot scale experiments were performed, to determine the optimum condition, and to evaluate the performance of struvite reactors in terms of effective phosphorus removal. The original objective was to evaluate the performance of a fluized bed crystallizer (FBC) for phosphorus removal from swine manure and the potential application of the collected struvite. However, after several operations, the pilot plant was found ineffective for treating presettled swine manure, but only suitable for diluted swine manure. So a new struvite reactor, named enhanced phosphorus crystallizer, was designed, assembled, and evaluated with both pre-settled and diluted swine manure. Pilot experiments were carried out to study the phosphorus removal performance of these two crystallizers.

2 Literature review

Swine waste treatment and management has been studied widely in the past, since swine production is a very ancient industry. A wide range of literature review was performed for this project, including the general characteristics of swine waste and the swine farms operation, as well as swine manure treatment / management methods and their advantages and limitations. Finnally, it was focused on the struvite crystallization process, for phosphorus removal/recovery from manures.

2.1 Swine farms operation and manure management

2.1.1 Swine farms operation

Swine production is an important agriculture enterprise throughout the United States and all over the world. In 1995, over 60 million pigs were produced in the US, and over 638 million swine were produced in the top ten swine- producing countries (Mikkelsen 1997a). As the swine production is becoming more and more centralized, the proper handling and disposal of the manure has become an important concern for the swine production industry. There could always be a risk of surface or/and ground water pollution, if the manure were not managed properly (Ra et al. 2000; Ritter and Chirnside 1990).

There are three kinds of swine manure, for the different operation of the various facilities, they are solid manure, semi-solid manure and liquid manure. This research would deal with the liquid manure only, as it is most popular in North America.

2.1.2 Swine manure characteristics

The swine manure characteristics vary widely, depending on the operation mode of the facility, types of feeding, cleaning methods, and age of pigs etc.. Swine manure contains very high level of organics, nutrients, solids, as well as various kinds of microorganism, which makes the swine manure treatment more complicated. According to ASAE Standard(2003), 1000 kg live stock pigs generate 84 kg manure per day, which includes 11 kg total solids, 3.1 kg BOD_5, 8.4 kg COD, 0.52 kg TKN, 0.18 kg TP, 0.12 kg Ca, and 0.07 kg Mg. It was also reported that a market pig could weigh 260 pounds or more, and could produce up to 16 pounds of manure each day, which is equivalent to 7.6L per day (USEPA 2005). Liquid manure is usually less than 8.0% solids, as wash water, runoff, precipitation and so fourth are added to dilute the manure and lower the solids content. (USEPA 2005). Swine generates more quantity of manures, compared to other animals (Mikkelsen 1997b), it was reported that about 6~8% of manure be produced each day for pigs in weight unit (ASAE 1997).

High concentration of phosphorus, magnesium and calcium were found in the swine manure, which is beneficial to the struvite formation. Based on the estimates of the material flow of P, Mg and Ca in the average swine husbandry system in Japan, the concentrations of P, Mg and Ca were calculated as 11.3 mmol/L, 6.2 mmol/L and 10.2mmol/L, respectively, when feces excreta was mixed into urine and washing water (Suzuki et al. 2001).

2.2 *Swine manure treatment and management*

Although high concentration and variability make it almost impossible for a universal treatment process satisfied for all swine manures, many wastewater treatment processes have been studied to treat swine manure, including different physical, chemical, biological processes and their combinations.

2.2.1 Physical / chemical treatment processes

Sedimentation has been widely investigated to treat swine manure, either as natural settling process in the lagoons, or in plain settling tank, or by enforced solid separation processes (Gronauer and Neser 2003; Powers et al. 1995; Sheen et al. 1994; Yang et al. 1997). As the characteristic of swine manue varied, the reported settling time was different between the researches. Moore et al. (1975) reported that 70% solid was removed in approximately 16 hours. Zhu (2003) found that TSS removal of swine manure is a function of settling time, and 75% removal was reached within 24 hours of primary settling. Ford and Fleming (2002) reported enhanced solids removal by using centrifuges.

Screen and filtration processes were also extensively investigated to treat swine manure (Glerum et al. 1971; Singh 2005). Szogi (1997) used a marl gravel filter to treat swine wastewater from stabilization tank and achieved 54% and 50% removal of TSS and COD, respectively. Singh (2005) reported that the Martin filter unit was very effective in removing solids from swine manure after coagulation and floculation treatment.

Chemical coagulation and flocculation have been studied extensively to treat swine manure for the reduciton of solids and other pollutants (Dou et al. 2003; Gao et al. 1993; Powers et al. 1995; Sievers et al. 1994; Vanotti et al. 2003; Zhu 2003). Although the process can achieve high percent removal of both suspended solids and phosphorous, it is not a proper treatment, because of the high operation cost of chemicals addition, increased sludge volume and increased difficulty for sludge disposal (Zhu 2003).

To reduce the biohazard level of the treated swine wastewater for safe reuse or disposal, several disinfection methods have been investigated. Because of the high organic concentration, and high potential of DBPs, chlorine was supposed not suitable for swine wastewater disinfection. Alternative methods have been reported using UV and ozone disinfection. UV was found to be effective for properly treated swine manure (Hill et al. 2002; Singh 2005; Zhu 2003). Hill et al. (2002) reported that approximately 2~2.5 log reduction of indigenous fecal coliform, *E-coli* in aerobically treated swine wastewater can be achieved by UV irradiation at incident dose of 40~60 mJ/cm^2. Watkins et al. (1997) reported that ozone was effective for disinfection and odor reduction for swine manure treatment.

2.2.2 Biological treatment processes

Biological processes, both aerobic and anaerobic, were extensively investigated to remove organic matter from swine manure. It was reported that 75% of swine production facilities in North America use anaerobic or liquid-slurry systems for waste holding or disposal (Harper et al. 2000). Anaerobic lagoon and land application were most commonly used for swine manure treatment, because of the easy operation and cost efficiency (Pfost et al. 2000). While many other treatment alternatives have been studied and reported, to remove contamination from swine manure successfully.

Sevaral aerobic processes have been studied treating swine manure. The aquatic plant system and constructed wetlands have been studied and found to be efficient in removal of BOD, TSS, nitrogen and phosphorus. (Cronk 1996; Hill et al. 2002). Intermittent aeration process was reported to remove nitrogen successfully from swine manure (Cheng and Liu 2001). Biological aerated filter was reported to be effective in reducing enteric microbial concentrations in flushed swine waste (Hill et al. 2002). SBR was also studied to treat swine manure by many investigators (Angenent et al. 2002; Bicado and Svoboda 1995; Bortone and Gemelli 1992; Fernandes 1991; Jern 1987; Osada 1991; Zhang et al. 2000). Edgerton et al. (2000) reported 79% and 49% removal of COD and phosphate, respectively, by using SBR.

Anaerobic process has been considered as an attractive strategy for swine manure treatment, because of its potential to recover energy, as a large quantity of methane can be produced due to degradation of organic content in the manure. ASBR were the most investigated biological treatment reactors and were reported to be suitable for treating swine manure because of the flexible operation modes (Angenent et al. 2002; Bicado and Svoboda 1995; Bortone and Gemelli 1992; Fernandes 1991; Jern 1987; Osada 1991; Zhang et al. 2000). A full scale, on-farm ASBR was studied for the treatment of swine waste, and it was found that careful monitoring of total ammonia, and total VFA levels during startup were essential to successfully operate the anaerobic digester (Angenent et al. 2002). UASB was also reported to be effective in treating swine manure (Ferreira et al. 2003; Kalyuzuyi 1999; Oliverra 1997). About 92% COD removal was reported using a combination of UASB and stabilization pond (Ferreira et al. 2003).

A swine waste treatment system, consisting of a solid/liquid seperation tank, two anaerobic reactors, one aeration unit, and one rock bed filter with the aquatic plant reactor, was reported with significan removal of both COD and nutrients (Yang et al. 1997).

2.2.3 Gaseous emission contol

Concentrated animal production operations could also have a significant effect on the atmospheric environment (Sharpe et al. 2002). Gaseous emission from swine lagoon is considered as nuisance and has been discussed in several studies (Adler 1994; Cullimore et al. 1985; Harper and Sharpe 1998; Harper et al. 2000; Sharpe et al. 2002). Non-invasive techniques were used to evaluate trace gases without disturbing the meteorology of a lagoon system by Harper et al. (2000). It was found that ammonia emissions varied diurnally and seasonally and were highly correlated with wind speed and water temperature. Methane emissions from two swine waste holding lagoons were measured under ambient conditions with little disturbance to the natural environment. It was found that under natural conditions, methane emissions were related to wind speed, air and water temperature etc. The emissions followed a diurnal pattern with high emissions during the day when effluent temperature was high, while greatest emissions were observed during the spring period when the sludge depth was the deepest. (Sharpe et al. 2002)

2.3 *Alternatives for phosphorus removal/recovery from animal manures*

As the discharging limit for nitrogen and phosphorus has become more strict, efficient nutrient removal systems are required to enable farmers to meet this criteria. Many studies have been conducted for effective removal and recovery of nutrients from swine manure, including physical, chemical and biological processes.

2.3.1 Physical / chemical Phosphorus removal

Physical processes have not been reported to be used solely for removing phosphorus from animal manure, because the phosphorus exists mostly as soluble orthophosphate. However, plain settling has been proved as effective pre-treatment to remove part of the phosphorus from swine manure (Singh 2005; Zhu 2003). Buchanan et al. (1994) reported that 38% phosphorus was removed without alum addition, by using a settling basin with skimmer. With addition of 0.5% alum, 75% phosphosrus removal was achieved. It was also reported that settling basin could work more efficiently by adding organic polymers or metal salts, such as alum or ferric chloride (Gao et al. 1993; Sievers et al. 1994; Zhang and Lei 1998).

Chemical removal of phosphorus has widely been investigated and recommended as effective method treating swine manure (Dou et al. 2003; MetCalf and Eddy 2003; Zhu 2003). The phosphorus removal can be achieved by precipitation involved in addition of alum, ferric or ferrous iron salts to form settable solids, while some times, polymer is added to enhance the removal efficiency.

The removal efficiency mainly depends on the dosing location, chemical type and its dosage (MetCalf & Eddy, 2003). Approximately 60% TP removal could be reached by alum addition in treating pre-settled swine manure and it could be enhanced by adding polymer additives (Zhu 2003). About 75% TP removal was reported by Singh (2005) by alum coagulation and filtration. Although the phosphorus can be efficiently removed by 90% or higher with good design and operation, this practice should be carefully applied, because of the increased amount of the generated sludge, and high alum concentration in the sludge.

2.3.2 Biological Phosphorus Removal

Enhanced biological phosphorus removal (EBPR) has become more popular to replace the chemical phosphorus removal. Alternative anaerobic and aerobic zones are required in EBPR process. Under anaerobic conditions, phosphorus accumulating organisms (PAOs) assimilate fermentation products into storage products within the cells, releasing phosphorus from shred polyphosphates. Under aerobic conditions, energy is produced by the oxidation of storage productswhile the polyphosphate storage within the cell increases (Metcalf & Eddy, 2003).

Combined UASB reactor and DAF/BF/Anoxic/Aerobic process for the removal of high-concentration organic matter and nutrients from slurry-type swine waste was studied by Kim et al. (2004b). Phosphorus was removed in the ratio of 0.16 g PO_4-P per 1 g addition of ferric iron (Kim et al. 2004b). 75~85% phosphorus removal was reported with sufficient aeration by biological aerobic treatment of pig slurry (Daumer et al. 2003). A pilot scale sequencing batch reactor was studied to treat piggery wastewater, and 49% of phosphate removal was achieved on a mass balance basis (Edgerton et al. 2000). A specific parameter of oxidation reduction potential (ORP) was studied to control the biological treatment process to achieve stable operation with satisfied removal of both C, N, and P from swine waste (Ra et al. 1997).

2.3.3 Phosphorus recovery

Although, the above discussed technologies, can successfully remove phosphorus from sewage and meet the regulation requirements, they are not environmental friendly ways, because all the phosphorus removed from the sewage is transferred into solid form, with increased sludge volume, and potential risk of pollution, if it is not handled properly. Technologies for phosphorus recovery is highly required, with the main advantages of (1) improvement of the total waste management, (2) sustainable development concept, (3) profit of the recovered products, and (4)extended land application without nutrient pollution to water bodies. Through a life cycle assessment study, Maurer (2003) found that nutrient recovery technology is more energy efficient than conventional nutrients removal from wastewater, while the phosphorus and nitrogen have to be produced from natural resources. The phosphorus can be recovered by either precipitation or crystallization from the wastewater, and the generated solids should be easily collected and ready to be used as fertilizer. Many processes have been studied and reported on phosphorus recovery from wastewater, including calcium phosphate precipitation, struvite precipitation, etc. (Adnan et al. 2004; Adnan et al. 2003; Battistoni et al. 2001; Booker 1999; Carlsson et al. 1996; Shimamura 2003; Vanotti et al. 2003). The precipitation reactions can be expressed simply as:

$10\ Ca^{2+} + 6\ PO4^{3-} + 2\ OH^{-} \leftrightarrow Ca_{10}(PO_4)_6(OH)_2$ Equation 2-1

$Mg^{+} + NH_4^{+} + PO_4^{3+} \rightarrow MgNH_4PO_4*6H_2O$ Equation 2-2

Among them struvite precipitation is a well studied process, and it can become a most promising technology for nutrient removal and recovery from farm wastes, due to the presence of high concentration of phosphate, ammonia and magnesium. This could not only increase the phosphorus recovery, but also minimize the need of chemical addition.

2.4 Struvite precipitation

Struvite is white crystalline substance, consisting of magnesium, ammonium and phosphate in equal molar numbers, expressed as $Mg(NH_4)PO_3*6H_2O$, with formula weight of 245.41g. Struvite crystals have distinctive orthorhombic structure and can be identified via X-ray diffraction by matching the intensity and position of the peaks to a database (Dayle and Parsons, 2002). It can be large single crystals, very small particles, large curds and a gelatinous mass (Munch and Barr 2000).

Struvite precipitation was first identified as operational problem, for blocking sludge supernatant pipelines in the wastewater treatment plants, and was highlighted in 1963 (Borgerding 1972). Many researches have been reported to avoid undesired struvite precipitation within sludge supernatant pipelines (Doyle et al. 2003; Dunn et al. 2004; Neethling and Benisch 2004; Rensburg et al. 2003). However, struvite could also be used as an effective and practical method for phosphorus removal and recovery. Struvite can be diectly used as fertilizer, if it were conditionally formed and collected, a market price has already been obtained by Unitika Ltd in Japan (Yasanori et al., 2001), which has become a world leader in the development and application of struvite and phosphorus recovery technologies. Several studies have been reported to generate struvite under controlled condition to avoid unwanted formation, while enable phosphorus removal and recovery in struvite crystal (Battistoni et al. 2002; Celen et al. 2004; Stratful et al. 2004; Ueno and Fuji 2001; Yoshino et al. 2003).

Struvite precipitation is a very complex reaction, which depends on pH value, ion activities and several other environmental factors. Although struvite can be readily formed in wastewater or manure treatment systems, high efficient struvite crystallization can not be easily achieved at designated location. The following literature review gave a general concept of the struvite chemistry and its applications.

2.4.1 The equlibrium and kinetics of the struvite precipitation

2.4.1.1 K_{sp} value and supersatuation level

Equilibrium is the point of a reaction, where the reactants and formed products reach balance. The equilibrium constant is the product of the activities of the reaction ions, it is used to predict the direction of the chemical reactions (Sawyer et al. 1994). When the solution is much diluted, the activities of solutes can be represented by their molar concentrations approximately. The solubility product value (Ksp) is often used for reactions involving solids, because no matter how insoluble the solids is, they are all soluble to some degree (Sawyer et al. 1994). The solubility product constant of struvite precipitation process can be expressed as: Ksp= [Mg]*[NH4]*[PO4]. It is an important parameter for struvite precipitation studies, and has been reported in the range of $5.50*10^{-14} \sim 4.36*10^{-13}$ (Ohlinger 1998; Burns 1982; Taylor 1982; Buchanan 1994; Aage 1997), and was summarized in table 2-1.

Table 2-1. Reported solubility products of Struvite

Ksp	Water characteristics	References
5.50 * 10-14	Sludge digestion supernatant	Ohlinger et al., 1998
7.08 * 10-14	Sludge supernatent	Taylar et al., 1963
7.58 * 10-14	Swine manure	Burns J R, et al, 2003
1.00 * 10-13	Anaerobic digestion supernatant	Mamais et al, 1994
1.15 * 10-13		Aage et al, 1997
2.51 * 10-13	Anaerobic treated sewage	Loewenthal et al., 1994
4.36 * 10-13		Buchanan et al., 1994
3.98 * 10-10	Sludge digestion supernatant	Borgerding J. 1972

Struvite precipitation can not occur, until the multiplied value of the activities of magnesium, ammonium and phosphate ions exceed the value of Ksp, this condition is termed as *supersaturation*. But the precipitation may still not occur, even in a supersaturation solution, because crystals are needed to be introduced into the solution or internal faces allow the formation of crystal nuclei, then precipitation will occur until the ionic concentration are reduced and become equal to that of a saturated solution (Reynolds and Richard 1996). Although higher supersaturation level could increase the reaction rate, if the degree of supersaturation is too high, crystallization reaction would produce fine crystals, which are hard to settle and separate from the wastewater and lead to lower removal efficiency (Adnan et al. 2004; Bowers 2002; Shimamura et al. 2001). Shimamura et al. (2003) found that higher phosphate concentration may result in the formation of fine crystals and thus, reduce the recovery ratio. A linear relationship was developed between phosphorus recovery rate and influent phosphate concentration, as shown in Figure 2-1.

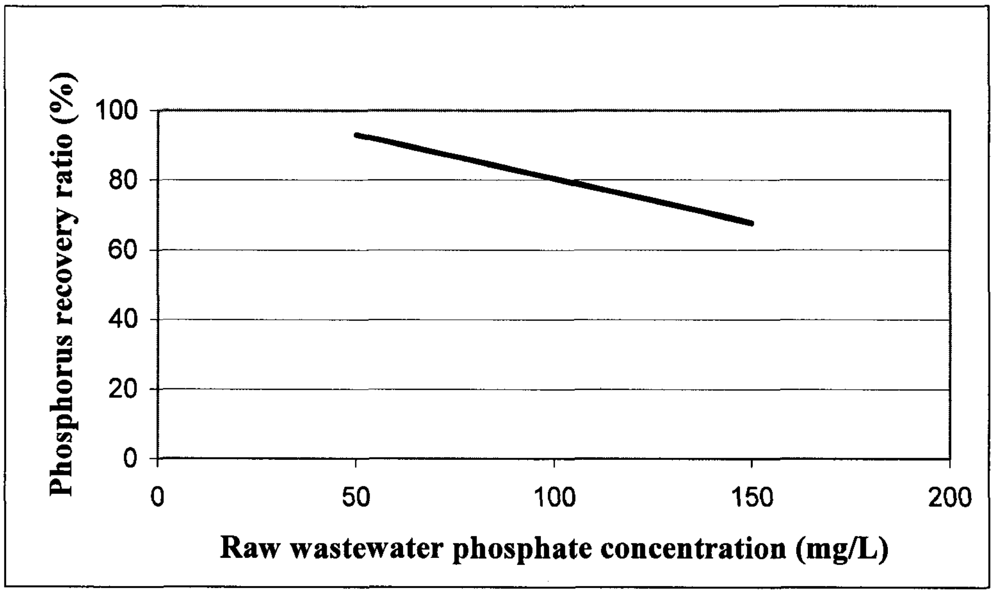


Figure 2-1 Phosphorus removal efficiency versus influent phosphate concentration (modified from Shimmamura et al. 2003)

To maintain a stable and high phosphorus removal efficiency, supersaturation level should be kept in certain range. Shimamura et al. (2003) used circulated flow at a rate of 0~2, to keep the influent phosphate concentration around 50~150 mg/L, to keep the supersaturation level and maintain the P-recovery higher than 84% for all the test. Keith (2002) used the term "critical supersaturation level" for the limitation of the supersaturation level. If struvite precipitates from a solution that is above the critical supersaturation level, many nuclei will form rapidly and simultaneously, which will result in a large amount of small particles. He pointed out that too high levels of pH or Mg dose would produce fine particles and reduce the P-removal. The struvite process should be operated near or below the critical supersaturation level (Bowers 2002). Although the critical supersaturation level is very important for struvite precipitation, this level is very hard to be determined, no method has been found in the literature on how to accurately determine the critical supersaturation level. The only way have been reported is to observe the first appearance of fine particles, but it is almost impossible with real wastewater. Several experiments are needed to find the operational limitations with different wastewater sources.

The equilibrium concept and Ksp value can only be used to estimate the possibility of the reaction to occur, it does not tell that how long it would take to complete the precipitation process. For better understanding of struvite process, the study of reaction rate kinetics is also very important to predict the reaction time.

2.4.1.2 Kinetic of struvite precipitation and modeling

Kinetic is the process constant used to characterize the reaction rate. A good estimation of process kinetic can help design the reactor and process conditions. Under constant temperature and agitation, the reaction rate can be expressed as

$$dx / dt = K * [Mg^{2+}]\cdot[NH_4^+]\cdot[HPO_4^{2-}]\cdot[OH^-], \qquad \text{Equation 2-3}$$

Where K is the kinetic

And it can be simplified as:

$$dx / dt = K' * [Mg^{2+}]\cdot[HPO_4^{2-}]\ , \qquad \text{Equation 2-4}$$

when the concentration of ammonia is much higher than the phosphate, and pH is maintained at a constant level (Battistoni et al. 2002).

Because of the complexity of the struvite process, the reported struvite precipitation kinetics may not be consistant with each other, although it is well established that struvite precipitation is a fast process and is highly affected by pH value. Different struvite reaction times have been reported in various studies, ranging from few minutes to hours. The reaction times are affected by several factors. Beal et al. (1999) reported 15 minutes for the struvite reaction in a bench scale test, while Liao et al. (1995) and Brionne et al. (1994) reported one and two hours, respectively, for struvite reactions. Shin and Lee (1997) reported the completion time of less than one hour for MAP precipiation.

The difference in kinetic values published by several researchers could be due to different operational pH values, wastewater characteristics, and the reaction mixing energy levels etc. Yoshino et al. (2003) reported that the reaction kinetic was influenced by the agitation intensity and the concentration of struvite during the reaction. Adnan et al. (2004) also reported that the slower kinetics of struvite crystallization could be attributed partly to the lack of high energy mixing in the bench scale experiments. A follow-up pilot scale version of a similar reactor design was operated at a higher degree of turbulence to validate this hypothesis. Ohlinger et al. (1999) reported the doubling of mixing speed led to halving of the induction time. Several studies have been conducted to determine the reaction rate. Burns et al. (2003) tested the reaction time of struvite precipitation from 0 to 40 minutes and found that the phosphate removal was increased with the increase in reaction time, but after 10 minutes the increase was very limited. Stratful (2001) reported that struvite particle size increased with reaction time. As reaction time increased from 1 to 180 minutes, struvite particle size increased from 0.1 to 3.0 mm. According to Battistoni et al. (2002), 90% of the total struvite was generated in the first 10 minutes of the reaction and the reaction tended to be stable after half an hour.

Several commercial models have been used to estimate the struvite process, such as MINTEQA 2 model (Nelson et al. 2003), MINTEQ model (Lee et al. 2002) and STRUVITE (version 3.1) (Jaffer et al. 2001). Nelson et al. (2003) reported the reaction times of 35, 45 and 60 minutes and pH values of 9.0, 8.7 and 8.4 respectively to reach steady state for struvite precipitation for anaerobic swine lagoon effluent. The precipitation rate was found to be a first-order kinetics reaction and the rate constant was calculated as 3.7 hr^{-1} at pH of 8.4 and that further showed an increase with increasing pH values. Ohlinger et al. (2000) discussed a struvite reaction process for a sludge lagoon supernatant which followed the pseudo-first order kinetics with a rate constant of 4.2 hr^{-1} at pH of 8.3. Bouropoulos and Koutsoukos (2000) reported the kinetic following a second-order dependence on the solution supersaturation implying to a surface controlled mechanism.

2.4.1.3 Struvite precipitation – nucleation and crystal growth

Struvite precipitation process can be separated into two stages: nucleation and crystal growth. Particle formation is referred to as nucleation. There are two types of nucleation: *homogeneous and heterogeneous*. Homogeneous nucleation occurs when no nucleus exist in the solution. Homogeneous nucleation could generate fine particles that are too small to be retained by gravity. . If other suitable nuclei are present, it is heterogeneous (Parsons, 2001), which is termed as seeding reaction. As solid struvite surfaces already present, then the precipitation will occur by crystal growth, and subsequently will form large-grained products. Struvite process is a self-seeding process, when the system is mature, the generated struvite particle can work as a seeding (Adnan et al. 2003; Bowers and Westerman 2003; Nelson et al. 2003).

Nucleation was found to be the controlling process for struvite formation during the induction period in both pure solutions and in wastewater (Ohlinger et al, 1999). It was also demonstrated that nucleation was primarily affected by the degree of supersatruation and therefore, was a reaction-controlled process, while the crystal growth rate was transport-controlled. Once nucleation has occurred, crystal growth rate exceeds the nucleation rate because of greater activation energy required for nucleation of non-associated ions as compared to the activation energy for deposition of ions on a crystal surface (Gunn, 1976). A high degree of supersaturation can maximize the nucleation rate and the proper mixing can increase the crystal growth. Crystal growth rate is believed to be a function of turbulence or mixing energy. Preferential accumulation of struvite was observed to occur in locations with high mixing energy. (Ohlinger et al. 2000). Once nuclei was generated, crystal growth continued until equilibrium was reached and the system was continuously replenished with struvite constituents (Parsons et al. 2001)

2.4.2 pH effects

Struvite precipitation is highly pH dependent, because the activities of both NH_4+ and PO_4^{3-} as well as the solubility of struvite are pH dependent. The pH effects are complicated, there is a minimium Ksp value in certain pH points for different wastewater. According to Stumm and Morgou (1970), as pH increased from 7 to 9, the percent of NH_4+ decreased from 99% to 64%, while the fraction of PO_4^{3-} increased 250 fold, because of this overwhelming increase in the proportion of PO_4^{3-}, the struvite precipitation was greatly enhanced. But when the pH exceeded 10, the struvite process was retarded, mainly because ammonia was unavailable for the reaction as it escaped as ammonia gas (Salutsky et al. 1972).

Although struvite precipitation can happen in natural to alkaline environment, with presentation of magnesium, ammonia and phosphate (Parsons 2001). An optimum pH value is essential for maximum struvite crystallization. As a major factor, optimum pH value was studied by many researchers, and was reported in the range of 8.8 ~ 10.7 depending on the characteristics of the wastewater (Buchanan et al. 1994; Ohlinger et al, 1998; Shin & Lee, 1997). Phosphorus removal was reported to increase by almost 50% at a pH range of 8.1 and 8.8 in a fluidized bed reactor (Adnan et al. 2003). By several bench scale experiments, the study conducted by Nelson et al. (2003) concluded that the pH for minimum struvite solubility was between 8.9 to 9.25 and was not affected by Mg/P ratio . Another study determined the optimal pH for mineral formation was between 9.0 and 9.5 (Salutsky et al. 1972). It was also found that within first 5 minutes, there was little defference observed in the removal under different pH conditions, but as reaction time increased, higher removal values were achieved with higher pH range of 8.1 to 9.1 (Battistoni et al. 2002). Using the Struvite Model (version 3.1), precipitate struvite versus pH curves were drawn by Parsons et al. (2001) (Figure 2-2). From the figure, it can be noted that the most efficient precipitation happens at a pH of around 9.0, with higher and lower (than 9) pH values resulted in less precipitation. This model was tested in seven wastewater plants in U.K. Although the optimum pH values could be different for different wastewater types, the shape of the curve would be very similar with the struvite formation.

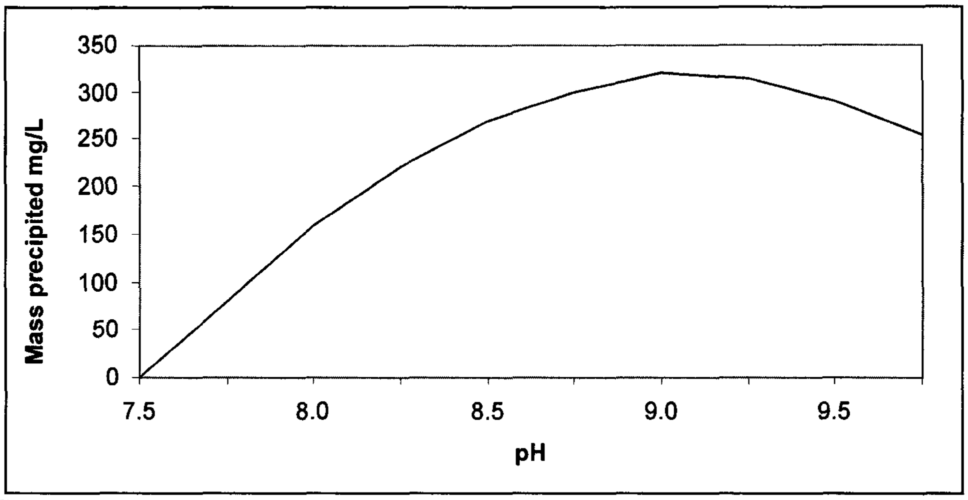


Figure 2-2 Phosphate removal versus pH value

(modified from Parsons 2001)

For any given set of conditions, there was a definite working limit with respect to pH, which was referred to as "the maximum allowable pH" by Adnan et al. (2004). A low value of pH_{lim} would possibly restrict the struvite recovery. It was hypothesized that the restriction of pH_{lim} and the occurrence of fines outside the reactor were the result of an incomplete chemical reaction inside the reactor (Adnan et al. 2004). When operated at pH values exceeding pH_{lim}, poor quality crystals were produced and reactor plugging often occurred. The pH_{lim} value mainly depends on influent phosphate concentration and Mg/P ratio. It was also reported that real wastewater had a lower optimum pH than that of the value indicated by tests on synthetic wastewater. It may be because the organic particles in the wastewater might have provided more crystallization nuclei. The same amount of precipitate deposited upon more nuclei would result in smaller, more numerous grains, which would be hard to separate from the wastewater (Bowers 2002).

As one of the main driving forces of the struvite formation, pH can be increased by the addition of a base or by degassing. Sodium hydroxide is mostly used for pH adjustment in laboratory and pilot scale experiments. This is a simple method, but the chemical cost could be very high. To reduce the chemical cost, magnesium oxide, magnesium hydroxide and ammonia have been used for pH adjustment by many investigators. (Bowers, 2002, Beal et al., 1999, chimenos et al., 2002). But there are limitations with these replacements: (1) the magnesium oxide is not so easily dissolved, (2) the pH value may not reach its optimum point at a controlled Mg/P ratio, if Mg was used for both Mg addition and pH adjustment, and (3) ammonia may increase the nitrogen level in the effluent, which is unwanted in most cases.

A number of researchers have used carbon dioxide stripping to enhance struvite precipitation as a mean to recover phosphorus. The phosphorus removal efficiency can be as high as 80% without chemical dosing, or even higher when combined with chemical dosing (Battistoni et al. 1997). Suzuki et al. (2001) used air flow of $16m^3/hr/m^3$ to treat screened swine wastewater and found that the pH was increased from 7 to 8 in half an hour and reached 8.5 at the end of 3 hours, 65% phosphate removal was achieved with 2 hours of aeration. By combining the air stripping and quartz sand seeding, up to 80% of phosphate removal was achieved without any chemical dosing by Battistoni et al. (1997). Table 2-2 summarises various studies using degassing for pH raising.

Carbon dioxide stripping can be performed by aeration or by pumping the liquid to increase the trubulance while stripping out the air. Ohlinger et al. (2000) reported that increasing turbulence could lead to carbon dioxide liberation and increase in the pH and hence, enhancement of struvite precipitation. The raise in pH (due to turbulence) depends on the type of wastewater, and primarily depends on the alkalinity. The water with an alkalinity of 100 mg/L aerated until in equilibrium with the carbon dioxide in air, would have a pH of about 8.6. (Reynolds and Richard 1996). Parsons et al. (2001) plotted the effects of stirring on the pH of centrifuge liquors with different alkalinity values, as shown in figure 2-3.

Table 2-2. P-removal efficiency by means of aeration

Wastewater type	Scale	P removal	Reference
Digester liquor		88% after 2 hrs	Waki et al. 1987
Synthetic Digester liquor	bench	>90% at pH =9.5	Somiya et al. 1989
Digester liquor	Bench FBR	>80% with seeding	Ohlinger et al. 2000
Textile waste	bench	90% ammonia	Kabdasli et al. 2000
Belt press liquors	Pilot FBR	80%	Battistoni et al. 1998
Belt press liquors	Full scale FBR	61~89% phosphate	Battistoni et al. 1998
Swine manure holding pond	Field scale	90% dissolved P 2 hours aeration	Burns et al 2001
Screened swine waste	Pilot plant	65% phosphate,	Suzuki et al. 2001

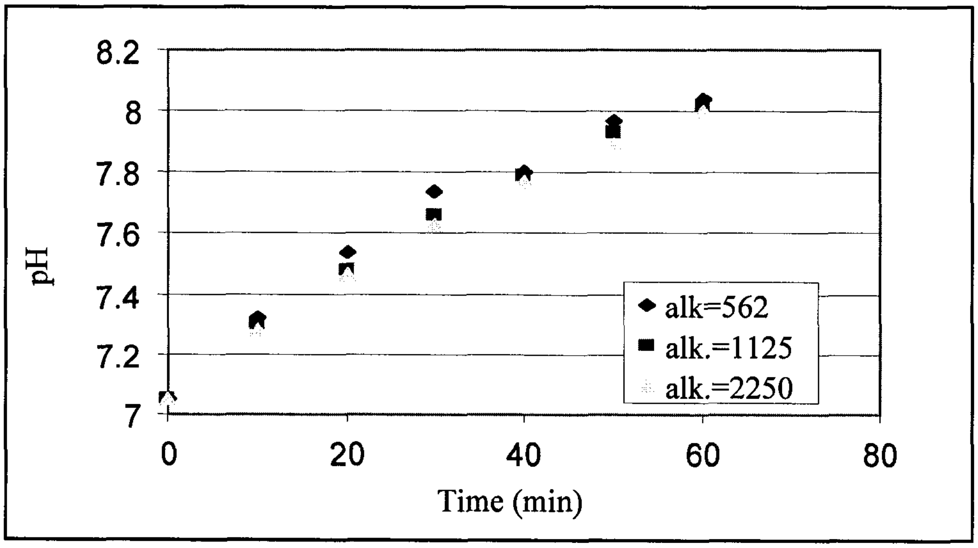


Figure 2-3. pH increase versus stirring time

(Adapted from Parsons et al. 2001)

2.4.3 Mg concentration effects

The concentration of magnesium is another important factor for struvite procipitation. It is one of the ions that precipitate the struvite, as a result, it also affects the supersaturation level and the progress of precipitation process. Because the struvite precipitation requires equal quantities (moles) of magnesium, phosphate and ammonia ions, the concentration of magnesium is usually calculated and used by Mg/P ratio in the struvite process. While unwanted struvite crystallization could occur at any Mg/P molar ratio, resulting in the formation of hard scales of struvite that can block the sludge pipe lines in wastewater treatment plants. For intentional struvite crystallization, the Mg/P ratio should be at least unity. Higher magnesium concentration could increase the P-removal. At a given pH, any increase in the Mg/P ratio would increase the degree of saturation with respect to struvite formation, which in turn would enhance the phosphorus removal (Adnan et al. 2004). But it does not always happen with higher magnesium dosage. But, too high level of magnesium concentration could cause high level of supersaturation and cause generation of numerical fine particles leading to reduced P-removal. Several studies were conducted to determine the optimum Mg/P ratio for intended struvite formation process. Magnesium concentration is often described as a limiting factor for phosphorus recovery from wastewater. A wide range of Mg/P ratio has been reported for struvite precipitation, depending on the pH value, wastewater characteristics, and the ion complex effects. Due to the effect of ions, the process could require high Mg dose, because some of the supplemented magnesium could bind with other compounds and become unavailable to the struvite reaction. Generally, Mg/P ratio of 1.1~1.6 was considered as optimum in most reports. With factorial experiments using livestock waste lagoons effluent, it was found that increasing Mg addition in the range of 0~60 mg/L and increasing ammonia addition in the range of 0~200ppm were significantly associated with increasing phosphorus removal (Bowers 2002).

The following chemicals are mostly used for magnesium source: magnesium chloride, magnesium hydroxide, and magnesium oxide. Magnesium chloride is generally used as it can easily be dissolved in water. Also, it requires a short reaction time, which is required to bring Mg^{2+} into solution. Magnesium oxide and magnesium hydroxide could be used to function as both Mg source and as a mean to increase the pH. However, to perform two functions with a single chemical, may not be suitable for process optimization under different conditions. Keeping the Mg/P ratio and other conditions constant, higher P-removal efficiencies were achieved by using magnesium chloride than that of magnesium oxide. (Antakyali et al. 2004; Hoffwann et al. 2004). However, magnesium oxide and magnesium hydroxide are still preferred by some investigators because of less chemical cost, and decreased chemical requirement for pH adjustment. Beal (1999) reported that when magnesium oxide was used as a source of Mg, the pH was increased to 8.3~8.8, and with an additional NaOH dosing (to increase pH to 9.0~9.5), there was no enhancement in the struvite formation. Possibly, the pH before NaOH addition had already achieved the optimum. Taruya et al.(2000) developed the Phosnix process, using magnesium hydroxide as Mg source and sodium hydroxide to control the pH. This is an optimized process with less NaOH requirements.

To reduce the chemical cost, studies were conducted by Beal et al. (1999) to find other cheap substitutes for magnesium, and it was found that anaerobic digestion significantly increased the magnesium concentration, thereby enhancing the struvite process because of the relaease of soluble magnesium by hydrolysis. Mg concentration was reported to be increased from 88 mg/L to 313 mg/L by ASTR anaerobic digestion for 36 days. Several substitutes have been studied for magnesium source, such as sea water, bittern and magnesium industrial by-products. A by-product of magnesium oxide production was studied to precipitate struvite from wastewater treatment liquor, and it was found to be more economical than using pure chemical (Quintana et al. 2004). Food grade bittern was used to treat effluent from activated sludge swine wastewater treatment and achieved about 80~90% phosphate removal (Lee et al. 2002). Sea water was also used as magnesium source for struvite precipitation and produced promising results (Matsumiya et al. 2000). Low-grade magnesium oxide obtanied from the calcination process (in rotary kiln at 1100 °C) was studied as a magnesium source to treat cochineal extract process wastewater and achieved higher than 90% phosphate removal (Chimenos et al. 2002). Alternative magnesium source requires greater quantity and longer reaction time, compared to pure magnesium oxide, but it still demonstrates a significant cost advantage.

2.4.4 Other affecting factors

A major obstacle in the recovery of phosphate via struvite is the complexity of struvite crystallization. The process highly depends on local conditions, ionic strength effects and the effects of foreign ions that further complicates the process (Andrade and Schuillig, 2001). Besides the pH and Mg concentration, many other factors could affect the phosphorus removal efficiency in the struvite crystallization, such as, temperature, ion strength, seedings, and the quality of produced struvite crystal etc., as discussed below.

- **Effects of ion strength and foreign ions**

Ionic strength of solutions affects the solubility of struvite, because it influences the activity of individual ions. Not all phosphate, ammonia and magnesium ions in the solution exist as free ions, it depends on the concentration of the solution and some other conditions. The interaction of ions in solution leads to an increase in solubility (Doyle and Parsons, 2002). The ionic strength can be calculated simply as:

$$\mu = 0.5 \Sigma Ci*Zi, \qquad \text{Equation 2-5}$$

where Ci is the concentration of each ion in the solution, and Zi is the valence of that ion.

Ion effect may influence the process by forming some complex compounds, and therefore, reduces the availability of ions for struvite formation. It was also found that grain size was smaller when real wastewater was used instead of synthetic water, because of the suspended organic particles. The organic particles produced large amount of crystallization nuclei, which resulted in numerous but small grains (Liao et al. 1995).

The induction time of struvite precipitation for low ammonia concentrations and in the presence of ions that are commonly found in natural waters was investigated by Kabdasli et al. (2004). The induction time was determined from absorbance measurements, while conductivity and pH of the solutions were monitored throughout the process. It was found that struvite crystal structure and dimension were affected by supersaturation and the presence of foreign ions. The induction time varied in a wide range depending on the composition of solution.

The calcium ions have been found to retard the struvite process (Corre et al. 2004; Kabdasli et al. 2004). Corre et al. (2004) reported that the presence of calcium ions in the media can significantly affect the struvite crystal growth and the quality of the crystals produced. It was found that by increasing the concentration of Ca, the size of struvite crystals was reduced, because Ca particles started to stick on the surface of struvite crystals, preventing further crystal growth and thus forming an amorphous product in the end (Corre et al. 2004). Kabdasli et al. (2004) also found that calcium ions at concentration of 0.25mM did not cause a remarkable change.

The effects of various other ions on struvite precipitation were also reported. It was found that the presence of sodium ions over 50mM retarded the induction time significantly; while carbonate ions had a slight effect, sulfate ions increased the induction time. Malonic acid had no significant effect on the rate of struvite precipitation at pH of 8.5 and constant supersaturation.

- **Temperature effects**

Temperature has less significance in the struvite process, although it is an important factor for many water/wastewater treatment processes. Since most studies were conducted at ambient temperature, only a few researchers investigated the temperature effects on struvite formation. Ideally, lower temperature should favor the struvite precipitation because the solubility product constant (Ksp) decreases with the decrease in temperature, but the real situation is more complicated. The temperature may affect pH, conductivity and other characteristics of the wastewater. All types (negative, positive or natural) of temperature effects have been reported. The different conclusions found in the literature could be due to different source wastewaters used. Adnan et al. (2004) concluded that lower temperature (15 °C) was more favorable to the struvite formation than the higher temperature (25 °C). Chol (1997) studied the nitrogen removal from piggery waste treated with SBR at temperature between 25 ~ 45 °C, and reported that struvite formation could not be observed at 30 °C or above. While Beal et al. (1999) reported that higher temperature could enhance the struvite process by increasing the temperature from 25 to 35 °C, as a result, the phosphate removal efficiency was increased from 28% to 42% with only stirring and settling of the swine manure was performed. However, Burns and Finlayson (1982) concluded from their experiments that temperature would not influence the process significantly in the general range of the wastewater temperature, and ambient temperature was recommended for most cases.

- **Seeding effects**

The effects of the seeding have been studied by several investigators to enhance the struvite crystallization (Ohlinger et al. 2000; Shimamura 2003; Webb and Ho 1992). Ideally, the seeding material should possess sufficient size and a crystal structure similar to that of the precipitating substances. Sand, borosilicate glass filings, and the struvite itself have been studied to be used as struvite precipitating seeding materials. (Webb and Ho, 1992, Momberg and Oellermann, 1992). Seeding was considered to enhance the struvite process by supplying the reaction surface. It has been suggested that the specific surface area of the seed could be one of the factors influencing P-removal, and therefore, a seed with a larger specific surface area could promote phosphorus removal (Ohlinger et al., 1999). Although large particles are desirable as it is easy to separate them from the solution. Excessive growth of MAP crystals could degrade the fluidized effect, and reduce the MAP surface areas necessary for reactions and thus decrease the MAP recovery ratio (Shimamura et al., 2001).

However, seeding were supposed to be needed only during the start-up period of the struvite process. A number of studies suggested that external seeding were not required when the system became stable (A.Seco 2004; Adnan et al. 2003; Bowers and Westerman 2003), because the generated struvite crystals would now act as seeding for the struvite crystallizetion.

2.4.5 Struvite precipitation from swine manure

Struvite formation was widely known as operational problem, blocking the pipelines in the swine manure collection and treatment facilities. (Booram 1975; Buchanan et al. 1994; Edgerton et al. 2000). Lately it has been recognized as an effective method to remove and recover phosphorus from the manure, due to the presence of high concentration of phosphate, ammonia. Because of the high concentration of magnesium in swine manure, the quantity of chemical added for manure treatment could be minimized. Because of its great potential for phosphorus precipitation, it could not only recover phosphorus from manure, but also could contribute to a scale-free purification system for swine manure (Suzuki et al., 2001).

Although struvite can be readily formed in swine wastes, it is not easy to precipitate at controlled locations, with high phosphorus removal efficiency. High contents of solids and organics in the manure interfere with struvite precipitation, therefore many of the previous studies were conducted with lagoon treated swine manures, rather than the fresh manures (Bowers and Westerman 2003; Mikkelsen 1997a; Nelson et al. 2003; Suzuki et al. 2004). Suspended solids concentration higher than 1000 mg/l may interfere the struvite precipitation (Schuiling and Andrade, 1999), while the organic compounds in the lagoon liquid have the potential to form soluble complexes with Mg^{2+}, thereby reducing its activity and increasing the equilibrium phosphate concentration (Schulzekettmer, 1991). Anaerobic digestion in the lagoon could also enhance the struvite formation by bringing more of the reaction limiting ions into solution.

By adding100 ppm ammonia and 30 ppm magnesium, Keith (2001) used struvite precipitation to treat liquid from swine manure holding pond and achieved 74% and 58% reductions of OP and TP, respectively. He also found that the decrease in flow rate (341~586 L/hr) was significantly associated with increase in P-removal in field-scale system, while the effect of flow rate was insignificant in the range of 41 to 57 L/hr in lab-scale system (Keith, 2001). From bench-scale experiments, Burns et al. (2003) concluded the optimum condition of pH of 8.6 and Mg/P mole ratio of 1.6:1 for struvite precipitation from swine waste. About 96% phosphate removal was achieved with swine waste pond supernatant. The study demonstrated a 90% reduction of soluble phosphorus (via struvite precipitation) in a 140,000 L swine slurry holding pond under field-scale conditions, with magnesium chloride dosage increased the mole ratio of Mg/P to 1.6:1. The treated manure was used for land application. Nelson et al. (2003) decreased the phosphate concentration in anaerobic swine lagoon liquid from an initial concentration from 51 mg/L to a steady state concentration of 7.6 mg/L in approximately 30 min at pH of 9.0 and Mg/P ratio of 1.2:1.

Several modeling techniques such as MINTEQA2 have been used to model struvite precipitation at various pH and molar ratios. From bench-scale tests, optimal pH was determined between 9.0~9.5 (A. Miles and Ellis, 2001)

Struvite process has been demonstrated as a promising technology for nutrient removal and recovery from swine manure. Table 2-3 summerized various applications of struvite process treating swine manure:

Table 2-3 **Struvite application with animal manures**

Scale	**WW character**	**Reactor type**	**Reactor volume (L)**			**Flow rate L/m**	**HRT** (Min)	**Mg/P**	**pH**	**DP remove %**	**Seed**	**Ref.**
			Mix	**Clari.**	**T**							
Pilot	Screened swine waste 195(TP)	Middle aeration cylinder	9.9 1.4m	34 1.54m	54 2.43 m	0.4	135	0.9 No chemical	*8.5 18m/h/m	65		Suzuki et al. 2001
Bench	Swine waste 230~570	Beaker 500ml			0.4		10	1.6	8.5	90	No effect	Burns et al 2003
Bench	Secondary treated swine ww P=13	Beaker	10 min	10 min	1			3.86 Seawater bittern	9.6	76 81		Lee et al. 2002
Bench	Swine waste lagoon effluent:50~64	Beaker	20 min					1.2	9	85		Nathan et al. 2003
Bench	Swine wastewater		5hr	pH was raised by aeration no NaOH was dosed				1:1	8.5	88		Loewenthal et al, 2004
	Digested		3hr					1:1	8	44		
Lab	Swine waste lagoon 60~80	Cone shaped FBR			35.6	0.82	43	0.54 ~ 1.9	8.1 ~ 8.5	36~74		Keith 2003
Pilot					23.6	7.4	3.2	0.9~1.7	8.3	56~82		
Bench	Swine manure	Beaker 500ml	15 min	15 min				1.1	8.5	92		Beal et al, 1999
	Digested									98		

2.4.6 Quality of recovered struvite crystals and its potential application

The recovered struvite can be utilized as fertilizer for land application and raw marterial for phosphorus industries, depending on the quality of the struvite crystal. The quality of the crystal struvite is described by its size, structure, mechanical strength or brittleness etc. The good quality crystals do not exhibit any attraction among themselves, unlike the dendrite crystals.

The quality of the struvite crystals depends on the supersatuation of the solution and many other factors. Adnan et al. (2003) found that the quality of the growing and harvested crystals was independent of the shape of the seed used, and there was no relationship established between crystal quality and magnesium feed concentration. It was also observed that the runs, where pH was slightly less than or equal to the pH_{lim}, always produced good quality crystals (Adnan, et al, 2003). To facilitate the generation of high purity struvite, a struvite accumulation device was developed by Suzuki et al. (2004). The device was made of stainless steel wire mesh, and was submerged in the struvite reactor. The accumulated struvite was easily scraped off with only a light brushing. About 95% pure struvite was produced, and the purity could be increased to 99.5% by washing with tap water before air-drying.

The quality of crystal struvite can affect the P-removal efficiency, because poor quality struvite would be hard to separate from the solution. In their study, Shimamura et al. (2001) found that by decreasing the mean particle size form 1.18 nm to 0.54 mm, the

P- recovery ratio was increased form 85% to 92%. The study also suggested that in order to maintain a stable operation and P-recovery ratio, the particle size in the reactor should be kept stable.

The potential applications of struvite precipitated from different waste streams have been widely investigated (Heinzmann 2004; Johnson et al. 2004; Schipper and verhoek 2004; Sothen 2004). It has been found to be a effective source of P, N, and Mg for plants through foliar and soil application (Lierti et al. 1981; Priestley et al. 1997; Salutsky et al. 1972). Because of its low solubility in water and soil solution, it can be applied to soil at higher rates than those of conventional fertilisers without the danger of burning of plant roots (Booker 1999). A full scale test was conducted with 250 tons of struvite cake precipitated from a calf manure treatment plant (Schipper and verhoek 2004). 3% of struvite was added to the usual phosphate rock feed for 70 hours. There were no adverse effects found by replacing part of the phosphate rock feed of the phosphate production with struvite (Schipper & Verhock, 2004). The potential for inclusion of struvite in a palletized compound fertilizer was investigated by Johnson et al. (2004) for the horticultural market. A trail batch of fertilizer pellets was successfully produced and plant growth trials were also carried out. The results indicated the use of the struvite as a fertilizer ingredient to be a realistic commercial opportunity. The study also addressed that the crystals need to be washed to remove organic solids and remaining bits of shredded plastic that were carried in the centrate and settled along with the struvite. The struvite was washed immediately after removed from the reactor because the organic solids could tend to congeal and trap the struvite crystals (Johnson et al. 2004).

Sothen (2004) investigated the marketing potential of fertilizer make out of recovered phosphorus by telephone-interview with all German organic farming associations. The survey showed an enormous interest in these new approaches, but suggested further public relation work required to inform and convince the farmers and consumers (Sothen 2004). Heinzmann studied several processes to recover phosphorus from either liquid, sludge or ash, and concluded that no phosphorus recycling with a defrayal of costs was possible. Acording to his study, the future importance of phosphorus recycling would depend on the market price for raw phosphate, the recycling costs and furthermore, on the general political framework (Heinzmann, 2004). Although the phosphorus recovery by struvite crystallization may not appear economically realistic at present, but it could be an effective way to offset some of the unavoidable costs associated with waterwater treatment and sludge disposal.

2.4.7 Pilot / full scale operations and struvite reactor design

A good design of a struvite reactor is foundamental for effective recovery of phosphorus from waste stream. Although, several processes have been developed and applied to recover phosphorus, either from the sludge supernatant or directly from the P-rich wastewater streams, an integrated struvite theory has not been formulated. The information on the reactor design and operation optimization is still not readily available.

Several studies have been reported with significant phosphorus removal, but operational problems, such as pipeline plugging, have also been mentioned. Adnan et al. (2004) found that when the solution saturation levels were high, the rate of primary nucleation increased accordingly, which resulted in the formation of fine crystals. The recycle line and the injection port were plugged within 20 hours and required constant cleaning to maintain successful operation (Adnan et al. 2004). It was also reported that by operating the struvite plant under strict meta-stable condition (pH = 7.6 ~8.2), scaling up of pipelines could be avoided (Battistoni et al. 2004).

Several types of struvite reactors have been developed and studied, and most of them were fluidized bed reactors (FBR) and pellet reactors, or developed from the similar concept. A stepped cylinder FBR with an external clarifier was developed by Adnan et al. (2003). The external clarifier was used to recycle the effluent back into the reactor and to trap the washed out fine crystals from the reactor. To accomplish the best possible mixing, an injection port build of stainless steel was provided at the base of the bottom section. Synthetic water was used for the study. It was found that by increasing the pH gradually to a higher value, smoother operation of the reactor was achieved with higher phosphorus removal. Over 90% P-removal was achieved with both low and medium phosphorus concentrations tested. The generated crystal size was mainly affected by the crystal retention time (Adnan et al. 2004) and without chemical dosing (Battistoni et al. 1997)

A demontration plant was developed and reported by Battistoni et al. (1997) to treat anaerobic supernatants in municipal wastewater treatment plant. The plant consisted of a large equalizatin tank, a decanter, a mixer, stripping and deaeration columns, and the FBR combined with a top cone clarifier. The effluent was recylced in a ratio of 3.5 ~ 7.0 to maintain certain flow rate (Battistoni et al. 2004). A crystallization reactor with two cylinders was developed by Suzuki (2004) to treat swine manure. The inner cylinder is the struvite reactor, where aeration is used for mixing and carbon dioxide stripping. Optional $MgCl_2$ was dosed as Mg addition. The outer cylinder is the clarifier to separate the generated struvite. An average of 66 ~ 86% phosphate removal was achieved under different operational conditions, and total hydraulic retention time of 22.3 hours (Suzuki et al. 2004).

The Phosnix process, based on an air agitated column reactor fitted with ancillary chemical dosing equipment, was developed by Brett et al. (1997).. Digester effluent was fed into the base of the tower where it was mixed with a magnesium solution to provide an Mg/P ratio of 1:1.3. Alkali was used to ensure a pH range of 8.5~9. Air sparked into the base of the column provided the necessary agitation for mixing and for maintaining the growing particles in suspension. The MAP slurry usually occupied about 12 liters of reactor volume after settling. About every five days of reactor operation, approximately 2~4 liter of settled MAP slurry were removed (about 16% solid content), which was about 320 g dry MAP per day, little less than the theoretical value (327 g /day), because some MAP was continuously lost as fine particles in the effluent. (Brett et al. 1997)

A full scale FBR struvite plant was reported with three years operation data (Ueno and Fuji 2001). Mg was added in the form of $Mg(OH)_2$, and pH was controlled by both aeration and NaOH addition. More than 90% phosphate removal was achieved with effluent phosphate concentration of less than 10 mg/L. The generated struvite, collected and purified by a rotation seperator, was sold as raw material for fertilizer.

Although lots of efforts have been made to study struvite process with reasonable success (as discussed above), further research is still required to study struvite process design, operational control and generated struvite applications. A good understanding of the struvite process chemistry, combined with parsimonious design, has the potential to produce a cost effective process for phosphorus recovery.

Table 2-4 Pilot scale or full scale operation summary

Wastewater	Reaction time	pH	Mg/P	P removal	Ref.
Anaerobic supernatant	4 min.	8.5	1.1	92%	(Yoshino et al. 2003)
Sludge dewatering centrate	1~2 hr	8.5	1.3	94%	(Munch. et al. 2000)
Diluted swine waste	> 30 min	8~10	2	Up to 99.2%	(Kim, et al. 2004a)
Swine wastewater	3.6 hr	8		66~86%	(Suzuki et al. 2004)
Pretreated swine waste	30 min.	8.5		98%	(Laridi et al. 2004)
Anaerobic sludge filtrate	42 hr.	8.2~8.8	1	≥ 90%	(Ueno and Fuji 2001)
Synthetic wastewater	10 min	8.3		90%	Adnan et al. 2003
Lagoon effluent		8.5~8.9	1.9	74	Bower et al, 2003
Anaerobic supernatant	2~2.5 hr	7.9~8.6		≤ 80%	(Battistoni et al. 1997)

2.5 Research objectives, methodology and future needs

According to the needs and objectives of the overall project, this research was focused on struvite crystillization to remove phosphorus from pre-treated swine manure. The research was conducted to achieve the following objectives:

1 Batch experiments to observe the struvite precipitation from pre-settled swine manure, and to determine the important affecting factors,

2 Pilot experiments to investigate the performance of the fluidized bed crystallizer for phosphorus removal from pre-treated and diluted swine manure,

3 Development of an enhanced phosphorus crystallizer with improved phosphorus removal,

4 Investigation of the performance of the new crystallizer at pilot scale in terms of phosphorus removal from swine manure

5 Economical analysis of the reactors for phosphorus recovery/removal

Based on the literature review and the time limitation of this research, future needs need to be addressed as following:

1 To find out the operation and maintenance requirements of the EPC, by pilot scale experiments,

2 To set up the optimum operation condition for the struvite process through long term continuous operation on farm site, using swine manure with varied characteristics,

3 To establish design principle for EPC plant, based on pilot experiments and long term operation results,

4 To estimate proper land application rates of the recovered struvite mixture, and the long term effects of the plants and soil,

5 To develop efficient method to recover more purified struvite from the manure and find the feasibility for their application in the phosphorus industries,

6 To investigate feasible substitutes of magnesium chloride to lower the operation cost,

7 To investigate the proper pretreatment for struvite system, to optimize the phosphorus recovery process.

3 Experimental methods

3.1 *Materials*

3.1.1 Source of the swine manure

In this research, raw swine manure was obtained from the Swine Research and Technology Center in the university farm located at the university of Alberta in the city of Edmonton, Alberta. The research center houses approximately 1500 pigs, including 300 fully grown pigs and 1200 growing pigs and piglets. The average water consumption was approximately seven liters per pig per day, according to Mr. Jay Willies, the supervisr of the research centre operation.

The swine manure was collected and stored in a holding tank outside the housing facility, and was pumped out periodically for further treatment and disposal. Three underground tanks, each with volume of 2000 gallon (about 7.5 cubic meter), were located near the holding tank. The raw swine manure was pumped out from the holding tank into one of the underground tanks, where it was settled for at least 24 hours, and the supernatant was transported to our pilot plant operation site for next treatment operation, or to the laboratory in the Environmental Engineering Building at University of Alberta for batch scale experiments.

All the swine manure used in this research, unless specifically described, was taken from the underground tank after 24 hours of settling, and was called pre-settled or primary settled (swine) manure in this thesis. This manure was transported from holding tank to the pilot plant or to the laboratory. The pre-settled manure might be diluted with tap water, depending on the experimental requirement.

3.1.2 Laboratory Studies

3.1.2.1 Jar test

To investigate the feasibility and to determine the optimum conditions of the struvite precipitation from swine manure, several jar tests were performed in the laboratory.

The premary settled swine manure was brought and stored into a 50 gallon (about 200 liter) barrel at the cold room with temperature of 4 °C. The manure samples were brought to the room temperature before the experiment (around 20°C).

Phipps & Bird^{TM} (PB-700^{TM} Jar tester) six-paddle stirrer with illuminated-base jar test apparatus was used to perform jar tests. Six 2-L square jars were used for the test. The swine manure was mixed thoroughly before the jar tests. The samples were collected from the top of the supernatant level in the jars using a pipette. The paddle mixing speed was controlled to the pre-set values, and the mixing time was monitored by a stop watch. The pH of the manure was adjusted by using NaOH and was monitored by a pH meter. A known amount of $MgCl_2$ was added into the jars. The original supernatant and treated supernatant samples were taken and analyzed to determine the effects of mixing, settling and chemical dose.

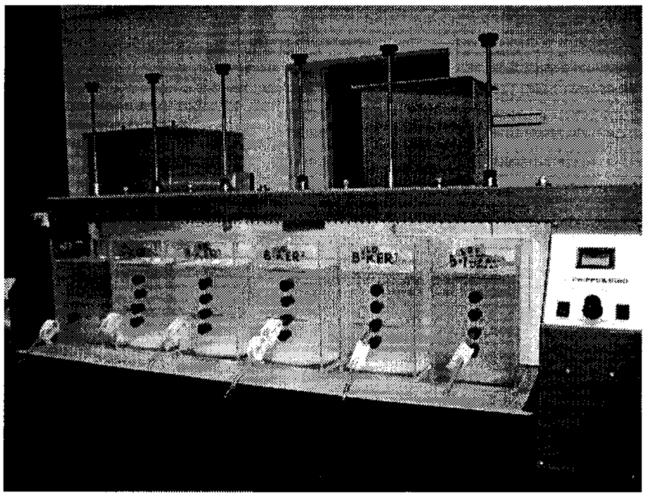


Figure 3-1 Jar test apparatus

(Adapted from Singh 2004)

3.1.2.2 Aeration test

To investigate the aeration effect on pH adjustment of the swine manure, and to monitor the pH changing trends during aeration, batch scale aeration test was conducted with pre-settled and fresh manure before the pilot experiments.

Fresh swine manure and pre-settled manure were taken from the swine manure holding tank outside the swine facility and the underground tank, respectively. These samples were transported to the laboratory in separate barrels. The manures were aerated in four liter jars with fine bubble diffuser. The air supply was controlled and monitored by valves and gas phase flow meter, as shown in the Figure 3-2.

Samples were taken before and after aeration. During the whole aeration period, pH was periodically monitored in predetermined intervals. A part of this aerated liquid (about 500 ml) was taken from the jar after 2, 4 and 6 hours interval. These mixed liquor were settled in 500 ml beakers for 2 hours. The settled supernatant was sampled for analysis of phosphorus and magnesium concentrations.

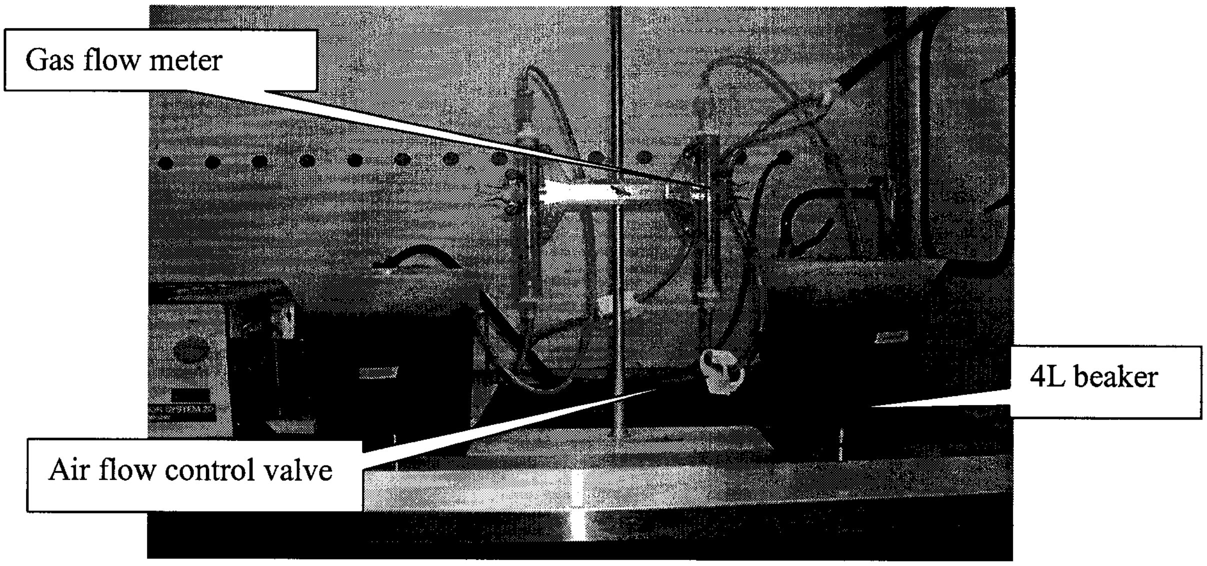


Figure 3-2 Laboratory aeration test apparatus

3.1.3 Pilot plant study

Two pilot plants were set up in a building located at the research farm of the University of Alberta, Edmonton, Canada. The first pilot plant was consisted of a cone shaped fluidized bed crystallizer, which was designed and assembled by Mr. Bowers according to his patent, and the other was an enhanced phosphorus crystallizer, which was developed druing this research to compensate the limitations of the first pilot plant.

3.1.3.1 Pilot plant accessories

The following accessories were used for the two pilot plants: a storage tank (2 m^3 capacity), with mixing pump inside, peristaltic pumps with controller, Mg solution barrels, pH meter, flexible hoses, valves, and connecting pipes, as shown in the following pictures in figure 3~6.

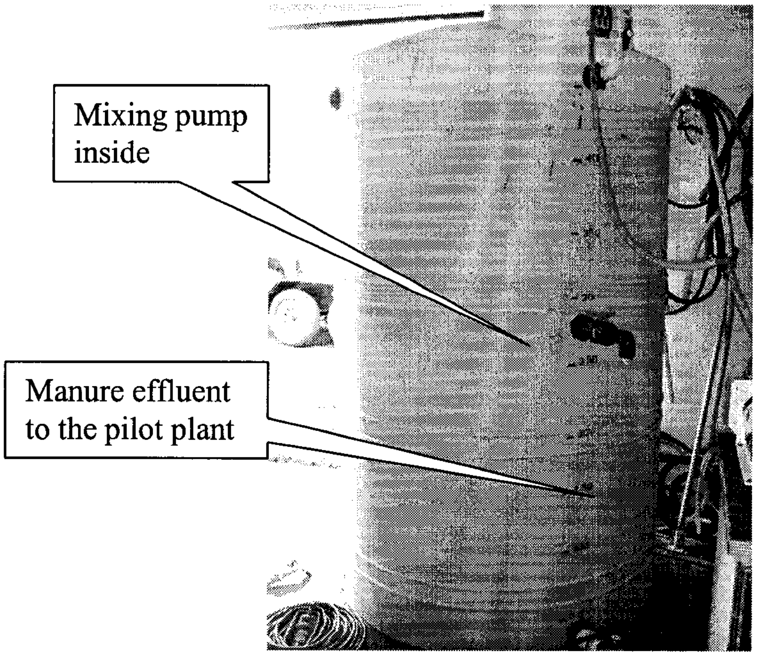


Figure 3-3 Pre-settled swine manure storage tank (2 m^3)

Figure 3-4. Mg solution bucket (about 20 liter)

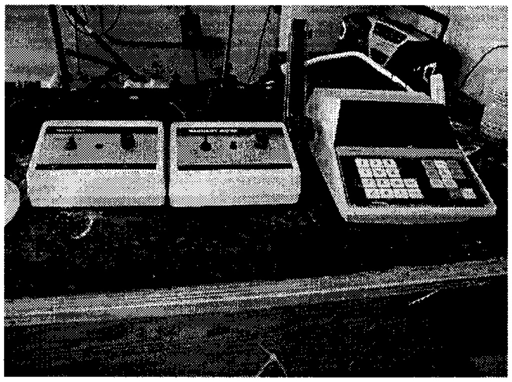


Figure 3-4 Peristaltic pump controllers and pH meter

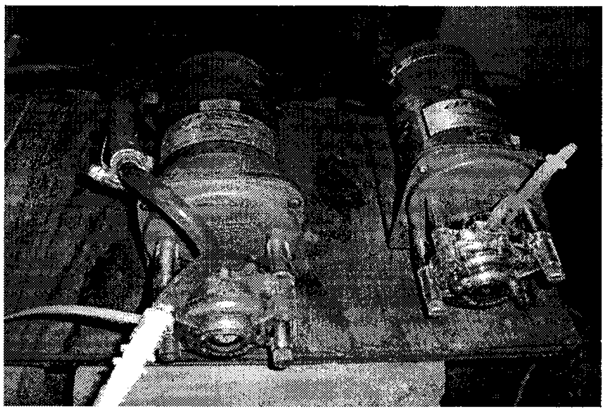


Figure 3-5 Peristaltic Pumps for manure and solution dose

3.1.3.2 Fluidized Bed Crystallizer

A cone shaped fluidized bed crystallizer was designed and assembled, based on the patented North Carolina University struvite system. The crystallizer was mainly consisted of a cone shaped reactor on the top, and a cylinder shaped struvite collector at the bottom, both were made of PVC plastic (Figure 3-6). The two parts were connected at the middle by a Tee pipe, where the influent was pumped into the reactor.The magnesium and alkaline solution (or ammonia gas) was introduced from the bottom of the cone through a flexible hose, where it was mixed with the influent manure. A rubber plug valve was installed at the bottom of the cone reactor, which could be opened periodically to collect the settled struvite into the bottom cylinder, while the influent manure could go up to the systemcontinuously. The effluent was collected through a hose provided at the top of the reactor.

The pilot plant was first operated with the pre-settled swine manure, which was taken from the underground settling tank and stored in the 2 cubic meter tank on site. Then the plant was tested with diluted swine manure at the suitable flow rate. Before the plant started up, some struvite scrapped from some discarded swine manure collection pipe was put into the reactor as seeding.

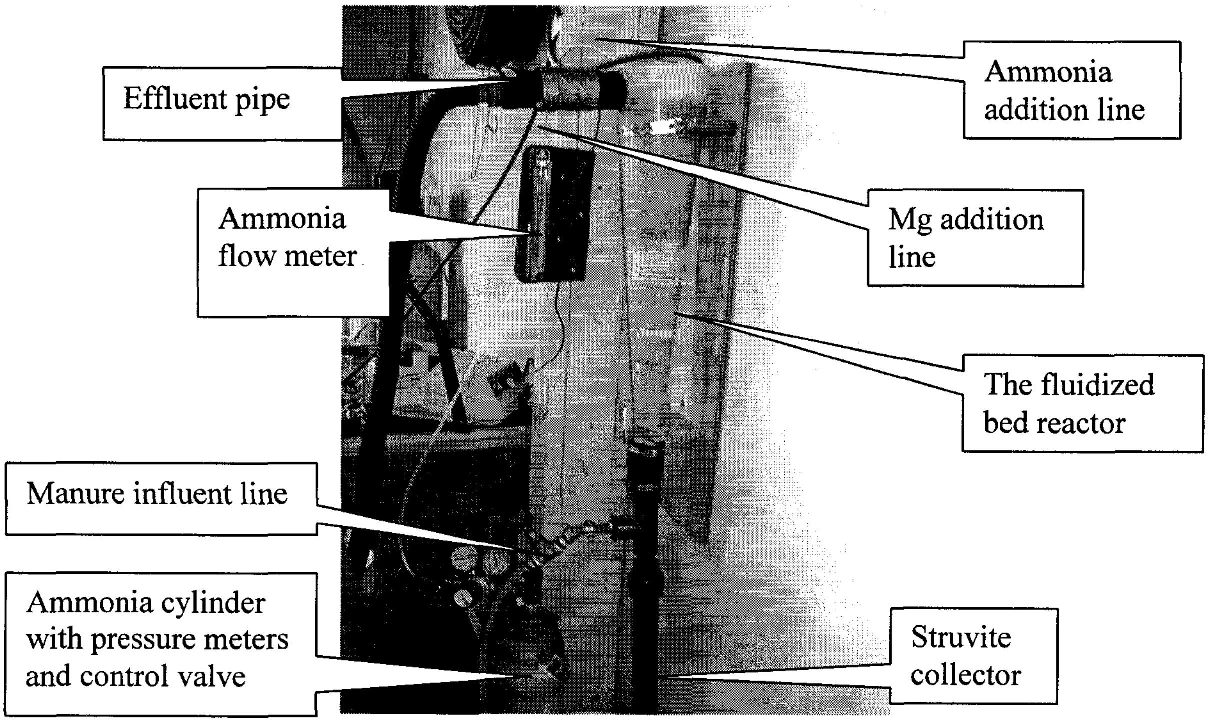


Figure 3-6 The Cone Struvite System

During the initial trial operations, no significant phosphorus removal was observed with this system, because the fluidized bed was not formed completely. Therefore, the two feet (0.6m) long cylinder was reassembled to be used as the reactor to create the fluidized bed, and the cone was now used mainly as a clarifier, as shown in the Figure 3-7. The alkaline and magnesium doses, and the manure influent were pumped into the bottom of the cylinder, mixed and flow up to form a fluidized bed in the cylinder for struvite formation. The grown struvite was seperated and settled down in the clarification cone. The generated struvite was discharged periodically from the bottom of the cylinder. This new assembled reactor was then tested with diluted pre-settled swine manure.

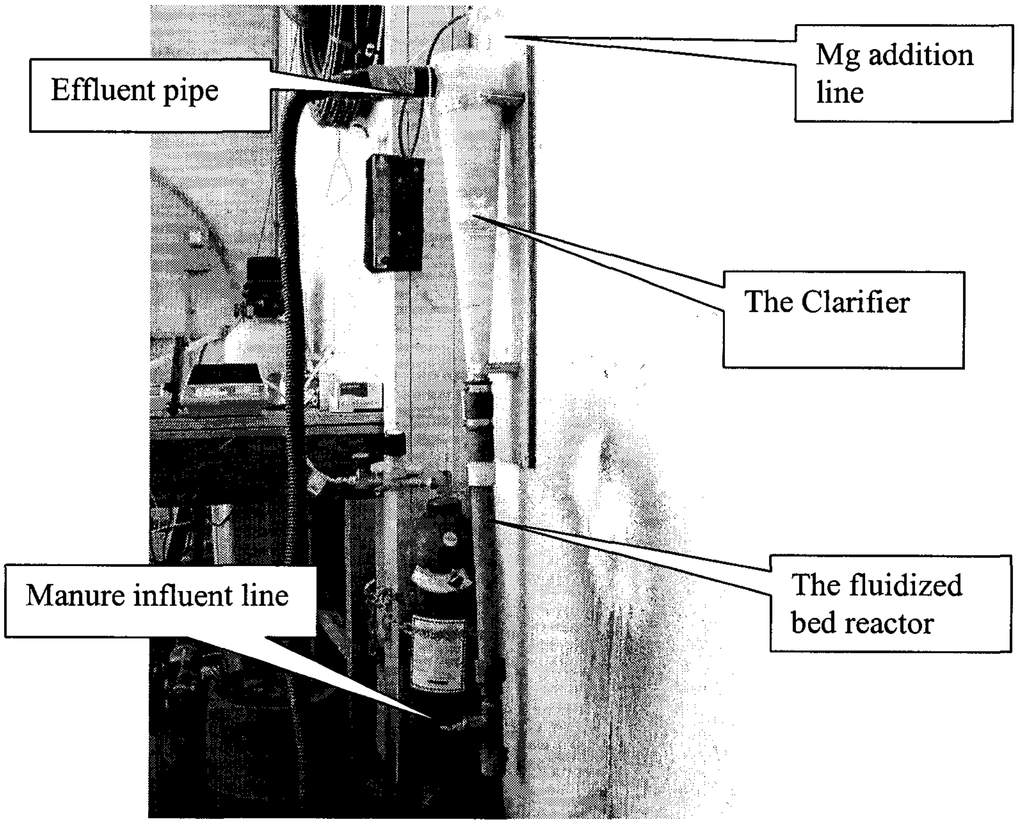


Figure 3-7 The Cone system after reassembling

The settled swine manure was diluted with tap water in ratio of about1:1 in a 200 liter plastic barrel. A centrifugal pump was used at a constant flow rate of 4 L/min to cycle insufficient phosphorus removal. The original diluted manure was collected from the barrel, while the treated wastewater was sampled from the effluent pipe.

$MgCl_2 \cdot 6H_2O$ was used as Mg source, which was first dissolved into tap water to make100g/L Mg solution in the laboratory. Then it was brought to the pilot plant site and diluted with tap water to make solutions with Mg concentration of 1000~3000 mg/L, depending on the operation requirements. The diluted Mg solution was put into a 20 liter bucket and pumped into the bottom of the reactor by a peristaltic pump at a pre-determined flow rate.

The pH was adjusted by adding ammonia at the early stage of the experiment. The ammonia was supplied from a compressed ammonia steel cylinder. A valve and gas flow meter were used to adjust the dosage. In the later experiments, ammonia was replaced by sodium carbonate solution, because ammonium content in the swine manure was sufficient for phosphorus removal by struvite formation. Also, high concentration of ammonia presents environmental hazards. Chemically pure sodium carbonate was used to make one mole solution in the lab, then it was diluted to 0.1 M when used in the pilot plant. The pH probe was put into the settling cone to monitor the pH throughout the process.

3.1.3.3 Enhanced Phosphorus Crystallizer (EPC)

An enhanced phosphorus crystallizer (EPC) was designed, assembled and tested in this research, to treat swine manure for phosphorus removal/recovery. This crystallizer was consisted of two chambers in one tank, they are reaction chamber and struvite separation chamber, connected through bottom opening. The reaction chamber is in rectangular shape, where carbon dioxide was stripped by fine bubble aeration to create an alkaline environment and create CSTR conditions. Here the influent manure and Mg solution were throughly mixed with the liquor. Subsequently, the mixed liquid flowed into the seperation chamber. The struvite separation chamber has one side wall inclined in 60° to enhance the settling and removal efficiency. A struvite "blanket" was formed with the generated struvite, which help to separate the generated struvite from the treated effluent effectively. The structure of the EPC is shown in the Figures 3-8 and 3-10. There are four advantages of this reactor: (1) no chemicals was needed for pH adjustment that saved the operation cost; (2) increased mixing condition for adequate struvite formation; (3) enhanced struvite seperation by the filtration function of sludge blanket; and (4) auto-seeding with gravity concentrated struvite, which ensured a relatively stable operation and enhanced phosphorus removal without effluent recycle. The unique features of EPC are easy assembling and robust operation, with less maitenance.

In EPC, the pH value was adjusted by aeration without chemical dosage, because aerating water can remove carbon dioxide, thus raise the pH, as:

$$H_2CO_3 + H_2O \leftrightarrow HCO_3^- + H^+ \qquad \text{Equation 3-1}$$

The increasing range and rate depends on the air flow rate, characteristic of the water and hydraulic retention time. It can be calculated that water with alkalinity of 100 mg/L, aerated until in equilibrium with the carbon dioxide in air, would have a pH of about 8.6. (Sawyer et al. 1994)

During the plant operation, the pre-settled manure and magnesium solution were pumped at designed flow rate into the reaction chamber, where they were throughly mixed, and flowed into the seperation chamber through the bottom connection. The mixed liquor flowed up and passed through the struvite blanket, resulted in the struvite crystals to grow and then settle at the bottom and partly flow back into the reaction chamer as seeding to enhance the struvite crystatlliztion. While the treated effluent was filtered by the struvite blanket and flowed over the effluent weir into the collection pipe. The generated struvite was periodically discharged from the bottom, while the struvite blanket was always kept between 0.05 ~ 0.25 m in height.

The samples were taken from the influent and effluent pipes during the plant operation. The influent samples were mixed throughly, and analyzed as the original manure, and the effluent samples were analyzed seperately and treated as duplicated data. Some of the discharged solids were collected for SEM analysis to analyze the crystal structure and compositions.

The air was supplied by a commercial fish raising aerator, with capacity of 2.5 ~ 3.0 L/min, and fine bubble diffuser as shown in Figure 3-9. The supplied air was continuously monitored with a gas flow meter. The Mg was supplied at a pre-determined rate using Mg solution of 1000~3000 mg/L. The Mg solution was introduced to the top of the reactor.

The air was supplied by a commercial fish raising aerator, with capacity of 2.5 ~ 3.0 L/min, and fine bubble diffuser as shown in Figure 3-9. The supplied air was continuously monitored with a gas flow meter. The Mg was supplied at a pre-determined rate using Mg solution of 1000~3000 mg/L. The Mg solution was introduced to the top of the reactor.

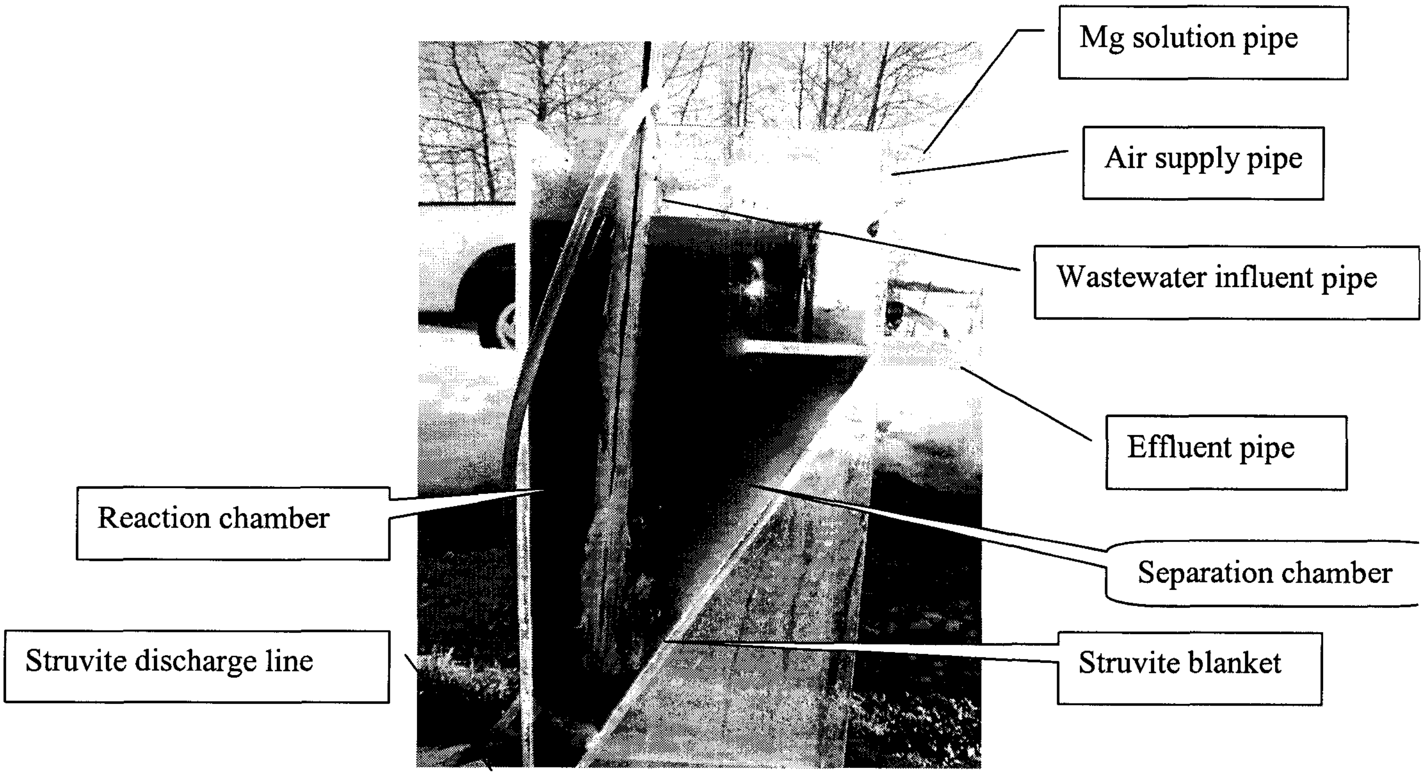


Figure 3-8 The pilot plant of aerated struvite formation system

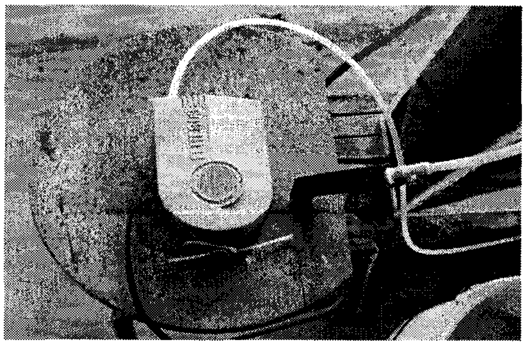


Figure 3-9 The aerator and fine bubble diffuser

3.2.1 Solids

3.2.1.1 General discussion

"Total solids" (TS) is the term applied to the material residue left in the vessel after evaporation of a sample and its subsequent drying in an oven at a defiend temperature. The total solids consist of all dissolved solids and suspended solids. The disolved solids is the portion of solids that passes through a filter of 2.0 um (or smaller) nominal pore size under specified conditions, and suspended solids is the protion retained on the filter (APHA, 1995).

The TS is analyzed by evaporation of a known volume of the well-mixed sample in a pre-weighed dish and drying to a constant weight at 103 ~105° C (APHA, 1995). The TDS is tested by filtering of a known volume of the well-mixed sample through a standard glass fiber filter. The filtrate is evaporated to dryness ina weighed dish and dried to constant weight at 180 °C, and the increase in dish weight represents the TS or TDS.

3.2.1.2 Apparatus

- *Evaporating dishes*, 40 mL capacity
- *Gooch crucibles*, 20 mL capacity
- *A/E Glass fiber filters*, special cut with 1.0 μm pore size and 33.8 mm diameter
- *Analytical balance*, Mettler AE 163
- *Drying oven*, BLUE M Gravity Oven
- *Vacuum Filtration assembly*, vacuum suction pump, volumetric flasks and holding unit for Gooch crucibles

3.2.1.3 Procedure

3.2.1.3.1 Total Solids (TS)

a. Evaporation dish preparation: The evaporation dish was heat cleaned at 103~105 ° C for one hour. Stored and cooled in the desiccator, and immediately weighed before use.

b. Sample analysis: A certain volume of well-mixed sample (usually 10~20 mL) was transferred to previously weighed dishes and the dishes were left to evaporate overnight in the oven at 103~105 ° C. The dishes were cooled to room temperature in the Desiccator for at least one hour and then weighed again. The samples were analyzed in duplicate.

c. *Calculation:*

$$TDS\,(mg\,/\,L) \;=\; \frac{(W_f\;-\;W_i)\times 1000}{sample\;volume\;(mL)} \qquad \text{Equation 3-2}$$

Where:

W_i = Initial weight of the evaporating dish, mg

W_f = Final weight of evaporating dish + weight of residue, mg

3.2.1.3.2 Total Dissolved Solids (TDS)

a. Sample preparation and filtration: All the samples were diluted before filtration. A number of dilutions (5, 10, 20, 25 and 50 times) were selected depending upon the quality of the sample. The same steps were followed for the filtration of samples as is described in section 2.2.1 (TSS determination), except the higher volumes (100 to 200 mL) of sample were filtered and the filtrate was not discarded.

b. Sample analysis: A known volume (usually 20 mL) of filtrate was transferred to previously weighed dishes and the dishes were left to evaporate overnight in the oven at 180° C. The dishes were cooled to room temperature in the Desiccator for several hours and then weighed again. The samples were analyzed in duplicate.

c. Calculation:

$$TDS\,(mg\,/\,L) = \frac{(W_f - W_i) \times 1000}{sample\ volume\ (mL)} \qquad \text{Equation 3-3}$$

Where:

W_i = Initial weight of the evaporating dish, mg

W_f = Final weight of evaporating dish + weight of residue, mg

3.2.1.3.3 Total Suspended Solids (TSS)

The TSS value was determined by substracting the TDS value from TS value.

3.2.2 Total and dissolved phosphorous

3.2.2.1 General discussion

- Phosphorus occurs in wastewaters almost solely as phosphates (APHA, 1995). But the phosphorus in the swine manure consists of both soluble phosphate and solid phosphorus. Total phosphorus includes both soluble and solid phosphorus, and can be analyzed with the well-mixed samples after dilution. Dissolved phosphorus (DP) were analyzed with the filtrate of the diluted samples. Phosphorus analysis basically requires two steps for determination: (1) sample digestion in the autoclave at 121° C and 137 kPa for 30 min to convert all phosphorus forms to the dissolved orthophosphate, (2) colorimetric determination of dissolved orthophosphate. In this project, the Ascorbic Acid Method (APHA, 1995) was used to determine the phosphorus concentration.

3.2.2.2 Apparatus

- *Spectrophotometer*, Ultraspec® 2000 Pharmacia Biotech
- *Autoclave*, for operation at 121° C, 137 kPa
- *Vacuum Filtration assembly*, vacuum suction pump, volumetric flasks and holding unit for Gooch crucibles
- *Glass fiber filters*, special cut A/E glass filter with 1.0 μm pore size and 33.8 mm diameter
- *Glassware*, Acid washed glassware

3.2.2.3 Procedure

a. Sample storage: All the samples were stored in the refrigerator and analyzed within 24 hours. Since the solubility of struvite depends on pH, the samples were not storded by adding acid as described in the Standard Methods.

b. Sample preparation: Most of the samples were diluted with a factor of 100, with some highly concentrated samples were diluted 125 to 150 times. The diluted samples were filtered with 1 μm fiber glass filter (same used for TDS test), and the filtrate was collected for analysis. Blank and phosphate standard solutions were run each time to ensure the reliability of the test. For a quality check, all the samples were run in duplicate.

c. DigestionI: 50 mL of each of the diluted samples (or samples filtrate) was poured into Wheatman Bottles (125 mL) through volumetric pipettes. Then one drop of phenolphthalein indicator solution was added. The sulfuric acid (11N H_2SO_4) was added if red color appeared after adding the indicator. Finally, 1 mL of 11N H_2SO_4 and 0.4 g (one scoop) of solid ammonium persulfate were added. The bottles were covered with aluminum foil paper and digested in the autoclave for 30 minutes at 121° C and 137 kPa pressure.

d. DigestionII: After cooling to the room temperature, the samples were neutralized with 5N NaOH, in the presence of phenolphthalein indicator, until a light pink color appeared. Then the samples were made to a volume of 100ml by adding DI water, and 50 mL of each sample were transferred to 250 mL Erlenmeyer flasks. The sample were acidified with 1N H_2SO_4, until the pink color disappeared. Finally, 8 mL of combined mixed reagent (Sulfuric acid, potassium antimonyl tartrate solution, ammonium molybdate and ascorbic acid) was added into each sample.

e. Sample analysis: The phosphorus concentrations were read in the spectrophotometer at a wavelength of 880 nm using 1 cm cuvette. All the readings were determeinted within 10 to 30 minutes after the addition of reagent.

f. Calculation: A standard calibration curve was generated from the readings obtained from the standards. The phosphorus concentrations for all the samples were computed from this standard curve.

3.2.3 TKN and Ammonia

3.2.3.1 General discussion

Nitrogen in the environment exists in two forms – organic and inorganic. High concentration of both organic and inorganic was contained in the swine manure. TKN is an important parameter for nitrogen in wastewater, it includes organic nitrogen and ammonia nitrogen, but does not include nitrate and nitrite. The TKN test consists of three main steps: *Digestion, Distillation* and *Titration.* The distillation and titration steps are needed to determine ammonia concentraion. Digestion is used to transfer organic nitrogen to ammonia-nitrogen form, distillation was used to absorb all of the ammonia nitrogen into an absorbent solution (4% boric acid), and finally, tritration was performed with 0.005N HCl using an auto titrator. The volumetric method of analysis in the Standard Methods was selected for the samples analysis. Ammonia-free water was used during the experiments.

3.2.3.2 Apparatus

Digestion apparatus, Tecator Kjeldahl 2020

Distillation apparatus, Tecator 1026

Titration apparatus, Mettler Toledo DL 50 autotitrator

3.2.3.3 Procedure

a. Sample preparation: All samples were diluted 100 times with DI water. Each sample was prepared in duplicate. For accuracy, precision and quality assessment, blanks and standards were run each time along with regular samples.

b. Digestion: 50ml of prepared samples were transferred into the digestion tube (250ml), then two Kjeltabs (tablets consisting of 3.4 g of K_2SO_4 and 0.4 g of $CuSO_4$) and one boiling rod were added to each tube. Then, 12 mL of concentrated sulfuric acid was added carefully with a dispensing pump to each tube. All of these tubes were then placed into a stainless steel frame which held the tubes over the Kjeldahl 2020 digestion apparatus, where the digestion occurred at 420° C for 70 minutes. The operating instruction manual "Tecator Application Note AN 300 for the determination of nitrogen according to Kjeldahl using block digestion and steam distillation" was followed.

c. Distillation: The Tecator 1026 apparatus was used for distillation and the operating instruction manual "the Tecator Application Note AN 300" was followed. 25 mL aliquot of 4 % boric acid in a 250 mL beaker was used as an absorbent to receive the condensate from the Tecator 1026.

d. Titration and sample analysis: Hydrochloric acid (around 0.005N) was used for ammonia titration. The titration was performed by Mettler Toledo DL50 autotitrator, and a printer was connected with the titrator to print the results. The operating manual "Tutorial: Mettler Toledo DL50/DL53/DL55 Titrators" was followed. Blank and standard samples were analyzed during each batch of sample titration. The ammonia concentration was calculated by the quantity of hydrochloric acid used for titration.

e. Calculation:

$$TKN / NH4 - N\,(mg\ N / L) = \frac{(T - B) \times N \times 14.007 \times 1000}{sample\ volume\ (mL)}$$ Equation 3-4

Where:

T = Volume of titrant used for sample, mL

B = Volume of titrant used for blank, mL

N = Normality of titrant to 4 decimal places

3.2.4 COD and BOD_5

3.2.4.1 Biochemical Oxygen Demand (BOD_5)

3.2.4.1.1 General Discussion

BOD measures the molecular oxygen utilized during a specified incubation period for the biochemical degradation of organic material and the oxygen used to oxidize inorganic material such as sulfides and ferrous iron (APHA,1995). It is the most popular parameter to determine the organic pollution in water. It involves the measurement of the dissolved oxygen used by microorganisms in the biochemical oxidation of organic matter. Generally, five days are used for the incubation period, which is termed as BOD_5, because most bio-degradable organics are oxidized in five days and it avoids the nitrification process that normally occurs after 5 to 7 days.

3.2.4.1.2 Apparatus

BOD incubation bottles, 300 mL

Air incubator, thermostatically controlled at 20 ± 1° C

DO meter: YSI Incorporated Model 50B

3.2.4.1.3 Procedure

a. Dilution buffer and seed solution preparation: Buffered water was used for samples dilution to supply enough oxygen and nutrients for the bacteria during incubation. To prepare dilution buffer, phosphate (PO_4) buffer, $MgSO_4$ solution, $CaCl_2$ and $FeCl_3$ solutions were added into DI water in the ratio of 1ml/1L. The dilution buffer was left for overnight aeration with organic-free oxygen. Seed solution was prepared from fresh swine manure by continuously aerating and adding the nutrients. A few mg of glucose was added every second day.

b. Sample preparation: Samples were analyzed within the same day of collection. Some trial experiments were carried out to determine the best dilution for the swine manure sample. 0.67mL seed solution was added into each incubation bottle, including blank and standard. Two dilutions (3000 and 1500) were used to ensure a residual DO of at least 1 mg/L and a DO uptake of at least 2 mg/L after a 5-day incubation period. The blank samples (seed checks), standards (Glucose-glutamic acid) and the regular manure samples were run in duplicate to ensure quality and accuracy.

c. BOD determination: DO experiments were performed on the same day. DO_1 readings were measured on the same day and rest of the bottles were capped and kept for 5-days (DO_5) incubation at 20° C. The DO_5 concentrations were calculated after five days incubation.

d. Calculation:

$$BOD\ (mg\ /\ L)\ =\ \frac{[(DO_1 - DO_5)\ -(DO_{sc1} - DO_{sc5})] \times 300\ (mL)}{sample\ \ volume\ \ (mL)} \qquad \text{Equation 3-5}$$

Where:

DO_1 = DO reading of the first day samples, mg/L

DO_5 = DO reading of the five day samples after incubation, mg/L

DO_{sc1} = 1-day DO of seed check (blank) sample, mg/L

DO_{sc5} = 5-day DO of seed check (blank) sample, mg/L

3.2.4.2 Chemical Oxygen Demand (COD)

3.2.4.2.1 General Discussion

The COD test is a measure of the oxygen equivalent of the organic matter content of a sample susceptible to oxidation by a strong chemical oxidant (APHA, 1995). It is also widely used to measure organic pollution of wastewater. Close reflux colorimetric method was used in this project. Capped vials were used for acid digestion and the readings were measured with a spectrophotometer at a wavelength of 600nm.

3.2.4.2.2 Apparatus

Digester, HACH COD reactor

Spectrophometer, Pharmacia Biotech Novaspec II

COD vials, 10 mL

3.2.4.2.3 Procedure

a. Sample preservation and preparation: The samples for the COD test were stored at a temperature of 4°C or less and pH below 2. The samples were allowed to reach room temperature before analysis. All the samples were diluted (100 times) before analysis.

b. Digestion: 3.5 mL of COD digestion reagent (mixture of 10.216 g $K_2Cr_2O_7$, 167 mL conc. H_2SO_4, 33.3 g $HgSO_4$ diluted in 1 L DI water), 2 mL of sulfuric acid reagent (10 g Ag_2SO_4 in 1 L conc. H_2SO_4) and 2 mL of sample were added to COD vials in sequence. The digestion was performed at 140°C for two hours.

c. Standard curve: Four different concentration of standard solutions made with phtassium hydrogen phthalate, and blanks were used to draw the standard curve, which was used to determine the COD of all the samples.

d. Sample analysis and COD determination: After digestion and cooling, the COD was determined by reading the absorbance at 600 nm wavelength. Standard solutions and blanks were also run every time the samples were analyzed. All the samples were analyzed in duplicate.

e. Calculation: COD values were computed from the standard curve.

3.2.5 Magnesium analysis

3.2.5.1 General Discussion

The magnesium was determined by atomic absorption spectroscopy method (USEPA method 3010A).

3.2.5.2 Apparatus

Hot plate: adjustable to maintain a temperature of 90~95 °C

Griffin beakers: 150 ml

Qualitative filter paper and graduated cylinder

Atomic absorption spectroscope: SPECTRAA 880 (VARIAN)

3.2.5.3 Procedure

3.2.5.3.1 Samples digestion

a. *Samples preparation*: Samples were digested after collection. The samples were not stored (by adjusting the pH below 2), because of pH dependence of the struvite process. With varying pH, fine struvite in the samples may dissolve and increase the Mg concentration. After mixing, 10 mL of samples were transferred into the Griffin beakers and mixed with 90 mL of DI water and kept for digestion.

b. *Acid digestion*: 3 mL of concentrated nitric acid was put into each Griffin beaker and the samples were digested on the heat plate. The temperature was regularly adjusted to avoid complete evaporation of samples. This step was repeated with additional 3 mL nitric acid, until the digested residue is light in color or the color has stabilized. The residue was brought to a low volume (5~10mL), refluxed with 10 mL hydrochloric acid and brought back into 100 mL in the volumatric flask.

c. *Digestate filtration:* filter the diluted digestate with quantitative filter paper to remove any possible solids, which may interfere the atomic absorbance reading.

3.2.5.3.2 Magnesium analysis

The magnesium concentration was determined by reading the automatic absorbance.

3.2.6 Particle counting

3.2.6.1.1 General Discussion

Particle counting and size distribution tests were conducted to characterize the swine manure. The samples were analyzed on the same day of sample collection, because long time storage and temperature changes could develop entrained air bubbles that could interfere with measurement accuracy. (APHA,1995). The particle classification ranges were chosen as 3,5,7,10, 15, 20, 50 and 75 um in this project.

3.2.6.1.2 Apparatus

Particle counter, PACIFIC SCIENTIFIC, HIAC/ROYCO® INSTRUMENTS 8000

3.2.6.1.3 Procedure

a. *Sample preparation:* the samples were diluted before analysis. The dilution ratio was determined according the solids concentration. Generally, 100 times dilution was used for the pre-settled swine manure in this project.

b. *Particle counting:* DI water was used for running blank samples. The diluted samples were analyzed with the particle counting instrument and the results were printed out automaticaly at the end of each run. The operator manual for particle counter was followed during the analysis.

3.2.7 Others

3.2.7.1 Temperature

Temperature is an important parameter for majority of reactions. In the laboratory, temperature was monitored together with pH, using a temperature probe attached to the pH meter. In the pilot plant, the temperature was monitored with a commercial temprature meter.

3.2.7.2 Conductivity

Conductivity is a measure of the ability of an aqueous solution to carry an electric current. The conductivity is ususally related to the TDS concentration because it depends on the concentration, mobility and valence of ions. It also depends on the temperature. The conductivity was measured directly by a conductivity meter.

3.2.7.3 pH value

pH is an very important factor for the struvite process. The pH was monitored every 2~3 hours during pilot plant operation, by the FISHER ACCUMET® pH meter (Model 805 MP). In the laboratory, pH was monitored with FISHER ACCUMET® RESEARCH pH meter AR20.

3.2.7.4 SEM analysis

To examine the crystal structure and their composition, Scanned Electron Microscope (SEM) analysis was performed on some of the generated crystal settlements with the pilot plant. The sediment samples were taken from the bottom of the reactors. The SEM machine (Model # JSM6301FXV, Japan Electron Optics Ltd.) used in this project was located in Earth Science Building at the Department of Earth and Atmospheric Sciences, University of Alberta. The samples were air dried and stuck on the special dishes to facilitate SEM scanning and X ray analysis.

3.3 Safety work procedures

As swine manure is a biohazardous waste, extra safety mesaures was taken during this project. All the students who worked on this project successfully completed a special biosafety training course received the certificate, before the project started on site. A safe work procedure manual was issued to all the students and personals, who would take part in this project.

4 Results and Discussion

4.1 The characteristics of primary settled swine manure

Based on the results of the previous stage of this project, that the character of the swine manure chages in a wide range. This lage variation can be attributed to several factors such as the pig diet, pig age, barn conditions, flushing method, season of the operation and manure management practices (ASAE 1997; Ra et al. 1997; Ra et al. 1998; Singh 2004; Zhu 2003). It has also been reported that most of the suspended solids (around 75%) and part of the phosphorus (around 20%) in swine manure was removed by plain settling within 24 hours in the previous research of this project (Singh 2005; Zhu 2003). But by further pilot and full-scale experiments it was found that plain settling reached a stable state in the initial 10 hours (Jin, 2005). However, 24 hours settled swine manue were still used in this research to keep the consistance of the whole project.

The characteristics of the pre-settled swine manure and the diluted swine manure were studied in this research, as they were used for most experiments in this researh. The raw swine manure was not studied, because it was thoroughly characterized in the previous studies (Singh, 2004; Zhu, 2003). A total of thirteen parameters were ananlyzed for the characteristic study, including nutrients (TKN, NH4-N, TP and DP), organics (BOD and COD), solids (TS, TSS, TDS), metal (Mg), and general parameters such as temperature, pH and electrical conductivity. The results are shown in Tables 4-1 and 4-2.

These parameter were chosen, as TP and DP were the target removal pollutant of this research, and solids and organic level were supposed to affect the struvite process. The following experimental results did show that the characteristic of swine wastewater affected the struvite formation and phosphorus removal, although the exact reason was still unclear in this stage. It was assumed that high solids concentration could interfere the struvite formation because of the ion strength effects, and the solids and organic matter could react with magnesium ion and form some complexes, which would reduce the available magnesium concentration, thus retard the reaction sequencely.

Table 4-1 The characteristics of the pre-settled swine manure

Parameters	**Sample #**	**Ave.**	**S.D.**	**Max.**	**Min.**
TP	17	185	30	244	143
DP	16	158	28	207	107
TKN	9	2742	600	4066	1809
NH4-N	13	2265	454	2723	1407
Mg	8	76	20	111	55
COD	14	22543	6277	32619	11416
BOD	6	7653	2050	9670	4185
TS	14	10159	2218	15800	7670
TDS	14	7420	2250	11800	3800
TSS	14	2762	1230	6320	1035
pH	14	7.7	0.62	8.37	6.68
Temp.	14	19.8	2.34	22	14.4
Cond.	11	13.87	5.41	17.6	8.65

Table 4-2 The characteristics of the diluted pre-settled swine manure

Parameters	Sample #	Ave.	S.D.	Max.	Min.
TP	8	74	43	150	38
DP	8	65	46	135	32
NH4-N	5	1090	458	1850	785
Mg	8	35	25	92	14
COD	5	7360	2595	11417	4358
TS	8	3721	1471	5320	1400
TDS	8	2620	1237	4350	1000
TSS	8	1104	598	2050	400
pH	8	7.9	0.15	8.08	7.64
Temp.	8	17.0	2.5	20	12.3
Cond.	8	5.55	2.41	8.55	2.48

Particle counting of the pre-settled swine manure was conducted. It was found that most particles, contributing to the suspended solids, were comprised of very fine particles, with about 50% of the particles were less than 3 μm, and more than 95% of the particles were less than 10μm. The larger particles were seperated during the primary settling. The results are shown in the Table 4-3 and Figure 4-1.

The results indicated that pre-settled swine manure exhibited a wide range of variations. Therefore, an equalization tank was recommended for the swine manure treatment, which could be very helpful for the following treatment processes. This equalization tank should be equipped with coarse aeration and locate before the primary settling tank to enhance the settling performance and struvite precipitation process.

Table 4-3 Particle analysis results of pre-settled swine manure

Particle size (um)	**<3**	**3~5**	**5~7**	**7~10**	**10~14**	**14~20**	**20~40**	**40~80**	**Total**
Sample number	15	15	15	15	15	15	13	14	15
STDEV	1065	710	475	319	88	22	2	0	2371
max.	5830	3453	1827	976	326	95	7	1	12172
min.	1497	384	89	19	4	1	0	0	2594
average	2728	1305	728	375	107	25	2	0	5270
% of total	51.76%	24.77%	13.81%	7.12%	2.03%	0.47%	0.04%	0.00%	100.01%

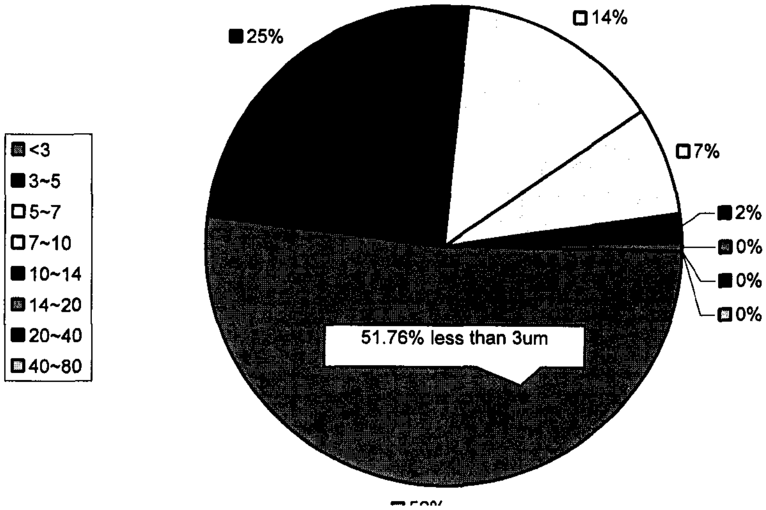

Particle size distribution pie

Figure 4-1 Particle size distribution pie of pre-settled swine manure

4.2 Laboratory experiments of struvite precipitation

Total four batches of laboratory experiments were carried out to observe the struvite formation visually before the pilot experiments and to study the effects of the main factors. The first batch was conducted to evaluate the effects of different magnesium addition without pH adjustment. The second was a factorial experiment designed to study the significance of the main affecting factors and/or their interactions. The third experiment was designed to find the optimum condition of pH value and Mg/P ratio, based on thefactorial experimentResults; the fourth experiment was conducted to evaluate the pH raising effect and phosphorus removal performance by means of aeration.

The laboratory experiments showed that phosphorus could be effectively removed from the pre-settled swine manure by struvite precipitation. Removal efficiencies of 62% and 64% were achieved for TP and DP, respectively. It was also found that the generated struvite was effectively separated from the manure by plain settling of two hours.

4.2.1 Effect of pH adjustment on struvite precipitation

During the first batch of jar test, only magnesium was added with seven different doses. The pH value of the original manure was 7.67, and no chemical was used for pH adjustment. $MgCl_2$ doses of 500, 900, 1200, 1500, 1800, 2200, and 3000 mg/L were selected, increasing the Mg/P mole ratio to 0.82 ~ 2.95 and up to a maximum of 4.95. Duplicate experiments were conducted for each magnesium dose. The mixing speed and the mixing time were 100 rpm and 10 minutes, respectively. The settling time was set at two hours as it was expected that two hours settling was enough to block out the settling effects for all experiments.

From the first jat test, pH adjustment was found to be critical for effective struvite formation and phosphorus removal. Only up to 25% of TP removal was achieved without pH adjustment, no matter how much magnesium was dosed, as shown in figure 4-2.

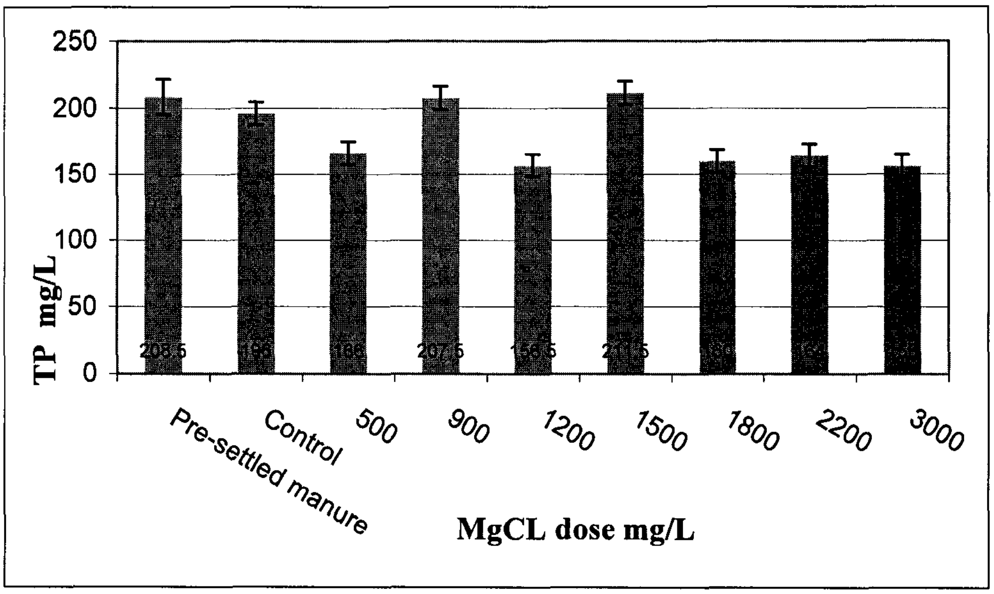


Figure 4-2 P concentration without pH adjustment at different Mg dosages

The significance of magenesium dose was not observed in this jar test, the reason was because that there was already enough magnesium present in the swine manure needed for struvite reaction. Initially, the magnesium concentration in the swine manure was not considered important. It was later confirmed that the Mg concentration of the pre-settled swine manures was about 80 mg/l in average.

There was no effective removal of other parameters observed with these jar tests(Figures 4-3 ~ 4-5). The solids concentration of a few samples increased after adding magnesium, because magnesium dose increased the inorganic salt concentration, and the reduced ion concentration by precipitation could not compensate this increase of Mg and Cl ions, thus increasing the TDS and TS concentrations. However, the suspended solids level, which is equal to the difference of TS and TDS, were almost stable between the samples.

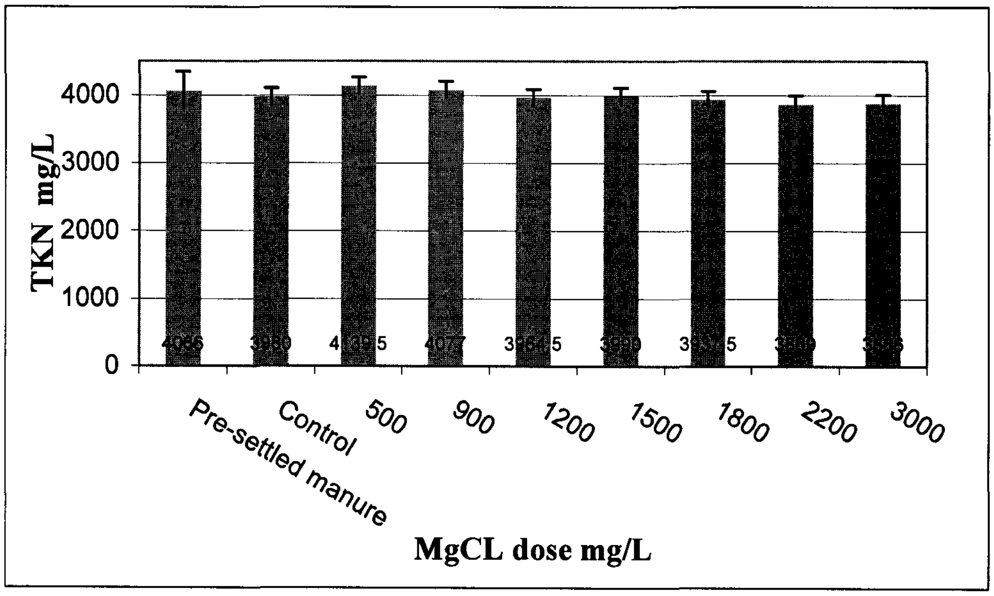


Figure 4-3 Nitrogen concentration at different Mg dose

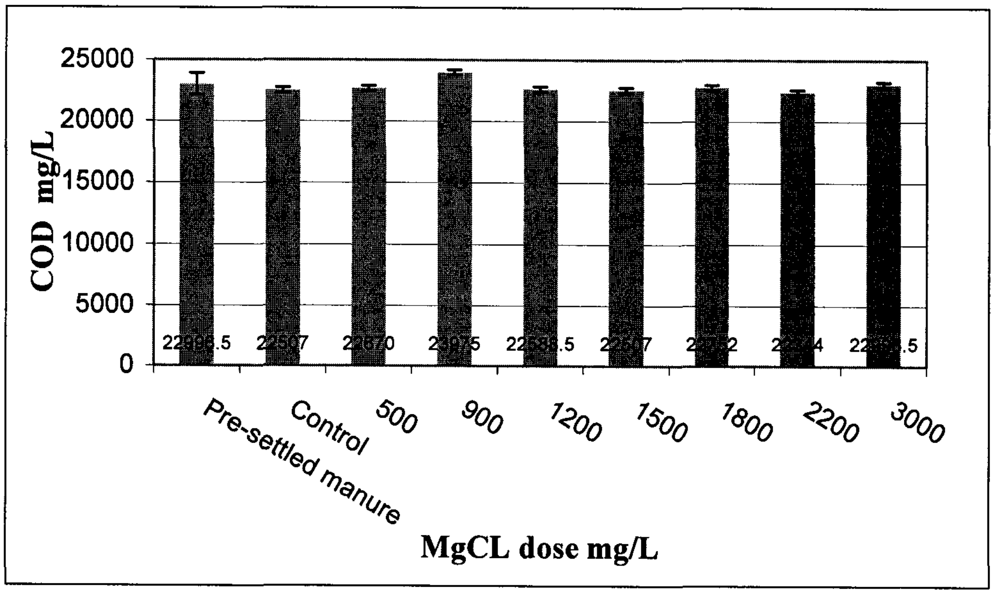


Figure 4-4 COD level at different Mg dose

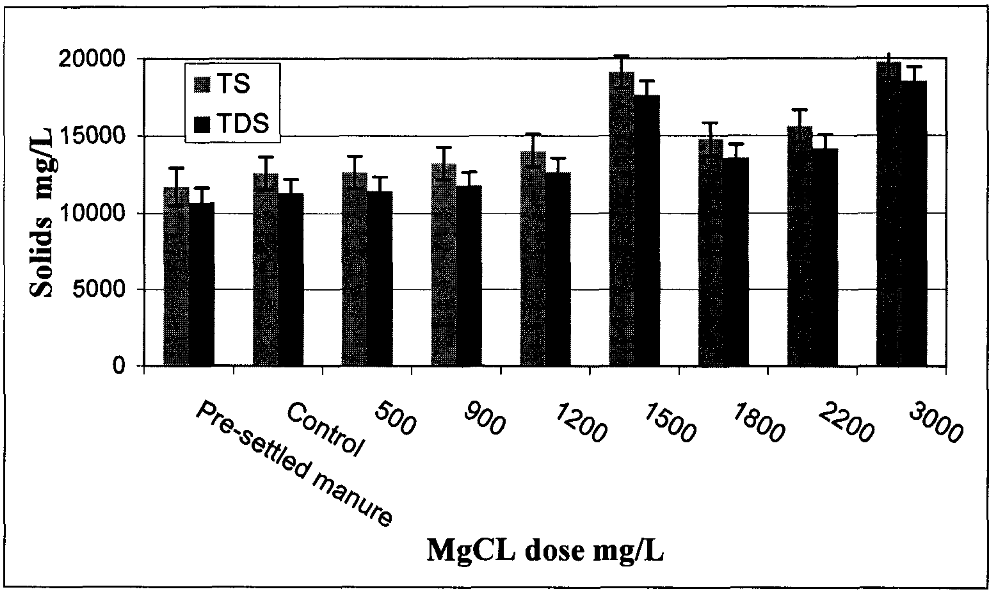


Figure 4-5 Solids concentration at different Mg dose

4.2.2 Factorial experiments

Based on first jar test results, pH adjustment was found to be critical for the struvite process. A 2^5 full factorial experiment was designed with five factors, which were pH value, Mg dose, mixing speed, mixing time and settling time. Two levels of each factor were conducted with 2 replicate central points. The setting of the factors is shown in Table 4-4 and the experimental design matrix is shown in Appendix 3.

The pH value was monitored in each jar during NaOH addition to reach the required value. The $MgCl_2$ solutions were poured into each jar after pH reached stable level. All the experiments were conducted in random order. Total 18 jar tests were conducted, and the samples were taken from the supernatent from each jar after one and two hours intervals. A total of 36 samples were obtained according to the design. TP and DP were monitored for each sample. The test results are shown in Appendix 3

Table 4-4 Setting of the factors

Factor level		-1	0	1
pH	A	7.8	8.5	9.2
MgCL2·6H2O (mg/L)	B	400	1000	1600
Reaction time (min)	C	10	15	20
Mixing speed (rpm)	D	50	100	150
Settling time (hr)	E	1		2

There was no significant difference observed between TP and DP removal in this jar test. The DP/TP ratio was nearly 95% in the pre-settled swine manure. This indicated that most phosphorus in solid form could be removed during pre-settling, and two hours settling time was sufficient for the generated struvite settling. The highest phosphorus removals (>60%) were occurred at high pH condition and longer settling time, with at least two of the other three factors at low level. This indicated that the pH should be kept high to achieve high phosphorus removal, while the Mg dose should be kept low to maintain the supersaturation level at certain range.

ANOVA regression analysis was peroformed on TP removal. The first regression was conducted with all five factors and their two-level interactions, then some most insignificant two-way interactions were removed, and other three-way and four-way interactions were added to obtain more accurate results. The results are shown in Table 4-5.

The regression results were significant because the F value (4.29618) was much greater than the F critical value (0.00147). The settling time and pH value were found to be most significant factors at 95% confidence level. The two-way interaction of pH with mixing time, pH with mixing speed, and three-way interaction of Mg dose, mixing time and speed, were also found to be significant. Theriotically, if a three way interaction was significant, at least one of its mother factors was also significant. From these results, magnesium dose was selected as significant factor. In Table 4-5, various significant factors and their interactions (at 95% confidence level) are presented in bold font, while others significant factors (at 80% confidence level) are also presnted in italic bold font.

Based on the ANOVA regression results presented in table 4-5, a correlation equation was developed at 95% confidence level:

$$\text{TP removal (mg/L)} = 46.56 + 10.68 * A + 4.38 * B + 9.48 * E - 6.53 * A * C - 7.67 * A*D - 7.83 * B*C* D \qquad \text{Equation 4-1}$$

where A, B, C, D, and E presents the pH value, Mg dose, mixing time, mixing speed, and settling time, respectively. However, this model can only be used as a reference, it can not be used to predict the pilot operation results, because the conditions were different. In the pilot plant operation, as seeding were used, the struvite process, the reactor volume was substantially reduced.

From the correlation equation, it was evident that longer settling times were always preferred for high phosphorus removal, while high pH was preferred when other factors were kept low, and lower pH was preferred when other factors were kept high. It was concluded that in order to maintain a certain supersaturation level, a balanced pH value and Mg dose were required. While lower mixing speed was preferred at high supersatuation level, because the latter would result in fast reaction, and vice-versa.

Table 4-5 Regression analysis of TP removal

	df	*SS*	*MS*	*F*	*Significance F*
Regression	15	17274.3	1151.6	4.29618	0.00147
Residual	20	5361.1	268.1		
Total	35	22635.5			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 80.0%*	*Upper 80.0%*
Intercept	46.5622	2.7287	17.0636	**0.0000**	40.8701	52.2542	42.9457	50.1787
A	10.6784	2.8943	3.6895	**0.0015**	4.6410	16.7157	6.8425	14.5143
B	4.3836	2.8943	1.5146	0.1455	-1.6537	10.4210	***0.5477***	***8.2195***
C	-2.5236	2.8943	-0.8719	0.3936	-8.5609	3.5138	-6.3595	1.3123
D	-5.0301	2.8943	-1.7380	0.0976	-11.0675	1.0072	***-8.8660***	***-1.1942***
E	9.4818	2.7287	3.4748	**0.0024**	3.7898	15.1739	5.8653	13.0983
AB	5.8467	2.8943	2.0201	0.0570	-0.1906	11.8841	***2.0108***	***9.6826***
AC	-6.5272	2.8943	-2.2552	**0.0355**	-12.5646	-0.4899	-10.3631	-2.6914
AD	-7.6728	2.8943	-2.6510	**0.0153**	-13.7101	-1.6354	-11.5087	-3.8369
AE	-4.6899	2.8943	-1.6204	0.1208	-10.7272	1.3475	***-8.5258***	***-0.8540***
CD	3.3515	2.8943	1.1580	0.2605	-2.6858	9.3889	-0.4844	7.1874
DE	2.1493	2.8943	0.7426	0.4664	-3.8880	8.1866	-1.6866	5.9852
ACD	-1.3554	2.8943	-0.4683	0.6446	-7.3927	4.6820	-5.1912	2.4805
BCD	-7.8316	2.8943	-2.7059	**0.0136**	-13.8689	-1.7942	-11.6675	-3.9957
CDE	-3.7145	2.8943	-1.2834	0.2140	-9.7518	2.3229	-7.5504	0.1214
ABCD	-4.8260	2.8943	-1.6674	0.1110	-10.8633	1.2114	***-8.6619***	***-0.9901***

4.2.3 Aeration test

Laboratory scale aeration test was performed to investigate the possibility of phosphorus removal from swine manure without chemical addition. Since the aeration can strip out the carbon dioxide from the liquid, which can result in raising the pH value. The concentration of magnesium and calcium in the swine manure can precipitate the phosphorus effectively. The test was conducted on both fresh and primary settled swine manure. The fresh manure was taken directly from the lift pump station (holding tank) outside the pig barn at the university farm, stored in the room temperature at Environmental Engineering Laboratory, and was used within four hours after taken; the primary settled swine manure was taken from the settling tank, and store in the cold room, and put in the same laboratory hours before the experiment to raise the temperature to same level. All the maunure were manually mixed before the experiment. Two identical 4-L beakers were used. The air was supplied from the the bottom by air diffuser. Two gas flow meters and adjustable valves were used to monitor/control air supply to each beaker. The air flow was maintained at 90 ml/min for each jar. No chemical was added in this experiment.

The results confirmed that aeration was sufficient for raising pH and struvite precipitation from the swine manure. Up to 72% and 42% total phosphorus removal were achieved for fresh and settled manure, respectively. The mole reduction of phosphorus was found to be higher than the reduction of magnesium, with an average ratio around 1.6. Not all of the phosphorus reduction was due to struvite precipitation, some phosphorus might have precipitated with calcium in the manure, forming HAP (hydroxyl-apatite) and finally settling out with the generated struvite.

Table 4-6 Phosphorus and Magnesium reduction during aeration

	Concentration				Reduction		P/Mg reduced
	mg/L		mole/L		mole/L		
	P	Mg	P	Mg	P	Mg	
Fresh manure	338.6	136	10.92	5.67			
2 hr	122.5	31.4	3.95	1.31	6.97	4.36	1.60
4 hr	121.2	31.9	3.91	1.33	7.01	4.34	1.62
6 hr	93.5	23.2	2.69	0.97	8.23	4.70	1.68
Settled manure	172.8	91.8	5.57	3.83			
2 hr	153.0	82.3	4.93	3.43	0.64	0.40	1.61
4 hr	117.8	62.8	3.80	2.62	1.77	1.21	1.47
6 hr	99.6	52.1	3.21	2.17	2.36	1.65	1.43

Higher phosphorus removal was found with fresh manure than the pre-settled manure, because the most non-soluble phosphorus would be removed already with the pre-settled manure.

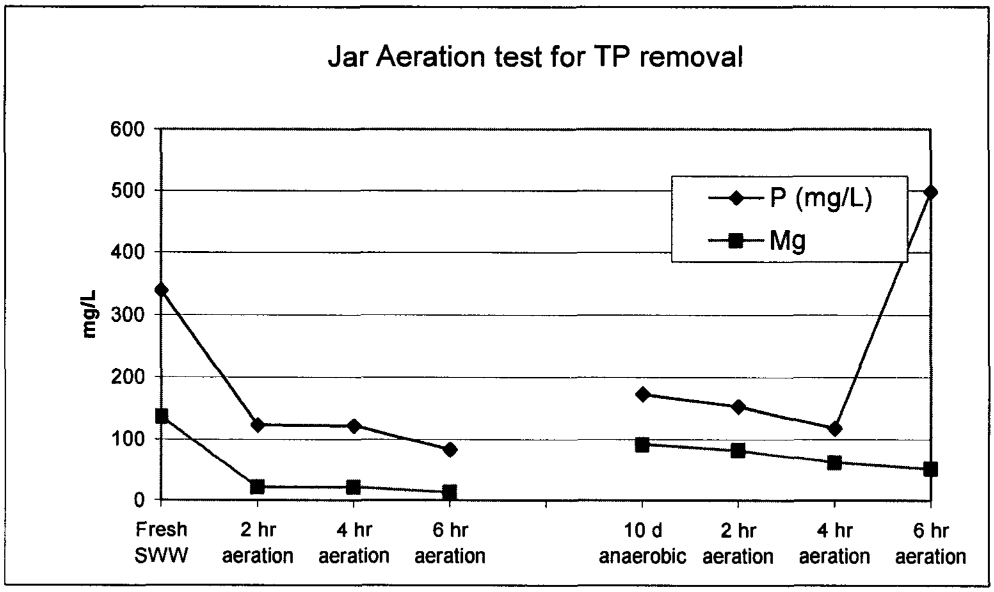


Figure 4-6 Total Phosphorus and Magenium reduction

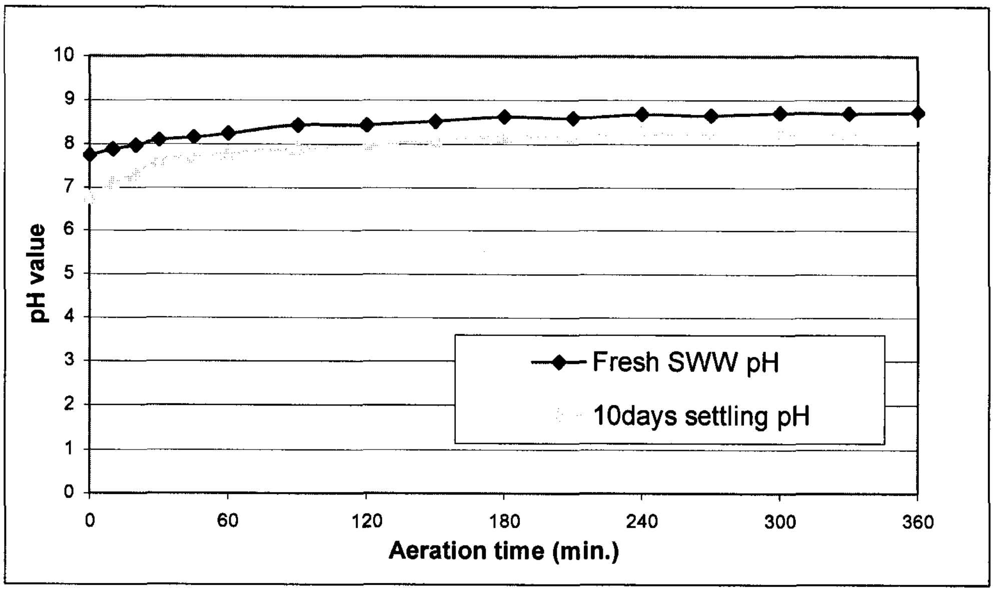


Figure 4-7 pH monitoring results

The pH value and temperature monitoring results are shown in Figur 4-7 and Appendix 4. The pH value increased continuously during the aeration, especially during the first one hour. It was found that more than 0.5 unit of the pH increase within the first hour and total 1 unit was raised after 6 hours aeration for the fresh manure, while more than 0.5 unit of the pH raise happened within only half hour, and total 1.5 units of pH was raised after 6 hours aeration for the pre-settled manure. The odor problem was not observed during the aeration, but removal of excessive foaming should be considered in the design of the pilot reactor design.

4.3 Pilot experiment – Fluidized bed crystallizer

The fluidized bed crystallizer, a cone shaped FBR, was designed by Keith Bowers, according to his patent, which has been successfully proved to treat animal manure lagoon effluent by several lab or pilot scale experiments (Bowers 2002). The plant was manufactured by ZeeBest Plastics of Canada Inc. in Edmonton, and was set up in the agriculture building at the university farm in the early July by Mr. Bowers.

The cone shape reactor provided a wide range of up-flow velocity and increased ratio of surface area to reactor volume, thus leads to greater volume efficiency, a similar crystallizer had been successfully tested with swine manure lagoon effluent. (Bowers and Westerman, 2003). The main purpose of this pilot scale experiment was to confirm the capability of this crystallizer treating swine manure, find out the significant factors and the operational condition. The experiment was devided into three stages. The first stage was conducted with aluminum fluculated swine manure and primary settled swine manure at flow rate of 2~3 liter per minute. However, the plant could not work properly as it was designed. In the second stage, the plant was operated with the diluted swine manure with reduced flow rate, to confirm if the reactor was sutitalbe for treatment of the swine manure and to find out the limit of the treatment flow rate; then in the third stage, a factorial experiment design was performed, to find the significant factor and/or interactions affecting the phosphorus removal.

However, all these experiments was only to confirm the capability of the reactor to remove phosphorus from the swine manure and to primarily find the suitable condition for the plant operation, more experiments should be conducted to find the optimum condition for this reactor operation. A long term operation should also be conducted to check the long term operation effects before a full scale operation.

4.3.1 Plant Operation

The pilot plant was first operated with the pre-settled swine manure, which was taken from the underground settling tank and stored in the 2 cubic meter tank on site. Then the plant was tested with diluted swine manure at the suitable flow rate. Before the plant started up, some struvite scrapped from some discarded swine manure collection pipe was put into the reactor as seeding. The peristaltic pumps were calibrated with graduated cyclinder.

The generated struvite sludge was planned to be removed, when the settled sludge reached a certain height after operation, but as the seperation layer of sludge was hardly observed, the sludge dischage were performed after every two operation runnings. About half of the mixtures were removed though the hose from bottom by the end of the operation through gravity flow.

4.3.2 Stage I experiments -- with pre-settled swine manure

There was no significant phosphorus removal observed in the operations with pre-settled swine manure, so it was preliminary concluded that the plant could not work with presettled swine manure, and the design flow rate is seems over the capability of the plant too. This is because that the presettled swine manure is very concentrated, with high concentration of organic matters, solids etc, which make the struvite crystallization more difficult, because the vesicosity could be increased with high organic concentration, which intervene the precipitation and settling of the struvite, and the high organic and small particle contents could aggregate around the fine crystals and prohibited further crystallization. The plant operation monitoring data is shown in Table 4-7. The possible prohibitation factors were assumed to be high organic contents, high TDS and TSS concentrations.

Table 4-7 Experimental results with pre-settled manure

Date	Flow rate L/min.	Pre-settled manure			Removal %	
		TP	TS	TDS		
		mg/L	mg/L	mg/L	TP	TS
9, July	3	85	5760	5560	0	-14
17, July	3	162	13283	12116	3	-9
22, July	2	315	27340	14800	0	-3
27, July	2	227	8220	6700	7	5
17, Aug	0.5	213	8560	5800	11	-10
1, Oct	0.2	185	7670	6100	11	

The high organic concentration can diminish the struvite process because organic matter can prohibit crystal growth by surrounding the newly generated fine struvite particles. Donnert et al. (2002) reported the organic carbon in water caused deterioration of phosphorus removal. The study assumed that this was due to partial covering of the struvite particles by the organic compounds.

The high concentration of TDS may inhibit the struvite formation, because of the ion effects. The high TSS concentration can also inhibit the struvite process, because the TSS in the swine manure mainly consist of fine particles of less than 3µm size (Table 4-3). This large amount of fine particles suspended in the liquid would inhibit the settling and separation of struvite crystals, as they could inhibit crystal growth.

The limited reactor size can be one of the reasons for limited phosphorus removal. To keep a fluidized bed reactor working effectively, there should be sufficient upflow velocity to fluidize the solids, and sufficient settling time and/or surface area to separate the solids effectively from the effluent. Due to its small size, the reactor may not have maintained these conditions.

Based on these observations, in the second stage, the pilot plant was operated with diluted presettled swine manure at a reduced flow rate. For full scale operation, the dilution could be conducted with UFFBC or soil column treated effluents.

water was filled full in the reactor, before plant started. The feeding flow rate was set at 4L/hr, to ensure adequate reaction and settling times. No seed was used in this run. The Mg dose was set at 100mg/L, which gave a Mg/P ratio of 1.29. The ammonia was used to raise the pH to 8.4. The operation was successful, as white crystal formation was clearly observed (Figure 4-8). The white crystal was assumed to be pure struvite, as the reduction of magnesium and phosphorus from the solution was about the same in mole. Effluent concentration was 24 mg/L and 38 mg/L for phosphorus and magnesium, respectively.

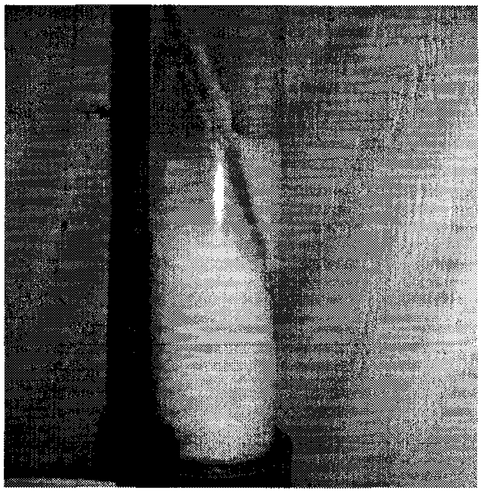


Figure 4-8 The precipited struvite from pure solution

Some of the generated white struvite crystals were used for seeding, before the plant started for experimental runs in scond stage. A total of seven runs were performed with the diluted swine manure. The fluidized bed crystallizer was proved for effective removal of phosphorus from diluted swine manure. Up to 62% and 61% removal was achieved for TP and DP respectively. The pH ranged between 8.2 ~ 8.5 and Mg/P ratio around 1 ~ 1.4

the diluted swine manure. The fluidized bed crystallizer was proved for effective removal of phosphorus from diluted swine manure. Up to 62% and 61% removal was achieved for TP and DP respectively. The pH ranged between 8.2 ~ 8.5 and Mg/P ratio around 1 ~ 1.4 was found to be prefered condition for the struvite crystallization. In some runs, TP removal was lower than DP removal, because some of fine struvite particles were washed out with effluent. And in some other runs, TP removal was found to be higher than DP removal, due to adsorption and/or co-precipitation phenomena. It was found that pH value was decreased, once after magnesium addition, because the ammonia was precipitated out of the solution.

The experimental operation conditions are shown in Table 4-8, and the results are presneted in Table 4-9 and Figure 4-9. It was found that higher phosphorus removal was achievable with increasing pH value or magnesium dose.

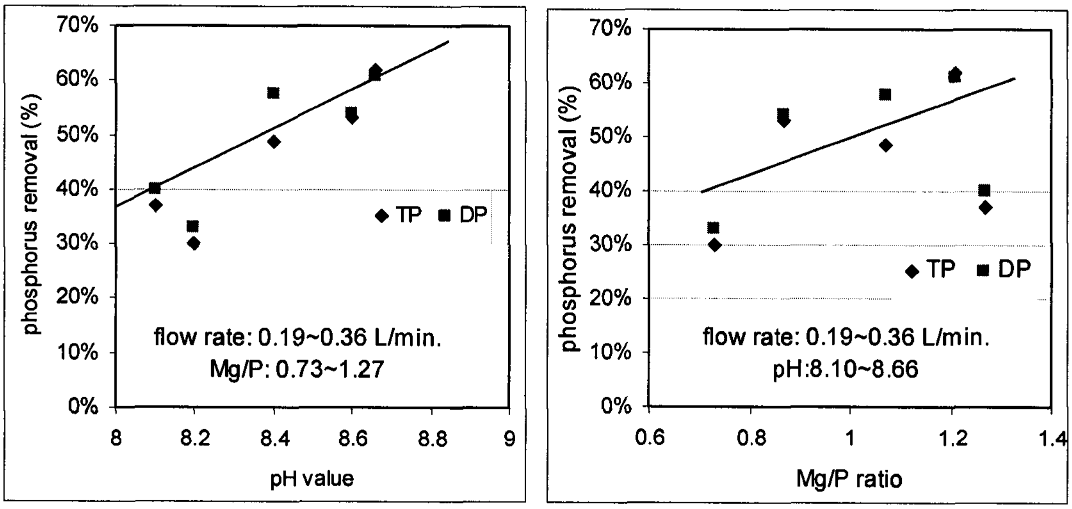


Figure 4-9 Phosphorus removal vs. pH value and Mg/P ratio

Table 4-8 Operation conditions of each experiment run

#	Date	TP reduced / Mg dose g/g	Operation condition			
			pH	Mg dose mg/L	Mg/P	Flow rate L/min
1	23, Aug.	8.4	8.1	19	1.27	0.2
2	27, Aug.	13.8	8.4	18	1.07	0.21
3	3, Sep	15.5	8.6	19	0.87	0.28
4	13, Sep	11	8.2	32	0.73	0.36
5	20, Sep		8.4	22	1.21	0.39
6	24, Sep	19.6	8.66	20	1.21	0.19
7	25,Sep		8.8	20	1.21	0.43

Table 4-9 Experimental results of each run

#	Date	Influent manure		Phosphorus Removal			
		TP	DP	TP		DP	
		mg/L	mg/L	mg/L	%	mg/L	%
1	23, Aug.	43	40.5	16	37%	16	40%
2	27, Aug.	49.5	43.5	24.1	48.6%	25.2	57.6%
3	3, Sep	55.7	39.2	29.8	53%	21.3	54%
4	13, Sep	60.5	53.4	17.9	30%	17.7	33.1%
5	20, Sep	38.3	31.8	1.37*		0.72*	
6	24, Sep	58.3	43.9	37.8	62%	26.8	61%
7	25,Sep	61.3	39	11.2*		14.3*	

During some operation runs, the effluent was trapped into a 20 liter bucket, and supernatant from the bucket was taken, to find if an exernal clarifier could help for more phosphorus removal. It was found that no significant further removal were achieved, with flow rate less than 300ml/min, but when flow rate was greater than 300ml/min, the TP removal was increased with external settling, and the results standard deviation was reduced, that means that the effluent became stable.

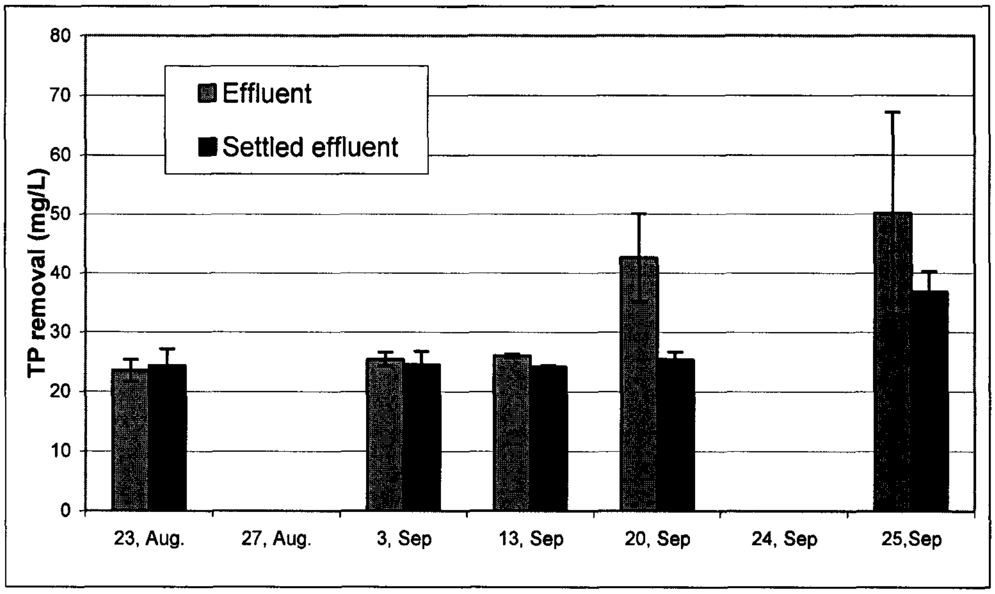


Figure 4-10 TP removal of effluents after further settling

However from these limited pilot operations, it was difficult to establish any relationship among phosphorus removal, pH value, and magnesium dose. The objective of these experiments at this stage was only to examine the effectiveness of this kind of crystallizer treating diluted swine manure. A factorial experiment was conducted during the third experimental stage to determine significant factors for phosphorus removal.

4.3.4 Stage III -- Factorial Designed experiments

As a complicated process, there were several factors could affect the struvite crystallization, such as, pH value, Mg/P ratio, ammonia/phosphorus ratio, temperature, solution concentration, seed, and reaction time etc. They could affect the struvite formation individually, or by combined interaction effects. Most of the reported experiments on struvite formation, whether in lab or pilot scale, were designed and conducted in a one-factor-at-a-time basis, which could give a clear idea of how one factor could significantly affect the process separately, as all the other conditions were fixed during the experiment, but the interactions of the factors could not be signified, even they were exist. So a factorial experiment was designed and performed in this project to determine the magnitude of the effects of the chosen factors and their interactions, and to build a mathematical model if possible. Factorial design is a powerful tool, to estimate the main effects and interactions independently. The strength and beauty of this design arise from its economy and balance. Each data point dose triple duty (at least) in estimating main effects. Each observation is used in computation of each factor and each interaction. This is the result of varying all experimental factors simultaneously (Berthouex and Brown 2002).

The factorial experiments have not been generally used for pilot experiments, because the operation conditions were hard to control at a particular setting point. In this project, a 2^3 full factorial experiment with two duplicate central points was designed as shown in Table 4-10 and 4-11. Three parameters were chosen as main affecting factors: pH value, Mg/P ratio, and flow rate (reaction and settling time). pH value and Mg/P ratio were chosen, because they are the most important control factors affecting the struvite process. The flow rate factor was selected, because it is an important design factor for all the continuous flow reactors.

There were total 10 runs in this factorial experiment. Each run lasted for about 9 hours. Three samples were taken from the effluent pipe with interval time of 3 hours. The three effluent samples were analyzed individually, and the results were averaged for each run. The influent was sampled for 3 times and analyzed for each run. The pre-settled swine manure was diluted in the 2m^3 holding tank. All the 10 runs were conducted in random order for10 continuous days. However, the operational conditions were not maintained as they were designed. The real operation conditions are shown in Table 4-12.

Table 4-10 Settting of the factors

	High level	Low level	Mid point
pH value	8.4	8.0	8.2
Mg/P	1.4	1.0	1.2
Flow rate (L/min.)	0.3	0.1	0.2

Table 4-11 Factorial experiment design matrix

Experiment run	pH value	Mg/P ratio	Manure flow rate (ml/min)
1	8.4	1	300
2	8.0	1	300
3	8.0	1.4	300
4	8.4	1.4	300
5	8.4	1.4	100
6	8.4	1	100
7	8	1	100
8	8	1.4	100
9	8.2	1.2	200
10	8.2	1.2	200

The influent and effluent samples were analyzed for phosphorus, ammonia nitrogen, magnesium and solids concentrations. One mixed influent sample and three effluent samples were analyzed for each run. The gram TP removal with every gram of magnesium dose was calculated and listed in table 4-12. It was found that efficient TP removal occurred when pH value was high and the Mg/P ratio was low. The experimental results are shown in the Table 4-13.

Table 4-12 Factorial experimental operation conditions

Run #	NH4-N/TP reduction mol/L	TP reduced / Mg dose g/g	Operation condition			
			pH	Mg dose mg/L	Mg/P mole ratio	Flow rate L/min
1	10.58	1.03	8.24	30	0.9	0.3
2	6.18	1.49	8.06	30	0.9	0.3
3	8.61	0.60	8.01	54	1.2	0.3
4	7.00	0.57	8.33	54	1.0	0.3
5	3.81	1.52	8.42	54	0.9	0.1
6	2.78	2.71	8.51	30	1.0	0.1
7	4.11	2.58	8.08	30	0.8	0.1
8	8.43	1.42	8.04	54	1.3	0.1
9	2.11	1.90	8.22	42	1.0	0.2
10	3.47	1.82	8.24	42	1.2	0.2

Table 4-13 Factorial experimental results

Run #	Influent manure			Phosphorus Removal			
	TP	DP	NH4-N	TP		DP	
	mg/L	mg/L	mg/l	mg/L	%	mg/L	%
1	142.5	129.5	1227.8	30.8	21.6%	41.1	31.7%
2	154.0	127.0	1158.2	44.8	29.1%	42.3	33.3%
3	135.3	130.2	1267.3	32.6	24.1%	46.4	35.6%
4	150.6	135.7	1380.5	31.0	20.6%	36.0	26.5%
5	155.8	117.7	1297.2	82.3	52.8%	74.5	63.3%
6	147.8	124.7	1274.0	81.3	55.0%	76.1	61.0%
7	162.2	142.4	1331.3	88.1	54.3%	84.9	59.6%
8	147.9	129.5	1262.3	76.9	52.0%	77.7	60.0%
9	157.3	144.1	1244.5	79.8	50.7%	96.3	66.8%
10	136.2	130.6	1196.4	76.3	56.0%	84.4	64.6%

The phosphorus and magnesium concentrations were monitored after each experimental operation, and there was moderate fluctuation during each run. The Mg/P ratio was not kept exactly as designed. The pH value was also very hard to control and varied around a certain range. Therefore, this experiment was not an exact facotrial experiment. In this case, least square regression (instead of ANOVA) method was used to develop a correlation equation for phosphorus reduction. Based on the understanding of the struvite process and the preliminary analysis of the results, important factors such as flow rate, pH value, Mg dose and interactions of pH and Mg dose were included in the correlation. The equation is shown below:

$$\text{DP removal (\%)} = [-8.04 - 1.34*Q + 1.06*pH + 6.67*Mg/P - 0.8*pH*Mg/P] * 100\%$$

Where, Q is the treatment flow rate in L/min
Mg/P is the magnesium to phosphorus mole ratio

This correlation equation was kept as simple as possible, while keeping the sum of squares of the residuals minimum. The sum of squares of the model residuals was 22.5%. The results showed that the DP removal increased with reduced flow rate, at higher pH or Mg concentration, but if both the pH and Mg concentration were in high level, the removal would be decreased. Equation for TP removal results was not established because the TP removal could be highly affected by adsorption, co-precipitation, and insufficient seperation. It also indicated the unstable performance of FBC.

The correlation equation was tested by drawing residuals plots, and showed good fit with experiment data (Figure 4-11). The estimated values by above modle were also compared with the experiment results (Figure 4-12). For a perfect case, all the points would be on the line (Y=X). Here all the DP plotted points were randomly distributed around a straight line of equation y=0.955x, with R square of 0.6137.

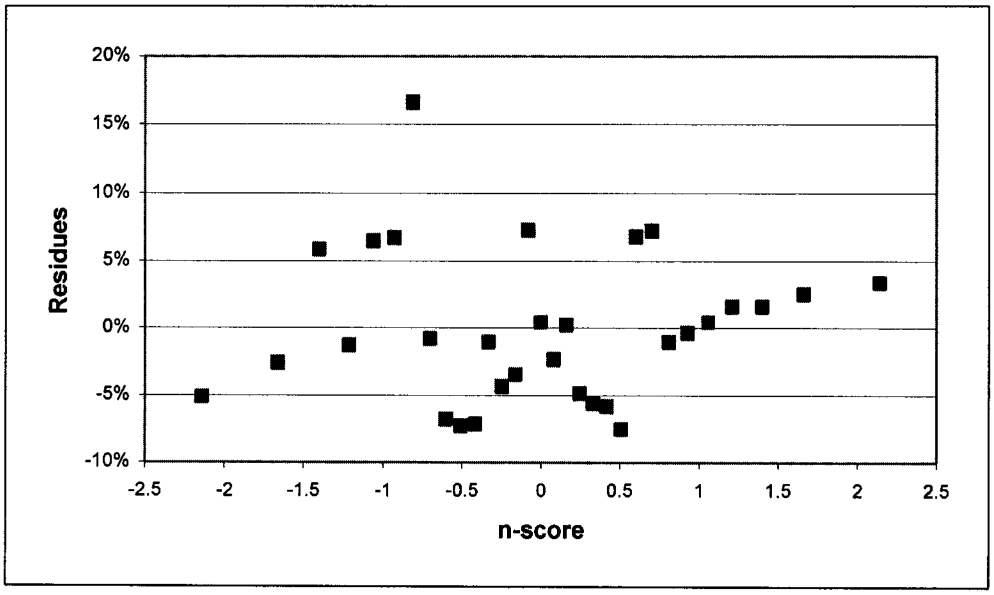


Figure 4-11 TP and DP residuals plot

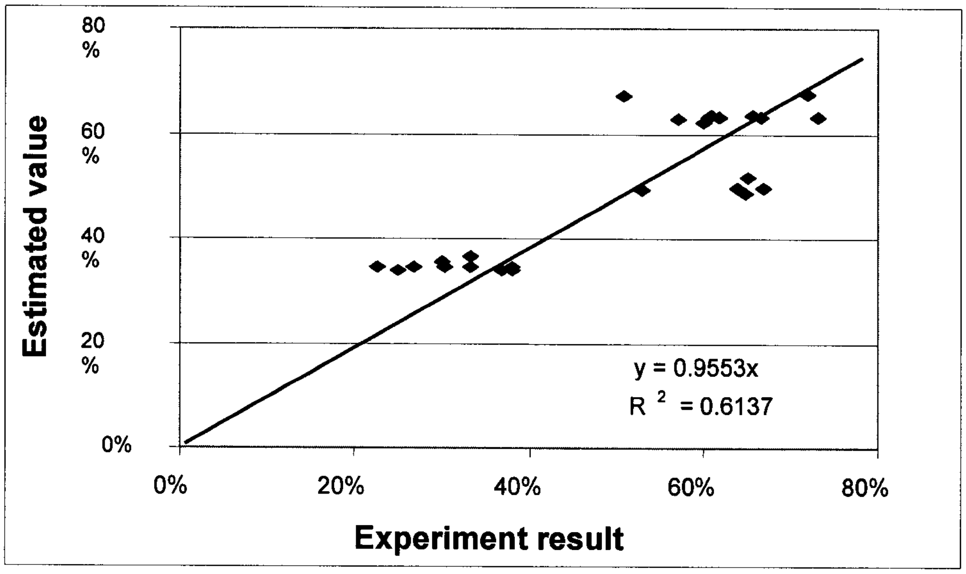


Figure 4-12 Model estimation comparison with experiment results

4.3.5 SEM and X-ray analysis

Some of the settled solids collected from the bottom of the FBC were analyzed by SEM technique. The solids were drawn from the bottom through the influent pipe, when the FBC were not operated. The solids were diluted with tap water, stirred gently and filtered through quantatitive filter paper, and finally air-dried. Then the air-dried sample was fixed on a small special dish for surface goldening and analyzed with SEM. The electro micro image of these solids is shown in the Figures 4-13 and 4-14.

From Figure 4-13, it was apparent that struvite crystals were distributed randomly with other stuff and some were embedded into the organic and other solids. The size of the crystals were less than 100μm. In Figure 4-14, the crystals are clearly shown in prism shape, with relative straight edges, although the surfaces were uneven and looked fragile. Also, they were embeded in other organic and solid materials, and stopped to grow larger. This could be a reason for less struvite formation from the swine manure. The size of the large crystals (in figure 4-17) was about 40 μm in length.

The crystals (as shown in figure 4-14) were confirmed to be struvite by X-ray analysis. The main elements of these crystals were found to be phosphorus and magnesium (Figure 4-19). Nitrogen was not shown, because it could not be detected by the X-ray. Besides struvite crystals, some other elements were also detectd by the X-ray analysis, such as calcium, aluminum, iron, and potassium (Figure 4-20). These elements are also present in the swine manure.

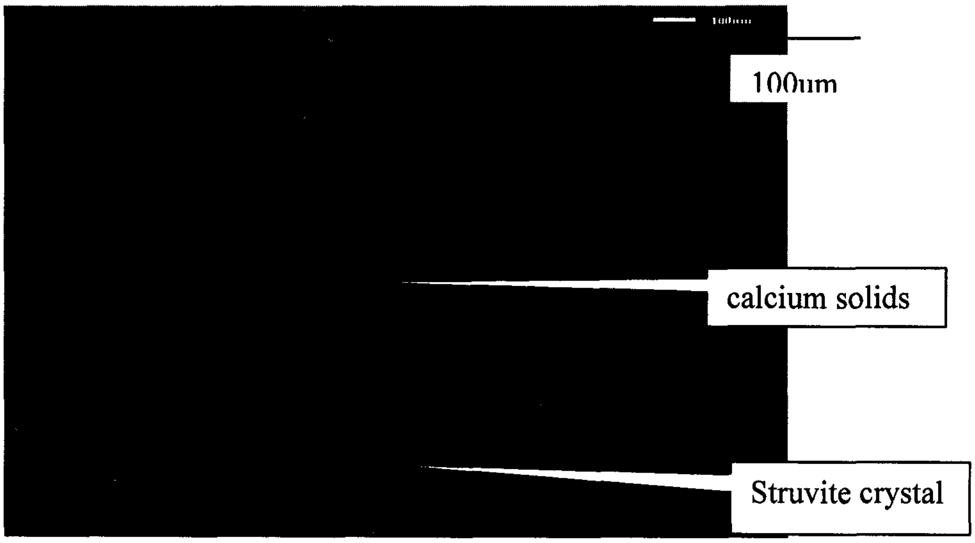


Figure 4-13 SEM image of collected struvite mixture

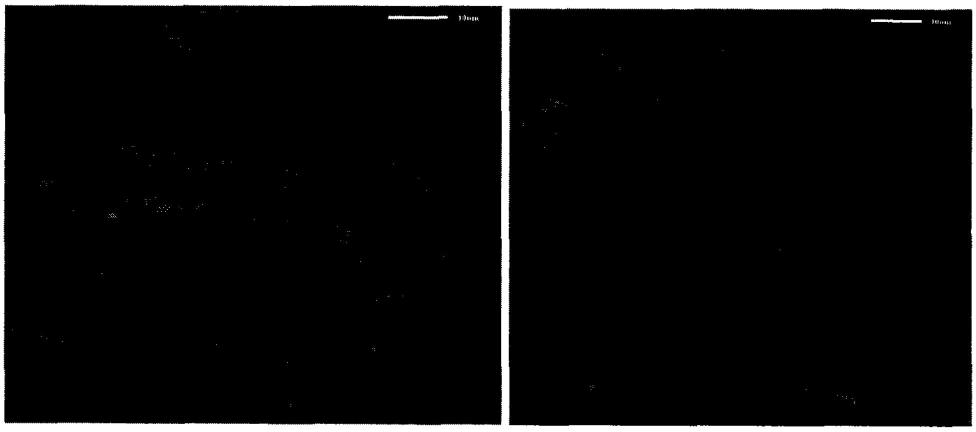


Figure 4-14 Enlarged SEM images of Struvite crystals

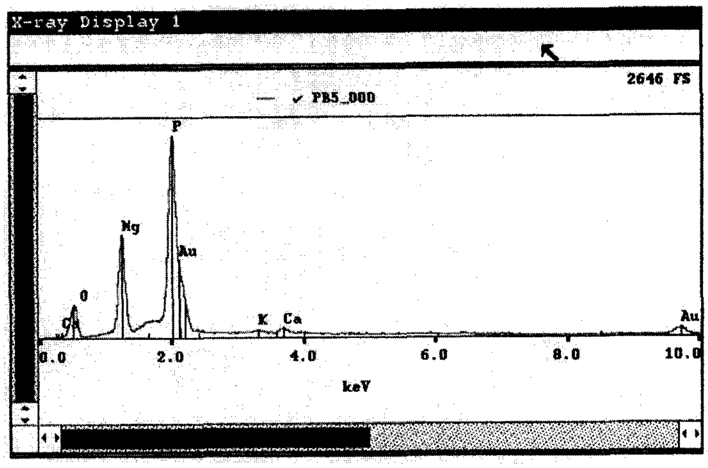


Figure 4-15 X-Ray analysis of the crystal in figure 4-14

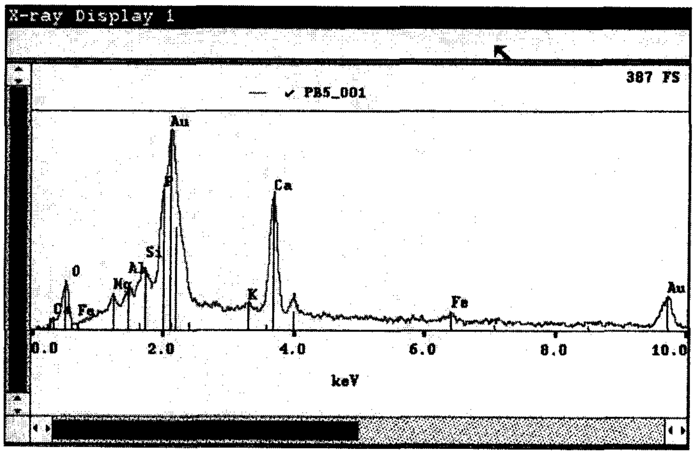


Figure 4-16 X-ray analysis of calcium solids in figure 4-13

4.4 Pilot experiment – Enhanced phosphorus crystallizer

Although the FBC successfully removed phosphorus from the diluted swine manure, it could not work well with the primary settled swine manure without dilution. It did not work smoothly and the performance varied for individual run(s). Therefore, to enhance the phosphorus removal performance and to reduce the chemical consumption, a new struvite reactor was designed and assembled. This new reactor was named enhanced struvite crystallizer (ESC). The ESC performance was investigated with three stage pilot scale experiments. The first stage experiment was conducted to investigate the effectiveness of the EPC to treat the swine manure (i.e., both primary settled and diluted swine manure). The second stage was designed to find significant factors and to build a phosphorus removal mathematical model through a factorial experimental design. And the third stage esperiment was conducted to test the stability of the operation through a long term continuous plant operation (10 days) with pre-settled swine manure.

4.4.1 Stage I -- Trial plant operations

The first run with the aeration struvite system was conducted to find out whether this reactor could effectively remove phosphorus from the non-diluted swine manure. For this purpose, the plant was run at two flow rates of 190 ml/min and 110 ml/min. Mg addition rate was kept constant at 17 ml/min with concentration of 550mg/L in Mg, which gave a Mg dose of 49 and 85 mg/L, and Mg/P ratio of about 0.8 and 1.0, respectively. Struvite settling from the cone system was used as seed in this run. Three samples were taken at each running condition with time interval of 2 hours. The first sample of each condition were taken after 3 hours of the plant start-up, or condition changed.

The operation was very successful. TP removal of 35 and 41% and DP removal of 24% and 35% were achieved for the two operating conditons. TP removal was higher than DP removal, because not only the phosphorus, which formed struvite, was totally removed, but some other phosphorus was also removed by co-precipitation, adsorption, and filtration through the “sludge blanket”. Aeration, not only raised the pH value, but also provided good mixing for the struvite crystallization. It was also clearly observed that the solid build up in the settling chamber, the generated struvite and the solids existing in the swine manure formed a clear solid/liquid seperation layer, as shown in Figure 4-17. The generated struvite mixture was removed, when the mixture reached 0.2 ~ 0.25 m height. During the plant operation, the struvite mixtures were discharged during the plant operation through a flexible hose by gravity flow, until the sludge seperation layer was reduced to 0.06 m. The sludge removal frequency differed according to the operations, which depended on the Mg dose, treated flow rate, and character of the influent manure. Generally, the sludge was removed after several hours of running.

Two another runs with diluted swine manure were conducted to test whether this reactor could work effectively with different wastewaters. The experiment was conducted at a flow rate of 400 mL/min. with Mg doses of 40 mg/L and 80 mg/L, which gave a Mg/P ratio of 0.9 and 1.2. TP and DP removal of 34% and 38% were achieved, respectively with the lower Mg dose, while 49% and 57% TP and DP removals were achieved with higher Mg dose. The TP and DP removal were almost same in these two runs, it indicated that the precipited phosphorus were effectively removed by the sludge blanket.

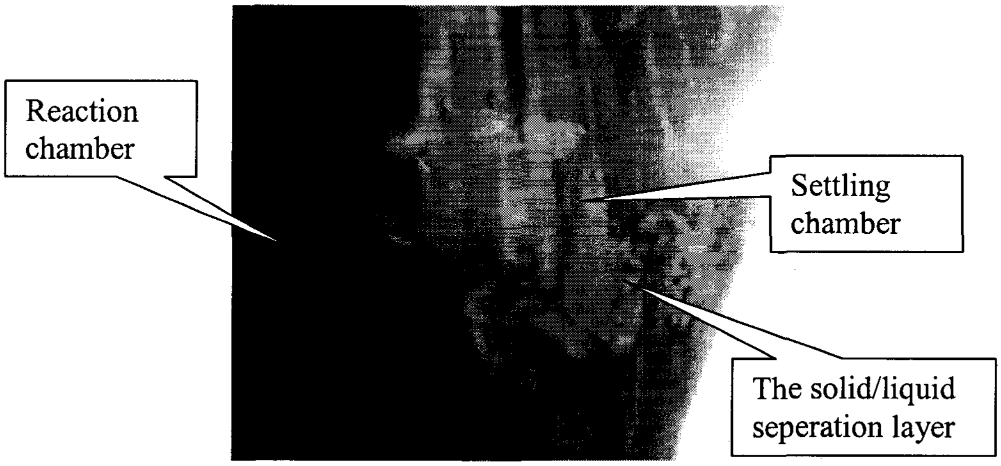


Figure 4-17 The Solid / liquid seperation line in the settling chamber

Table 4-14 Operation condition of the experiments

Date	TP reduced / Mg dose g/g	Operation condition			
		PH	Mg dose mg/L	Mg/P	Flow rate L/min
6. Oct.	1.59	8.28	49	0.8	0.19
	1.05	8.28	85	1	0.11
17. Nov.	1.24	8.17	40	0.9	0.4
18. Nov.	0.98	8.15	80	1.2	0.4

The experimental results are shown in the Table 4-15 and Figures 4-18 and 19. From Figure 4-18, it was found that phosphorus removal was increased with higher Mg dose, because the supersaturation level was limited by Mg concentration level, and the reaction was not completed within the limited retention time. In Figure 4-19, phosphorus removal per unit magnesium addtion were compared. It was found that phosphorus removal per unit Mg dose were decreased with the increased magnesium dose, because more dose of magnesium would only increase the supersaturation level, but would not be utilized for precipitation of struvite.

Table 4-15 Experiments results

Date	Influent manure		Phosphorus Removal			
	TP	DP	TP		DP	
	mg/L	mg/L	mg/L	%	mg/L	%
6. Oct.	219.2	177.3	77.9	35.5%	43.4	24.5%
			89.5	40.8%	69.3	39.1%
17. Nov.	147.8	130.2	49.8	33.7%	50.1	38.5%
18, Nov.	160.6	144.8	78.8	49.1%	82.7	57.1%

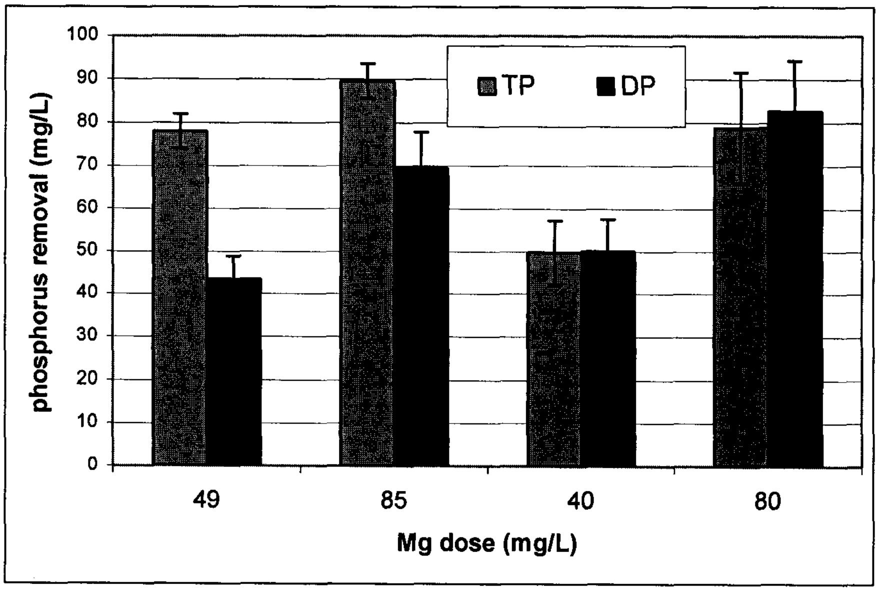
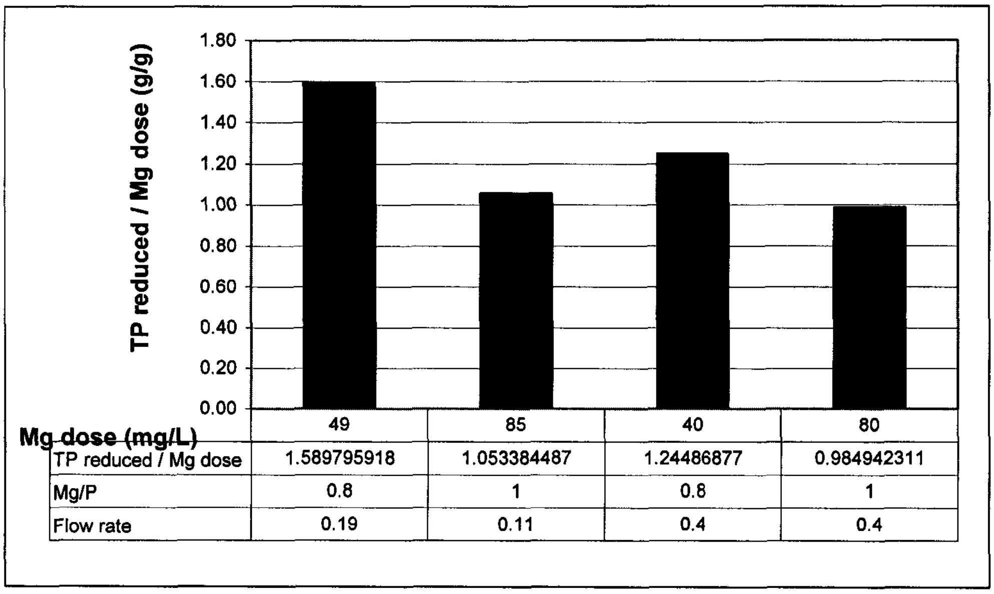


Figure 4-18 Phosphorus removal with different magnesium dose



Mg dose (mg/L)	49	85	40	80
TP reduced / Mg dose	1.589795918	1.053384487	1.24486877	0.984942311
Mg/P	0.8	1	0.8	1
Flow rate	0.19	0.11	0.4	0.4

Figure 4-19 Phosphorus removed (g) per gram of magnesium dose

4.4.2 Stage II -- Factorial designed experiments

4.4.2.1 Factorial experiments design and operation

2^2 factorial experiment was performed, to find the significant factors and interactions. The two factors selected were treatment flow rate and Mg dose. pH was not selected, becuause it was not a control factor, as no chemicals was added for pH adjustment. The pH was only adjusted by the carbon dioxide stripping. And the pH will depend on the charactristic of the manure and aeration time. These factors were tested at two levels. The factor setting is shown in Table 4-16. The low level was chosen to set the Mg/P around 1:1 same for the two experiments, and the high level was chosen to set the Mg/P ratio of 1.4 and 1.6 for the first and second run, respectively. Based on the monitoring results of the first run, higher value was set for Mg dose in the second run. The same factorial experimental design matrix was used for the two runs, as shown in Table 4-17.

For each factorial designed experiments, the experiment was conducted for 4 days in sequence, the same manure was used for the all four experiments. The experiments were conducted in a random order. Three effluent samples were collected from the effluent hose with 3 hours interval time during each run. The raw wastewater samples were collected from the influent hose four times with the same 3 hours interval. The real experimental conditions are shown in Table 4-18.

Table 4-16 Setting of the factors

Factors		Run #1		Run #2		Unit
		low (-1)	high (+1)	low (-1)	high (+1)	
A	Flow rate	0.1	0.2	0.1	0.2	L/min
B	Mg dose	65	127	80	140	mg/L

Table 4-17 The factorial design matrix

Setting	A	B	AB
1	-1	-1	1
2	1	-1	-1
3	-1	1	-1
4	1	1	1

The gram of the phosphorus reduced per gram of magnesium added was calculated and listed in Table 4-18, because it is an important fincancial consideration to reduce the magnesium dose while optimumly reduce the phosphorus. It was found that Mg/P ratio of about 1.2 produced optimum usage of added magnesium, any lower or higher dose decreased the efficiency. The results were consistent with the stage I experimental results

.

Table 4-18 Operation conditions of the experiments

Experiment date	NH4-N/TP reduction mol/L	TP reduced / Mg dose g/g	Operation condition			
			pH	Mg dose mg/L	Mg/P mole ratio	Flow rate L/min
Oct. 25	11.40	0.65	8.13	65	0.89	0.1
Oct. 26	12.26	0.64	8.06	65	0.89	0.2
Oct. 27	8.80	0.74	8.19	127	1.23	0.1
Oct. 28	8.62	0.72	8.04	127	1.38	0.2
Feb. 1	4.36	1.03	8.19	80	1.23	0.1
Feb. 2	7.97	0.80	8.33	140	1.57	0.1
Feb. 3	9.33	1.05	8.08	80	1.19	0.2
Feb. 4	7.97	0.78	8.24	140	1.51	0.2

The ammonia reduction per unit phosphorus removal (in moles) were calculated and listed in table 4-17. The ratio was found varied around 8, which was more than that required for struvite precipitation. Some ammonia was escaped through air stripping. However, the amount of escaped ammonia was limited, and would not cause any serious environmental concern (see section 4.4.4).

4.4.2.2 Experimental results – phosphorus removal

The phosphorus removal results are shown in the table 4-19. Up to 70% and 72% removal efficiency was achieved for TP and DP, respectively. The phosphorus removal values were different for the two batches (with different manure samples) of runs.

Table 4-19 Experimental results

Experiment date	Influent manure				Phosphorus Removal			
	TP	DP	Mg	NH4-N	TP		DP	
	mg/L	mg/L	mg/L	mg/l	mg/L	%	mg/L	%
Oct. 25	174.0	129.5	55	1227.8	42.0	24.2%	36.6	28.2%
Oct. 26	177.2	164.4	57	2661.7	41.3	23.3%	34.3	20.9%
Oct. 27	193.7	181.5	57	2709.7	94.0	48.5%	96.6	53.2%
Oct. 28	191.7	176.0	78	2722.9	92.1	48.0%	104.1	59.1%
Feb. 1	146.8	107.3	60	2355.1	82.6	56.2%	51.3	47.8%
Feb. 2	160.0	137.4	55	2491.0	112.0	70.0%	96.2	70.0%
Feb. 3	143.2	118.1	52	2514.5	84.0	58.7%	78.4	66.4%
Feb. 4	166.3	132.9	55	2552.3	109.6	65.9%	96.0	72.2%

The flow rate in the range of 100~200 ml/min was found to affect the phosphorus removal. The pH was a little higher with lower flow rate. When the pH was raised to a certain value (~ 8.1), further increasing of pH did not enhance the struvite precipitation as now supersatuation was sufficient for efficient precipitation. The effect of Mg dose on phosphorus removal is shown in Figure 4-20.

The experiments were designed into two batches of factorial experiments. Since the real operational conditions were different from the design assumption, ANOVA was not used for results analysis. Correlation equations were developed using least square regression method, as follows:

$$\text{TP removal (\%)} = (63.2 * \text{Mg/P} - 18.6 * Q - 25.9)\ \% \qquad \text{Equation 4-2}$$

$$\text{DP removal (\%)} = (66 * \text{Mg/P} - 17.2 * Q - 28.8)\ \% \qquad \text{Equation 4-3}$$

Where, Mg/P is the unitless and Q is the flow rate in L/min

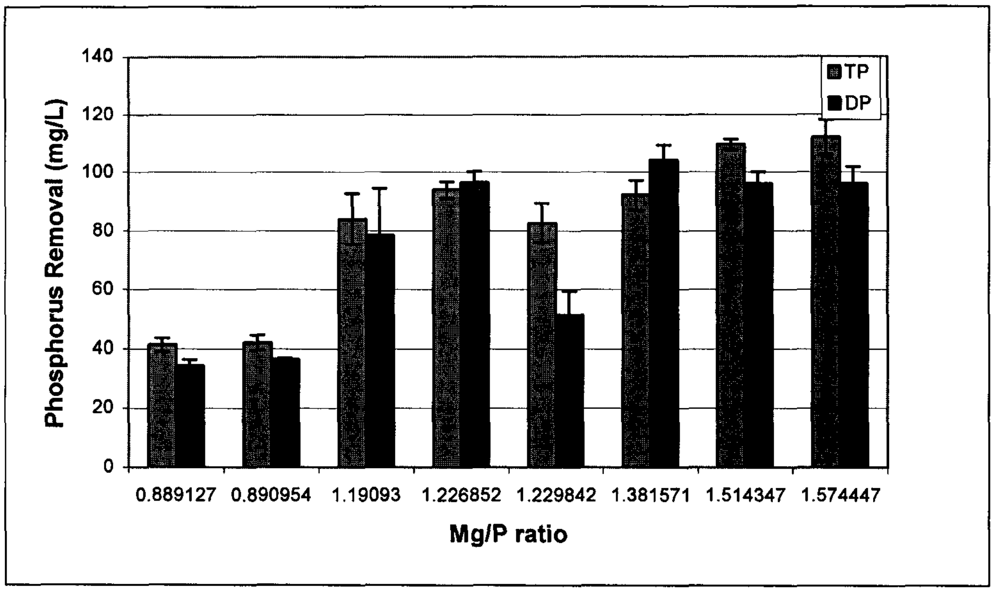


Figure 4-20 Phospborus removal at different Mg/P ratios

There were only two parameters included in the equations, because they were the only controlled factors, and the equations were built as simple as possible, with satisfactory residual sum of squares. The least sum of squares were 0.035 and 0.039 for TP and DP, respectively. The equation was checked by plotting normal probability graph of the residuals. The residual points were evenly distributed around the zero percent (y=x) line. From the equation, phosphorus removal increased with the increase in Mg/P ratio and decrease in flow rate.

In figure 4-22, the X-axis is the experiment results and Y-axis is the the estimated removal value. All the plotted points were distributed around the zero percent line (y=x), with.the R^2 values of 0.838 and 0.8436 were obtained for TP and DP, respectively. The results indicated that the equation estimation was reasonable, and reflected the experimental results quite well. The R^2 values were much greater than those obtained in the FBC model results, which indicated that this operation was relatively more stable and consistent than the FBC system.

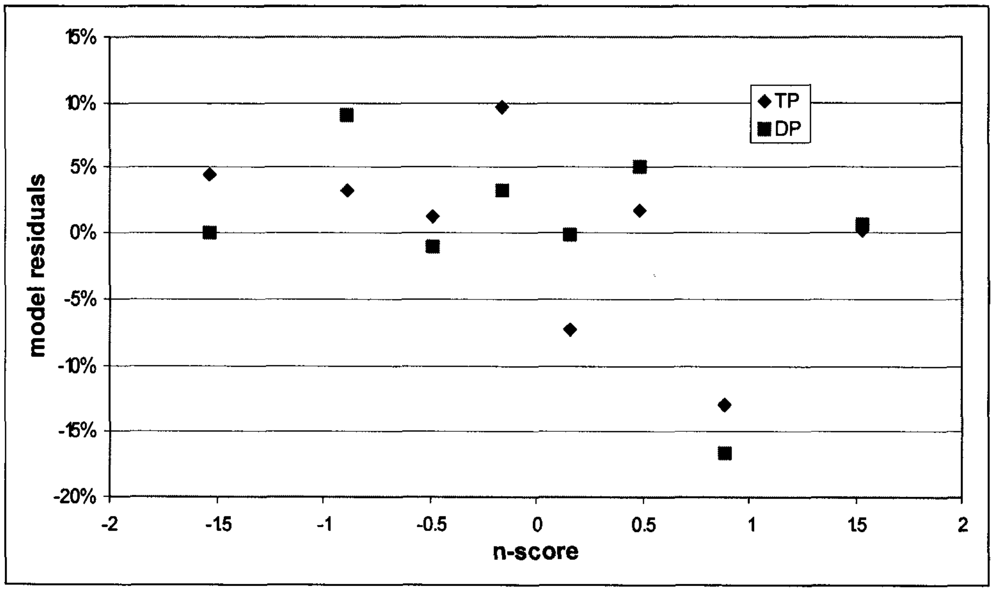


Figure 4-21 Normal probability plot of the residuals

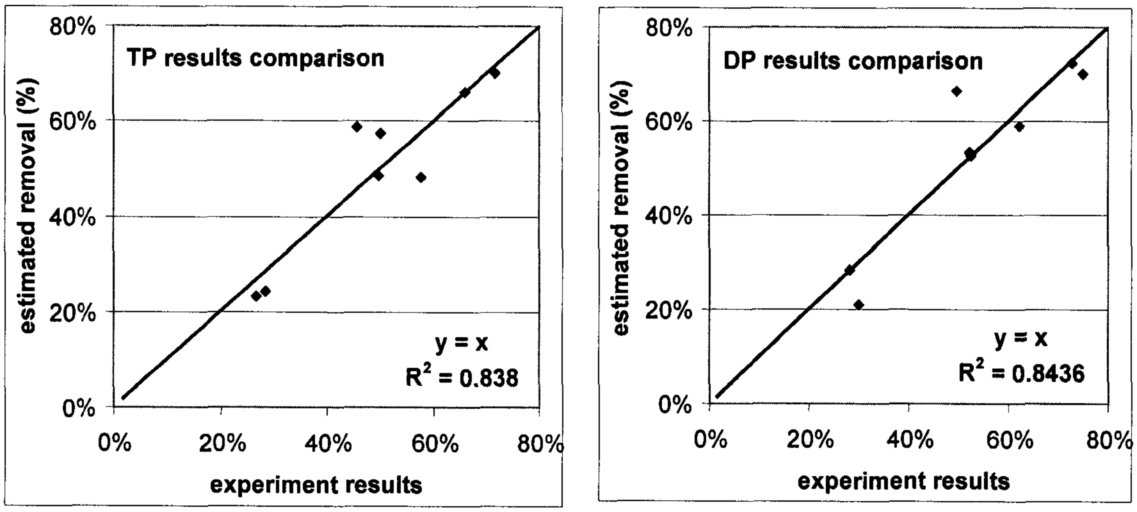


Figure 4-22 Comparison of the model estimated value and experiment results.

(Mg/P ratio and flow rate were 0.89 ~ 1.57, and 0.1 ~ 0.2 L/min, respectively)

Sensitivity analysis was performed on the experimental results using the main equation parameters. The results showed that Mg/P ratio was more sensitive than the flow rate.

Table 4-20 Sensitivity analyis of the equation parameters

Parameter		TP removal %	Δ	DP removal %	Δ
Mg/P ratio	1.4	59.8		61.0	
	-10%	51.9	-7.9	51.8	-9.2
	-20%	43.0	-16.7	42.5	-18.6
	10%	69.6	9.8	75.9	14.9
	20%	78.4	18.6	85.2	24.2
Flow rate (L/min.)	0.15	59.8		61.0	
	-10%	60.1	0.3	61.3	0.3
	-20%	60.3	0.6	61.5	0.5
	10%	59.5	-0.3	60.8	-0.3
	20%	59.2	-0.6	60.5	-0.5

4.4.2.3 Experimental results – organic and solids removal

The percentage removal efficiencies of solids and organic matter were also determined. The results of COD, total solids and dissolved solids are shown in Table 4-21. Up to 52% and 81% of removal efficiency was achieved for COD and TSS, respectively. The COD and TS removal results were plotted in Figures 4-23~24. No relationship was developed for COD and solids removal under varying flow rate and magnesium dose. It could be noted that total solids removal was marginally higher than the suspended solids removal, indicating that the dissolved solids concentration remained stable during the process. It was suggested that higher COD removal would have resulted in higher phosphorus removal, but no conclusion could be drawn from these limited runs.

Table 4-21 COD and solids monitoring results

Experiment date	Initial				Removal	
	COD mg/L	TSS mg/L	TDS mg/L	TS mg/l	COD %	TSS %
Oct. 25	32619	2640	7900	10540	18.3%	66.7%
Oct. 26	31151	1775	6450	8225	10.8%	52.0%
Oct. 27	25863	2990	7150	10140	13.8%	69.2%
Oct. 28	25168	2190	6050	8240	11.3%	46.3%
Feb. 1	26095	2600	5400	8000	49.4%	81.4%
Feb. 2	24790	2800	5900	8700	51.8%	74.4%
Feb. 3	16799	5850	4200	10050	39.4%	50.0%
Feb. 4	15168	1930	6170	8100	34.4%	48.2%

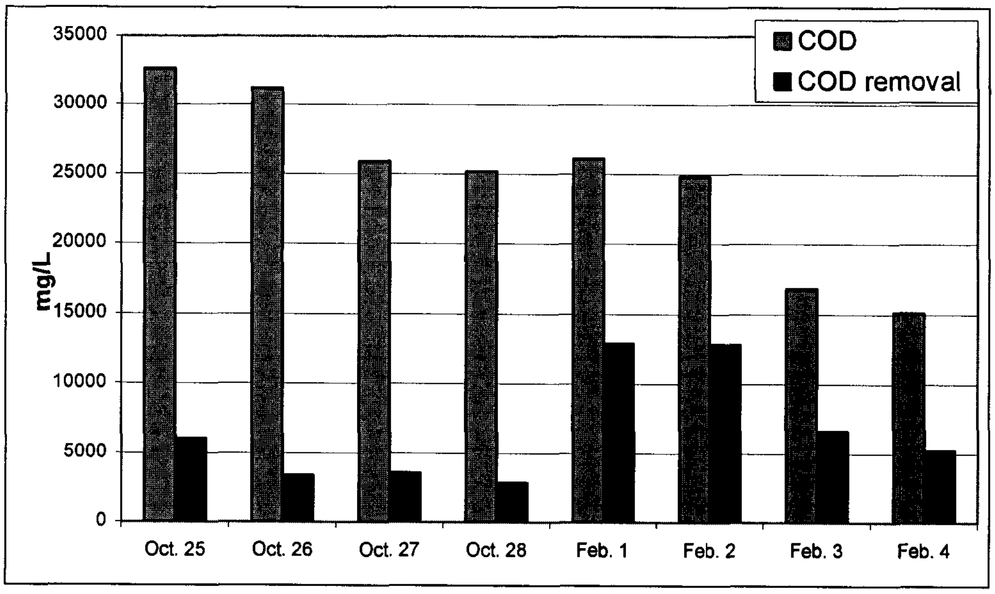


Figure 4-23 COD concentration in the manure and its removal

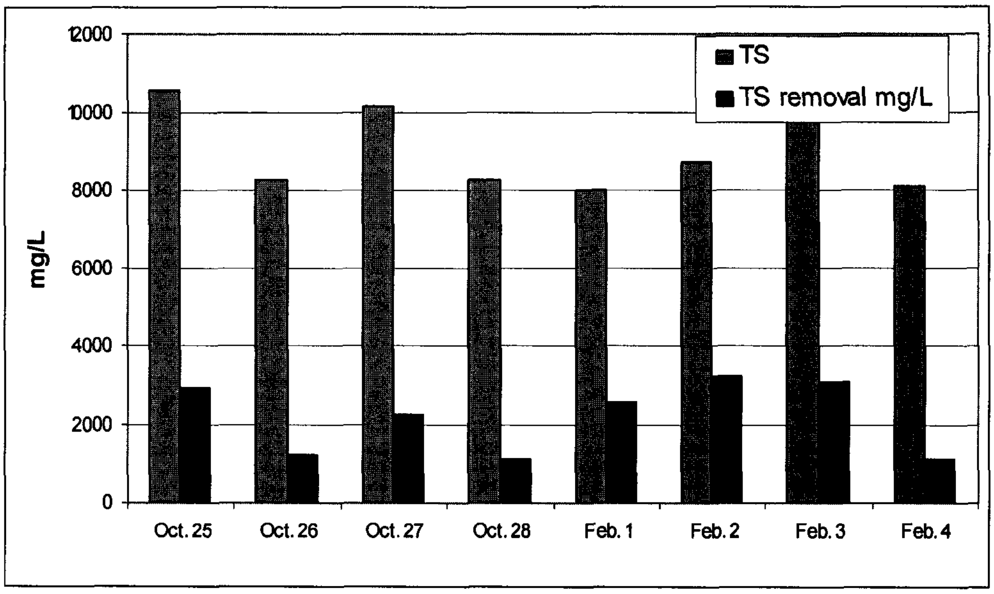


Figure 4-24 Total solids in the manure and its removal

4.4.3 Stage III -- 10 days continuous operation

The enhanced struvite crystallizer was operated continously for 10 days to test its performance stability. The plant operation was started on 14th Feberury (3:00 pm) with influent flow rate of 150 ml/min and ended on 24th February (3:00 pm). The Mg solution of 2000mg/L was introduced at a flow rate of 7 ml/min, which increased the Mg/P ratio to about 1.6. Presettled swine manure was used as influent, which was sampled every day and then mixed and analyzed by the end of the plant operation. The effluent was sampled once a day at afternoon, and analyzed individually. During some special events, ex. power failure, pipe broken etc., more than one samples were taken on the same day.

Table 4-22 Phosphorus and ammonia results

Sampling time	TP		DP	
	mg/L	Removal	mg/L	Removal
RWW	125.2		93.6	
16-4	34.5	72.5%	27.5	70.6%
17-4	111.1	11.3%	91.2	2.6%
17-8	48.3	61.4%	39.7	57.6%
18-4	63.9	49.0%	46.0	50.8%
19-8	33.4	73.3%	31.3	66.6%
20-2	109.1	12.9%	79.0	15.6%
20-5	46.8	62.6%	27.5	70.6%
21-3	55.9	55.4%	33.3	64.4%
22-9	38.1	69.6%	20.8	77.8%
22-4	64.1	69.6%	20.8	77.8%
23-9	51.5	58.8%	27.5	70.6%
23-1	51.4	59.0%	30.9	67.0%
24-2	34.1	72.8%	17.9	80.9%
Average	55.4	55.8%	37.2	60.2%

The system ran smoothly with average removal efficiencies of 56% and 60% for TP and DP respectively, the monitoring results were shown in Table 4-22. The average removal in the bottom of the table, were calculated without the three abnormal operation samples, which were greyed in Table 4-22. Ammonia concentration in the effluent was monitored each day. The average ratio of the removed ammonia to total phosphorus was about 8 mole/L. Some ammonia escaped to the atomsphere through air stripping. The phosphorus removal was very stable with removal efficiency of 50 to70% for both TP and DP.

The enhanced struvite crystallizer was found to be very stable under variable conditions. It went back to normal operation quickly after unexpected system failure, ex. power failure, pipe failure and dried solution etc, once it was corrected. Too high Mg concentration would decrease the phosphorus removal efficiency, because the high supersaturation level would result in generation of too fine crystalls, which were difficult to separate from the liquid stream. On 17th Februry, the influent pipe was blocked for a long time, the TP removal was reduced to 11%. And the phosphorus removal would decrease without Mg dose, as on 20th, the Mg solution was dried for several hour, and TP removal was reduced to 12.9%. it was also found that variation within 17% of air flow would not affect the phosphorus removal efficiency, as on 23rd, the air diffuser was cleaned after first sampling, which resulted air flow from 25 to 30 units, and there was no significant difference with the phosphorus removal.

On 22nd, the influent pipe blocked for a short time, which resulted in the increase of Mg/P, and hence higher phosphorus removal (70% for TP and 78% for DP) was achieved. This indicated that a little increase in magnesium dose could increase the phosphorus removal.

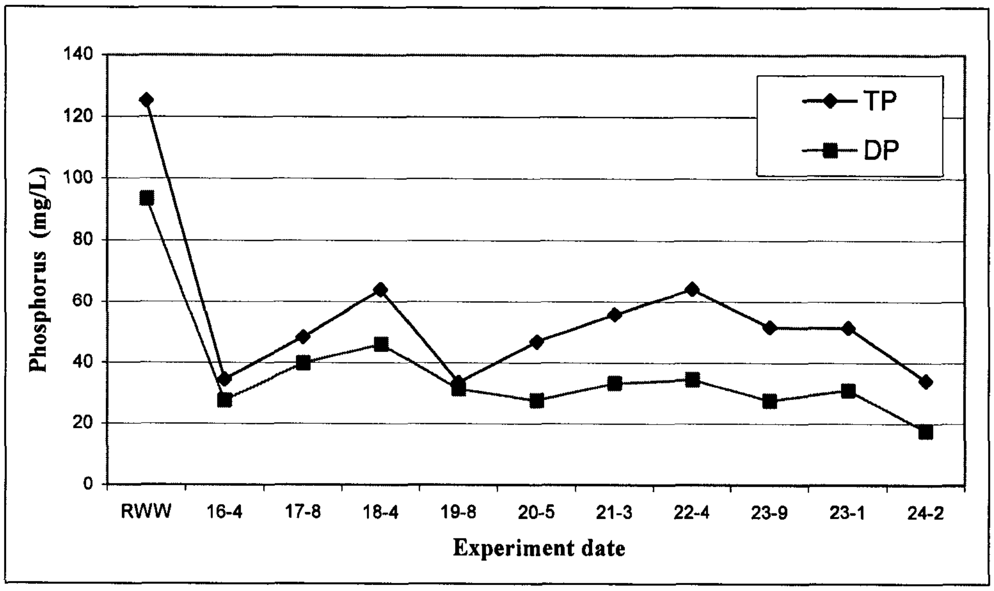


Figure 4-25 Phosphorus monitoring results

Not only the phosphorus, but also organic matter and solids were significantly removed through the enhanced struvite crystallizer. 37% of COD removal was achieved in average, with maximum removal of 60 %. The COD monitoring results are shown in Table 4-23, and plotted in Figure 4-26.

The average total solids (TS) concentration was removed for 475 mg/L in average. It consisted mainly suspended solids because dissolved solids were not removed significantly. An average of 83% suspended solids were removed. The monitoring results of total solids were shown in Table 4-23 and plotted in Figure 4-27.

Table 4-23 Solids and COD monitoring results

Sample	TS	TDS	TSS	TS	TDS	TSS	COD	
		Mg/L			Removal		Mg/L	Removal
RWW	4400	3500	900				7665	
16-4	5050	4750	300	-15%	-36%	67%	6361	17%
17-4	4000	3500	500	9%	0%	44%	6035	21%
18-4	3800	3350	450	14%	4%	50%	3425	55%
19-8	3800	3400	400	14%	3%	56%	4567	40%
20-2	3650	2900	750	17%	17%	17%	3588	53%
20-5	3950	3200	750	10%	9%	17%	6850	11%
21-3	3400	3250	150	23%	7%	83%	4730	38%
22-9	4150	3750	400	6%	-7%	56%	5708	26%
22-4	4050	3400	650	8%	3%	28%	3588	53%
23-9	4100	3650	450	7%	-4%	50%	4567	40%
23-1	3550	3150	400	19%	10%	56%	5708	26%
24-2	3600	3100	500	18%	11%	44%	3099	60%
Average	3925	3450	475	11%	1%	47%	4852	37%

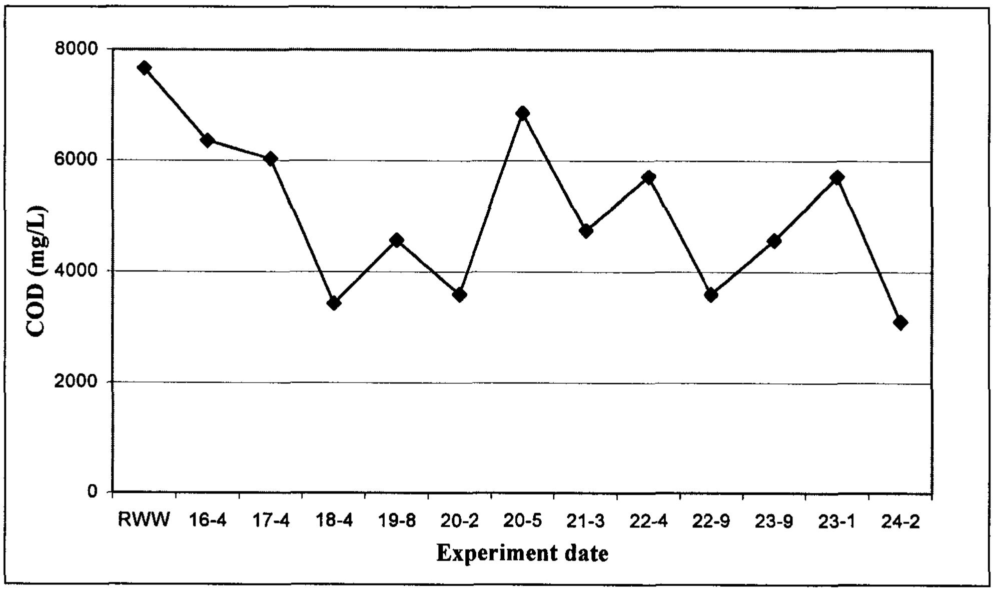


Figure 4-26 COD monitoring results

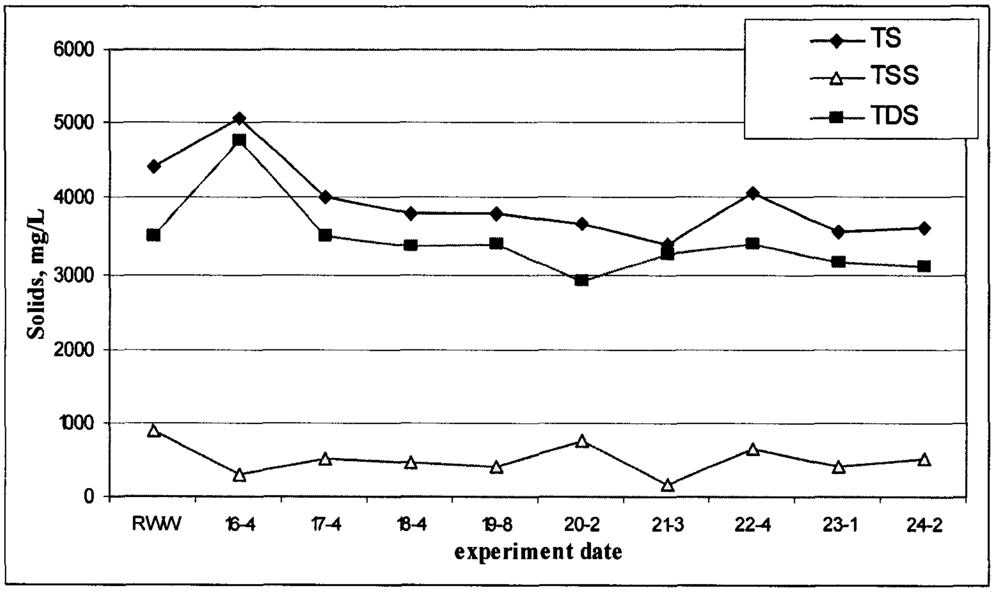


Figure 4-27 Solids monitoring results

4.4.4 Other operational concerns

4.4.4.1 Ammonia emmission

Ammonia emmision is a serious environmental problem for animal manure treatment lagoons. The emission may cause disturbance to the neighbourhood. Ammonia, with a Henry' constants of 0.75 atm in the natural water or wastwater, is marginally strippable (MetCalf and Eddy 2003). So the aeration was warried to increase the ammonia emmision to the atmosphere. However, during the pilot plant operation, there was no amminia smell noticed, and therefore was not be a problem for the aeration system.

Ammonia has to be in gaseous form before it can escape from the manure. The equilibrium of the ammonium ions and gaseous ammonia in the manure is expressed as:

$NH_4^+ = NH_3 + H^+$ Equation 4-4

With $K_a = 5.7*10^{-10} = [NH_3]*[H^+] / [NH_4^+]$ (Reynolds and Richard 1996)

As the pH increases, the equilibium tend to shift to the left. As a result, more ammonium ions get converted to ammonia gas. The aeration system was supposed to operate in the pH range of 8.2 to 8.5, the possible ammonia emmision was calculated as following:

Assuming the total ammonia/ammonium concentration in the primary settled swine = 2500mg/L.

At pH = 8.5, $[H^+] = 10^{-8.5}$, so the ratio of $[NH_3] / [NH_4^+] = Ka / [H^+] = 0.18$

In this case, the gaserous ammonia calculated in the manure was around 380 mg/L. According to the Henry's constants of ammonia, it was assumed that 25% ammonia (about 95 mg/L) was emmitted out of the liquid phase. The air supply was about 10 L air per L manure. A mass balance equation can be developed:

$L (C - Ce) = G (Y - Yo)$ Equation 4-5

Where: L = the manure treatment flow rate

G = the air supply rate for aeration

C - Ce = ammonia concentration reduction in the manure

Yo = ammonia concentration in the supplied air

Y = ammonia concentration in the emmitted air, assumed to be zero

From the mass balance equation, the possible ammonia emmision was calculated to be 9.5 mg/L. Similiarly at pH = 8.2, the possible ammonia emmision was around 5.2 mg/L.

4.4.4.2 Foam control

Foaming has been reported as an operational problem in swine manure treatment. Some experiments have reported the use of oil to control foaming with reasonable success (Edgerton et al. 2000; Suzuki et al. 2004). In this experiment, the foam was contained in the aeration chamber by a cover, while the air still could escaped from the hose holes in the wall. The aeration chamber was cleaned regularly during the experiments, as the cover is removable. For a full scale operation, washing pipes could be arranged in the top of the aeration chamber and wash the walls and cover periodically.

4.4.5 SEM and X-ray analyses results

The generated struvite mixtures were collected and analyzed by SEM and X-ray method. The solids were discharged from the bottom of the clarifier through the flexible hose, diluted or washed with tap water, then it was filtered through quantatitive filter paper, and air-dried. The air-dried sample was stuck on a small special dish for surface goldening and SEM analysis. The SEM images are shown in the following figures 4-28 ~ 4-32.

Figure 4-28 is the image of the struvite aggregated with other solids. As compared to the sample images of the struvite from the FBC, the ESC struvite crystals were more distinguished. The crystals were of prism-like shape, but looked more stronger and larger than the crystals generated in the fluidized bed crystallizer.

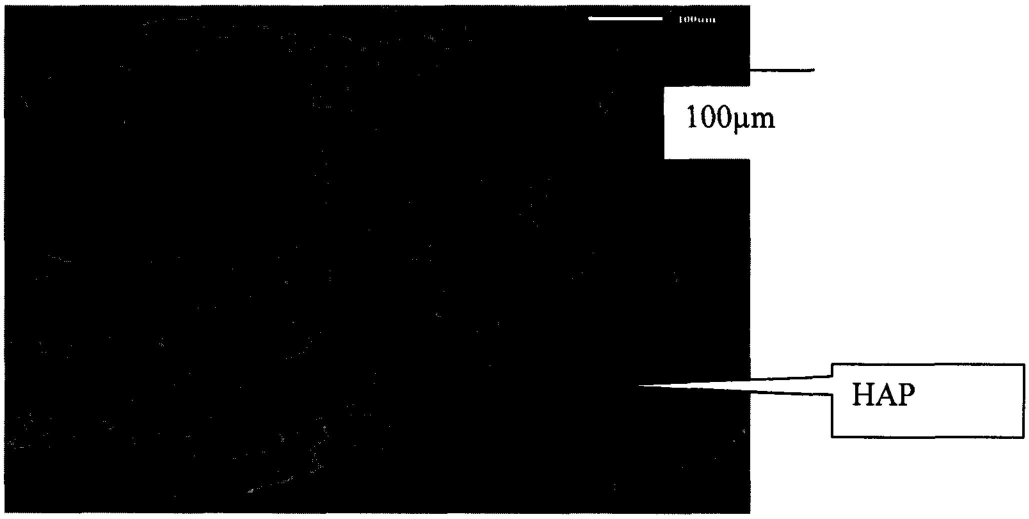


Figure 4-28 The aggeragated solids of struvite crystals

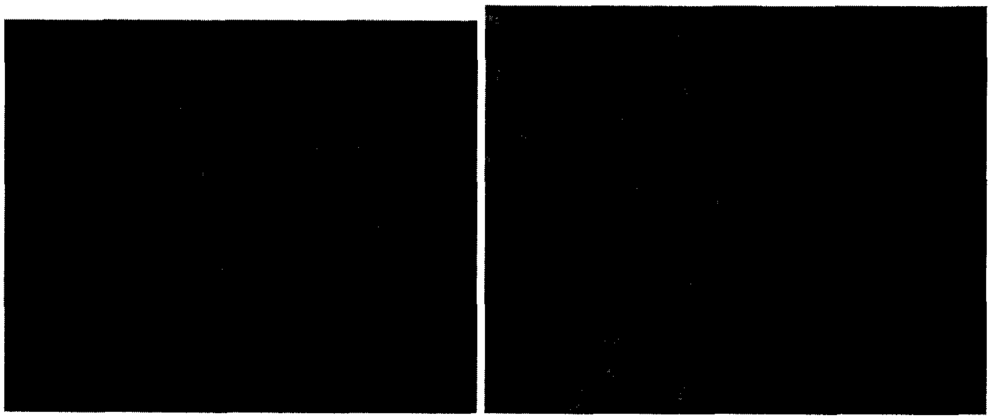


Figure 4-29. SEM image of the struvite crystals (washed sample)

Some samples were washed with tap water for several times, then filtered and air-dried for SEM analysis. The images are shown in Figure 4-29, where the crystals looked more clear in semi-transparent color. The enlarged image (Figure 4-29 right) is also shown in figure 4-30. The crystals were confirmed struvite crystals by X-ray analysis, the results are shown in figure 4-31.

Figure 4-30. Enlarged image of the struvite crystals

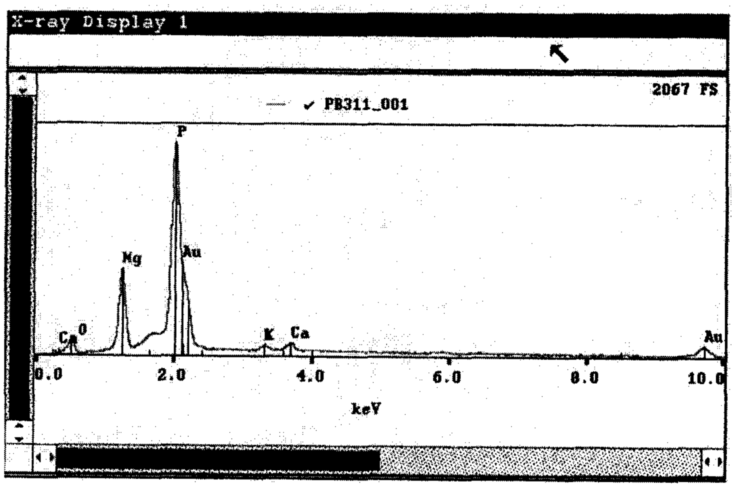


Figure 4-31 X-ray analysis of crystal in figure 4-33 (left)

Calcium phosphate (HAP) was also found in the collected solids. HAP crystal appearance was different from the struvite crystal. It looked more rough on the surface, and the edges was irregular, not forming a straight line as in case of struvite crystals. The SEM image and X-ray results of the HAP particle are shown in figure 4-32 and 4-33.

Figure 4-32 enlarged SEM image of HAP particle

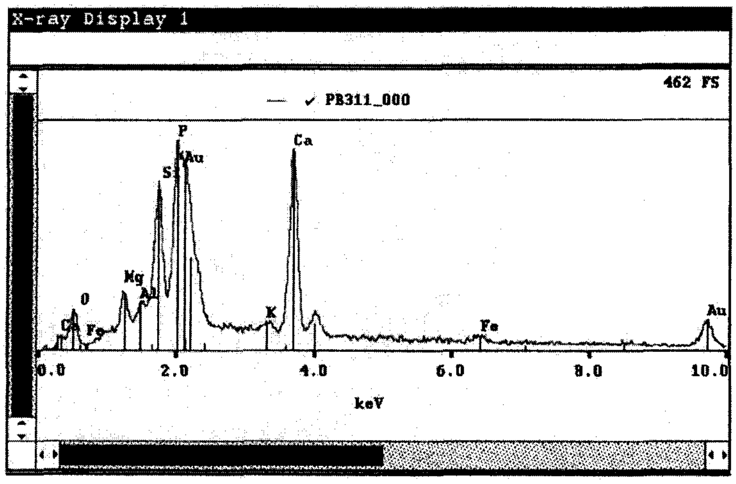


Figure 4-33 X-ray analysis of crystals in figure 4-35

4.5 Economical analysis of the struvite process

The technical feasibility of controlled struvite precipitation has been proposed by several researchers (A.Seco 2004; Adnan et al. 2004; Antakyali et al. 2004; Battistoni et al. 2004). The struvite has been studied extensively for its attractive agronomic properties and excellent fertilizer value (Schipper and Verhoek, 2004, Beal et al., 1999, Driver, J et al. 1999). However, the market price of struvite has not been established, and the commercial application of struvite precipitation are still very limited in North America. The main reason is high cost involved with chemicals required for magnesium addition and pH adjustment. A general economical analysis was carried out for an assumed swine farm with 1,000 pigs, with two kinds of struvite crystallizer. The theoretical benefit/cost factor was calculated based on the stoichiometry of the reactions.

According to USEPA (2005), 2 gallon (~ 7.6 L) manure is generated per pig each day. Considering a swine farm with 1,000 pigs, the manure flow rate was assumed to be about 7600 liter per day, that is 5.3 L/min. The concentration of the pre-settled manure was assumed to be 200, 80, and 2000 mg/L for total phosphorus, magnesium and ammonia nitrogen, respectively. Therefore, the required size (volume) of the EPC and FBC reactors are 400 and 265 L, respectively, based on the retention times of 75 and 25 minutes. Although the required volumes were different for FBC and EPC reactors, their manufacturing cost was assumed to be same ($10,000). It is because the height and shape of FBC makes it more difficult for manufacturing. Other accessaries were assumed to be same for the two reactors. The estimated construction costs are shown in table 4-24.

While EPC system needs only magnesium addition, the FBC system needs both magnesium and sodium carbonate, therefore, to account this the chemical pump and solution tank costs were doubled for FBC system (Table 4-24). The reactor costs included manufacturing and assembling costs. Submersible centrifugal pump (flow rate around 5L/min.) would be used as the sewer pump, and Chem-feed adjustable pump (flow rate 20~200 ml/min.) from BLUE-WHITE would be used as chemical pump. Fisher accumet

AB15 pH/mV/°C meter would be used for pH monitoring. The air flow required for the blower would be around 80 L/min. with pressure greater than 4.3 psi. (30 kPa)

Table 4-24 Estimation of the construction cost of the two struvite systems

Items	EPC	FBC
Reactor	10,000	10,000
Manure pump	300	300
Chemical pump	500	1000
Air blower	500	
Solution tank	100	200
pH meter	1,100	1,100
Total	12,500	12,600

The operational cost of struvite precipitation mainly depends on the labor and chemical addition requirement, and the cost of power. Assuming the plant needs to be maintained every two hours in a day for struvite collection and for general plant maintenance, the lobor cost is assumed $25 per hour. the labor cost would be $18,500 for each plant per year. The power cost mainly from the manure pump and blower. The total power required for EPC and FBC. were assumed 2 and 2.5 hp, respectively. EPC uses one sewage pump for manure influent and one air pump for aeration with one horsepower, while FBC uses one sewage pump (1.5 hp) for diluted manure influent (doubled flow rate) and another pump (1 hp) for dilution water. If the unit price of electricity is assumed $0.06/kwh, the cost of power can be estimated as $784 for EPC and $ 980 for FBC reactor. More power is needed for FBC, because it is operated with diluted manure, which needs an extra pump for dilution water and larger pump (1.5 hp in this case) for influent.

The chemical cost mainly depends on the operational conditions of the plant, e.g. the pH value and Mg dose. The most frequently used chemicals for struvite precipitation are: magnesium oxide, magnesium chloride, and sodium hydroxide. In this study, magnesium chloride and sodium hydroxide were used. The chemical dose and cost estimates under different operation conditions are calculated and presented in Table 4-25. Magnesium chloride hexahydrate crystalline was used to prepare solution. The price of natural flake magnesium chloride (with minimum 12% Mg) was estimated to be $290/ton (www. ravensdown.co.nz 2005). The pH adjustment was performed by adding sodium hydroxide. Sodium hydroxide flakes were used to prepare solution. The price of sodium hydroxide flakes was $92.50 per 50 lb, derived from www.chemistrystore.com (2005).

The revenue obtanied from struvite precipitation can be calculated by the price of the produced struvite and by saving the maintenance cost by reducing the pipe blockages. The sale price of struvite is an important factor for cost-benefit analysis, although the market price has not been established. The market value of recovered phosphates primarily depend on the quality of the recovered product, and on the local market conditions. The price estimates of struvite as suggested in several studies vary significantly, and are summarized in Table 4-26.

Table 4-25 Chemical dose and cost under different conditions

Desired Mg/P ratio	1	1.2	1.4	1.6	1.8
Required Mg dose (mg/L)	59	87	115	143	171
Daily usage of Mg (g)	451	663	875	1087	1298
Daily cost ($)	1.09	1.60	2.11	2.63	3.14
Yearly cost ($)	398	585	772	958	1,145
Desired pH value	8	8.2	8.4	8.6	8.8
Required dose of NaOH (mg/L)	40	63	100	159	252
Daily usage of NaOH (g)	304	482	764	1210	1918
Daily cost of NaOH ($)	2.81	4.45	7.06	11.18	17.72
Yearly cost ($)	1025	1625	2575	4082	6469

Table 4-26 Estimated struvite prices

Price	Description	Country	References
198~330	Suggested market value	Australia	Munch and Barr, 2001
283	Suggested market value	UK	Jaffer et al, 2001
310	Obtained by Unitika Ltd.	Japan	Yasanori Ueno, 2001
206	Based on fertilizer N&P value	US	Beal et al., 1999

Here the price of the generated struvite from swine manure was estimated at $150 per ton, as their purity would be lower, even after further purification, because of the high concentration of contaminants in swine manure. The potential sale benefits of struvite are presented in Table 4-27.

Table 4-27 Potential sale benefit of the recovered struvite

Estimated phosphorus removal (%)	40%	60%	70%	80%	85%
Daily generated struvite (kg)	4.33	6.50	7.58	8.66	9.20
Daily income of sale ($)	0.65	0.97	1.14	1.30	1.38
Yearly income for sale ($)	237	356	415	474	504

From the above economic analysis, the most important operation cost is the labor cost, which was about $18,500 per year. Based on our experiments, for a smooth operation, 70% phosphorus removal could be reached with EPC at Mg/P ratio of 1.6, and 60% phosphorus removal with FBC at Mg/P ratio of 1.4 and pH of 8.2. In this case, the power and chemical costs would be $1742 and $ 5774 for EPC and FBC respectively, the alkaline usage was doubled for FBC, because it operated with diluted manure. Also, it can be noted that the revenue obtained from struvite sales was very limited (Table 4-28).

Table 4-28 Cost/Benefit analysis of the struvite process operation

	Estimated TP removal %	Required Mg dose mg/L	NaOH dose mg/L	Labor cost	Chemical and electricity cost	Sales revenue	Benefit
EPC	70	1.6		18500	1742	415	-19827
FBC	60	1.4	8.2	18500	5774	356	-23918

Note: the units for all the cost, revenue and benefit are in Canadian dollar.

However, the benfits of struvite application are not limited to its sale, but other potential benefits, such as phosphorus management, improved waste management, sustainable development concept, and reduced sewage plant maintenance costs by avoidance of the unwanted struvite formation. So struvite process still could be widely applied, although the sale price of the product of recovered phosphate can not compensate the cost of the operation of the process. The application of struvite process, mostly depends on the education of the farm owners and the relative regulation.

5 Conclusion and recommendations

In this research, the effectiveness of struvite crystallization for phosphorus removal/recovery from swine manure was studied, at laboratory and pilot scale experiments. Two types of pilot plants were evaluated for their performance in terms of phosphorus removal and easy operation. Following points were concluded from this research:

- There is great potential to recover phosphate from swine manure, and struvite crystallization was demonstrated as a promising technology with satisfied results. Up to 73% phoshphrus removal was achieved when the EPC reactor was used to treat the premary settled swine manure. Up to 64% phosphorus removal was achieved when FBC reactor was used to treat diluted swine manure;

- Struvite precipitation is a complicated process. It could be affected by many factors such as pH value, Mg/P ratio and their interactions. The study concluded that higher pH (8~8.8) resulted in higher phosphorus removal, and higher Mg/P ratio increased the phosphorus removal in the range of 0.8~1.8 treating pre-settled or diluted swine manure. Howevr, When the two parameters were both in high levels, the phosphorus removal decreased;

- Aeration was found to be an effetive method for struvite crystallization from swine manure. It was not only useful to control the pH, but also removed some organic matter and solids, which could enhance the struvite formation too.

- Seedings were used only at the initial start-up of the plants. It was not necessary for the later stages. The struvite generated after precipitation worked as seeding;

- The generated struvite mixtures can be used as fertilizer. These mixtures are rich in phosphorus, and also contain calcium and potassium, which are the essential elements for plant growth;

- The SEM and X-ray analysis confirmed the generated solids were struvite crystals. The results showed that struvite crystals were mixed with the other crystals containing calcium phosphorus, and some other solids. Main elements such as P, Ca, Mg and K were found in the solid mixture;

- The reactor design is critical for effective removal of phosphorus from different kind of wastewater. The fluidized bed crystallizer was suitable for treating dilute swine manure, while the enhanced struvite crystallizer worked well with both types of swine manures (diluted and pre-settled);

- Enhanced struvite crystallizer (ESC) significantly removed the suspended solids and organic matter, while insignificant removals were observed with fluidized bed crystallizer;

- Equalization tank is strongly recommended for the swine manure treatment system. It can be helpful to improve the efficiency of succeeding treatment processes; and
- Primary settling is recommended for an effective preliminary treatment for swine manure.

Based on above conclusions, following recommendations are made for further investigations:

- Further study in pilot scale are needed to investigate the effects of reactor hydraulics, and organic and solids concentrations on struvite crystallization;
- Long term continuous operation studies of the pilot/full scale plant are needed to evaluate the plant performance in terms of long term effects and set up the operational and manitenance requirements of the plant, for further commercial applications;
- Further research could be conducted on land application potential of the struvite mixtures or purified forms. These studies can be useful to evaluate the struvite fertilizer value and its effects on the land products and soils;
- Further investigation are needed to develop potential market strategies for the recovered struvite and their application feasibility in phosphorus industries, and to develop effective purification methods for the collected struvite mixtures.

6 References

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Apendix 1

The characteristic of the primary settled swine manure

Sample date	TP	DP	TKN	NH4-N	Mg	COD	BOD	TS	TDS	TSS	pH	Temp.	EC
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L			
6, May	208.5		4066			22996		11705	10670	1035	7.67	20.7	
20, May	147	130									7.34	20.4	
19, June	162	147	1809	1407	96			13282	11116	2167	6.68	20.2	8.65
17, July	184	148	2884	1521		26095	7705	15800	11800	4000	7.4	17.8	13.34
22, July	244	207	2702	2104		29031	8806	10120	3800	6320	7.4	20.4	13.07
27, July	227	196	2440	1801		17777	4185	8220	6700	1520	6.8	20.7	15.72
17, Aug	213	172	2936		111	17940					7.54	18.9	17.6
1, Oct	185	175	2588	2014	72	11416		7670	6100	1570	8.17	20	14.06
6, Oct	219	178	2786		78						8.06	22	12.07
25,Oct	174	162		2594		32619	9111	10540	7900	2640	7.91		14.6
26, Oct	177	164	2466	2662		31151		8225	6450	1775		15.6	14.55
27,Oct	194	182		2710	57	23863	6442	10140	7150	2990	8.08	14.4	14.49
28,Oct	192	176		2723	78	19867		8240	6050	2190	8.11		14.47
1. Feb.	146	107		2355	60	26095	9670	9200	6200	3000	8.08	22	
2. Feb.	160	137		2491		24790		8900	6000	2900		22	
3. Feb.	143	118		2514		16799		10050	6800	3250	8.17		
8. Feb	166	132		2552	55	15168		10140	7150	2990		22	

Appendix 2 The characteristic of the diluted swine manure after settling

Sample date	TP mg/L	DP mg/L	NH4-N mg/L	Mg mg/L	COD mg/L	TS mg/L	TDS mg/L	TSS mg/L	pH	Temp.	Cond.
23, Aug.	43	40		23.4					7.89	20	5.41
27, Aug.	49.5	43.5	785	22.8	9214	1800	1350	450	7.85	16.7	
3, Sep	55.7	39.2		18.6		2320	1550	770	7.64	15.8	4.16
13, Sep	60.5	53.4	828	22.2	8318	2310	1100	1210			
20, Sep	38.3	31.8		14		1400	1000	400	7.87	17.8	3.03
24, Sep	61.3	43.4	790	37.5	2383	2320	1550	770	8.03	18.5	2.48
17, Nov.	135	130	1850	48.9	4358	4780	3200	1580			
18. Nov.	150	135				4530	2950	1580	8.08	12.3	7.33
23, Nov			1196	92	8325	4300	2250	2050	8.04	18.9	8.55

Appendix 3 Lab scale factorial experimental results

Run #	A	B	C	D	E	TP removal		DP removal	
	pH	Mg	Reaction time	Mixing speed	Settling time	%	mg/L	%	mg/L
1	1	1	1	1	1	31.8	47.0	23.4	30.5
2	**1**	**1**	**1**	**-1**	**1**	**62.2**	**91.8**	**63.5**	**82.8**
3	**1**	**1**	**-1**	**1**	**1**	**60.6**	**89.5**	**55.4**	**72.2**
4	1	1	-1	-1	1	58.1	85.8	55.7	72.6
5	1	-1	1	1	1	28.1	41.6	13.1	17.1
6	1	-1	1	-1	1	28.5	42.1	29.5	38.5
7	1	-1	-1	1	1	19.8	29.2	17.5	22.9
8	**1**	**-1**	**-1**	**-1**	**1**	**62.3**	**92.0**	**60.7**	**79.1**
9	-1	1	1	1	1	33.9	50.1	35.7	46.5
10	-1	1	1	-1	1	34.3	50.6	35.4	46.1
11	-1	1	-1	1	1	40.0	59.2	39.0	50.8
12	-1	1	-1	-1	1	28.6	42.3	27.0	35.2
13	-1	-1	1	1	1	46.6	68.8	43.2	56.3
14	-1	-1	1	-1	1	33.0	48.8	33.4	43.6
15	-1	-1	-1	1	1	42.5	62.8	46.5	60.6
16	-1	-1	-1	-1	1	27.5	40.6	23.4	30.5
17	0	0	0	0	1	19.0	28.1	23.7	30.8
18	0	0	0	0	1	26.0	38.5	23.1	30.1
19	1	1	1	1	-1	25.3	37.4	9.7	12.7
20	1	1	1	-1	-1	53.2	78.6	57.4	74.8
21	1	1	-1	1	-1	45.5	67.1	52.6	68.6
22	1	1	-1	-1	-1	48.4	71.5	53.2	69.3
23	1	-1	1	1	-1	26.0	38.5	4.7	6.2
24	1	-1	1	-1	-1	25.4	37.6	3.9	5.1
25	1	-1	-1	1	-1	23.7	35.0	8.4	10.9
26	1	-1	-1	-1	-1	58.7	86.7	56.0	72.9
27	-1	1	1	1	-1	25.2	37.2	49.0	63.9
28	*-1*	*1*	*1*	*-1*	*-1*	*13.3*	*19.6*	*20.1*	*26.1*
29	*-1*	*1*	*-1*	*1*	*-1*	*10.8*	*16.0*	*25.9*	*33.8*
30	-1	1	-1	-1	-1	19.9	29.4	15.3	20.0
31	-1	-1	1	1	-1	32.1	47.4	43.2	56.3
32	-1	-1	1	-1	-1	17.3	25.6	18.1	23.6
33	*-1*	*-1*	*-1*	*1*	*-1*	*-2.8*	*-4.2*	*35.9*	*46.8*
34	-1	-1	-1	-1	-1	25.7	37.9	10.3	13.4
35	0	0	0	0	-1	-0.7	-1.1	3.3	4.4
36	0	0	0	0	-1	3.3	4.9	7.0	9.1
					Average	31.5	46.5	31.2	40.7

Appendix 4 pH and Temperature monitoring during the aeration

Time	Fresh SWW		10days settling	
Min.	pH	Temp	pH	Temp
0	7.74	18.3	6.78	19.4
10	7.89	18.2	7.07	19.2
20	7.96	18.1	7.3	19
30	8.1	18	7.65	18.2
45	8.2	18	7.72	18
60	8.25	18	7.79	17.8
90	8.43	17.9	7.91	17.3
120	8.44	17.8	7.97	16.9
150	8.52	17.7	8.08	16.5
180	8.62	17.5	8.19	16.6
210	8.6	17.7	8.17	16.7
240	8.68	17.6	8.24	16.9
270	8.66	17.4	8.21	17
300	8.71	17.4	8.25	17
330	8.69	17.4	8.21	17
360	8.72	17.4	8.24	17

◆

Appendix 4 pH and Temperature monitoring during the aeration

Time	Fresh SWW		10days settling	
Min.	pH	Temp	pH	Temp
0	7.74	18.3	6.78	19.4
10	7.89	18.2	7.07	19.2
20	7.96	18.1	7.3	19
30	8.1	18	7.65	18.2
45	8.2	18	7.72	18
60	8.25	18	7.79	17.8
90	8.43	17.9	7.91	17.3
120	8.44	17.8	7.97	16.9
150	8.52	17.7	8.08	16.5
180	8.62	17.5	8.19	16.6
210	8.6	17.7	8.17	16.7
240	8.68	17.6	8.24	16.9
270	8.66	17.4	8.21	17
300	8.71	17.4	8.25	17
330	8.69	17.4	8.21	17
360	8.72	17.4	8.24	17

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Appendix 3 Lab scale factorial experimental results

Run #	A	B	C	D	E	TP removal		DP removal	
	pH	Mg	Reaction time	Mixing speed	Settling time	%	mg/L	%	mg/L
1	1	1	1	1	1	31.8	47.0	23.4	30.5
2	**1**	**1**	**1**	**-1**	**1**	**62.2**	**91.8**	**63.5**	**82.8**
3	**1**	**1**	**-1**	**1**	**1**	**60.6**	**89.5**	**55.4**	**72.2**
4	1	1	-1	-1	1	58.1	85.8	55.7	72.6
5	1	-1	1	1	1	28.1	41.6	13.1	17.1
6	1	-1	1	-1	1	28.5	42.1	29.5	38.5
7	1	-1	-1	1	1	19.8	29.2	17.5	22.9
8	**1**	**-1**	**-1**	**-1**	**1**	**62.3**	**92.0**	**60.7**	**79.1**
9	-1	1	1	1	1	33.9	50.1	35.7	46.5
10	-1	1	1	-1	1	34.3	50.6	35.4	46.1
11	-1	1	-1	1	1	40.0	59.2	39.0	50.8
12	-1	1	-1	-1	1	28.6	42.3	27.0	35.2
13	-1	-1	1	1	1	46.6	68.8	43.2	56.3
14	-1	-1	1	-1	1	33.0	48.8	33.4	43.6
15	-1	-1	-1	1	1	42.5	62.8	46.5	60.6
16	-1	-1	-1	-1	1	27.5	40.6	23.4	30.5
17	0	0	0	0	1	19.0	28.1	23.7	30.8
18	0	0	0	0	1	26.0	38.5	23.1	30.1
19	1	1	1	1	-1	25.3	37.4	9.7	12.7
20	1	1	1	-1	-1	53.2	78.6	57.4	74.8
21	1	1	-1	1	-1	45.5	67.1	52.6	68.6
22	1	1	-1	-1	-1	48.4	71.5	53.2	69.3
23	1	-1	1	1	-1	26.0	38.5	4.7	6.2
24	1	-1	1	-1	-1	25.4	37.6	3.9	5.1
25	1	-1	-1	1	-1	23.7	35.0	8.4	10.9
26	1	-1	-1	-1	-1	58.7	86.7	56.0	72.9
27	-1	1	1	1	-1	25.2	37.2	49.0	63.9
28	*-1*	*1*	*1*	*-1*	*-1*	*13.3*	*19.6*	*20.1*	*26.1*
29	*-1*	*1*	*-1*	*1*	*-1*	*10.8*	*16.0*	*25.9*	*33.8*
30	-1	1	-1	-1	-1	19.9	29.4	15.3	20.0
31	-1	-1	1	1	-1	32.1	47.4	43.2	56.3
32	-1	-1	1	-1	-1	17.3	25.6	18.1	23.6
33	*-1*	*-1*	*-1*	*1*	*-1*	*-2.8*	*-4.2*	*35.9*	*46.8*
34	-1	-1	-1	-1	-1	25.7	37.9	10.3	13.4
35	0	0	0	0	-1	-0.7	-1.1	3.3	4.4
36	0	0	0	0	-1	3.3	4.9	7.0	9.1
					Average	31.5	46.5	31.2	40.7