

PILOT SCALE APPLICATION OF MICROWAVE  
TECHNOLOGY FOR DAIRY MANURE TREATMENT  
AND NUTRIENT RECOVERY THROUGH STRUVITE  
CRYSTALLIZATION

by

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## **Abstract**

Excessive use of nutrients in agriculture has been significant surface and groundwater pollution sources. A pilot scale treatment process was developed for the purposes of phosphorus and ammonia recovery from dairy manure slurry. A novel advanced oxidation process combining hydrogen peroxide, microwave, and sulphuric acid was studied for its abilities to solubilise nutrients and metals in manure. The treated manure was then used for struvite crystallization to recover phosphates and ammonia in a commercially viable fertilizer form.

Using dairy manure, as a phosphate source for struvite crystallization, had some foreseeable challenges. The majority of phosphorus in dairy manure slurry was insoluble, thus unsuitable for struvite crystallization. A synergistic nutrient solubilisation effect was found when manure was treated. As high as  $101.7 \pm 4.3\%$  of total phosphorus was solubilised as phosphate, and  $94.9 \pm 4.7\%$  of total nitrogen was solubilised as ammonia. High suspended solids concentration in manure slurry, thought to impede struvite crystallization, was also overcome through microwave treatment to destabilise manure solids from suspension. As high as 2.00 Log reduction in total suspended solids was achieved by gravity clarification. Manure contains high levels of calcium that would compete against struvite for phosphate precipitation. Oxalic acid was tested as a potential reagent to use for calcium removal from dairy manure. Up to 97.2% soluble Ca removal, by calcium oxalate precipitation was observed.

The treated dairy manure was then used as influent material for struvite crystallization. Under various reaction conditions, it was found that phosphorus reduction between 69% and 99% was achievable. Roughly 25% nitrogen removal was observed under all reactor conditions. An interesting observation from the crystallization experiments was that pellet morphologies and compositions varied with reaction conditions. The potassium containing mineral hazenite was

found to coexist in the struvite pellets. The ability to extract potassium from dairy manure was not only beneficial to the dairy industry, but may also create a fertilizer of higher economical and nutritional value, than struvite alone.

## **Preface**

This thesis is original, unpublished, independent work by the author, Hui Zhang. The apparatuses used in this study (as described in Chapter 2) were based on the design of Wayne Lo, and modified by myself to better suit the scopes of this research. The model used for predicting struvite crystallization was created by Daniel Potts. All data presented henceforth, were generated from my studies conducted at the Dairy Education and Research Centre (Agassiz, B.C), in collaboration with the Department of Environmental Engineering, at the University of British Columbia, Point Grey campus.

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## **List of Abbreviations**

$\varepsilon''$	Relative loss factor
$\varepsilon'$	Dielectric constant
AOP	Advanced oxidation process
B.C.	British Columbia
C	Carbon
COD	Chemical oxygen demand
CY	Struvite crystallization reactor
DERC	Dairy Education and Research Centre
DRP	Dissolved reactive phosphorus
DUP	Dissolved unreactive phosphorus
EBPR	Enhanced biological phosphorus removal
EDTA	Ethylenediaminetetraacetic acid
EPS	Extracellular polymeric substance
H <sub>2</sub> O <sub>2</sub> /MW-AOP	Peroxide/microwave advanced oxidation process
H <sub>2</sub> O <sub>2</sub> /MW/H <sup>+</sup> -AOP	Peroxide/microwave advanced oxidation process with acid
HRT	Hydraulic retention time
K	Potassium
K <sub>so</sub>	Conditional solubility product
K <sub>sp</sub>	Solubility product constant
MCP	Microbiological calcium precipitation
MW	Microwave
N	Nitrogen
NH <sub>3</sub> -N	Ammonium nitrogen
OA	Oxalic acid
·OH	Hydroxyl radical
P	Phosphorus
PAN	Plant available nitrogen
PO <sub>4</sub>	Ortho-phosphate
PO <sub>4</sub> -P	Phosphate P
PP	Particulate phosphorus
PTFE	Polytetrafluoroethylene
Q <sub>i</sub>	Influent flow
Q <sub>R</sub>	Recycle flow
Q <sub>T</sub>	Total flow
RR	Recycle ratio
SBR	Sequencing batch reactor
SCOD	Soluble chemical oxygen demand
SP	Soluble phosphorus
SS	Suspended solids
SSR	Supersaturation ratio
TKN	Total Kjeldahl nitrogen
TOC	Total organic carbon
TP	Total phosphorus
TS	Total solids

UBC  
WAS  
WWTP

University of British Columbia  
Waste activated sludge  
Wastewater treatment plant

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## **Chapter 1: Introduction**

The dairy industry in British Columbia is the third largest in Canada, producing roughly 8.3% of the national total milk production. The majority (68%) of B.C. dairy herds are located in the Lower Mainland. The average lactating herd size is 142, plus a total equivalent number of replacement calves, heifers and dry cows. In light of recent expansions/development of livestock industry and changes toward environmental regulations/awareness, manure management and treatment technologies have been capturing the attention of researchers worldwide.

The current study was located in Agassiz, B.C., at the University of British Columbia's (UBC) Dairy Education and Research Centre (DERC). The facility hosted roughly 500 cows, with about 250 lactating at any given time. Each lactating cow produced 12-15L of urine and 35kg of feces per day. In a combined collection system, approximately 50 L of manure slurry was generated per cow per day. Dairy manure slurry was composed almost entirely of water, thus making its transportation expensive. Therefore, all manure produced has been spread onto the land, locally, as soil amendments.

Trends in the dairy industry clearly show that the number of cows per herd is ever increasing, while the number of dairy farms has been decreasing. Contrary to some beliefs, the industrialization of dairy farming has had an overall positive impact on the environment. It was found that, for equivalent volume of milk produced, industrialization of dairy production led to 79% reduction of animals, 90% reduction of the land used, 76% reduction of manure, 67% reduction of CH<sub>4</sub>, and 44% reduction of N<sub>2</sub>O (Capper *et al.*, 2009). Although pollution has been reduced globally, the increased heads of cows per acreage has increased the potential for dairy farms to be an isolated pollution source, impacting the environment locally.

Increasing the herd density per acreage of land may have led to over-fertilization of the soil. For farms located close to surface water, runoff and soil erosion transport the excess nutrients to the local surface waters; groundwater can become contaminated from leaching. Elevated nitrogen and phosphorus levels have been a known cause of eutrophication.

The current chapter provided a general description of phosphorus use in agriculture, dairy manure, and the environmental impacts of both. Although treatment and management of dairy manure has been well studied in the past, recent world fertilizer production trends have highlighted the need for phosphorus recovery and recycle. The subsequent chapters give an in-depth look at a novel method of manure treatment with the goal of recovering excess phosphates from dairy manure. Phosphate recovery by such a method will not only produce a phosphate rich commercial fertilizer, but also allow dairy farms to have better control of their nutrient application management.

## **1.1 Phosphorus**

Carbon (C), nitrogen (N), phosphorus (P), potassium (K), and other trace elements have been essential for life. Both C and N have relatively short natural cycles that helped replenish itself in water and soils. The P biogeochemical cycle, however, has been amongst the slowest. Although ortho-phosphates ( $\text{PO}_4$ ) move quickly through plants and animals, their movement through the soil and oceans have been relatively slow. In nature,  $\text{PO}_4$  originates from the weathering of rocks rich in  $\text{PO}_4$ . After entering the soil,  $\text{PO}_4$  is absorbed on the surfaces of clay and organic particles where they can be remobilized and incorporated into plant tissue.  $\text{PO}_4$  in vegetation is consumed by other higher organisms, such as animals, before excreted as waste. The  $\text{PO}_4$  in excreted wastes, would have re-entered the soil through excrement disposal.

Therefore,  $\text{PO}_4$  would have been reused until it ultimately enters ocean waters before sedimentation occurs on the ocean floor. The sediments can be brought back to land over long periods of time, via geologic uplift, and thus completes the oversimplified cycle.

In the biosphere, the phytomass of plants, the hydroxyapatite of bones and teeth, as well as genetic materials of all organisms contain the most significant sources of P. The intensified mobilization of P has been mainly due to agricultural uses for risen food productions. The application of inorganic fertilizers, prepared from the treatment of phosphate rock, was substantially expanded after 1950. 13–16 Mt P/year of fertilizers was produced by 2000 estimates, which amounts to 80% of total P production from phosphate rock sources (Smil, 2000). The United States has been amongst the world's largest producer of phosphate rock since the late 1800's (US Dep. Agric., 1964). More recent evaluations determined that 85% of the phosphate market is controlled by Morocco. (Mavinic, pers. comm. 2013).

The consequence of P fertilizer usage had increased its potential to leave the fields and enter the aquatic ecosystem. Phosphorus in aquatic systems was divided into three categories: dissolved reactive phosphorus (DRP), dissolved unreactive or soluble organic phosphorus (DUP) and particulate phosphorus (PP) (Rigler, 1973). The sum of DRP and DUP was given the general term soluble phosphorus (SP); the sum of all phosphorus components was termed total phosphorus (TP). SP and PP were differentiated by whether or not they passed through a 0.45  $\mu\text{m}$  membrane filter. Of the SP fraction of phosphorus, DRP is largely composed of inorganic  $\text{PO}_4^{3-}$  and its hydrogenated ions whereas DUP comprises of certain organic form of phosphorus and/or chains of inorganic  $\text{PO}_4$  termed polyphosphates. An estimate from the year 2000 speculated that 27 Mt of P became waterborne due to soil erosion alone; a majority of which came from agricultural lands.

Anthropological use, and losses, of P are largely in urban settings where an annual 0.75 – 1 kg P/capita entered the sewer system (Smil, 2000). Wastewater treatment facilities traditionally precipitated  $\text{PO}_4$  in insoluble salts by addition of flocculating compounds, usually salts of iron (*e.g.*  $\text{FeCl}_3$  or  $\text{FeCl}_2$ ) to produce  $\text{FePO}_4$ , salts of Al (*e.g.*  $\text{Al}_2(\text{SO}_4)_3$ ) to produce  $\text{AlPO}_4$ , or lime ( $\text{CaO}$ ) to generate  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ . The  $\text{PO}_4$  precipitated in this manner was often unsuitable as soil amendments for two notable reasons:

- there may be heavy metals and
- the Fe and Al will remove dissolved  $\text{PO}_4$  in the soil as well.

For these reasons and more, biological P removal had gained popularity.

## 1.2 Dairy Manure

### 1.2.1 Manure Characteristics

Each lactating dairy cow produces roughly 50 L of waste (urine and feces) per day. The feces to urine ratio has been approximately 2.2 : 1 by weight (ASAE, 1982). Of the total solids (TS) found in manure, roughly 83% of which was volatile solids. Dairy cow manure varied in composition for a number of reasons. Cows on larger farms were typically kept separate as lactating cows, breeding cows, calves, heifers etc. Each of the cow types were fed differently and produced manures that varied in content (Toors *et al.*, 2005). Manure collection and barn arrangements also impacted the content of dairy manures. Mechanical or hydraulic scraping was often used for waste collection from the barn floors into the manure pit. The term “manure” was the material collected from barns and not only contained solid and liquid animal wastes, but also feed and bedding residues.

Bedding material for dairy cows consisted of sand, straw, or sawdust, in most circumstances, and depended on the choice of each farm. Straw and sawdust were typical choices for bedding since they were the most absorbent materials and were relatively inexpensive. Sand bedding had risen in popularity due to its effectiveness for lowered cases of clinical mastitis caused by coliforms and *Klebsiella* spp. However, it was found that *Streptococcus* spp. became more abundant on the teats of cows housed on sand, compared to sawdust (Zdanowicz *et al.*, 2004).

The feedstuffs for a dairy cow were classified into forages and concentrates. Concentrates were generally defined as having more digestible energy per unit weight or volume of food. Therefore, concentrates were mostly composed of cereal grains, milling by-products, protein sources and fats; the energy was mostly in the form of starches, sugars, fats, and other carbohydrates. On the other hand, forages had lower digestible energy per unit weight/volume of material. The energy in forages was in the form of cellulose and hemicelluloses. Hence, forages consisted of more fibrous and vegetative portions of a plant. Division of the two categories had not been fully defined and is more complex than energy density alone, but the exception will not be discussed further. Of the gross energy consumed by a lactating cow, an estimated 35% was lost in the solid and liquid waste stream. The organics in the waste stream tended to resist biodegradation, or does so only slowly.

The mean physical and chemical characteristic of manure had been reported by many. All records emphasized that the nutrient content of dairy manure differentiated greatly and depended on digestibility of the rations, animal age, amount of feed and water wasted, the amount/type of bedding used, and the amount of water used for manure removal from the buildings. In order to



give the reader a general idea of constituents in manure, Tables 1.1 and 1.2 showed the compiled dairy manure characteristics from a number of facilities in both the Carolinas, United States.

### 1.2.2 Dairy Manure Treatment and Uses

Uses for manure are relatively few. In majority of cases, it was applied to the land as fertilizer due to its high phosphorus and nitrogen content. The manure, in combination with other fertilizers was used to increase the fertility of the soil and increase crop yield (Hadas *et al.*, 1983). The physical disadvantages of manure as a fertilizer are two-fold. First, the texture of manure was irregular and thus, made it difficult to broadcast in the field. Second, the high moisture content of the manure made it expensive for transport. As a solution to these problems, manures had been made into pellet forms that had more uniform particle size and lower moisture content. The pellet forming process involved four steps: drying, compression, heating, and cooling. Since this study used the liquid manure after the liquid/solid separation process, manure in solid forms will not be discussed in detail.

In barns with mechanical scrappers, like the one at DERC, the liquid and solid waste streams were combined in the manure collection pits. From there, separation of liquid and solid fractions of the waste was a desirable operation in the treatment process. Transportation costs were decreased and the energetic yield was increased for combustion processes through dewatering. High TS content and high VS/TS ratio in the solid fraction, was found desirable if the material was used for compost (Lo *et al.*, 1993) or energy production (Moller *et al.*, 2004). The large volume of separated liquid fraction (known as manure slurry) was spread on fields for most of the year with minimal environmental impacts if the solids and ammonium contents are low (Rico *et al.*, 2007). The more concentrated dry-matter, however, should only be spread

Table 1.1 Nutrient content of solid and semi-solid dairy manure (Barker, 1990).

	Fresh manure	Scraped paved outside lot	Solids from settling basin	Solids from stationary screen
Moisture	86%	67%	89%	80%
TS	14%	33%	11%	20%
	(kg / tonne)			
NH <sub>4</sub> -N	0.77	0.91	0.18	0.09
NO <sub>x</sub> -N	0.01	0.05		0.00
Organic -N	3.76	5.90	2.63	2.13
Total-N	4.54	6.85	2.81	2.22
TP	1.00	1.58	0.80	0.62
K	3.05	5.31	0.38	0.72
Ca	1.68	11.16	2.49	2.27
Mg	0.77	1.36	0.32	0.54
Zn	0.02	0.05	0.09	0.03
Cu	0.00	0.01	0.06	0.05
Mn	0.02	0.04	0.03	0.02
S	0.54	0.91	0.50	0.36
Na	0.54	0.68	0.09	0.23

during the growing season. Manure management in B.C. is governed by the Environmental Management Act.

In recent years, cattle herd sizes per land area had dramatically increased. Direct land application of such large quantities of manure per acreage led to an imbalance of nutrients on the field; with the scale tipped towards more nutrients than crops needed. For example, Edwards and Withers (1998) reported that operation of intensive livestock farming imported a surplus of greater than 20 kgP·ha<sup>-1</sup>·yr<sup>-1</sup>; in New Zealand, soils that received effluent from dairy operations accumulated between 16 – 47 kgP·ha<sup>-1</sup>·yr<sup>-1</sup> (Toors *et al.*, 2004). In such cases, manure treatment methods, such as nutrient recovery, was attractive for environmental load reduction.

Table 1.2. Nutrient content of slurry and liquid dairy manure (Barker, 1990).

	Fresh Liquid Manure	Slurry	Milking Center Manure and Wastewater	Lagoon Surface Water	Lagoon Sludge	Agitated Lagoon Liquid & Sludge
Moisture	96.20%	93%	98.30%	99.40%	93.90%	97.00%
TS	3.80%	7%	1.70%	0.60%	6.10%	3.40%
	(mg/L)					
NH <sub>4</sub> -N	659	1126	755	383	743	563
Organic-N	779	1630	455	216	1054	635
Total-N	1438	2756	1210	599	1797	1198
TP	411	738	179	148	1160	654
K	766	2089	766	716	786	756
Ca	959	1198	324	35.9	1438	743
Mg	336	575	132	156	539	347
Zn	14.4	25.2	4.79	8.39	46.7	27.6
Cu	10.8	5.99	1.20	1.20	43.1	22.8
Mn	12.0	21.6	3.59	5.99	35.9	21.6
S	180	371	65.9	108	431	276
Na	288	383	156	216	168	192

Phosphorus recovery technologies, such as struvite ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ) crystallization, had been established for centrates of digested sludge in municipal wastewater treatment plants (WWTP) as a substrate (e.g. Gaastra *et al.*, 1998; Wu and Bishop, 2004; Britton *et al.*, 2005; Battistoni *et al.*, 2005). Qureshi *et al.*, (2006) studied dairy manure treatment, with sequencing batch reactors (SBR) that were operated in anoxic/aerobic modes, for enhanced biological phosphorus removal. The effluent from the SBR was then anaerobically digested for release of phosphates before subjected to struvite crystallization. Under the operational parameters used, a phosphate recovery yield of 82% was observed.

Liquid/solid separation of manure using mechanical separators and settling has been well studied (Burcham *et al.*, 1997; Gilbertson and Schulte, 1987; and Mohri *et al.*, 2000).

Coagulation-flocculation by  $\text{Fe}^{3+}$  or  $\text{Al}^{3+}$  together with polymers should be used if better separation was desired. Zhang and Lei (1998) have reported an optimum polymer dosage that was linearly correlated to the total solids (TS) content of manure and the amount required for dairy manure was 7.4% of TS. It was also found that the use of a combination of metal salts and polymers greatly reduced the phosphorus content of the liquid manure.

Dairy manure has also been used for biogas production. It was found that the liquid manure, after screening, produced equivalent amounts of methane per volatile solids (VS) loading as unscreened manure in a mesophilic anaerobic digester, with a 16 day hydraulic retention time (HRT). However, screened manure showed significantly higher biogas production rate per gram of VS when the HRT was lowered (Lo *et al.*, 1983). Lo *et al.* (1985b) was able to show that there was no benefit to thermophilic anaerobic digestion of screened manure compared to mesophilic temperature ranges.

### 1.2.3 Environmental Implications

In the province of B.C, there were approximately 147 000 heads of dairy cows spread over 545 farms. The dairy industry generated \$493.7 million, farm gate value in the year 2010, plus an additional \$56 million to the beef industry. Environmental problems potentially caused by the dairy industry mainly lay in the fact that the number of animals per acreage of land has been increasing. Manures produced on dairy farms were used locally, as soil amendments, for feed crops to the cows. Manure spreading required management based on crop demand for nutrients. Too much applied nutrients may potentially result in pollution of both surface and ground waters.

Manure storage capacity has been a limiting factor on dairy farms. Direct land application of manure has led to environmental damage mostly during periods when the soil does not benefit

from nutrient addition. For this reason, manure spreading was forbidden during the winter months in B.C. Williamson et al. (1998) came to the conclusion that intensive-production farms should use specialised technologies, if they wish to operate in sensitive zones, where the traditional method of land fertilization with wastes was either inapplicable or exceeded the land acceptance capacity.

Animal manure management has been crucial for available nutrients exploits for crop growth, while avoiding harm to the environment. Currently, land spreading has been the most common means to animal manure management. Land spreading, however, has been found as the cause for surface and groundwater contamination, as well as odor emissions (Miner, 1977; Powers and Schepers, 1989; Ghaly and Singh, 1991; Voorburg and Kroodsma, 1992; Meinardiet *al.*, 1995; Hayes *et al.*, 2006)

Nutrient management has also been difficult for most farms in North America. Vegetation grown on dairy farms, for feedstuffs, required more N compared to P; often at a ratio of 9 to 1 for N and P, respectively, by weight. However, the N to P ratio found in dairy manure was found to be on average 4 : 1. If the dairy farms were to base their nutrient management on P, then excess nitrogen fertilizers would have been required to balance plant demands. On the other hand, if the dairy farm were to manage its soil based on nitrogen, then P would have been loaded at roughly twice the amount required. Based on a cow's intake and amount of crops grown, the nutrient balanced farm would require roughly 0.43 acres/cow to remain environmentally sound. DERC currently holds space at roughly 0.50 acres/cow, only slightly above average and should not be considered a cause for concern.

Recent studies conducted in Maine compared the characteristics of manure from conventional versus organic dairy farming. Interestingly enough, it was found that the manure

from organic farming had double, sometimes triple, the concentration of most environmental pollutants tested. The only manure contaminant from conventional practice that had higher concentrations than organic farming was iron (He *et al.*, 2009).

#### 1.2.3.1 Phosphorus

Phosphorus is an essential nutrient for life, and has been found to be (and most often thought of as) a limiting factor for the growth of algae in lakes and reservoirs. Therefore, phosphorus has been widely studied in freshwater aquatic sciences. Numerous correlations and regressions have been constructed linking phosphorus, especially total phosphorus, with variables such as algal chlorophyll, and algal weight. The use of P as soil amendments traditionally came from two sources: manures or mineral fertilizers.

Although animal manure P was valuable for plant growth, it may also have been a major contributor to the P responsible for eutrophication (He *et al.*, 2004). Animal wastes remained a relatively large source of recyclable P in modern agriculture and amount to roughly 40–50% of the P now distributed as fertilizers. Of the animal wastes, dairy manures generally have the lowest P content (Smil, 2000).

Agricultural lands were potential nonpoint-sources of P lost to the environment. “Source” and “transport” are two groups of factors that affected P loss from agricultural lands (Kleinman *et al.*, 2002). Major source factors included soil P concentration, rate, method and timing of P additions, and inherent properties of manure P amendments (Kleinman, 2000). In soils amended with manure, phosphorus chemical fractionation will likely affect DRP concentrations in the runoff. It was found that water extractable soil P was strongly correlated with DRP concentrations ( $r > 0.9$ ) in surface runoff (Pote *et al.*, 1999). P application methods also played a

role in runoff losses. DRP concentrations may be increased in the runoff of fields where manure has been applied to the surface. The use of injection or knifing may remove manure from the effective depth of interaction zone of the soil. Once P was applied, it will interact with the soil and be transformed into increasingly recalcitrant forms (Edwards and Daniel, 1993). The potential for P loss was observed to peak shortly after manure application and decreased with time. Therefore, manure should not be applied during or before rain events.

The runoff DRP and TP concentrations from soils amended with dairy manure was higher, but not always significantly different than from soils without amendments. However, it was found that majority of the P in the runoff were from manure sources, rather than the P originally in the soil (Kleinman *et al.*, 2002). It was possible that surface applied dairy manure is shielded the underlying soil from erosion, since suspended solids (SS) concentrations were much lower in the runoff of surface amended soil with manure, than without. In whatever the case, an estimated 33% of TP in dairy manure was soluble (Kleinman *et al.*, 2002), and the potential for runoff has been highly possible.

Potential for leaching of P into groundwater strongly depended on soil type. The saturation point of the soil was a function of the soil's ability to bind P. In the Fraser valley, soil has a relatively high saturation point for P and leaching has not been of any significance.

#### 1.2.3.2 Nitrogen

Manure has also been a rich source of N as well as all the other essential nutrients for plant growth. Only a fraction of the N in dairy manure was immediately available for plant use. The N that was available for plant use was aptly named plant available nitrogen (PAN). Nitrogen can be present in manure as ammonia-N, organic-N, and nitrate-N. The ammonium – ammonia

equilibrium in water has a pKa of 9.25 and is as shown in equation 1. Both species of ammonium and ammonia can rapidly interchange depending on the pH of the solution.



(Markou and Georgakakis, 2011)

Most dairy manures had a pH close to but slightly greater than 7.0. Therefore, both ammonium and ammonia are present. For the purpose of this study, unless otherwise stated, ammonium and ammonia will be reported as ammonia nitrogen (NH<sub>3</sub>-N), which was a sum value that includes both species. Organic-N was found in abundance for manure with a high TS content. Organic-N was not made available to plants until mineralized to NH<sub>3</sub>-N by microbes in the soil. Since organic-N is bound by solids, it will not leach and very little has been found in runoff.

Manure N can cause harm to the environment by a number of ways. Most notably are volatilization to the air, runoff into surface waters, and leaching into groundwater. Since the focus of study is on P recovery, the destiny of manure N will not be discussed here in detail.

### 1.3 Microwave Technologies

The microwave (MW) oven can be dated back to 1946 where the first was tested in a Boston restaurant. In the 1960's, use of the microwave for food processing became prevalent. After development and production of smaller and more affordable units in the 70's and 80's, the microwave oven became a household norm. MW themselves are electromagnetic wave within the frequency range of 300 GHz to 300 MHz. For most heating applications, 2450 MHz was the standard frequency used in order to prevent overlap with cellular phones and other telecommunications, which uses frequencies between 872-960 MHz. When MW was applied to



any material, the electromagnetic field caused polar molecules (or polar groups on macromolecules) to align with the electric field's direction in a mechanism called dipolar-polarization. MW's interaction and heating of materials depended on the specific material's relative loss factor ( $\epsilon''$ ) and its dielectric constant ( $\epsilon'$ ). The  $\epsilon'$  value characterized a relative measure of MW energy density in the material and  $\epsilon''$  represented the amount of MW energy that was lost in the material as heat. The ratio of  $\epsilon'' : \epsilon'$  is termed the dissipation factor. A material with large  $\epsilon''$  will then be easily heated by MW energy (Remya and Lin, 2011). Metals and plastics are generally unaffected by MW energy since MWs reflect off the surface of electric conductor. On the other hand, MWs are transparent to plastics. However, metals can be heated by MW if the particle sizes were fine; insulators can be heated by MW in the presence of heat facilitators, where MW energy is absorbed by the facilitator and heat is transferred to the insulator by conduction (George *et al.*, 1994). When a material is MW heated, hydrogen bonds may be broken and hydration zones become altered (Hong *et al.*, 2004). Since World War II, there have been major developments in the use of microwaves for heating selective materials. Compared with conventional heating techniques, microwave heating had advantages of rapid heating, ease of control, enhanced chemical reactivity, reduced equipment size and waste, and so on.

Microwave processing of various materials has been an ever-growing field. Research into waste handling by microwave irradiation has also become a relatively new field of study. The use of microwaves for immobilization of radioactive waste, in order to meet transportation and storage regulations, as well as volume reduction and the ability for remote processing, had been an important development at a laboratory scale (Schultz *et al.*, 2011). In addition to waste treatment, microwave technology had been tested for resources and materials recycle. For

example, the use of microwave energy in treatment of used tires had some promising aspects. Microwave energy, in this case, was able to de-vulcanize the rubber by breaking S-S and S-C bond while leaving the C-C polymer bonds alone. Therefore, more treated rubber can be incorporated in recycled tires (Schults *et al.*, 2011). Since C-C bonds were not affected by microwave irradiation, grafting of polyacrylamide side-chains onto a backbone of agar had been tried. The resulting polymers had potential uses as flocculating agents (Mishra *et al.*, 2011). Research into catalytic degradation, with MW irradiation as an enhancement tool, had been another emerging field. For better catalysis of organics, MW absorbing materials (*e.g.* granular activated carbon) were often used as “hot-spots” that caused greater molecular rotation and thus decreased the activation energy of the reaction (Remya and Lin, 2011). In the case where MW was used for the catalysis of organics with activated carbon, it was hypothesized that  $\pi$ -electrons on the surface of the activated carbon became delocalized and ionized the surrounding atmosphere, forming hot-spots and a phenomenon called plasma. The hot-spots only lasted temporarily but the temperature can reach 1200°C (Jones *et al.*, 2002; Menendez *et al.*, 2010).

Whether the effects of MW treatment are thermal or athermal is still debated. The thermal effects referred to the result of increased temperatures due to MW energy, whereas the athermal effects may be specific to the interaction between MW and the substrate irradiated. For example, one of the studied uses of MW had been the inactivation of microorganisms. However, the mechanism of MW interaction with microbes and biological systems is not fully understood. A number of studies suggested that microbial death was due to the thermal effects from oscillating electrical fields rotating the polar molecules (Fung and Cunningham, 1980; Vela and Wu, 1979; Welt *et al.*, 1994; Tong, 1996). Evidence for the athermal effects of MW on microbes consist of greater amount of cell death compared to conventional heating methods using similar

temperatures. Also, cell deaths were observed at temperatures lower than the thermal death point of the organisms when irradiated with MW (Dreyfuss and Chipley, 1980; Khalil and Villota, 1985; Kozempel *et al.*, 1998; Hong *et al.*, 2004).

MW heating had gained popularity over conventional heating in certain industrial applications, due to significant reduction in reaction time. Microwaves were particularly effective since polar bonds of molecules can be selectively excited and cleaved by microwave irradiation. Free radicals were thought to form at these sites of selective excitation. MW technology had been tested for many environmental applications, in the last decade or so, including pyrolysis (Huang *et al.*, 2008; Menendez *et al.*, 2002; Menedez *et al.*, 2005), phase separation and extraction processes (Haswell and Howarth, 1999; Punt *et al.*, 1999; Tai *et al.*, 1999; Ericsson and Colmsjo, 2003; Perez-Cid *et al.*, 1999; Perez-Cid *et al.*, 2001; Prevot *et al.*, 2001), soil remediation (Kawala and Atamanczuk, 1998; Abramovitch *et al.*, 1999; Abramovitch *et al.*, 2003; Jou, 2006), desulphurization of coal (Weng and Wang, 1992; Ferrando *et al.*, 1995; Hayashi, 1990), as well as chemical catalysis/syntheses (Bond *et al.*, 1993; Zhang *et al.*, 2003; Wu *et al.*, 2002; Chen *et al.*, 2005; Zhang *et al.*, 2007; Kappe, 2004; Kappe, 2008; Mallakpour and Rafiee, 2008). In the past, our group has extensively researched sewage sludge treatment with MW technologies (Wong *et al.*, 2006a; Yin *et al.*, 2007).

In many environmental engineering applications, MW has been used for its rapid and selective heating properties (Remya and Lin, 2011). Sludge (both primary and secondary) disposal has been a significant operational cost in WWTP and much effort has been made to reduce sludge volume. One method for sludge volume reduction has been by anaerobic digestion. In secondary waste activated sludge (WAS), however, one of the major components of microbes consists of a matrix of polymers called extracellular polymeric substance (EPS).

EPS is produced by and surround microbial cells to protect the organism from harm. In light of the function of this polymeric material, it became trivial to see that EPS inhibited anaerobic digestion of the sludge by acting as a chemical and physical barrier. In order to enhance the biodegradability of WAS, much effort has been made for developing pretreatment methods to disrupt the EPS (Muller *et al.*, 1998; Stuckey and McCarty, 1984; Gonze *et al.*, 2003; Chiu *et al.*, 1997; Barjenbruch and Kopplow, 2003; Valo *et al.*, 2004).

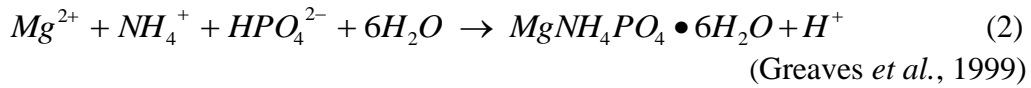
In recent years, MW irradiation has been studied as a novel method of WAS pretreatment with the goal of enhancing anaerobic digestability (Eskicioglu *et al.*, 2007a; Eskicioglu *et al.*, 2007b) and pathogen sterilization (Hong *et al.*, 2004). One way of determining EPS and cellular destruction was by measuring increased soluble chemical oxygen demand (SCOD). Eskicioglu *et al.* (2007c) reported that the WAS pretreated by MW irradiation was able to generate higher biogas than by conventional heating. In the same study, the authors also reported a linear relationship between the MW heating temperature (between 50 – 96°C) and degree of hydrolysis measured by the ratio of SCOD to total COD. Microwave treatment of sludge from the wastewater of poultry slaughterhouse produced a material that generated more hydrogen gas, when anaerobically fermented with *Enterobactor aerogenes* or mixed cultures from hot spring sediment as the inoculums (Thungklin *et al.*, 2011).

The use of MW has also been developed for advanced oxidation processes (AOP). AOP is a process that uses highly reactive free radicals, especially the hydroxyl radical ( $\cdot\text{OH}$ ), as reagents.  $\cdot\text{OH}$  can react both rapidly and non-selectively with most organic and some inorganic molecules due to its high oxidation potential of about 2.28 V. The advantage of AOPs, over conventional secondary treatment, for wastewaters was that it can effectively destroy and remove a wide variety of bio-refractory organics (Remya and Lin, 2011). Although the cost of AOP may

be high, it can be less energy intensive for select applications like phenol removal (Esplugas *et al.*, 2002). The need for finding new AOP processes has been driven by high cost of operations as well as secondary pollutants like iron, in the case of Fenton and Fenton-like reactions. The reasons for combining MW with AOP were many. For example, if MW irradiation were used alone for the catalysis of organic compounds in wastewater, the photons alone do not have the energy to break C-C bonds. When MW was combined with oxidants, not only did the temperature become higher in a shorter time period, it also stimulated free radical formation (Zhang *et al.*, 2007); both factors increased the degradation rate of wastewater constituents.

## 1.4 Struvite Crystallization

Struvite ( $MgNH_4PO_4 \cdot 6H_2O$ ) is a natural occurring mineral in animal manures and thus has the synonym guanite. The mineral is a white crystalline substance of relatively low solubility. Struvite precipitation can be simplified to the formula shown in equation (2).



Struvite crystallization, like the precipitation of any material, is governed by its solubility. The solubility and dissociation of a solid material in aqueous solution, at a given temperature, can be determined by the solubility product constant (usually termed  $K_{sp}$ ). The derivation of  $K_{sp}$  is shown in equations (3) to (4)

$$\text{Example: } MA_{(s)} \rightarrow M^{z+}_{(aq)} + A^{z-}_{(aq)}$$

$$K^o = \frac{\{M^{z+}_{(aq)}\}\{A^{z-}_{(aq)}\}}{\{MA_{(s)}\}} = \{M^{z+}_{(aq)}\}\{A^{z-}_{(aq)}\} \quad (3)$$

Where  $K^\circ$  is the thermodynamic equilibrium constant, and the activities are in brackets  $\{\}$ . Since the activity of a solid is equal to one by definition, and the activity coefficients of ions in dilute solution is approximately equal to one, the expression can be simplified to

$$K_{sp} = [M^{z+}_{(aq)}][A^{z-}_{(aq)}] \quad (4)$$

(Rossotti and Rossotti, 1961)

The values in square brackets  $[]$  are the concentrations.

When the products of the concentrations of struvite constituents (*i.e.* magnesium, ammonium and phosphate) exceed the  $K_{sp}$  value, the solution is oversaturated and precipitation occurs. The equilibrium solubility calculated using  $K_{sp}$  values will differ from actual values since factors such as pH, ion activity, and ionic strength are not considered. When the aforementioned factors are taken into consideration, the equilibrium constant can be expressed as a conditional solubility product ( $K_{so}$ ). Equation (5) describes how the  $K_{so}$  for struvite can be calculated

$$K_{so} = \frac{K_{sp} \text{ (struvite)}}{\alpha_{Mg} \alpha_N \alpha_P} \quad (5)$$

(Ohlinger, *et al.*, 1998)

Where  $\alpha$  is the fraction of magnesium, nitrogen, and phosphorus that can be used toward struvite crystallization.

For example, many groups have measured the  $K_{so}$  of struvite for different solutions and found that  $K_{so}$  decreased with increasing pH (Musvoto *et al.*, 2000a; Mustvoto *et al.*, 2000b; Booram *et al.*, 1975; Ohlinger *et al.*, 2000). Doyle and Parsons (2002) compiled a list of measured struvite

$K_{sp}$  values that are found in literature. The  $K_{sp}$  and their corresponding  $pK_{sp}$  ( $pK_{sp} = -\log K_{sp}$ ) values range from  $3.98 \times 10^{-10}$  to  $5.50 \times 10^{-14}$  and 9.4 to 13.26, respectively.

Struvite's use as a fertilizer has been limited to high value crops since struvite manufacturing costs are relatively high. Due to increased need for phosphorus recycling from waste streams, recovery of phosphorus as struvite has gained interest in recent decades. As mentioned earlier, struvite naturally occurs in animal manures. Isolating struvite from manure has been relatively difficult since it has a specific gravity of only 1.6, which was a value similar to but only slight greater than most suspended organic solids. As a fertilizer, the N:P:K ratio in oxide form is 5.7:28.8:0 with 9.9% Mg. Fertilizer chemistry and efficiencies in soils are well beyond the scope of this study, and will not be discussed further.

Struvite has been a known nuisance in WWTPs for many decades (Rawn *et al.*, 1939). The mineral forms inside pipes and caused blockages, especially following anaerobic digestion of solids, which released considerable ammonium and phosphate into the digester liquor. Recovery of phosphorus from anaerobic digester liquors and manures, in the form of struvite, was difficult since both substrates had low pH and were often deficient in magnesium. Of the WWTPs using struvite recovery facilities, the economic value of the added chemicals were often greater than the value of struvite as a fertilizer. However, those WWTPs tended to experience sufficient savings in operational costs, from decreased struvite-causing pipe obstructions, which made struvite recovery feasible (Ueno and Fujii, 2001; Jaffar *et al.*, 2002).

In earlier studies, using similar struvite crystallization reactors, it was found that an increase in pH led to an increase in P removal (Adnan *et al.*, 2004). If pH is too high ( $9 \leq \text{pH} \leq 10$ ), the solution becomes too supersaturated and rapid nucleation tended to occur. Fine struvite crystals have been observed to form in these cases, instead of crystal growth (Ohlinger *et al.*,

1999; Seckler *et al.*, 1996). As pH was increased beyond 10, it has been shown that the solubility of struvite increased (Doyle and Parsons, 2002). In this case, the ammonium ions in solution convert to ammonia, therefore, less nitrogen in solution would be available for struvite formation, in other words,  $\alpha_N$  decreases. According to equation (5), a decrease in  $\alpha_N$  will lead to an increased  $K_{so}$ , thus struvite was more soluble.

As previously mentioned, temperature also changed the solubility of struvite. Aage *et al.* (1997) looked at the solubility of struvite at various temperatures and found that struvite solubility increased as temperature increased. Maximum solubility was reached at 50°C, after which, the solubility decreased. In fact, the same study found that struvite's crystal structure changed when temperature reach 64°C. A change in crystal structure would inevitably change the material's solubility. Bhuiyan *et al.* (2007) studied the solubility of struvite at various temperatures and ionic strengths. The group then extrapolated their values of thermodynamic solubility products for zero ionic strength. Through this method, it was found that the  $K_{sp}$  values increased as temperature increases from 10°C, until it peaked at 30°C, after which  $K_{sp}$  decreased with increasing temperature. Unlike previously reported  $K_{sp}$  values, the ones reported by Bhuiyan *et al.* (2007) were consistently lower, most likely because they extrapolated for zero ionic strength. Since struvite crystallization depended on supersaturated conditions, knowing the correct  $K_{sp}$  for the specific solution may be helpful. If the conditional solubility product cannot be determined, the values reported by Bhuiyan *et al.* (2007) would be a reasonable approximation.

Previous attempts at recovering phosphorus from animal waste, by struvite crystallization, have been unsuccessful. In some cases where struvite recovery has been tested on swine manure slurries, chemical analysis of the precipitate that formed upon chemical addition has indicated



the N:P:Mg molar ratio to be 1:2:0.2. The numbers differed from that of the theoretical values 1:1:1, which indicated that majority of the phosphates removed was not struvite, but rather in the form of other phosphate minerals (Barak and Stafford, 2006). To further complicate matters, struvite crystallization chemistry is extremely complex and local conditions need to be tested before full scale operations can be considered (Andrade and Schuilling, 2001). A vast amount of studies have been performed, both at lab scale and at the pilot scale, for struvite crystallization with the purpose of phosphate recovery (e.g. Wu and Bishop, 2004; Battistoni *et al.*, 2000; Battistoni *et al.*, 2001; Mavinic *et al.*, 2003; Adnan *et al.*, 2003a; Adnan *et al.*, 2003b; Adnan *et al.*, 2004). Struvite crystallization has been a success story for a number of WWTPs when trying to recover P from anaerobic digester or filter press centrates.

Information on the recovery of phosphates from untreated dairy manure, via struvite crystallization, has not yet been published. However, some recent research has been conducted to extract struvite from digested dairy manures (e.g. Uludag-Demirer *et al.*, 2005; Huchzermeier and Tao, 2012). Anaerobic digestion is a slow process with HRT that can be as long as 40 days. Considering the volume of manure slurry produced on large scale production farms, anaerobic digestion reactors that can accommodate such long HRTs would require a significant footprint and capital investment. Since the purpose for anaerobic digestion was to liberate bound phosphates and release them as DRP, MW treatment of the manure slurry has shown much potential as a relatively fast alternative manure pretreatment process, prior to struvite crystallization (Qureshi *et al.*, 2008). Struvite crystallization, using dairy manure, is theoretically possible, but growth of struvite crystals to an appreciable size is highly unlikely for many foreseeable reasons. The main purpose of this pilot scale study was to make an attempt at

rapidly producing a material, using dairy manure slurry as a precursor, such that struvite can be recovered from it.

## 1.5 Purpose and Scope

Due to over exploitation of the raw materials for P, the world supply is dwindling. As mentioned earlier, raw materials for P comes from phosphate rock, a name collectively given to natural occurring calcium phosphates of various forms. Of the known phosphate rock reserves, it was estimated that commercially exploitable supply may peak in production from as little as 20 years (Grantham, 2012) to an optimistic reserve life of just less than 100 years (Fixen and Johnston, 2012). With that in mind, less conventional sources of phosphate, as well as the possibility of recycling this essential nutrient, has been and must continue to be explored. Animal manures are a rich source of phosphate and can potentially be a source of water pollution if the nutrient is not recovered.

Manures contain all the essential nutrients for plant growth. Traditional farming has used manures as amendments for soil long before chemical fertilizers became popular. Due to ever increasing herd sizes, manure nutrients have often exceeded crop needs on the land where it has been spread (Greaves *et al.*, 1999). An estimate done in the UK has found that, on a dairy farm of 129 lactating cows on 57 ha of land, a P accumulation of 1.5 tonnes was realized (roughly 60% of P imported to the farm) per year equalling  $26 \text{ kg P ha}^{-1} \text{ yr}^{-1}$  (Haygarth *et al.*, 1998). Contrary to old beliefs that P remained bound in the soils in which it was applied, it is now widely accepted that surface waters are receiving P from agricultural soils and may be the cause for eutrophication of water bodies. In order to mitigate the excess loading of P to agricultural soils, recovering P from manures should be considered. A long list of reasons for P recovery can be

found in a review by Greaves *et al.* (1999). Phosphorus recovery from dairy manure has been made more convenient since more and more livestock are reared under housed conditions, where the manure is collected and stored in confined areas.

Recovery of manure P is likely to occur in two stages: (1) extraction of P from bound to soluble forms and (2) convert the extracted P into a useful form. With that said, the scope of this pilot study was two-fold:

- (1) Extraction of organic/inorganic bound P into soluble orthophosphates using the  $\text{H}_2\text{O}_2/\text{MW}$ -AOP process developed by Dr. Victor Lo's group. Once the phosphates are in solution, we would have essentially produced an influent material suitable for recovery P in the form of struvite.
- (2) Use Dr. Donald Mavinic's patented fluidized bed crystallizer reactor to harvest the soluble orthophosphates as mineral struvite, which can be used as a phosphate rich fertilizer that is relatively inexpensive to transport.

## **Chapter 2: Pilot Plant Design and Operations**

The current study took place at the UBC's DERC facility, located in Agassiz British Columbia, Canada. The research station was a fully operational, commercial and research dairy production facility that housed 250 lactating cows, with a total of approximately 500 animals when calves, heifers, and non-lactating cows were included. The lactating and "dry-off" cows were housed in free-stall barns where their manure was collected. Each stall was lined with sand as the bedding and absorbent material. The animals defecated and urinated in central alleyways, where a mechanical scraper collected the waste plus other materials into a collection pit underneath the barn. The manure mixture was agitated by a mechanical mixer, before pumped to a rotary drum screen for liquid solid separation. The large particulate solids (mostly undigested fibres and some bedding) was collected and composted. The liquid manure slurry is sent to a clarifier to decrease the sand content of the slurry. After the majority of the sand/silt was sedimented, the liquid slurry was sampled for treatment. Otherwise, the remaining slurry was then pumped to a storage tank for storage before land application.

In the experiments conducted, several steps were taken for the pretreatment of manure, in order to prepare a material suitable for struvite crystallization. The overall pretreatment process involved manure acidification, peroxide/microwave advanced oxidation process ( $\text{H}_2\text{O}_2/\text{MW}$ -AOP), liquid-solid separation, and finally calcium precipitation with oxalic acid (OA). This chapter describes the process design, as well as the experimental apparatuses used. In later chapters, operation procedures and results from each pretreatment step were presented and discussed in detail, as well as the benefits they served for struvite crystallization.

It should be noted that the pilot plant was built in such a way that the hose connections could be taken apart with ease. The orientation and arrangement of each step used during the current study can be altered and rearranged, if future studies were to take place at these facilities.

## **2.1 Peroxide/Microwave Advanced Oxidation Process with Acid**

Manure slurry from the manure clarifier was pumped into a storage tank, termed raw manure storage, in close proximity to the pilot facility. As much as 1300 L batches of slurry were taken each time. Each time the raw manure storage tank was filled the contents were manually stirred, sampled, and analyzed for various constituents. Unlike previous experiments, which mainly looked at the combination of  $\text{H}_2\text{O}_2$  and MW irradiation, the current study deemed it necessary to add acid to the AOP process. Via a submersible pump placed in the raw manure storage tank, slurry was taken for the peroxide/microwave advanced oxidation with acid ( $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP) treatment process, following the schematic shown in Figure 2.1.

The raw manure slurry first entered the system into a 200 L tank where the manure pH was lowered with sulphuric acid. A mechanical mixer was in place to stir the contents of the tank. The water level of the acidification tank was controlled by a float switch. Therefore, the pump in the raw manure storage tank was turned on if the volume was below 40 L, and turned off when the tank was filled to roughly 160 L. Sulphuric acid was added to the raw manure by means of a pH controller. Sulphuric acid was diluted to a 30% v/v solution before use, since the pH controller could not tolerate higher concentrations of sulphuric acid. When making the stock sulphuric acid solution, the author recommends that it be done in a well-ventilated location (*i.e.* outdoors), with caution, to avoid inhaling irritating fumes.

While lowering the pH of the manure slurry, vast amounts of foam formed. It was speculated that the offset gas was carbon dioxide. If the manure was left unattended during acidification, the foam was likely to overflow. To avoid such spills, the pH controller was set to decrease pH at 0.5 increments; the pH controller was manually turned off if the volume of foam became too high. When no further acid was added to the slurry, mechanical mixing will slowly dissipate the foam.

The  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP process at the pilot plant was semi-continuous. Manure was first acidified in batches then pumped continuously through the MW system, at a predetermined flow rate, turned off when the acidified manure batch was depleted. A rotor/stator pump (Moyno) was used to deliver the acidified slurry to the MW chamber. Flow rate from the pump was adjusted by varying the pump's rpm. Due to presence of sand and silt in the manure slurry, wearing of the stator is significant, and regular flow monitoring was advised. Within the duration of this study, wearing of the rotor was not deemed significant enough for replacement.

Hydrogen peroxide was added to the process at the influent hose before the manure entered the MW chamber. The main reason for adding  $\text{H}_2\text{O}_2$  just prior to entering the MW was because of its short life in the presence of organic compounds. If  $\text{H}_2\text{O}_2$  was mixed into the acidified slurry, it would diminish over time and, thus, its concentration during the semi-continuous  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP. The  $\text{H}_2\text{O}_2$  was pumped to an injection port that was placed perpendicular to the main slurry hose. The pump used for  $\text{H}_2\text{O}_2$  was of the peristaltic type; the entry being perpendicular to the flow, allowed for best mixing conditions.

For each  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP experiment conducted, the flow rate of  $\text{H}_2\text{O}_2$  was always 10% of the total flow rate that entered the MW chamber. Stock  $\text{H}_2\text{O}_2$  solutions were made, so that a 10 fold dilution would produce the desired concentration in the  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP process.

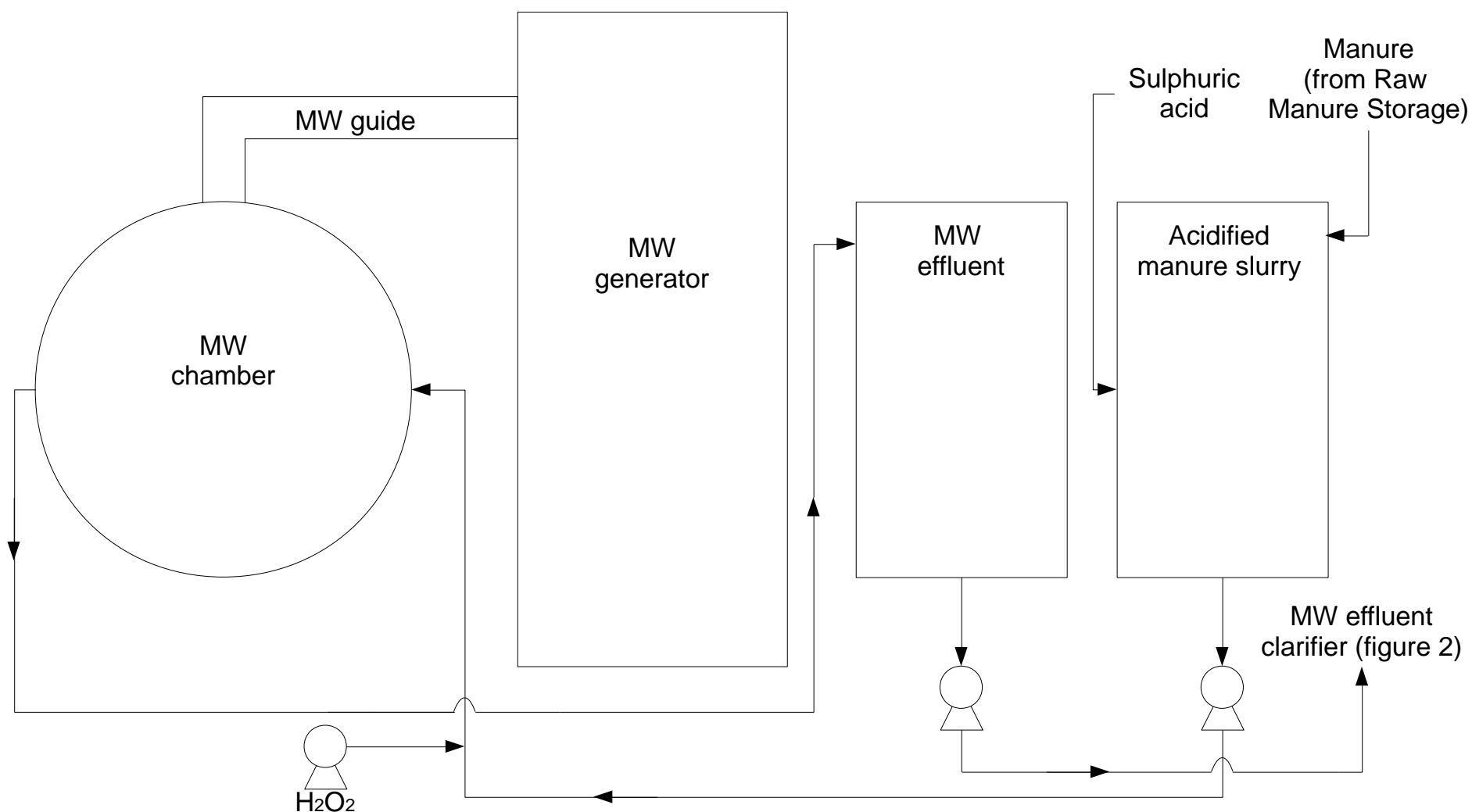


Figure 2.1.A schematic flow diagram of the H<sub>2</sub>O<sub>2</sub>/MW/H<sup>+</sup>-AOP treatment process (not drawn to scale). Raw manure slurry is brought into the system from a storage tank. The slurry is first treated with sulphuric acid before entering the H<sub>2</sub>O<sub>2</sub>/MW/H<sup>+</sup>-AOP process. H<sub>2</sub>O<sub>2</sub>/MW/H<sup>+</sup>-AOP effluent is moved along to the MW effluent clarifier for further processing.

This method insured that outcomes from the  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP processes were a product of various  $\text{H}_2\text{O}_2$  concentrations and not due to different dilutions of the slurry. Stock  $\text{H}_2\text{O}_2$  solutions were made fresh at the beginning of each experimental day. To avoid waste,  $\text{H}_2\text{O}_2$  solution volumes were made according to how much manure was prepared for treatment that day.

The MW generator had a maximum microwave power of 8 kW; adjustable between 1 – 8kW. The magnetron was water cooled, protected by a circulator and water load, and generated at a frequency of  $2450 \pm 10$  MHz. The anode to the magnetron had a voltage of DC  $10\,000 \pm 1000$  V. Each MW experiment used a specified power output. Therefore, the hydraulic retention time determined how much MW energy was received by the manure slurry. However, since the tubing inside the MW chamber was of constant diameter and cross sectional area, the flow rate of the manure slurry was used to control the energy input (*i.e.* effluent temperature). Throughout the duration of the study, the flow rate through the MW chamber had not exceeded 1.0 L/min. At that flow rate, MW power output of only 6 kW was needed to bring the slurry to a boil. Without pressurization, the boiling temperature of the slurry was the highest temperature that could be achieved. The controls on the MW generator allowed for a maximum reaction time of 9999 seconds. Taking into consideration the time required for acidification of every batch of manure slurry, two to three MW runs could be done in a work day. Effluent from the  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP process was temporarily stored in the MW effluent tank for cooling, before being pumped to the clarifier for liquid solid separation.

The MW chamber was made of stainless steel, resonant cavity type, and was cylindrical in shape. MWs were fed continuously by a WR430 type wave guide. Inside the MW chamber, the mixture of  $\text{H}_2\text{O}_2$  and acidified manure slurry flowed through a conduit made of polytetrafluoroethylene (PTFE). The PTFE tubing used had an inside diameter of 3/4 inch (19.05



mm) and was 300 inches (762 cm) in length, giving a total volume of roughly 8.7 L. The PTFE tubing was arranged in a helical coil configuration, with both the influent and effluent ends at the rear face of the chamber. Flow of the slurry mixture moved in an overall upwards direction.

Reasons for choosing the tubing configuration and the flow direction were two-fold:

1. In theory, and observed in previous practice, gases were likely to form when organics react with  $\text{H}_2\text{O}_2$ . In this case, foam will form when the gases escape the slurry at high temperatures. With the flow moving in the upward direction, foam was pushed out of the reactor, with relative ease, as opposed to being trapped and potentially causing air locks.
2. The helical coil configuration allowed for even distribution of MW irradiation. The nature of the MW photon allowed it to be reflected on metal surfaces. In the stainless steel MW chamber, reflection of the MWs will cause standing waves to form. The nodes and antinodes will be the cold and hot spots, respectively. Assuming the slurry moved through the conduit in a plug flow manner, rotation about the vertical axis allowed the content to avoid cold spots on the horizontal plane where no energy was received. Likewise, displacement along the vertical axis avoided cold spots in the vertical plane. A helical coil allowed the slurry to avoid both.

A strong recommendation for future operators of the pilot plant is that the MW reactor required consistent and rigorous cleaning. The liquid/solid separation system at DERC had its flaws and larger particulate solids (*e.g.* undigested fibrous feed stuffs, sand, and silt) remained in the slurry. The PTFE tubing, inside the reactor, sometimes became plugged due, to the small

tube diameter and low flow rate. If plugging did occur, temperatures inside the chamber could reach the melting point of PTFE and even create spontaneous combustion.

To avoid plugging, the operator must be vigilant for signs of plugging. Some signs that plugging was occurring were pressure build up in the influent hose outside the chamber, a dramatic reduction of flow at the effluent side, and/or failure of the peristaltic pump to deliver  $\text{H}_2\text{O}_2$ . It was observed that daily cleaning of the PTFE tubing, after each day of use, greatly increased the life of the tubing. Water was used throughout the study to clean the PTFE tubing. With water delivered through the reactor at a relatively low flow rate, the MW generator can be used to heat the water. Contents scaled to the sides of the PTFE tubing (that may normally cause plugging) can be easily removed with boiling water.

## **2.2 Liquid/Solid Separation and Calcium Removal**

$\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP treatment of the manure slurry allowed solids to destabilize from suspension and flocculate. A schematic flow diagram for the gravity clarification process and subsequent Ca removal was shown in Figure 2.2. The efficacy for solids removal by various  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP treatment conditions is discussed, in detail, in Chapter 3. Calcium removal from the liquid fraction of the  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP effluent by OA is discussed in Chapter 4.

After a short period of time for  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP effluent to cool, the effluent material was pumped to the MW effluent clarifier. The conical tank (Ace Roto-Mold, CB0200-42) used as a clarifier has a maximum capacity of 200 gal (757 L). The bottom conical section, ~120 L, was reserved for sludge. Therefore, approximately 600 L of the liquid fraction could be recovered per day. Due to time constraints, a maximum of ~500 L of manure slurry could be processed each day.

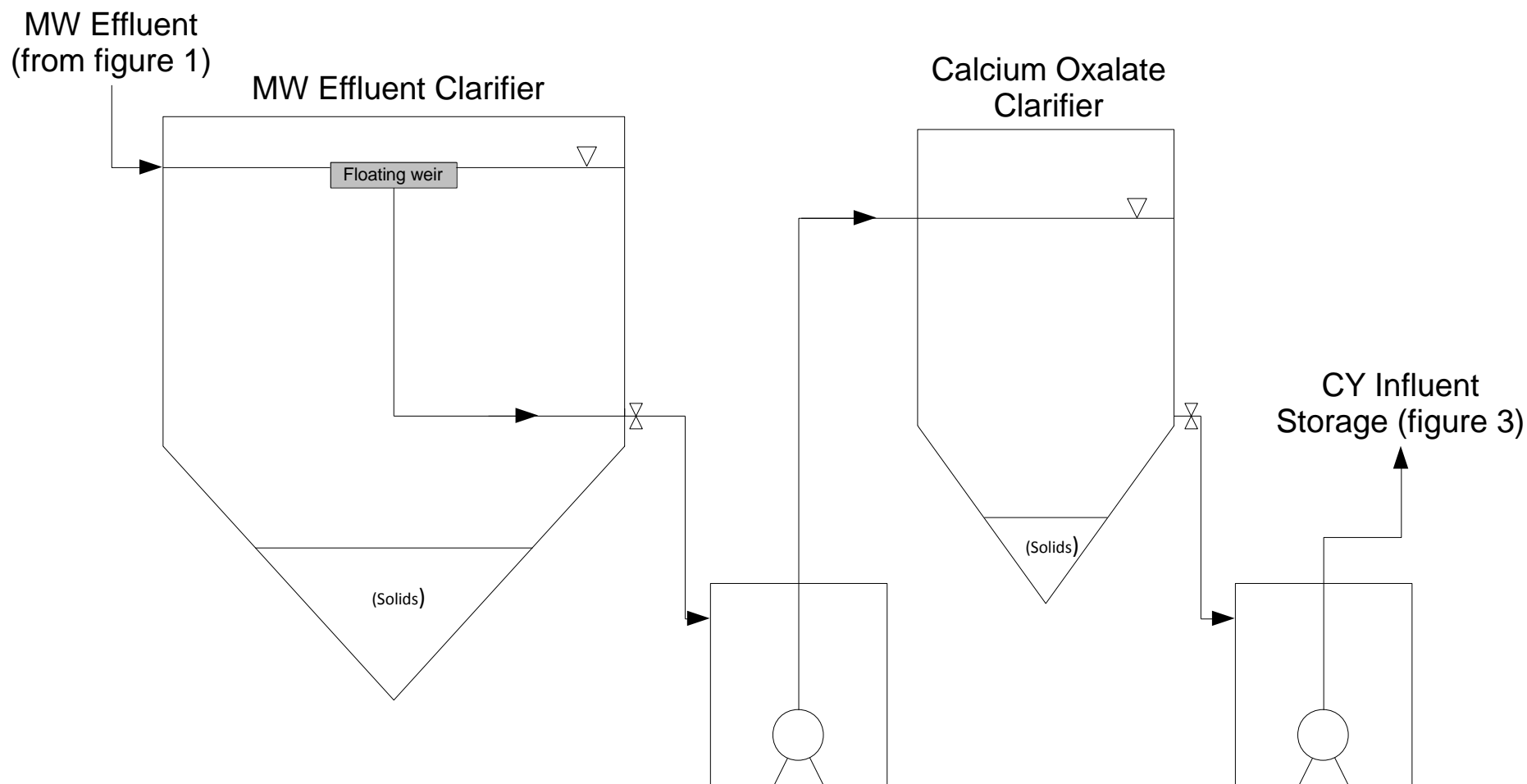


Figure 2.2.A schematic flow diagram for liquid/solid separation of the  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP effluent and calcium removal (not drawn to scale). The liquid fraction of the  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP effluent is recovered via a floating weir. The liquid fraction is then treated with OA and Ca is removed by gravity clarification of the calcium oxalate precipitate that forms.

With sludge taking approximately 40% of the total treated volume, a maximum of only 300 L of effluent liquid fraction could be harvested each day.

A floating weir was installed in the clarifier to draw the liquid fraction of the clarified  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP effluent. The conduit attached to the floating weir was longer than necessary to increase the head losses that would decrease flow. High volume flow could disturb the liquid inside the clarifier and cause the sludge to re-suspend.

Liquid drawn from the MW effluent clarifier was added to the calcium oxalate clarifier in 150 L batches. Given the time constraints, two batches could be processed per day. The appropriate amount of OA was added, and manually stirred until all the OA had dissolved. Oxalate was the reagent used to remove calcium that was solubilised by the  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP process. Calcium oxalate has a density of  $2.12 \text{ g/cm}^3$ , more than twice that of water. Therefore, gravity clarification of the calcium oxalate precipitate was relatively fast. All the noticeable precipitate settled within 5 hours, after OA addition.

Once calcium removal was complete, effluent from the calcium oxalate clarifier was pumped to a 1300 L storage container, until enough was collected for one struvite crystallization experiment. After treatment with OA, the solution pH was slightly below 2.0. In such acidic environments, microorganism growth was at a minimal and biochemical effects could be neglected. Therefore, storage for extended periods of time was not seen as an issue. Chemical analyses also showed negligible changes in soluble phosphate, ammonia, and Mg concentrations when stored for up to 4 weeks.

## 2.3 Struvite Crystallizer

Struvite crystallization was used as a method for phosphorus recovery from dairy manure. Struvite crystals were grown from manure slurry that was previously treated by  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP, gravity clarification and calcium removal. The method used in this study involved the struvite crystallization reactor previously designed, and patented, at UBC. Struvite crystallization theory and mechanisms have been described extensively in the past, and is not the focus of this study. However, the struvite reactor was used to verify whether or not the pre-treatment process used in this study produced a suitable material for phosphorus recovery, via struvite crystallization.

The crystallizer reactor (CY) itself, as shown in Figure 2.3, was designed and constructed based on the concept of a fluidized bed reactor. Clear polyvinylchloride was used to build the reactor, and it stood as a vertical column. The four sections of the reactor differed in the cross sectional area. The inside diameters were 1", 1.5", 2", 6" (2.54 cm, 3.81 cm, 5.08 cm, 15.24 cm), respectively, for each section from bottom to top. Therefore, for a given volumetric upflow rate, the upflow velocity changed, as the fluid moves through different sections of the reactor.

CY influent and the reactor recycle stream were injected together, from opposing directions, at the bottom of the reactor. Thus, the injection port maximized mixing in this manner. Similar injection ports also existed for adding Mg and/or sodium hydroxide to the reactor. Mg has been added to the reactor, with success, for increasing the molar ratio of Mg : P, when treating municipal wastewaters. However, molar concentrations of Mg were much higher than that of P in manure slurry. Thus, the Mg injection port was sealed for the duration of these experiments. NaOH solution was added to the reactor for maintaining the appropriate pH to reach the desired supersaturation for struvite. The CY influent stream, CY recycle stream, and

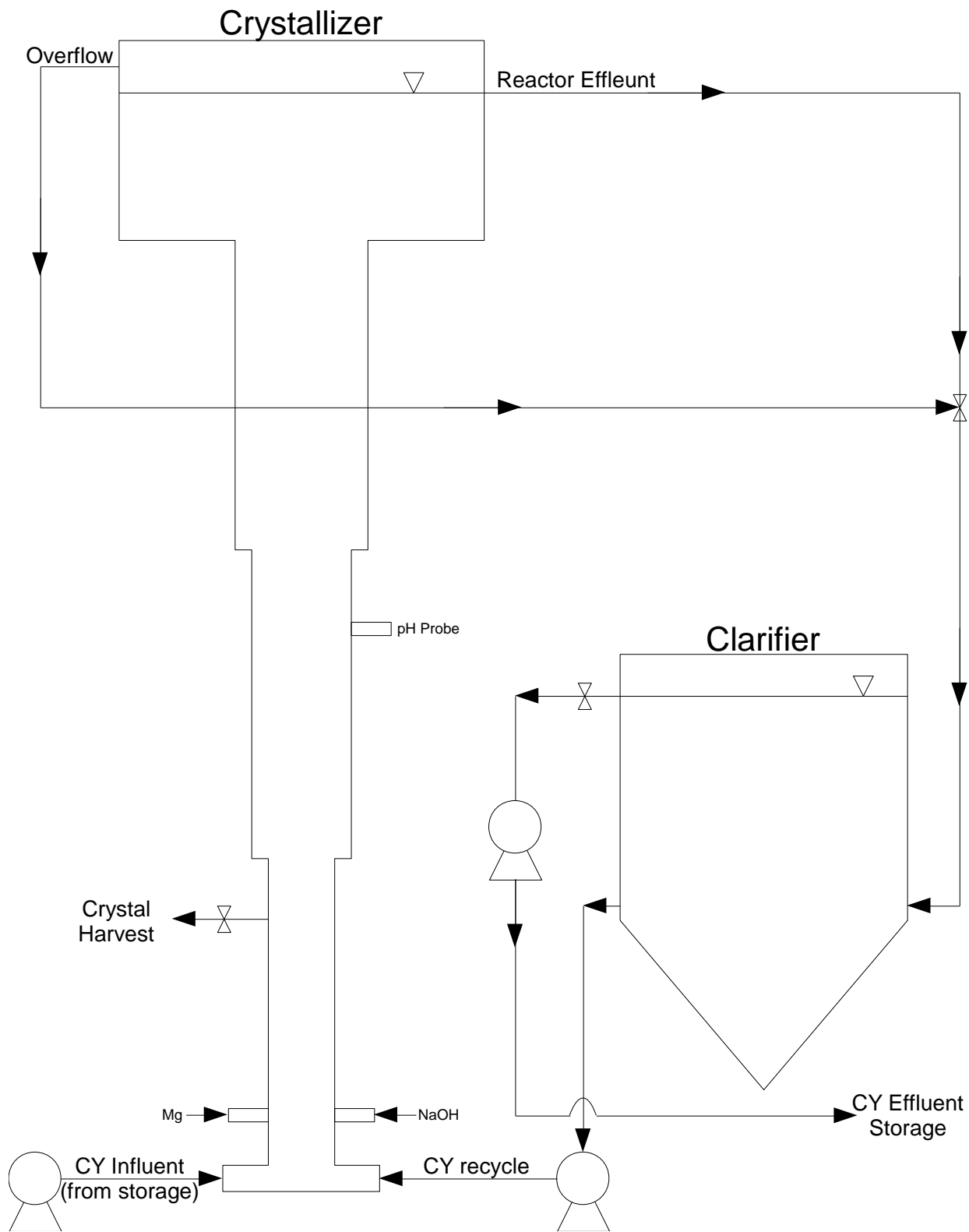


Figure 2.3.A schematic flow diagram of the struvite crystallizer reactor and the external clarifier used for this study (not drawn to scale).

the NaOH solution were delivered to the reactor by a peristaltic pump, rotor/stator pump, and pH controller, respectively. The reactor was operated in a continuous feed mode, and turned off only when the influent material was depleted.

With the CY influent stream, CY recycle stream and addition of NaOH entering at the bottom of the reactor, it was expected that the supersaturation ratio (SSR) of the struvite constituents would be highest within the bottom section. In this case, the term SSR is the quotient of the reaction quotient, divided by the solubility product constant. Therefore, struvite crystallization will occur if and when  $SSR > 1$ , and vice versa. Since crystal nucleation is reaction controlled and is positively correlated with SSR, nucleation is believed to occur at the lowest section of the reactor.

Struvite crystals can increase in size by either agglomeration of existing crystals, or crystal growth. Both mechanisms may occur in the reactor and may determine the morphology of the pellets produced. Upon entering the CY reactor, the pH of the mixed influent was raised by NaOH. Crystal nuclei that form are brought in close proximity of larger crystals by the flow and will agglomerate (Mavinic *et al.*, 2003). The small crystals that did not agglomerate are brought to the higher sections of the reactor. The crystals will remain in a section of the reactor if the fluid velocities are low enough in that section. Crystal growth was previously thought to occur more prevalently in areas of higher turbulence (Ohlinger, 1999). Relating turbulence to the Reynold's number, crystal growth should be enhanced in the bottom sections of the reactor, where fluid velocity was greater. Crystals, that have reached sizes bigger than what the fluid velocity can carry, will move to the lower sections of the reactor. Larger crystals were then harvested by isolating the upper three sections of the reactor while, opening the crystal harvest valve on the bottom reactor section.

The upper most section of the reactor had the largest diameter and lowest upflow velocity. Therefore, its main function was to act as an internal clarifier that would prevent small crystals from leaving the CY reactor. Clarification in the top section, however, is not perfect and an external clarifier was needed to avoid small crystals (fines) from leaving with the effluent. Although efforts were made to maximize struvite formation inside the CY reactor, it was inevitable that fine crystals would also form and build up inside the external clarifier. The fine crystals were cleaned out of the external clarifier, after each run of the CY reactor.

Trapping small crystals aside, the external clarifier had a second purpose of providing the reactor with its recycle stream. The recycle flow was drawn from the clarifier, at a port located below the liquid surface, by a rotor/stator pump. The final effluent from the system overflowed out of the external clarifier, by gravity, from a port near the top of the clarifier. It was then pumped to a storage tank for further experiments, or was disposed of.

Flow measurements were made at two distinct locations, in order to determine the ratio between influent and recycle flow. A three way valve was inserted just downstream of where the CY reactor effluent line meets the CY overflow line. The volumetric flow measured at this location is the total flow ( $Q_T$ ) of the CY reactor. A second three way valve was placed on the system effluent line, outside the external clarifier. The volumetric flow at this location is the influent flow ( $Q_i$ ) into the system. The recycle flow ( $Q_R$ ) was derived as the difference between  $Q_T$  and  $Q_i$ . The recycle ratio (RR) is then defined as  $RR = Q_R / Q_i$ . The RR was used as input parameter for the struvite crystallizer model.



## **Chapter 3: H<sub>2</sub>O<sub>2</sub>/MW/H<sup>+</sup>-AOP**

### **3.1 Introduction**

A brief on MW's history and its wide range of uses were presented in Chapter 1. The current chapter will describe the MW and how it was used as a treatment process in the current study. The microwaves used in this study are at a frequency of 2450 MHz. Waves at this frequency have energy of  $1.02 \times 10^{-5}$  eV. The expected penetration is about 3 cm. For larger applications, where increased penetration is needed, longer wavelength (*i.e.* lower frequency) waves should be considered.

One of the most studied oxidizing reagents coupled with MW irradiation is H<sub>2</sub>O<sub>2</sub>; with the other being persulfate (S<sub>2</sub>O<sub>8</sub><sup>2-</sup>). The homolytic dissociation reaction of H<sub>2</sub>O<sub>2</sub> and the subsequent reactions can be shown in equations (6) – (9).



(Meagher and Heicklen, 1974)

It is important to note that the hydroxyl radical formed in equation (6) can react with the hydroperoxyl radical formed in equation (7) to generate oxygen and water, as depicted in equation (9). In light of this, the degradation efficiency will increase with [H<sub>2</sub>O<sub>2</sub>], only at low concentrations. The use of high H<sub>2</sub>O<sub>2</sub> concentrations in the H<sub>2</sub>O<sub>2</sub>/MW-AOP process will not increase treatment efficiency, since the hydrogen peroxide will react with itself.

Disposal of sludge from water/wastewater treatment is expensive, and could account for 50-60% of operational costs (Spellman, 1997). Therefore, the drive for developing better sludge reduction methods led to the development of a novel AOP process, by our group at UBC. The AOP process combined MW irradiation to the oxidizer H<sub>2</sub>O<sub>2</sub> and was aptly termed

peroxide/microwave advanced oxidation process ( $\text{H}_2\text{O}_2/\text{MW-AOP}$ ) (Wong *et al.*, 2006a,b; Yin *et al.*, 2007). It was shown that the  $\text{MW}/\text{H}_2\text{O}_2$ -AOP process had an advantage of increased efficiency in sludge volume reduction, and nutrient solubilisation, in addition to sterilization (Liao *et al.*, 2005a,b; Wong *et al.*, 2006a,b; Wong *et al.*, 2007; Liao *et al.*, 2003). This process had been shown to solubilise previously insoluble substances such as ammonia, ortho-phosphate and carbonaceous compounds (*i.e.* chemical oxygen demand (COD)). The solubilised nutrients could be reused in subsequent processes, such as struvite crystallization; the solubilised carbonaceous compounds can be used in anaerobic digestion for biogas production. Since the current study involves the solubilisation of phosphorus, ammonia and select metals, only they will be discussed in detail further.

As was mentioned,  $\text{H}_2\text{O}_2/\text{MW-AOP}$  has had tremendous success in sludge destruction. Wastewaters containing phosphorus are commonly treated through an enhanced biological phosphorus removal (EBPR) process, which uses phosphate accumulating organisms to take up phosphorus (Mulkerrins *et al.*, 2004) and stored in polyphosphate (poly-P) form. Therefore, sludge from the EBPR process can alternatively be seen as a resource that is rich in phosphate. However, the phosphorus becomes inaccessible in the waste sludge since it is stored inside microbes that are protected by EPS mentioned earlier.  $\text{H}_2\text{O}_2/\text{MW-AOP}$  research, done at UBC, was focused on solubilisation of phosphates from secondary sludge for the purpose of struvite crystallization. It was found that MW treatment of sludge increased ortho-phosphate solubilisation (Liao *et al.*, 2005a; Liao *et al.*, 2005b). It was hypothesized that microwave irradiation enhanced the conversion of  $\text{H}_2\text{O}_2$  into highly reactive, hydroxyl radicals. The hydroxyl radical has higher oxidation potential and helped release nutrients into solution. However, the actual mechanism of free radical formation itself remains a topic of debate. Since

MW irradiation was thought to break down  $\text{H}_2\text{O}_2$  into hydroxyl radicals, as well as a heating source in the process, it can be used without the addition of metal catalysts as defined by conventional AOPs; this reduced the potential metal contaminant that would have been a by-product of the reaction.

$\text{H}_2\text{O}_2$  is an oxidizing reagent on its own and thus should have the ability of breaking down secondary sewage sludge. Secondary sludge from a biological nutrient removal (BNR) process was treated with about 1.5% wt  $\text{H}_2\text{O}_2$  to determine the effect of  $\text{H}_2\text{O}_2$  addition without microwave treatment. After 2 hours of reaction time, 43% of total phosphorus (TP) was released and remained constant over a period of 72 h. (Liao *et al.*, 2003). In the sludge solution prepared without adding  $\text{H}_2\text{O}_2$ , no soluble phosphate was observed in the first 6 h. About 10.5 mg/L of phosphate was obtained after 24 h. In this case, the small amount of phosphorus released into solution was most likely due to anaerobiosis (Liao *et al.*, 2003; Shapiro *et al.*, 1967).

Therefore, the results confirmed that the use of  $\text{H}_2\text{O}_2$ , alone, could be a means of solubilising phosphorus in the sludge, even in the absence of MW treatment. When MW heating process was applied alone, up to 76% of the TP in the sewage sludge was released into the solution with a MW heating time of only 5 min (Liao *et al.*, 2005b). In another study, Liao and colleagues (2005a) combined the use of  $\text{H}_2\text{O}_2$  and MW treatment in a batch MW/ $\text{H}_2\text{O}_2$ -AOP process, to test their possible synergistic effects. The results showed an increase in solubilised phosphate when both methods were combined, compared to either done separately. For the solubilisation of phosphate from secondary municipal sludge of an EBPR process, more than 84% of the TP was shown to be released at a MW heating time of 5 min at 170°C (Liao *et al.*, 2005a). At lower temperatures, however, phosphate release with or without  $\text{H}_2\text{O}_2$  addition, consistently reached a minimum at 60 - 100°C. The observed minimums appeared to be at a soluble

phosphate concentration less than that of the untreated (Liao *et al.*, 2005a). The decrease in soluble phosphate concentrations at this lower temperature range was speculated to be due to the initial release of polyphosphates (poly-P), until temperatures are high enough for further breakdown. Arguments for these findings were seen in a heating process to release poly-P from the activated sludge where almost all the poly-P could be released by heating the sludge for about 1 h at 70°C; after the poly-P release, only about 20% of the poly-P was degraded to soluble phosphate (Kuroda *et al.*, 2002; Takiguchi *et al.*, 2003). The released poly-P can be further degraded if treatment time was increased to about 2 hours, regardless of temperature. Although the phenomenon of poly-P release was likely to occur at lower temperatures, it does not explain why soluble phosphate concentrations should decrease to levels below that of initial untreated samples and further investigations should be done to identify the cause for soluble phosphate disappearance.

Previous studies have shown that poly-P could easily be degraded to orthophosphate by acid hydrolysis (Harold, 1960), and thus, is a potential method of solubilising phosphate at lower treatment temperatures. Further synergistic experiments of H<sub>2</sub>O<sub>2</sub>/MW-AOP with acid addition showed that, at microwave heating temperatures of 100 °C and 120 °C, for short reaction times of only 5 min, the combination of hydrogen peroxide and acid hydrolysis resulted in up to 61% of TP released as ortho-phosphate (Wong *et al.*, 2006).

The P speciation in dairy manure was holistically different from secondary wastewater sludge. One of the main contributors to excessive P in dairy manure was the excessive amount of P in the diet for the animals. One survey in the United States found that the average P content of dairy cow feed was 0.44% (Dou *et al.*, 2003), a value that was roughly 34% greater than what is recommended by the National Research Council. The concentration of orthophosphate in

dairy manures were highly variable from farm to farm, but was found to be linearly related to TP concentrations (Toors *et al.*, 2005). In the same study, it was found that orthophosphate represented between  $73 \pm 4.5\%$  of TP, orthophosphate monoesters (includes phytic acid, some phospholipids, etc.) made up  $18 \pm 5.7\%$  of TP, and orthophosphate diesters (some phospholipids, DNA, etc.) constitute  $7 \pm 2.6\%$  of TP.

A nearly ubiquitous component of cereals and grains, phytic acid was first discovered in 1903 (Posternak, 1903). Therefore, the phytate in manure slurry was sure to have come from feed sources. Phytates (inositol hexaphosphate) are six carbon rings with an orthophosphate attached to each member of the ring by a phospho-ester bond. In solution, the carbon ring is in a chair conformation, with five of the phosphate groups in the equatorial positions and one in the axial. The salt of phytic acid can form with a mix of calcium-magnesium-potassium cations. Phytates are major components of phosphate storage tissue in plants and also plays a role in a plant's structural integrity. Phytate associated P can comprise of up to 90% of P in seeds, and phytates could form 1 - 5% of the seeds' total weight. The long term viability of plant seeds were also attributable to phytates, since it may act as an antioxidant that blocks iron-catalyzed oxidation of unsaturated fatty acids (Graf *et al.*, 1987; Graf and Eaton, 1990). Although ruminant animals (*e.g.* dairy cows) contain enzymes for breaking down phytates, there are still abundances in the manure slurry.

Due to the antioxidant property of phytates, their presence could potentially cause any AOP to fail. Phytic acid is one of few reagents that inhibit ferrous iron-catalyzed formation of hydroxyl radicals from  $H_2O_2$ , by blocking its coordination site at the ferrous ion (Graf *et al.*, 1984). As a result, manure treatment, using the Fenton or Fenton-like reactions for oxidation, may be futile since production of hydroxyl radicals from hydrogen peroxide was almost com-

pletely blocked in molar phytate to iron ratios of 0.25 or more (Graf and Eaton, 1990). This inhibition was thought to be due to the equatorial-axial-equatorial conformation of phytic acid, since the stereoisomer, with all phosphates at the equatorial positions, showed less efficient blockage of the Fenton reaction (Hawkins *et al.*, 1993). Phytate further behaves as an antioxidant by diminishing the concentration of free ferrous ions. In the presence of phytate, the redox potential for oxidation of ferrous ions to ferric ions was lowered and thus the transformation was accelerated. Once the ferric ions were formed, they were firmly bound to phytate, its reduction back to the ferrous state was not possible (Graf *et al.*, 1987).

Phytic acid formed metal complexes with a variety of polyvalent cations, over almost the entire pH range (pH 1 – 12). Graf and Eaton (1990) reported the stability of phytates with metal ions as  $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Mn}^{2+} > \text{Fe}^{3+} > \text{Ca}^{2+}$ . Mono-ferric phytate was the only ferric salt of phytic acid that was soluble in water; the di- and tri-ferric phytates are insoluble. Therefore, as the phytate to ferric iron molar ratios increased, more mono-ferric phytate will form leading to higher soluble ferric ions in solution. Another way to deteriorate the antioxidant property of phytates was by hydrolysis of the monoester bonded phosphates on the hexane ring. The inositol compound lost its ability to bind metals, as more and more phosphates were cleaved.

The release of  $\text{PO}_4$  from phytatic acid could be done by enzymatic hydrolysis, and is often used as a method for quantifying its presence in manure (He *et al.*, 2004). Phillipy *et al.* (1987) tried an acid hydrolysis method for releasing phosphates from phytic acid at 121°C. The group found that the amount of hydrolysis increased as pH decreased, and that at pH 4.0, 81% of phytic acid lost at least one phosphate in the treatment process. Therefore, in order to increase the efficiency of the  $\text{H}_2\text{O}_2/\text{MW}$ -AOP process, the addition of an acid may increase the release of phosphates into solution.

Keeping in mind the chemical differences between secondary wastewater sludge and dairy manure slurry, combining the hydrogen peroxide/microwave advanced oxidation process with acid ( $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP) was experimented on, as a pretreatment of dairy manure for phosphate release. The acid may also increase the efficiency of the oxidation reaction since  $\text{H}_2\text{O}_2$  is more effective as an oxidant under acidic pH levels (Remya and Lin, 2011). The effluent from this process will contain the solutes suitable for phosphate recovery via struvite crystallization.

## **3.2 Materials and Methods**

### **3.2.1 Constituent analysis**

All analytical methods and sample preservation/preparation were done according to that which was described in Standard Methods. Total Kjeldahl nitrogen (TKN) (Standard Methods 4500-N<sub>org</sub> D),  $\text{NH}_3\text{-N}$  (Standard Methods 4500-NH<sub>3</sub> H), TP (Standard Methods 4500-P H), and  $\text{PO}_4\text{-P}$  (Standard Methods 4500-P G) was analyzed by the flow injection method. The analytical instrument used was the Lachat QuickChem 8000. Direct air/acetylene flame atomic adsorption spectroscopy (Standard Methods 3111 B) was done using the Varian SpectrAA 220 for Mg and K. Other metals were analyzed by inductively coupled plasma (ICP) atomic emissions spectroscopy (Standard Methods 3120 B). ICP was done on a PerkinElmer Optima 7300DV. The glass fibre filters used for select solids analysis was from Whatman. TS, TSS, and VS analysis was done according to Standard Methods 2540 B, 2540 D, and 2540 E respectively. All the constituents that were considered soluble were able to pass through a 0.45  $\mu\text{m}$  filtre (Millipore).

### 3.2.2 Manure

The manure used throughout this study was kindly provided by UBC's DERC facilities, located in Agassiz, British Columbia (Canada). For ease of access to manure, as well as demonstrative purposes, the pilot plant was constructed on the premises of DERC. As mentioned in Chapter 2, the manure slurry used for treatment was mostly devoid of large particulate solids and bedding material. During periods of machinery failure and/or when the manure separator was malfunctioning, it was common to find large undigested fibres and sand in the manure slurry. In such events, the manure slurry was screened with a mesh (roughly 2 mm pores) before use, in order to avoid pipe clogging. If too much large particulate material was found, then the slurry was discarded until the liquid/solid separator at DERC was fixed.

Manure slurry was pumped, in batches, to a 1300 L tank for storage before microwave treatment. The said batches were taken randomly according to when the storage tank required refilling. A sample of the manure slurry from each batch was taken for analysis of its constituents, to establish the initial conditions.

### 3.2.3 Chemicals

Reagent grade, concentrated sulphuric acid and 30% hydrogen peroxide used for these experiments were both purchased from Fisher Scientific.

### 3.2.4 H<sub>2</sub>O<sub>2</sub>/MW/H<sup>+</sup>-AOP

The microwave generator, chamber, and reactor were described in Chapter 2. The H<sub>2</sub>O<sub>2</sub>/MW/H<sup>+</sup>-AOP experiments were done to study the effects of both acid and of hydrogen



peroxide on manure slurry. Experiments were setup in a three by three factorial manner, shown in Table 3.1, where 3 different pHs were each paired to 3 different H<sub>2</sub>O<sub>2</sub> concentrations.

Table 3.1. Microwave treatment conditions.

	pH	H <sub>2</sub> O <sub>2</sub> % (w/v)
A	4.0	0.1
B	4.0	0.3
C	4.0	0.5
D	3.5	0.1
E	3.5	0.3
F	3.5	0.5
G	3.0	0.1
H	3.0	0.3
I	3.0	0.5

For each treatment condition, 160 L batches of manure slurry were acidified with 30% (v/v) sulphuric acid until the desired pH was achieved. Thirty percent sulphuric acid was used with the intent of keeping the manure slurry as concentrated as possible, while keeping in mind the capacity for acid tolerance of the pump used. In all cases, the volume of acid added was less than 0.5% of the manure volume.

Hydrogen peroxide was pumped directly into the MW influent line prior to entering the MW chamber. The reason was that the H<sub>2</sub>O<sub>2</sub> was expected to begin its reaction instantaneously. Since the batch of acidified manure did not enter the MW chamber all at once, pumping H<sub>2</sub>O<sub>2</sub> into the MW influent line was thought to produce more consistent H<sub>2</sub>O<sub>2</sub> concentrations throughout each experiment. The ratio of H<sub>2</sub>O<sub>2</sub> flow and acidified manure flow was set at 1 : 9, and the stock concentrations of H<sub>2</sub>O<sub>2</sub> were made, accordingly. This method of H<sub>2</sub>O<sub>2</sub> addition ensured that dilution of the manure slurry was not a factor affecting the MW treatment process.

### 3.2.5 Coagulation/Flocculation and Settling of Manure Solids

Sedimentation of manure solids after the  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP treatment was measured for each treatment condition tested. Samples of effluent material were taken in 250 mL bottles (Nalgene) and were stored at  $4^\circ\text{C}$ , before settling tests could be conducted. Settling tests were carried out using 100 mL graduated cylinders, as opposed to conical Imhoff cones. The sludge volume was defined as the portion of effluent in the cylinder that is not a visibly transparent liquid. The decrease in sludge volume was recorded at increasing time intervals, after pouring the effluent material into the graduated cylinders.

## 3.3 Results and Discussion

### 3.3.1 Untreated Manure Characteristics

Each batch of dairy manure slurry brought to the storage tank was sampled and analyzed for various constituents, as shown in Tables 3.2 and 3.3. Large variations in the manure's characteristics were observed throughout the experimental time period. The manure used for this study had much higher moisture content than the values observed by Barker (1990), with an average TS concentration of 12185 mg/L (max 19980 mg/L; min 8440 mg/L).

The manure slurry used in this study was similar to the “Fresh Liquid Manure” described by Barker (1990) in terms of the origin and amount of processing done to the manure. Although the manure slurry used for this study was analyzed for TKN (whereas total nitrogen was used to characterize the manure from the previous work) these two values can be comparable. The lack of  $\text{NO}_x$  ( $\text{NO}_x < 1\text{ppm}$ ) in all the manure slurry sampled at DERC allowed us to assume that TKN was a good representative of total nitrogen. In fact, the reported total nitrogen value, by Barker (1990), was the sum of  $\text{NH}_4\text{-N}$  and organic-N, which was TKN by definition. Nitrate/nitrite free

dairy manure is commonly found in facilities that stored manure with little agitation, thus creating anaerobic conditions. It is interesting to note that the TKN observed in this study was roughly 16.6% lower than the total nitrogen observed previously elsewhere; however, the amount of soluble  $\text{NH}_3\text{-N}$  is 34.6% higher. The percentage constituent of TKN as  $\text{NH}_3\text{-N}$  in the manure slurry at DERC was observed to have an average value of 74%, which is roughly 30% higher than those observed previously when comparing  $\text{NH}_3\text{-N}$  to total nitrogen (Barker, 1990).

Table 3.2 Solids and COD content of the manure slurry used.

	pH	TS (mg/L)	VS (mg/L)	TSS (mg/L)	TCOD(mg/L)	SCOD(mg/L)	SCOD/ TCOD
Mean	7.28	12185	6059	11193	12638	5719	0.453
$\sigma^*$	0.16	4015	1854	4113	4503	1084	0.174
Max	7.79	19980	8720	15950	18800	7588	0.894
Min	7.15	8440	3920	5550	6342	4723	0.315

\*  $\sigma$  = standard deviation

Table3.3 Nutrient content of manure slurry used.

	$\text{PO}_4\text{-P}$ (mg/L)	TP (mg/L)	$\text{PO}_4\text{-P/}$ TP	$\text{NH}_4\text{-N(mg/L)}$	TKN (mg/L)	$\text{NH}_4\text{-N/}$ TKN
Mean	91.3	220	0.415	887	1200	0.74
$\sigma^*$	19.0	63.8	0.051	74.8	103.2	0.084
Max	123.3	308	0.50	961	1364	0.92
Min	73.7	164	0.36	772	1042	0.66

\*  $\sigma$  = standard deviation

Phosphorus levels in the manure slurry found at DERC were also lower than those observed previously at other dairy facilities. In this case, the observed highest TP and average TP was only 75% and 54%, respectively, of the average TP reported by Barker (1990). The lower than expected TP content could be due to feedstuffs consumed by the cows. Dou *et al.* (2003) conducted a survey that suggested the average dairy farm fed their animals 34% more phosphorus than was required. The excess phosphorus in the feed was often advised by

veterinarians for preventative health measures. Since nutrient absorption by the cow is almost always lacking, it was believed that overdosing the feed with phosphorus will at least not affect the animals negatively. Since it was a well-known fact that phosphorus loading in the feed was positively correlated to its concentration in the manure, it was not surprising to see a lower than expected TP concentration in the manure slurry at DERC. Whatever the reason for the differences seen in the manure TP between DERC and other facilities, it was important to note that high variability in phosphorus existed from farm to farm. In fact, even at the same location, the phosphorus content can be expected to change dramatically, as shown by the wide range and large standard deviation in measured TP. With that said analysis for the phosphorus content of the manure should be done frequently at every location where manure treatment is needed.

In previous studies,  $\text{PO}_4\text{-P}$  concentrations in the manure have varied significantly from location to location. However, a linear correlation had been found between TP and  $\text{PO}_4\text{-P}$  concentrations where the ratio between the two was relatively constant within each farm (Toors *et al.*, 2005). At DERC, less than half of the phosphorus in the raw manure slurry was in soluble  $\text{PO}_4$  form (Table 3.3). The observed  $\text{PO}_4\text{-P}$  constituted roughly 41.5% of TP (max 50%; min 36%). The proportion of TP as  $\text{PO}_4\text{-P}$  was fairly constant, and was in agreement with previously findings, with a standard deviation of 5.1%. This information could be useful if certain analytical tests cannot be readily preformed. If either one of TP or  $\text{PO}_4\text{-P}$  concentration was known for the raw manure slurry, then an approximate can be made for the other. However, the TP :  $\text{PO}_4\text{-P}$  ratios were expected to differ from farm to farm. For example, Toors *et al.* (2005) found the manure they studied had  $\text{PO}_4\text{-P}$  representing  $73 \pm 4.5\%$  of TP, which is 76% greater than what was found at DERC. Therefore the TP and  $\text{PO}_4\text{-P}$  relationship should be established locally, before making such approximations.

### 3.3.2 Nutrient Solubilisation

The ultimate goal of the study presented in this chapter was to produce a suitable influent material for struvite precipitation and crystal growth, in order to recover phosphorus. Solubilisation of the struvite constituents needed to be maximized in order to maximize struvite yield downstream. With that said, methods should be considered for solubilising the metal magnesium, as well as the nutrients ammonium and phosphate. According to the struvite precipitation formula shown in equation (2), orthophosphate, magnesium ion, and ammonium are needed in 1 : 1 : 1 ratio. Figure 3.1 depicts the molar ratios between the various constituents of struvite that was found in raw manure slurry compared to the either orthophosphate or total phosphorus. It was not surprising to observe the large excess of ammonia in the raw slurry. The amount of soluble ammonia, even without further nitrogen solubilisation, was more than sufficient for extracting 100% of the TP as struvite.

The effects that MWs had on manure slurry were first tested, where raw manure slurry was subjected to MW irradiation. The effluent material was analyzed for TP, soluble  $\text{PO}_4\text{-P}$ , TKN and soluble  $\text{NH}_3\text{-N}$ . The percentage of TP as  $\text{PO}_4\text{-P}$ , and the percentage of TKN as  $\text{NH}_3\text{-N}$  are shown in Figure 3.2. Each sample was taken at a specified effluent temperature. The reactor volume and MW power were unchanged during these experiments. The flow rate (hydraulic retention time) was changed to vary the amount of energy received by the manure slurry. In other words, less MW energy was received by the slurry when flow rate was higher, which in turn led to lower effluent temperatures, and vice versa. Manure slurry that did not receive MW treatment had an initial temperature of  $10^\circ\text{C}$ . The experiments for each temperature were replicated a minimum of four times.

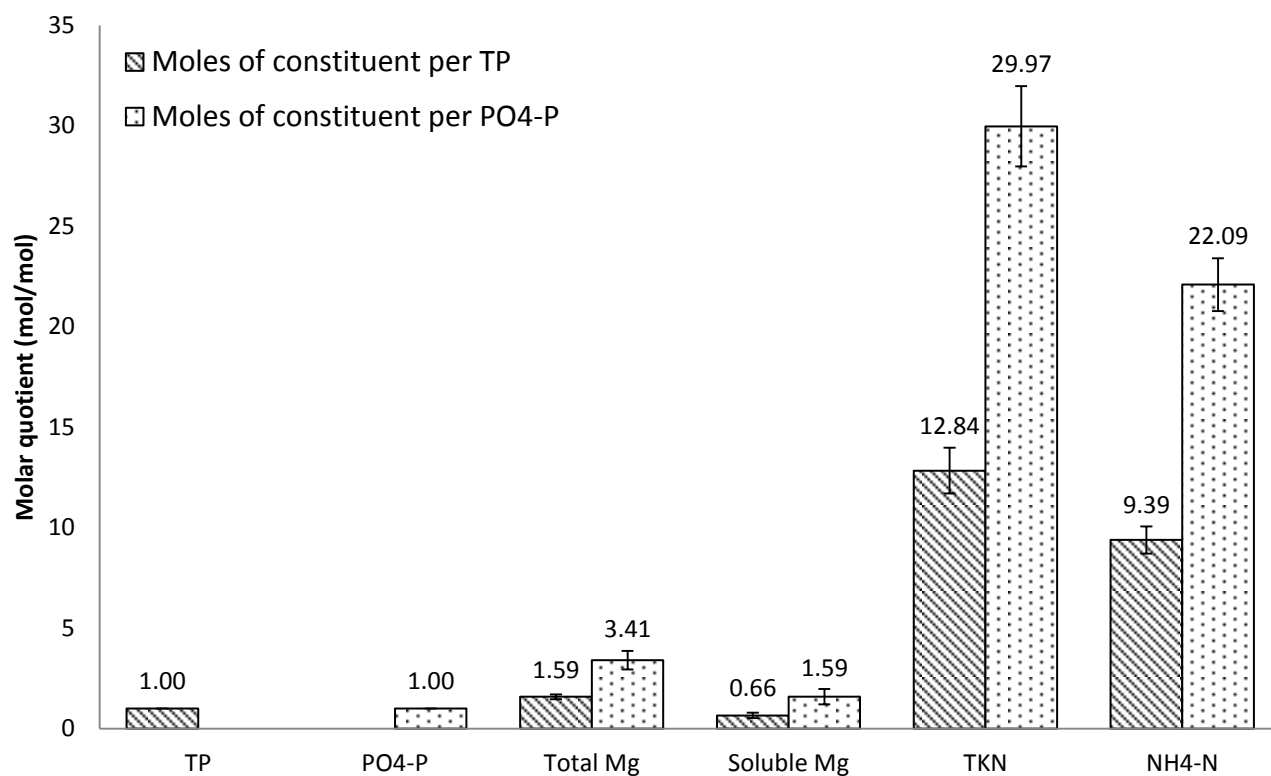


Figure 3.1. Molar quotient of each struvite constituent relative to either total phosphorus (shown in black) or orthophosphate (shown in stripes) that is found in raw manure slurry. Error bars represent standard errors about the mean.

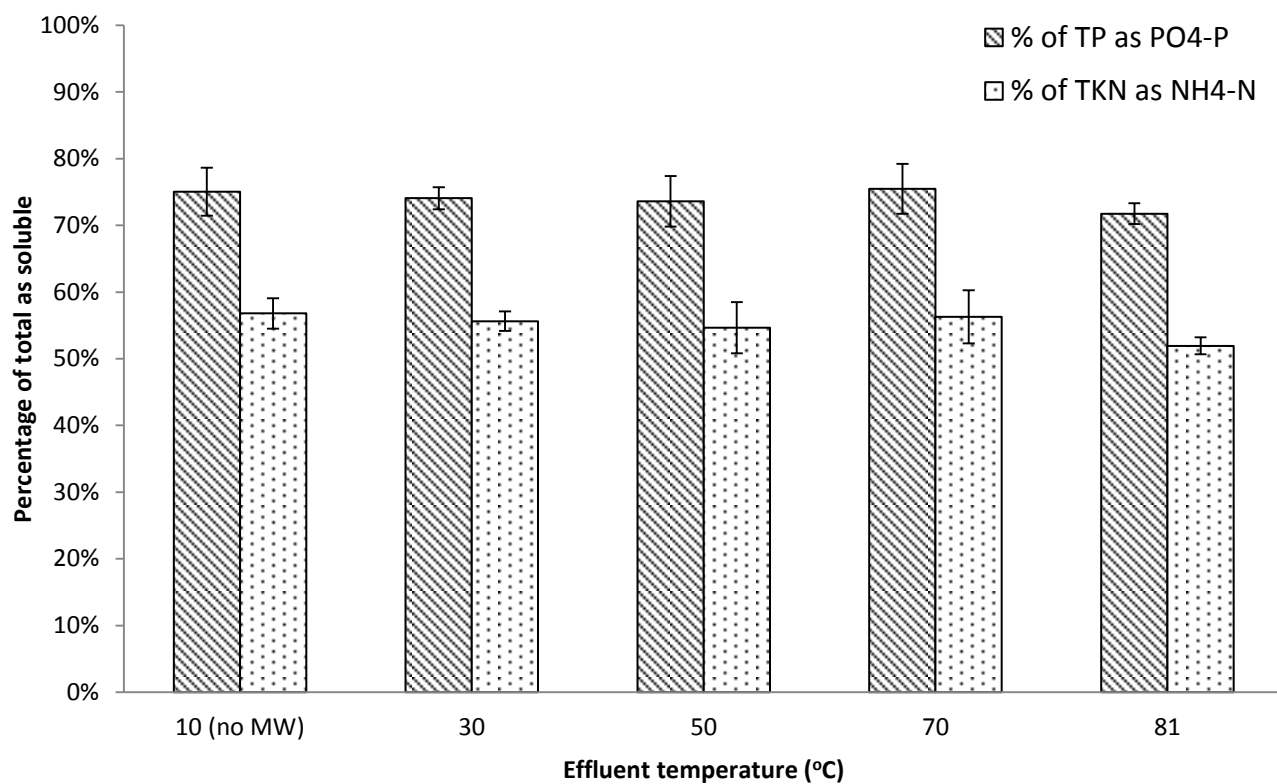


Figure 3.2. Effects of MW on raw manure slurry. Values presented are the proportion of either TP as PO<sub>4</sub>-P or TKN as NH<sub>3</sub>-N. No significant changes were observed for temperatures up to 81°C

The batches of manure slurry used for these experiments had a mean TP and TKN concentration of 178 mg/L and 1531 mg/L, respectively. Of the manure TP, 75.1% was soluble  $\text{PO}_4\text{-P}$ ; 59.1% of TKN consisted of  $\text{NH}_3\text{-N}$ . Increasing exposure time of the manure slurry to MW irradiation did not significantly increase soluble  $\text{PO}_4\text{-P}$  or  $\text{NH}_3\text{-N}$  levels. Unlike previous studies, where it was found that MW treatment of sludge increased ortho-phosphate solubilisation from secondary wastewater sludge (Liao *et al.*, 2005a; Liao *et al.*, 2005b), MW alone did not affect manure slurry in the same manner.

A possible explanation for this difference in effect must be due to the composition of the TP in the materials. Previous work on sewage sludge used waste sludge from EBPR processes, where the microorganisms harvest and store excess phosphorus inside the cell. The phosphorus would be stored in inorganic polyphosphate form. When the microbes are heated, the cells would likely undergo lysis. The thermally unstable polyphosphate would come into solution and hydrolyze into its phosphate monomers, due to heating. The insoluble phosphorus in manure slurry, however, was most likely bound to organic molecules. The phosphoester bond is relatively strong and stable. For most applications, the phosphoester bond is difficult to break, except in extreme conditions, or when biological enzymes were involved. Therefore, these results tell us that MW irradiation of manure, alone, will not be able to liberate more phosphate or ammonia into solution.

It is important to understand the various forms of phosphorus that exist in manure slurry, in order to understand how to increase soluble orthophosphate concentrations. Toors *et al.* (2005) reported that 98% of the phosphorus content from manures found in average dairy farms was either free orthophosphate, or is organically bound. More specifically, it was found that  $73 \pm 4.5\%$  was free orthophosphate,  $18 \pm 5.7\%$  were orthophosphate monoesters, and the remaining  $7 \pm$

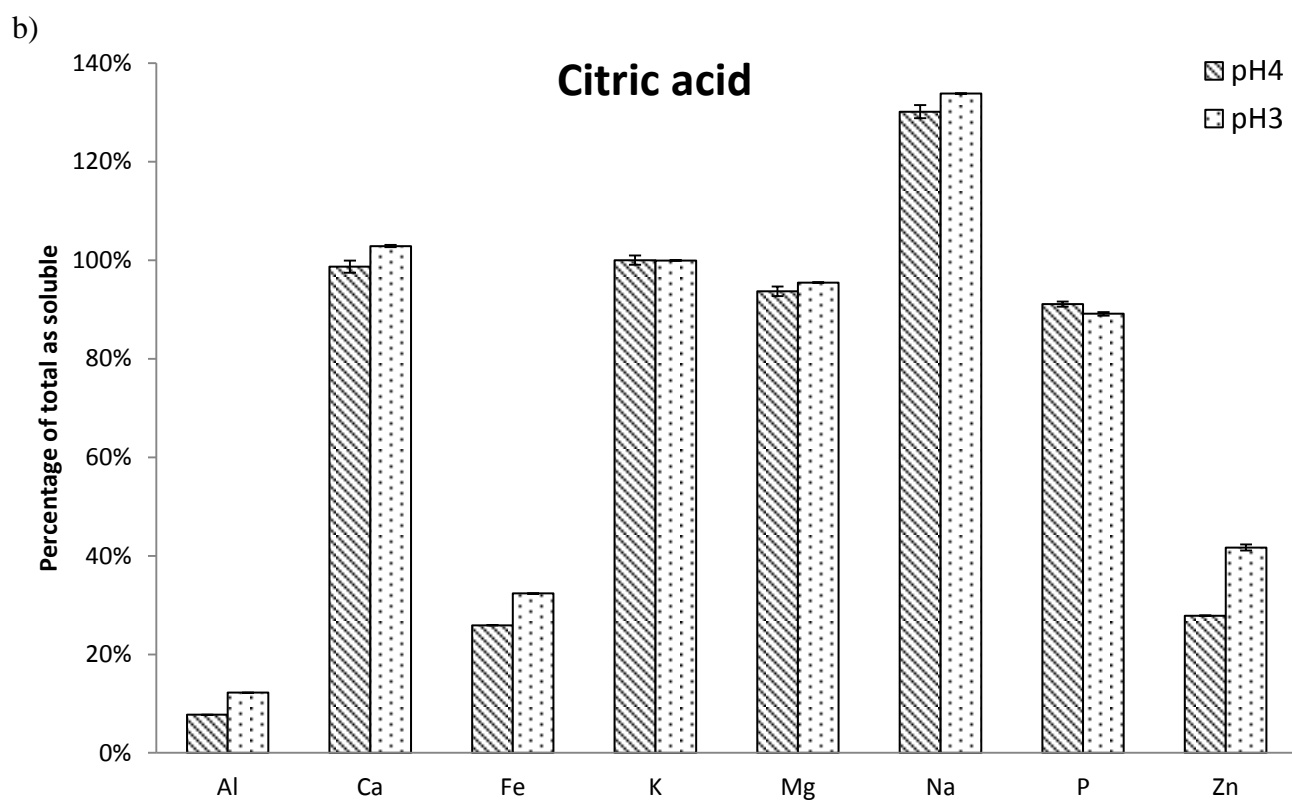
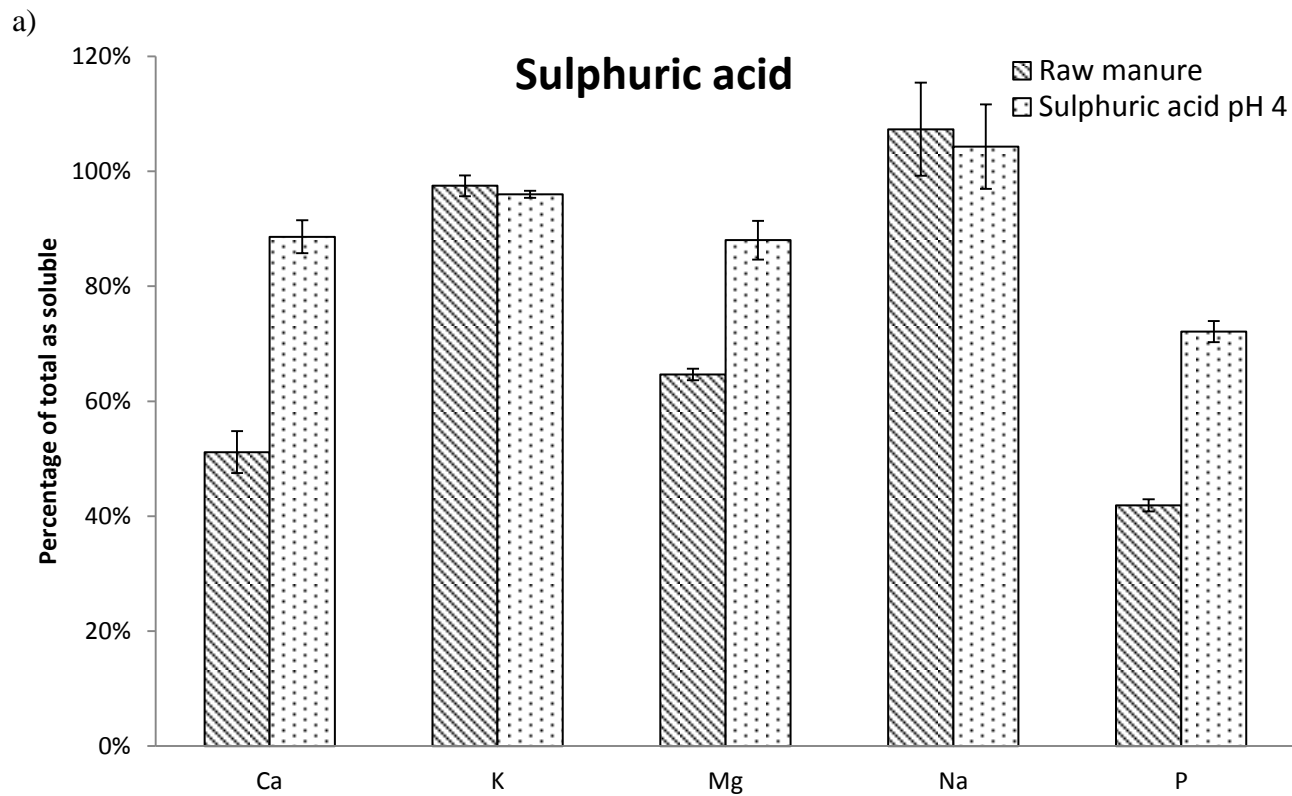


2.6% were orthophosphate diesters. Since other phosphorus forms were never in significant quantities, nearly all the phosphorus may be solubilised by cleaving the phosphoester bonds of organic molecules. This cleavage reaction then frees the orthophosphates into solution.

Despite being one of the most important reactions in biological systems, we still have limited understanding of phosphate monoester hydrolysis reaction mechanisms in solution. The problem stems from the fact that the energies of the transition states of phosphate hydrolysis reactions are relatively high, thus making it difficult to characterize such transition states and the reaction intermediates (Klahn *et al.*, 2006). The scope of this study was not to further our understanding of the reaction mechanism behind hydrolysis of phosphate monoesters, but rather to apply previous methods that showed potential in hydrolyzing the phosphoester bonds.

As previously mentioned, a known organic molecule that carries phosphate groups in a monoester bond is phytic acid. Phillipy *et al.* (1987) tried an acid hydrolysis method for releasing phosphates from phytic acid with great success. Therefore, in order to increase the efficiency of the H<sub>2</sub>O<sub>2</sub>/MW-AOP process, the addition of an acid was expected to increase the release of phosphates into solution. The H<sub>2</sub>O<sub>2</sub>/MW-AOP process was combined with acid treatment in this study, for maximizing phosphate solubilisation and increase H<sub>2</sub>O<sub>2</sub> efficiency.

Three different acids were used to examine the effects of acid on solubilising various constituents of the manure slurry. Manure slurry pH was lowered using one of sulphuric, citric, or oxalic acid. The changes in select soluble materials of the manure by the acids were presented in Figure 3.3 a), b), and c), respectively. Raw manure was used as a negative control. The concentrations of each soluble constituent analyzed were then divided by the respective total concentration of that constituent. The resulting values are the percentages of total as soluble; the errors shown are the standard error about the mean. In raw manure, the percentage of TP as



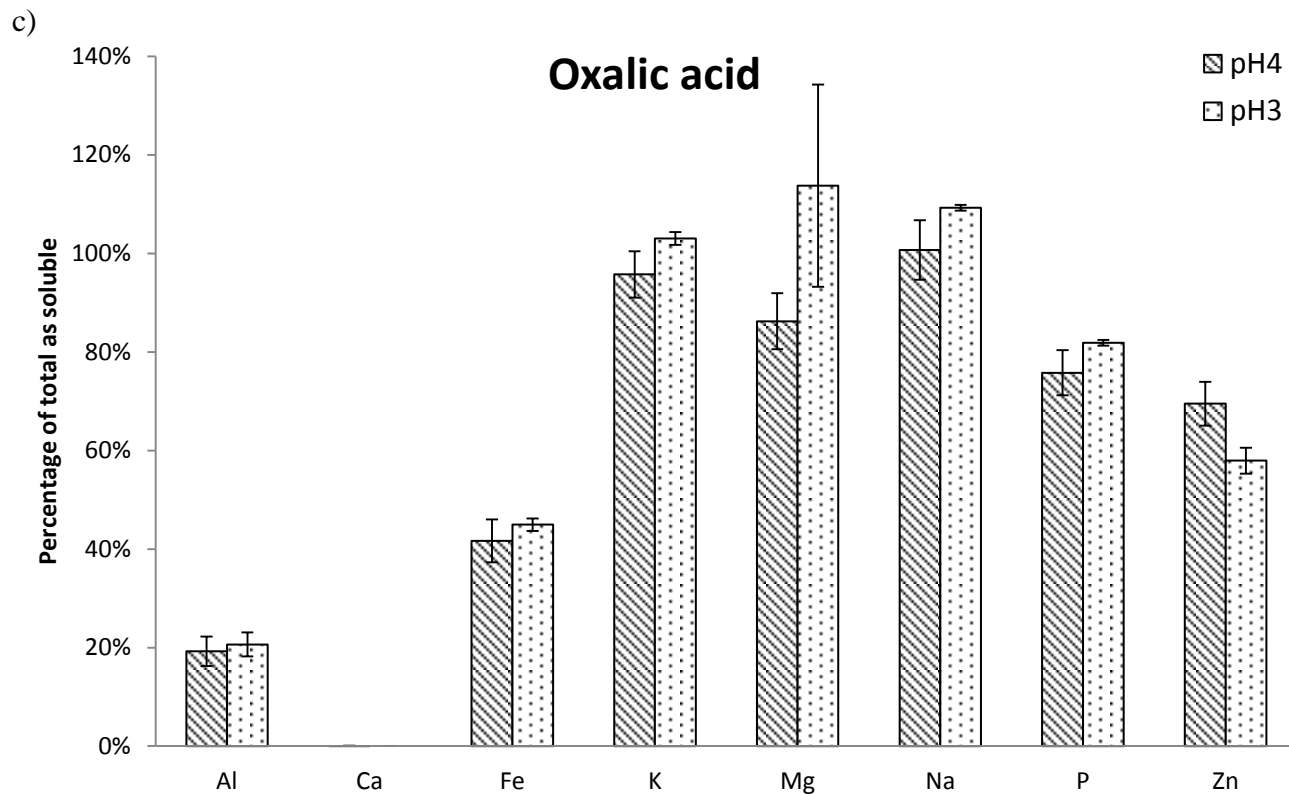


Figure 3.3. Effect of various acids on manure slurry. Graph a) shows the percentage of various manure constituents found as soluble in untreated and sulphuric acid treated manure. Graphs b) and c) shows the effects of citric and oxalic acid, respectively, on dairy manure. In all graphs, error bars represent standard error about the mean.

soluble  $\text{PO}_4\text{-P}$  was  $41.9 \pm 1.1\%$ ; soluble Mg concentration was  $64.7 \pm 1.0\%$  of total; soluble Ca was  $51.2 \pm 3.7\%$  of total.

Sulphuric acid was first used to lower the manure pH to 4.0; then the experiment was repeated 4 times. Both citric and oxalic acid was used for lowering the manure pH to either 4.0 or 3.0; these experiments were repeated twice. In the case where sulphuric acid was used, soluble phosphorus increased to  $72.1 \pm 1.8\%$  of TP, soluble Mg increased to  $88.0 \pm 3.4\%$ , and soluble Ca increase to  $88.6 \pm 2.9\%$ . When citric acid was used, soluble  $\text{PO}_4\text{-P}$  concentration increased to  $91.1 \pm 0.5\%$  of TP at pH 4.0; no significant change was observed when pH was further decreased to 3.0, where the soluble  $\text{PO}_4\text{-P}$  concentration was  $89.1 \pm 0.3\%$  of TP. The soluble portion of Mg also did not show significant differences at pH 4.0 and 3.0, where soluble Mg was  $93.7 \pm 0.1\%$  and  $95.5 \pm 0.04\%$  of total Mg respectively. Citric acid was able to solubilise  $98.7 \pm 1.2\%$  of Ca at pH 4.0 and complete Ca solubilisation ( $102.9 \pm 2.1\%$ ) was observed at pH 3.0. Treatment with oxalic acid showed a slight inverse relation between pH and constituent solubilisation. Soluble  $\text{PO}_4\text{-P}$  was  $75.8 \pm 4.6\%$  and  $81.9 \pm 0.6\%$  of TP at pH 4.0 and 3.0, respectively. Soluble Mg was  $86.2 \pm 5.7\%$  when pH was lowered to 4.0; soluble Mg increased to  $113.8 \pm 20.6\%$  of total Mg at pH 3.0. The greater than 100% of Mg observed as soluble Mg could be due to instrument measurement errors and was reflected by the high degree of error. It should be noted that soluble Ca was near to completely nonexistent when oxalic acid was used. Oxalic acid is a known compound that selectively sequesters soluble Ca, forming a precipitate of calcium oxalate.

Oxalic and citric acid both performed better than sulphuric acid in terms of P and Mg solubilisation in manure slurry. However, sulphuric acid was chosen as the acid to use for further experiments, for two important reasons.

- 1) Due to the strength of sulphuric acid ( $K_{a1} > 1$ ,  $K_{a2} = 1.2 \times 10^{-2}$ ), much less sulphuric was needed to decrease pH compared to using oxalic acid ( $K_{a1} = 5.9 \times 10^{-2}$ ,  $K_{a2} = 6.4 \times 10^{-5}$ ) or citric acid ( $K_{a1} = 8.4 \times 10^{-4}$ ,  $K_{a2} = 1.8 \times 10^{-5}$ ). Therefore, the cost for the necessary amounts of oxalic or citric acid is much greater than the cost for using sulphuric acid.
- 2) The second, but more important reason, for using sulphuric acid was related to  $H_2O_2/MW/H^+$ -AOP. For reasons this author cannot fully explain,  $H_2O_2/MW/H^+$ -AOP treated manure slurry show the phenomenon of flocculation if, and only if sulphuric acid was used (see Chapter 1.3.3 for details). It is possible that sulphuric acid was causing the proteinaceous substances in the slurry to denature and precipitate. Our findings support those reported earlier, where sulphuric acid was able to induce proteins to precipitate and form the largest particulate sizes amongst a variety of protein precipitating agents (Chan *et al.*, 1986). It is possible that other acids can also induce flocculation, but they were not tested in this study.

Sulphuric acid was then chosen as the acid to use for further  $H_2O_2/MW/H^+$ -AOP experiments. The 3 x 3 factorial experimental design mentioned above was conducted to observe the effects of  $[H_2O_2]$ , as well as pH on  $H_2O_2/MW/H^+$ -AOP treatment of dairy manure slurry. Each manure slurry batch was acidified to the desired pH (e.g. pH4.0, 3.5, or 3.0) before the start of each  $H_2O_2/MW/H^+$ -AOP run. The highest altered manure pH was chosen to be 4.0, since acid hydrolysis of phosphates was previously observed at this acid concentration (Phillipy *et al.*, 1987). pH 3.0 was the lowest value chosen, since the possibility of Fenton reaction (which may aid in oxidation) diminishes at lower pH values, since ferrous iron cannot be regenerated due to ferric iron precipitation (Sanz *et al.*, 2003). The raw slurry, pre-MW acidified slurry, as

well as  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP effluent material was sampled and analyzed for TP, soluble  $\text{PO}_4\text{-P}$ , TKN and soluble  $\text{NH}_3\text{-N}$ ; the results were presented in Figure 3.4. All experiments were replicated at least four times, and the error bars shown are the standard errors about the mean.

Raw manure slurry used for these experiments had a mean  $45.8 \pm 2.3\%$  of TP as soluble  $\text{PO}_4\text{-P}$ . One tailed student's t-tests were performed, using Microsoft Office Excel 2007, to find statistical significance of each treatment condition (see Appendix A). Acidification of the manure slurry alone was able to significantly increase soluble  $\text{PO}_4\text{-P}$  levels to  $59.4 \pm 4.8\%$  of TP at pH4.0 ( $p < 0.05$ ). The initial increase in soluble phosphate could have been attributed to the acid hydrolysis effect previously observed by Phillipy *et al.* (1987). However, the treatment temperature previously used was  $121^\circ\text{C}$  (Phillipy *et al.*, 1987), much higher than the  $\sim 7 - 15^\circ\text{C}$  manure slurry used in our current study. These findings suggest that the manure slurry at DERC contain high levels of easily broken orthophosphate monoester bound organic compounds, other than phytic acid. Further studies are required to characterize the phosphorus composition of the slurry.

Treatment of the manure by  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP process was able to further increase soluble  $\text{PO}_4\text{-P}$ . It was found that all treatments significantly solubilised more  $\text{PO}_4\text{-P}$  than that found in raw manure slurry ( $p < 0.05$ ). All  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP treatments were found to solubilise significantly more  $\text{PO}_4\text{-P}$  than acid alone ( $p < 0.05$ ). It was presented earlier that MW irradiation alone did not increase phosphate solubilisation. Therefore, it was found that the use of acid and hydrogen peroxide together in the  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP process had a synergistic effect on phosphate solubilisation.

As mentioned previous, increased levels of soluble ammonia was not necessary for struvite crystallization in this study. However, the effects of the  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP process on

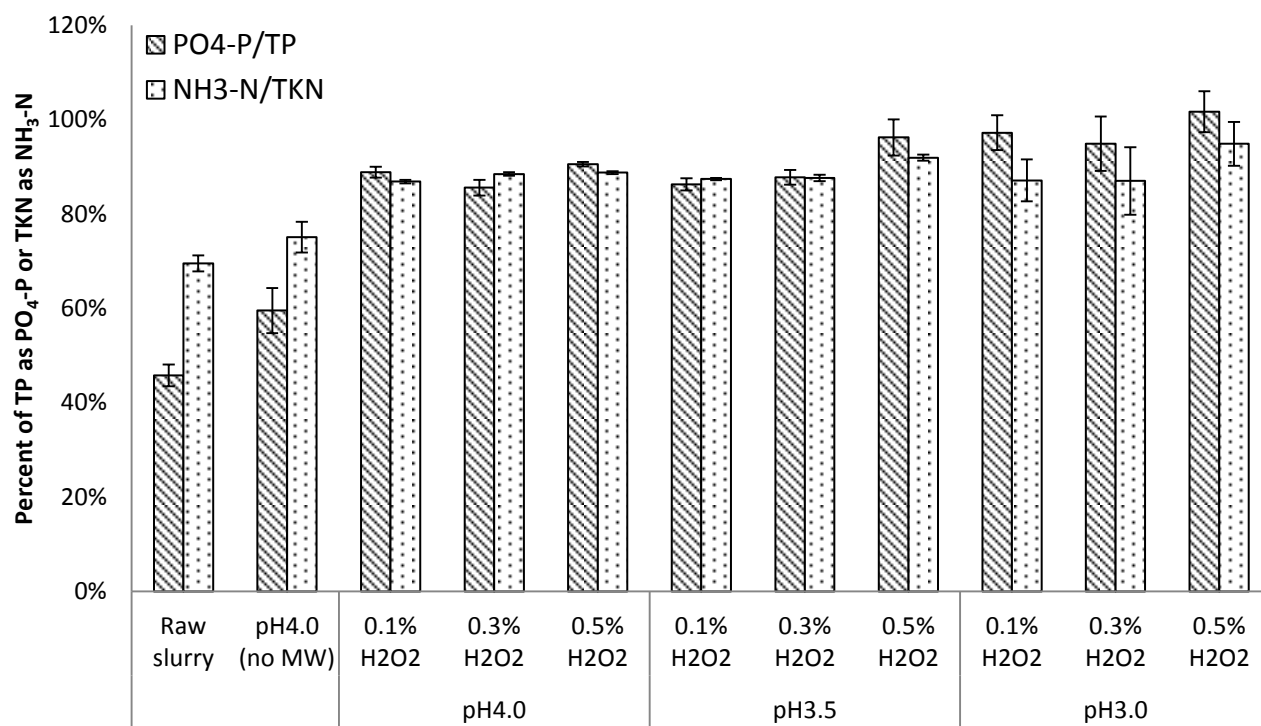


Figure 3.4. Changes in manure nutrients' solubility after  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP treatment under various treatment conditions. Three different pH values were each coupled one of three  $[\text{H}_2\text{O}_2]$ .

ammonia solubilisation was examined, since it may have applications elsewhere. Acidification of the manure slurry, using sulphuric acid, was able to increase soluble  $\text{NH}_3\text{-N}$  from  $69.5 \pm 1.7\%$  of TKN to  $75.1 \pm 3.3\%$  of TKN at pH4.0. The increase in soluble  $\text{NH}_3\text{-N}$  using acid alone was not found to be significantly different than that of raw manure slurry ( $p = 0.0903$ ).

$\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP treatment of manure, however, was able to significantly increase the percentage of TKN as soluble  $\text{NH}_3\text{-N}$  in all treatment conditions, when compared to raw manure ( $p < 0.05$ ). All  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP treatments also increased the fraction of TKN as soluble  $\text{NH}_3\text{-N}$  compared to acidification alone ( $p < 0.05$ ), save for pH3.0 + 0.3%  $\text{H}_2\text{O}_2$  ( $p = 0.10$ ).

One tailed t-tests were also conducted to verify whether changes in  $[\text{H}_2\text{O}_2]$  or initial pH affects the effluent soluble nutrients' concentrations. For each  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP treatment condition tested, a significant increase in the fraction of TP as soluble  $\text{PO}_4\text{-P}$  was observed for pH4.0, when  $[\text{H}_2\text{O}_2]$  increased from 0.3% to 0.5%, and pH3.5 when comparing 0.1% to 0.5%  $\text{H}_2\text{O}_2$ . Similarly, the percentage of TKN as soluble  $\text{NH}_3\text{-N}$  showed significant increases at pH4.0 when  $[\text{H}_2\text{O}_2]$  was increased from 0.1%; however, the difference made between 0.3% and 0.5%  $[\text{H}_2\text{O}_2]$  was not statistically significant. At pH3.5, 0.5%  $\text{H}_2\text{O}_2$  significantly increased soluble phosphate compared to the other  $[\text{H}_2\text{O}_2]$  used; no significant change was observed between 0.1% and 0.3%  $\text{H}_2\text{O}_2$ . At pH3.0, increases in  $[\text{H}_2\text{O}_2]$  did not show an increase in percentage of TP as soluble  $\text{PO}_4\text{-P}$  or an increased percentage of TKN as soluble  $\text{NH}_3\text{-N}$ .

It appears that at more neutral pH, where the acid has difficulties with phosphate and ammonia solubilisation,  $\text{H}_2\text{O}_2$  comes into play to solubilise those nutrients further. As the pH became lower, the acid effect becomes more pronounced. Maximum phosphorus and nitrogen solubilisation, achieved by the  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP process, was realized by using 0.5%  $\text{H}_2\text{O}_2$  at pH3.0, to yield  $101.7 \pm 4.3\%$  of TP as soluble  $\text{PO}_4\text{-P}$ , and  $94.9 \pm 4.7\%$  of TKN as soluble  $\text{NH}_3\text{-N}$ .



The amount of P solubilisation in this study did not reached its maximum potential under certain treatment conditions, in comparison to previous studies. However, the operating temperatures used in this study were in the range where the lowest amount of P solubilisation was observed in previous studies. Therefore, it could be assumed that, if operating temperatures were higher, then greater P solubilisation can be achieved. For further studies, the reactor should be modified to increase operating pressures to reach higher temperatures.

### 3.3.3 Gravity Clarification

To our surprise, the  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP process caused solids to destabilize from suspension; a phenomenon never before reported for dairy manure. The solids appeared to flocculate and would be removed by simple gravity clarification. To determine the rate and efficacy of gravity clarification, the effluents from each  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP experiments A to I were sampled. Each of the effluent materials sampled were well shaken before 100 mL were poured into 100 mL graduated cylinders. A time course experiment was conducted and the sludge volume from each  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP effluent was recorded at select time intervals. Experiments G – I were repeated 4 times whereas experiments A – F were repeated 6 times. A plot of the average sludge volume and settling time was presented in Figure 3.5 (a) – (c). It should be noted that MW application to raw manure, treating raw manure with the  $\text{H}_2\text{O}_2/\text{MW}/$ -AOP process, or microwaving acidified manure (except for pH3.0) did not lead to the observed destabilisation of solids in the slurry. The observed standard errors about the mean for all experiments are considerably high (see Appendix B). Therefore,  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP treatment of dairy manure for solids clarification should be tested for the specific manure being treated.

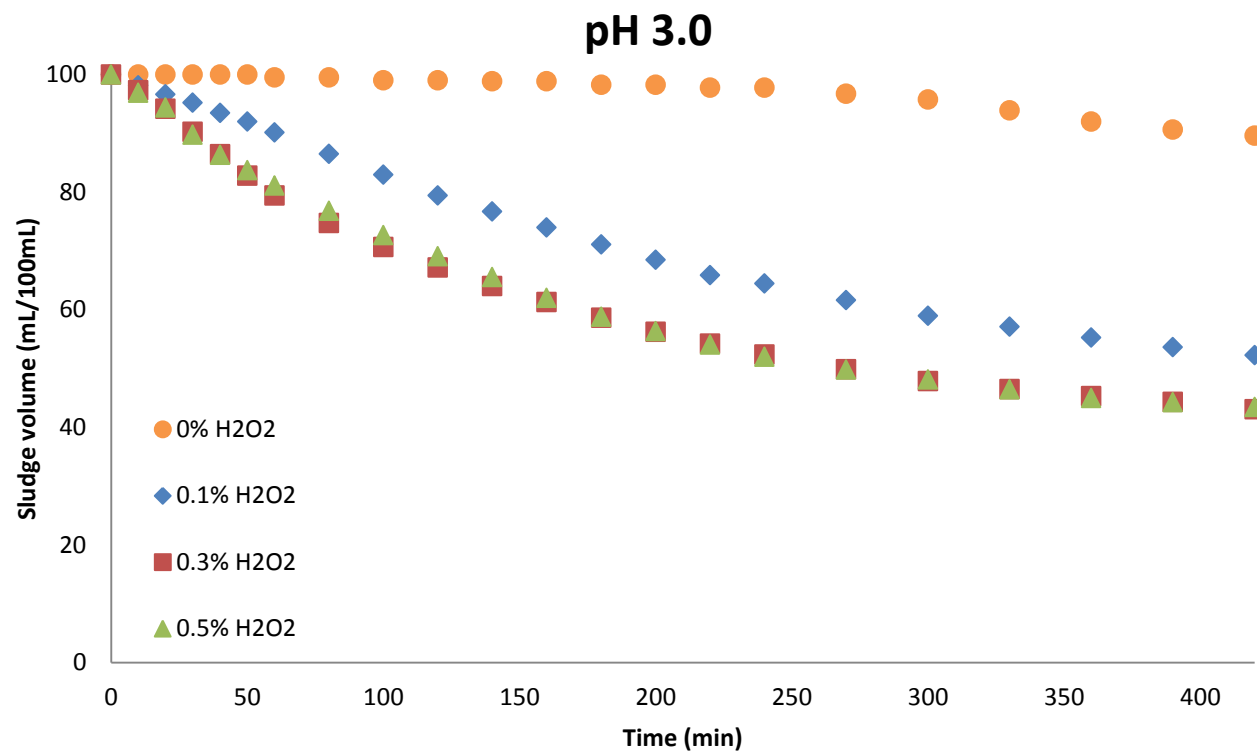
As shown in Figure 3.5 (a) by the circles, the microwave treated manure slurry at pH3.0, without using H<sub>2</sub>O<sub>2</sub>, showed an acid effect that allowed the solids to destabilize from suspension. However, the sludge volume averaged  $89.6 \pm 0.4\%$  of the total volume after the 7 hour experimental settling period. The slight solids settling observed at pH3.0 may be due to the effect of sulphuric acid acting as a protein precipitation agent (Chan *et al.*, 1986).

The fastest clarification, leaving the least volume of sludge, was for H<sub>2</sub>O<sub>2</sub>/MW/H<sup>+</sup>-AOP treated manure at pH3.5. Significant differences between the various H<sub>2</sub>O<sub>2</sub> doses, at pH3.5, were not seen in terms of solids settling. At pH4.0 and pH3.0, however, increasing H<sub>2</sub>O<sub>2</sub> concentration from 0.1% to 0.3% contributed to reduced sludge volumes. Further increase of H<sub>2</sub>O<sub>2</sub> concentration to 0.5% did not cause sludge volumes to decrease.

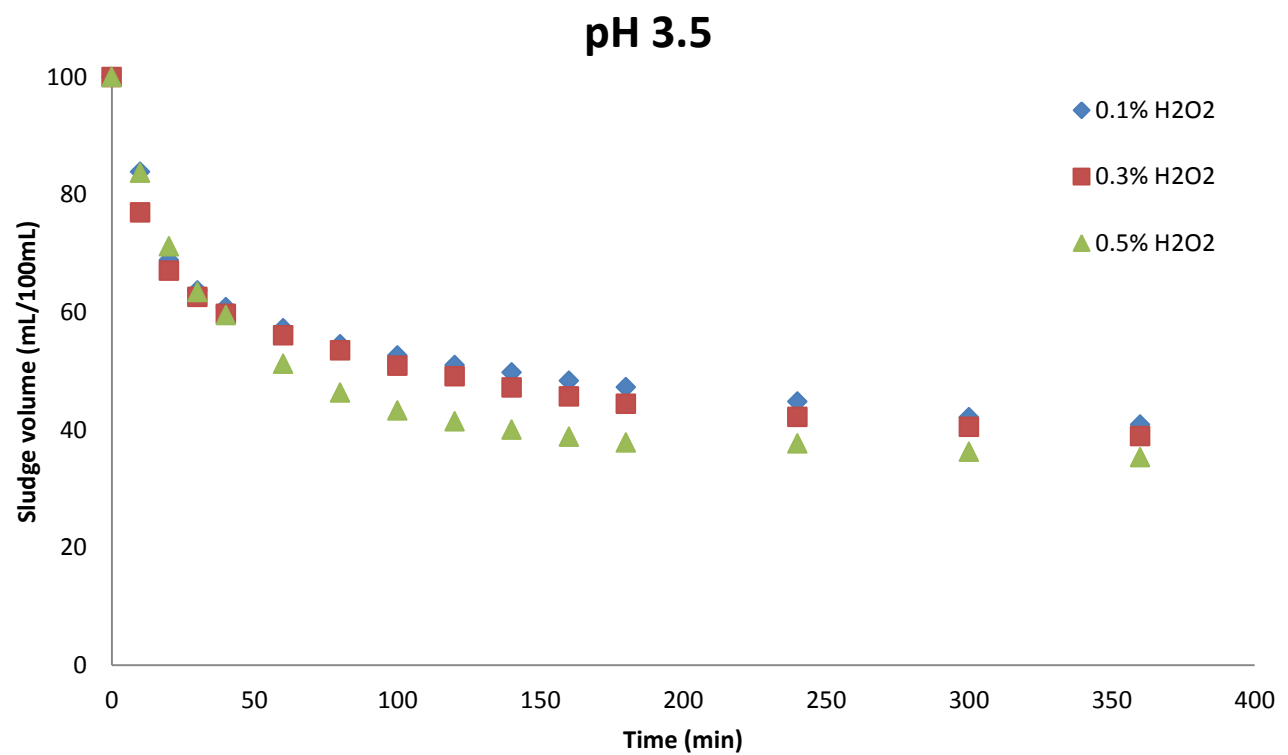
The mechanisms that cause slurry solids to sediment may be complex. However, from general observable appearances, coagulation/flocculation is a major mechanism. Due to the availability of aluminum and iron species in the manure slurry, the coagulating agents are present. Coagulation and flocculation occurs in two distinct steps. The solid particles suspended in a liquid normally hold a negative charge. As the particles come spatially together, the charges repel and cause the suspended solid particles to remain suspended. Coagulating reagents are commonly positively charged ions that would neutralize the negative charges on the suspended solid particles. Once the charges are neutralized, the particles come together to form microflocs, via Van der Waals forces, in a process called coagulation. The microflocs are then brought into contact by gentle mixing, where they bind to form large visible precipitate. The most latter step is termed flocculation.

Ferric (Fe<sup>3+</sup>) and ferrous (Fe<sup>2+</sup>) iron are the two most common oxidation states of iron, and both may be used as coagulants due to their positive charges. Since phytates in the dairy manure

(a)



(b)



(c)

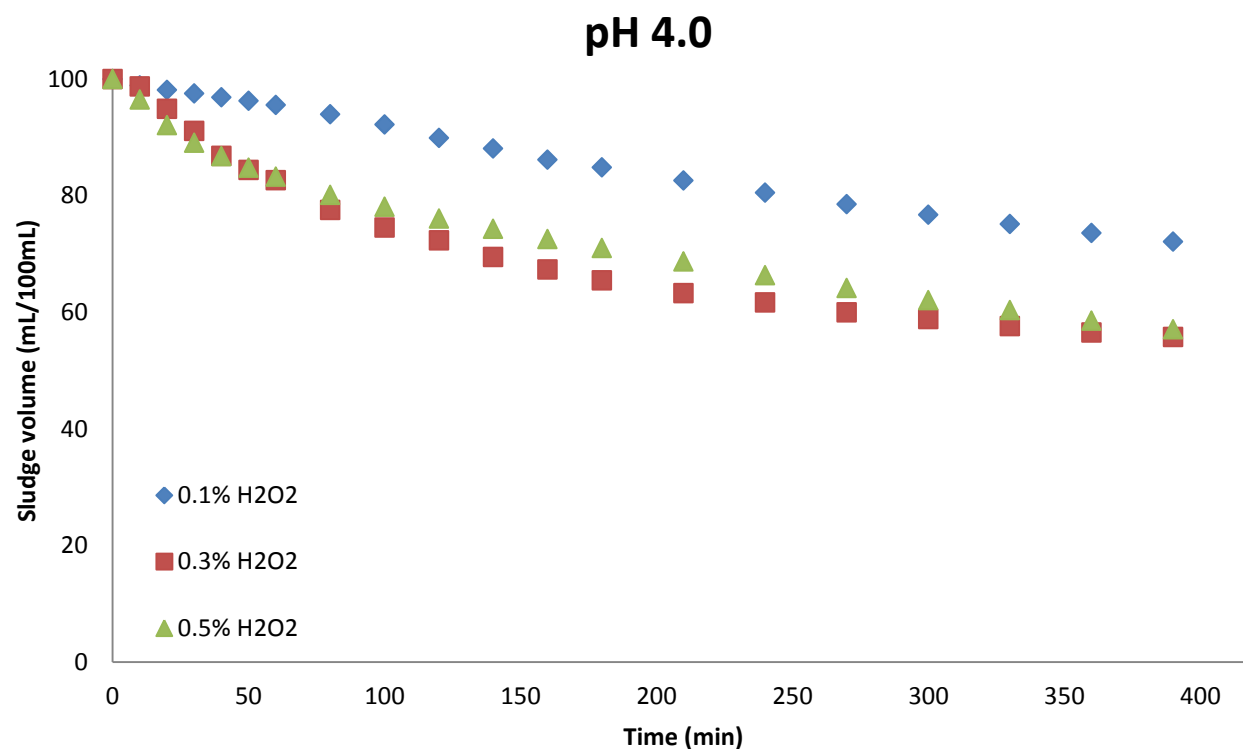


Figure 3.5. Plots of the average sludge volumes obtained for each settling test versus the respective time allowed for sludge to sediment. Graphs (a), (b), and (c) shows the sludge settling for manure acidified to pH3.0, 3.5, and 4.0 respectively. In each graph, the designated manure pH was coupled to various [H<sub>2</sub>O<sub>2</sub>] as described in Table 3.1. Although 0% H<sub>2</sub>O<sub>2</sub> was tested for each manure pH, sludge sedimentation was only observed when manure pH was lowered to 3.0 and is shown in graph (a).

normally form insoluble salts with iron (Urbano *et al.*, 2000), iron ions in the manure slurry are highly likely to be bound by phytates. As discussed earlier, the increases in soluble  $\text{PO}_4\text{-P}$  concentrations, after  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP treatment, are likely from the destruction of phytate molecules, through the hydrolysis of the monoester bonded phosphates. The inositol compound loses its ability to bind metals as more and more phosphates are cleaved (Graf and Eaton, 1990). In this case, the bound iron will enter solution, where they can behave as coagulants.

Experiments A-C and G-I were repeated to examine the effects and extent of initial pH and  $\text{H}_2\text{O}_2$  concentration in the  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP process on TSS levels. The  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP effluents underwent a gravity clarification process for 7 hours. Aliquots of the clarified liquid materials was taken and analyzed for its TSS concentration. The mean TSS concentrations from each of the six experiments are presented in Figure 3.6.

TSS concentrations of the, post clarified, liquid fraction appeared to decrease with increased  $\text{H}_2\text{O}_2$  dosage concentration. For equal  $[\text{H}_2\text{O}_2]$ , one-tailed student t-test does not find statistically significant decreases in TSS between the two pH values. For the three experiments where the slurry was acidified to pH3.0, a significant decrease in TSS concentration was found when  $[\text{H}_2\text{O}_2]$  increased from 0.1% to 0.3% ( $p < 0.05$ ); a further increase in  $[\text{H}_2\text{O}_2]$  to 0.5% did not significantly reduce TSS any lower. In the cases where the manure slurry was acidified to pH4.0 however, a significant decrease in TSS concentration was only observed when  $[\text{H}_2\text{O}_2]$  was increased from 0.3% to 0.5% ( $p < 0.05$ ). TSS removal reached as high as  $1.9974 \pm 0.0007$  Log-reduction at pH3.0 and 0.5%  $\text{H}_2\text{O}_2$ .

With the anticipated release of ferric and ferrous ions, the possibility of the Fenton and Fenton-like reactions exist in the  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP manure treatment process. The Fenton oxidation reaction was shown to be an effective method at destroying organic pollutants (Neyens

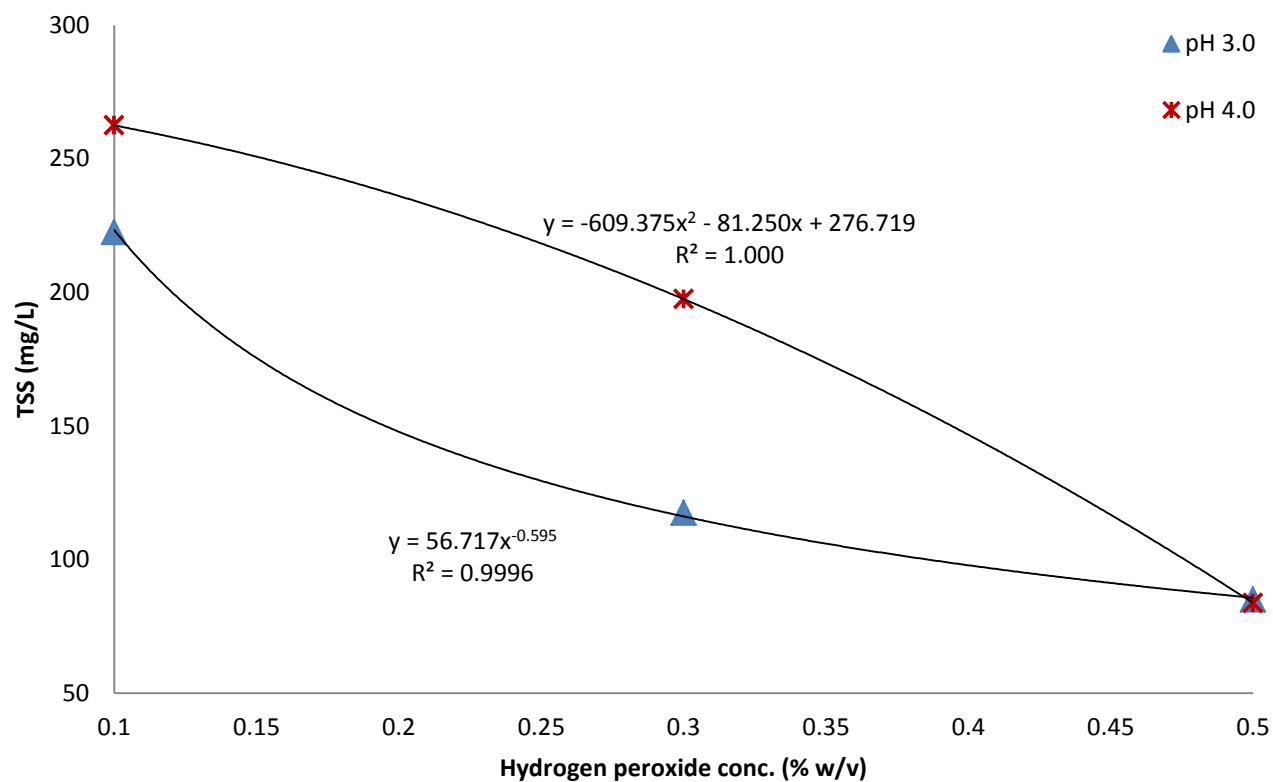
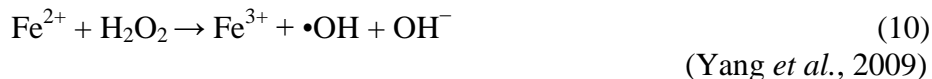


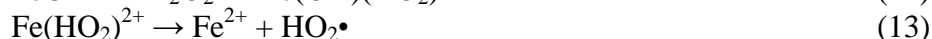
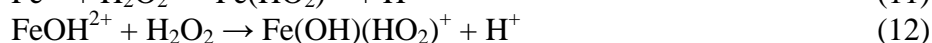
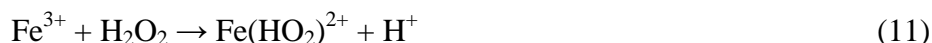
Figure 3.6.A plot of the TSS concentrations in the liquid fraction of the  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP effluent, after a 7 hours clarification period. The effluents were those of manure acidified to either pH3.0 or 4.0, and each were coupled to one of three  $[\text{H}_2\text{O}_2]$  for the  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP treatment process.

and Baeyens, 2003; Yang *et al.*, 2009; etc.). Fenton's oxidation reaction was suggested to follow that expressed in equation (10).



The ferrous ion in equation (10) can be substituted by a ferric ion when reacting with the  $\text{H}_2\text{O}_2$ .

In this case, aptly termed the Fenton-like reaction, radical generation and subsequent organic molecule decomposition/oxidation follows equations (11) through (15).



(Yang *et al.*, 2009)

In addition to its oxidative abilities, the Fenton-like reaction forms ferric-hydroxo complexes (Kuo, 1992; Kang and Chang, 1997). The ferric-hydroxo complexes may have played a role in the coagulation of manure solids seen in this study. The Fenton-like processes have been shown to reduce sludge volume when treating pharmaceutical wastewater (Yang *et al.*, 2009), as well as textile finishing wastewater (Meric *et al.*, 2005), compared to traditional coagulation.

### 3.4 Conclusions

The  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP process has been shown to solubilise  $\text{PO}_4\text{-P}$ ,  $\text{NH}_3\text{-N}$ , and Mg under the reaction conditions tested. All three needed for phosphorus recovery by struvite crystallization. Solids destabilisation from suspension in dairy manure slurry has never been reported. Nevertheless, this discovery may be critical for the downstream struvite crystallization

process. In past studies, it was reported that TSS >1000 ppm interfered with struvite production (Schuiling and Andrade, 1999). Some studies using dairy manure suggest that TSS > 4000 mg/L was not suitable for struvite crystallization (Shen *et al.*, 2010; Shen *et al.*, 2011). In any case, the TSS contents of most dairy manure slurries are too high. Sedimentation of solids after the H<sub>2</sub>O<sub>2</sub>/MW/H<sup>+</sup>-AOP process offers a possible solution to this problem. Liquid solid separation of dairy manure slurry has never been reported to achieve this level of quality.

The drawbacks of the H<sub>2</sub>O<sub>2</sub>/MW/H<sup>+</sup>-AOP process mainly reside in the installation and operation costs of the system. Energy usage is relatively high and thus, efficient use of energy should be considered. Heat exchangers could be installed either to recover heat or preheat the influent material in order to minimize operational costs.



## **Chapter 4: Calcium Removal**

### **4.1 Introduction**

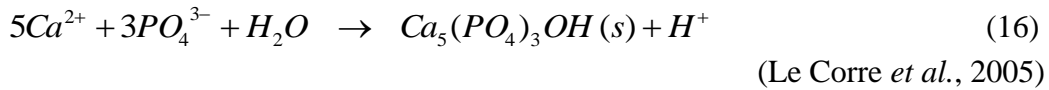
In the  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP process for nutrient solubilisation, pH of the manure decreased. Under the acidic treatment condition, metals that would normally be bound became soluble as well. The two metal ions, released into solution, worthy of note are Mg and Ca. Increase in soluble Mg will serve as a benefit for struvite crystallisation since it brought the soluble Mg to a concentration, whereby, additional Mg was not needed. Mg addition, in past experiences, has been a significant operational cost for full-scale struvite recovery. In the case of dairy manure, however, the soluble Mg to  $\text{PO}_4$  molar concentration ratio exceeded that of the necessary 1:1 after  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP treatment.

One foreseeable negative aspect of the  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP process was the release of Ca ions into solution. A number of studies conducted for the recovery of P, via struvite crystallization, suggest an inverse relationship between P recovery and soluble Ca concentration in manures (Shen *et al.*, 2010; Shen *et al.*, 2011; Zhang *et al.*, 2010). A recent P recovery study was conducted using anaerobically digested dairy manure for struvite precipitation. The pH of the digester effluent was decreased with the intention of P solubilisation; at the same time, an increase in soluble Ca was also observed. The study found that soluble P reduction levels could be increased, from 1 – 13% for the acidified effluent, to 30 – 82 % if further treated with ethylenediaminetetraacetic acid (EDTA) to chelate soluble Ca (Zhang *et al.*, 2010).

With that said, Ca removal is critical for downstream struvite crystallization and P recovery. Several methods for calcium removal exist. Microbiological calcium precipitation (MCP) is a method in which calcium is precipitated in the form of  $\text{CaCO}_3$ . MCP has been applied to a wide range of uses including sandstone monument restoration projects (Castanier *et*

*al.*, 1999; Le Metayer-Levrel *et al.*, 1999) and control of ground water flow by mineral plugging of soil pores (Stocks-Fisher *et al.*, 1999; Ferris and Stehmeier, 1992). MCP has also been experimented for calcium removal from industrial wastewaters, where soluble Ca concentrations were about 500 ppm. Although Ca removal reached beyond 90%, the hydraulic retention time (HRT) was 4 days and ammonia is a by-product and possible secondary pollutant of the reaction (Hammes *et al.*, 2003). HRT of such lengths are not feasible for the current study.

The majority of Ca removal techniques involve chemical treatment, since Ca precipitates readily in alkaline pH. To remove Ca, NaOH has been added to a variety of wastewaters such as nanofiltration/reverse osmosis concentrates (Sperlich *et al.*, 2010). However, to increase the solution pH with NaOH, for significant calcium precipitation, there will also be a depletion of PO<sub>4</sub>, since calcium phosphate will likely form following the formula in equation (16).



In fact, a number of innovative approaches have been developed in recent years, which use Ca minerals and alkaline conditions to remove phosphates from wastewaters (*e.g.* Bellier *et al.*, 2006). Therefore, NaOH is simply not practical for the current project since PO<sub>4</sub> recovery, via struvite crystallization, is the ultimate goal.

For our treatment purposes, removal of soluble calcium must be done selectively, so that Mg and PO<sub>4</sub> are left alone for struvite crystallization. A number of chemical precipitation and/or chelating methods have been proposed, which show potential. The removal of soluble calcium from concentrated brine after desalination has been tested by Yi and Dong (2009) using sodium carbonate. The study found a Ca reduction of 80%, while Mg was reduced by 20%. Shen *et al.* (2010) tried two different methods of removing soluble calcium, (1) chelating with EDTA and (2)

precipitation by oxalic acid (OA). It was found that both methods were able to reduce soluble free  $\text{Ca}^{2+}$  by 90% and Mg removal was no more than 10%.

Of the three reagents mentioned above, both EDTA and OA seem suitable in this study, since they are able to reduce the most soluble Ca while affecting Mg in the least. The reagent selected for reducing the soluble Ca in the supernatant of  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP effluent was OA.

The advantages of using OA over EDTA are numerous:

- (1) The ultimate fate of the liquid effluent from the manure treatment process will be spread on to crop fields as nutrient amendments for the soil. EDTA is a chelating agent that removes soil bound metals, chelate them and the EDTA-metal compound enters the liquid phase. Once in solution, the bioavailability of the heavy metals increases and is taken up by the vegetation; especially in the roots (Yang *et al.*, 1999; Chen *et al.*, 2004). Increased heavy metals in crops may lead to detrimental health impacts for the consumer.
- (2) Corn is an essential crop on most dairy farms since it is used to make the high-energy corn silage feed. EDTA induced metal uptake will inhibit the growth and wellbeing of crops such as corn (Chen *et al.*, 2004).
- (3) OA, on the other hand, has relatively less negative impact on plants. In some cases, the presence of oxalic acid has been shown to lower the potential for infection of tobacco and soybean plants by the ubiquitous pathogenic fungus *Sclerotinia sclerotiorum* (Cessna *et al.*, 2000). Enhanced release of P from soil apatites, by oxalic acid-producing mycorrhizal fungi, are especially critical during later stages of soil development when primary minerals have weathered away (Walker and Syers, 1976; Frossard *et al.*, 1998). This is especially true if limestone is present.

- (4) In theory, both EDTA and OA bind  $\text{Ca}^{2+}$  on a 1:1 molar basis. The price of EDTA is rather expensive. On a mole per mole basis, the current cost of decreasing soluble calcium ions using EDTA will be many times the cost of OA. Therefore, using EDTA was not feasible for our scale of operation.
- (5) The calcium oxalate produced can be used as a cattle feed supplement. Although rarely used in Canada as a Ca supplement, under the proper diet regime, calcium oxalate has been successfully used in cattle feed. However, calcium oxalate is not recommended for this purpose, since over feeding without a proper diet will prevent oxalate breakdown in the rumen. If oxalate is not broken down it can be absorbed by the digestive tract of the cow. Elevated oxalate levels have been a known cause for kidney stones.

## **4.2 Materials and Methods**

### **4.2.1 Treatment of $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP Effluent With OA**

In order to test the efficacy of OA for soluble Ca removal, 500 mL aliquots of clarified liquid  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP effluent were used. The manure slurry used for  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP treatment was acidified to pH4.0 with 0.5%  $\text{H}_2\text{O}_2$ . In a beaker, increasing quantities of OA (Fisher Scientific) were added while stirring. Ten minutes after each OA concentration increase, a sample was taken and passed through a nitrocellulose filter with 0.45  $\mu\text{m}$  pore size (Millipore), before being analyzed for its soluble constituents. Each filtrate was diluted immediately in order to avoid further reactions. After dilution, aliquots of each sample were made and preserved for their respective constituent analysis, according to Standard Methods. The experiment was repeated with 4 individual  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP effluents. OA additions to effluents 3 and 4 were

repeated twice for each effluent. Therefore, the OA treatment experiment resulted in a total of 6 experimental runs.

#### 4.2.2 Analysis

All samples were passed through nitrocellulose filters with a pore size of 0.45  $\mu\text{m}$ . Therefore, all constituents of the filtrate were considered to be soluble. Select metals, including Mg and Ca, were analyzed using ICP(Standard Methods 3120 B). ICP was done on a PerkinElmer Optima 7300DV. Both Mg and Ca were analyzed in replicates for each sample. Two different wavelengths were used for each metal. Therefore, each sample was analyzed 4 times for each metal. The presented values are the mean of the 4 values. Analysis for soluble  $\text{NH}_3\text{-N}$  (Standard Methods 4500- $\text{NH}_3\text{ H}$ ) and  $\text{PO}_4\text{-P}$  (Standard Methods 4500- $\text{P G}$ ) was analyzed by the flow injection method using the Lachat QuickChem 8000. All samples were analyzed in replicates and the presented values are the means.

### 4.3 Results and Discussion

Post clarified liquid  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+\text{-AOP}$  effluent was treated with various OA concentrations at increasing increments. Samples were taken at each OA concentration and analyzed for its soluble metals, as well as soluble nutrients. The actual OA concentrations were calculated according to the amount of OA added while taking into consideration of the volume extracted for sampling.

The soluble  $\text{NH}_3\text{-N}$  and  $\text{PO}_4\text{-P}$  concentrations after each OA concentration increment were divided by the original concentration, without OA treatment, to obtain a percentage remaining of each nutrient. The percent of remaining  $\text{NH}_3\text{-N}$  and  $\text{PO}_4\text{-P}$  in solution were plotted against the

ratio between molar concentrations of OA to initial molar concentration of soluble Ca in Figures 4.1 (a) and (b), respectively.

Minor decreases in soluble  $\text{NH}_3\text{-N}$  and  $\text{PO}_4\text{-P}$  concentrations were observed when post clarified liquid fraction of  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP effluent was treated with OA. The highest observed  $\text{NH}_3\text{-N}$  and  $\text{PO}_4\text{-P}$  loss was 7.2% and 17.1%, respectively. However, almost no decrease in either  $\text{NH}_3\text{-N}$  or  $\text{PO}_4\text{-P}$  were observable when OA was used at a molar ratio twice that of Ca in the original solution.

The soluble metals Mg and Ca were analyzed using ICP. Similar to nitrogen and phosphorus, the percent remaining of soluble Mg and Ca were calculated from dividing the constituent concentrations of each sample by the respective concentration from those untreated with OA. The percent remaining Mg and Ca were plotted against the molar ratio of OA and initial Ca concentrations (in Figure 4.2).

Unlike the results observed by Shen *et al.* (2010), OA treatment of post clarified liquid  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP effluent did not lead to a decrease in Mg concentration in solution. However, the increase in soluble Mg was surprising. Soluble Mg increases by as high as 25% were observed in the samples. The increased Mg concentrations were only observed for effluents 3 and 4, which indicated an error in the analysis process. Whatever the reasons may be for the observed Mg increase, it is not expected to negatively impact the downstream struvite crystallization process.

As high as 97.2% of soluble Ca was removed by OA and calcium oxalate precipitation. The level of removal was even greater than the 90% removal observed in previous studies (Shen *et al.*, 2010). The rate of Ca removal decreases to a minimal as OA to Ca ratio reached approximately 2. Further Ca removal may have been hindered by the low pH value, where the

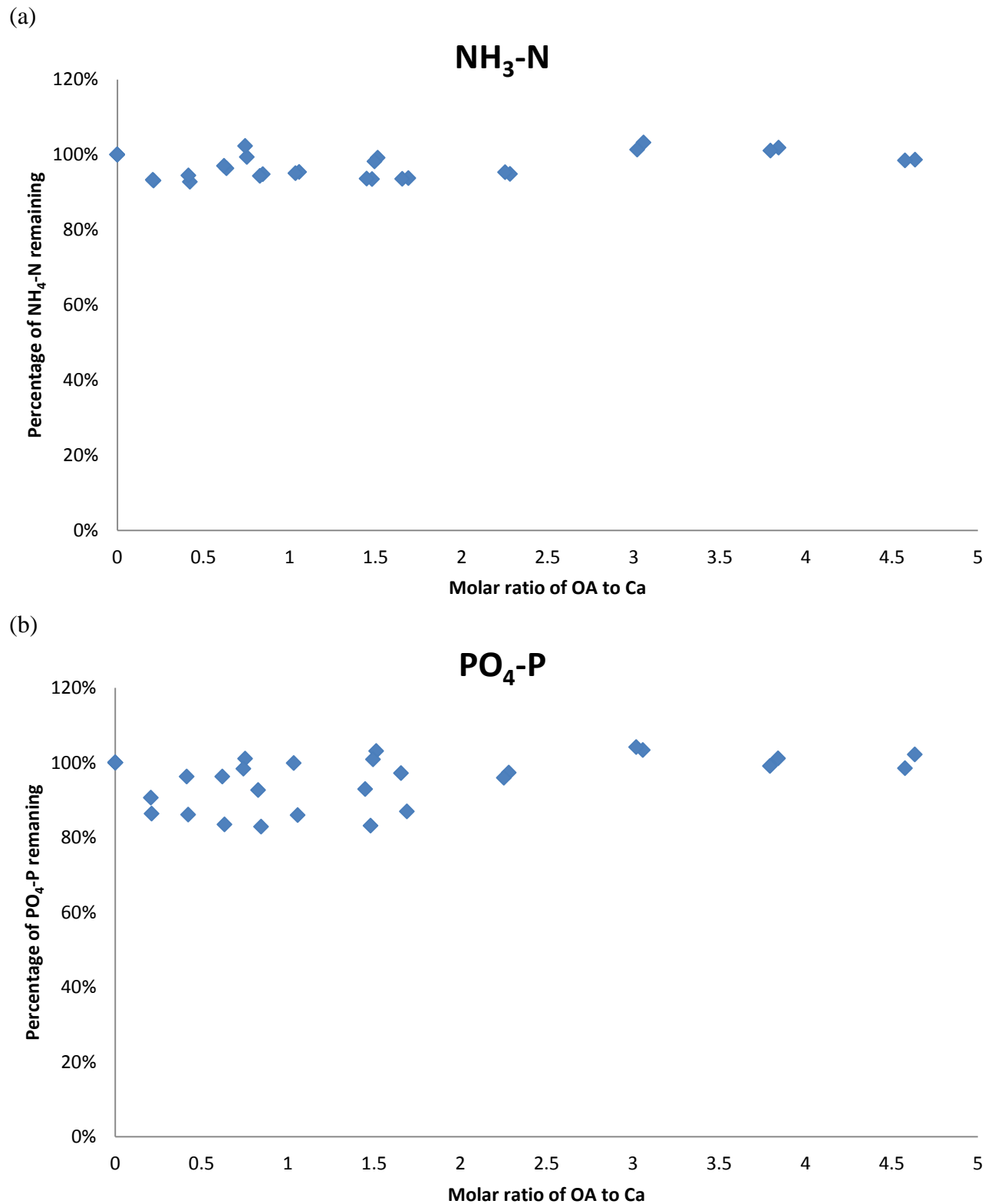


Figure 4.1. Percent of soluble nutrients remaining in the post clarified H<sub>2</sub>O<sub>2</sub>/MW/H<sup>+</sup>-AOP effluent after OA treatment. Graphs (a) and (b) show the remaining NH<sub>3</sub>-N and PO<sub>4</sub>-P, respectively.

proton concentrations are too high for additional OA to dissociate. In this case, the conjugate base of OA, the oxalate ion, does not form and thus cannot bind the  $\text{Ca}^{2+}$  ion in solution.

Throughout the experimental time period, the highest observed Ca concentration in the dairy manure was 967.5 mg/L. The scatter plot in Figure 4.2 allow us to estimate that only 10% of soluble Ca remains in solution at OA : Ca molar ratio of 2 : 1. However, calcium oxalate precipitate is expected to have an OA to Ca ratio of 1:1. The higher than expected need of OA could be due to its solubility equilibrium, or that OA is forming precipitates with other substances in the  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP effluent. ICP analysis (see Appendix C), however, did not show reductions in any of the metals selected for quantification. Whatever the case might be, 90% reduction in Ca left the clarified  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP effluent with no more than 100 mg/L (~2.50 mmol Ca/L) of soluble Ca.

The purpose of reducing soluble Ca in solution is to avoid removal of phosphates by Ca and maximize  $\text{PO}_4$  recovery by struvite. Calcium dihydrogen phosphate ( $\text{Ca}(\text{H}_2\text{PO}_4)_2$ ), out of all the calcium phosphates, has the highest molar P to Ca ratio. However, formation of  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  is less likely to occur. Formation of hydroxyapatite, as described in equation (16), is most likely to occur and has a P : Ca molar ratio of 3:5. Lowest observed  $\text{PO}_4$ -P concentration in the clarified  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP effluent was 110 mg/L (~3.55 mmol P/L). Therefore, in the worst possible situation, where the manure slurry has high Ca concentration coupled to low  $\text{PO}_4$  concentration, Ca levels may still be too high even after OA treatment. In the vast majority of the manure slurries treated with the  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP process, soluble  $\text{PO}_4$ -P ranged between 170 – 250 mg/L (5.49 – 8.07 mmol P/L). During average conditions, there is ample phosphate available for struvite crystallization.



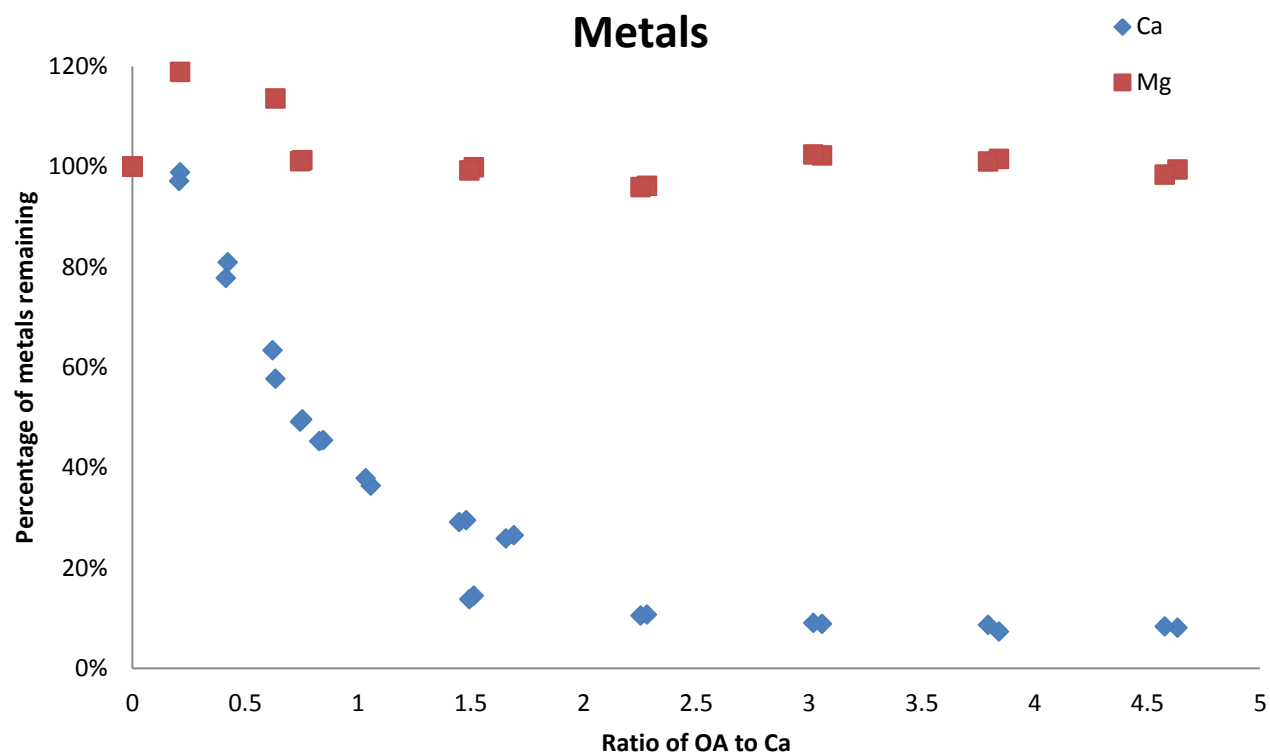


Figure 4.2. Effect of OA treatment on the soluble Mg and Ca concentrations in post clarified liquid fraction of  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP effluent.

## 4.4 Conclusions

The use of OA for treating clarified  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP effluent showed a 90% Ca removal, when OA was added at a molar OA to Ca ratio of 2:1. A maximum soluble Ca removal of 97.2% was observed in the OA concentration range used. With that said, manure Ca concentrations should be monitored for proper treatment with OA. Monitoring the total Ca concentration of the raw manure slurry is sufficient, since almost all of the Ca was observed to be solubilised by the  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP process. Soluble Mg was not significantly decreased in the experiments performed.

The level of OA addition led to a decrease in pH. The pH of the solution decreased from 4.03 in the case where OA was not used, down to 1.68 at the highest OA concentration of 4.63 mmol/L. The downstream struvite crystallization process requires caustic for pH elevation, to at least  $\text{pH} = 6.8 - 7.2$ . Therefore, knowing the final pH of the solution after OA treatment, will aid in optimization and calculation of the overall operational costs of the system.

## **Chapter 5: Struvite recovery**

A description of the mineral struvite was given in Chapter 1. A generalized version of its chemistry, as well as how struvite crystallizes, was discussed. The crystallization reactor used in these experiments was described in Chapter 2. The current chapter will describe the reaction conditions used for our pilot scale study. Phosphorus recovery efficiency from dairy manure, after the pre-treatment process, was tested and discussed.

### **5.1 Introduction**

In the past, struvite has commonly scaled on equipment/pipe surfaces of WWTPs, with anaerobic digestion and post-digestion processes. The scaling was thought to be caused by solubilisation of struvite constituents, during the digestion process, where the ion concentrations reached supersaturated conditions. To mitigate the problem of struvite formation on equipment, much research was done to find ways of recovering the struvite beforehand. A number of reactors exist for struvite crystallization, with fluidized bed reactors being the reactor type of choice. A variety of bench, pilot and full scale studies have been done for struvite recovery from wastewater and have been reviewed by Doyle and Parsons (2002). The chemical constituent of what enters the struvite crystallization reactor can be adjusted, often by chemical addition or pH change, so that concentrations reach beyond saturation  $K_{sp}$  for struvite to form.

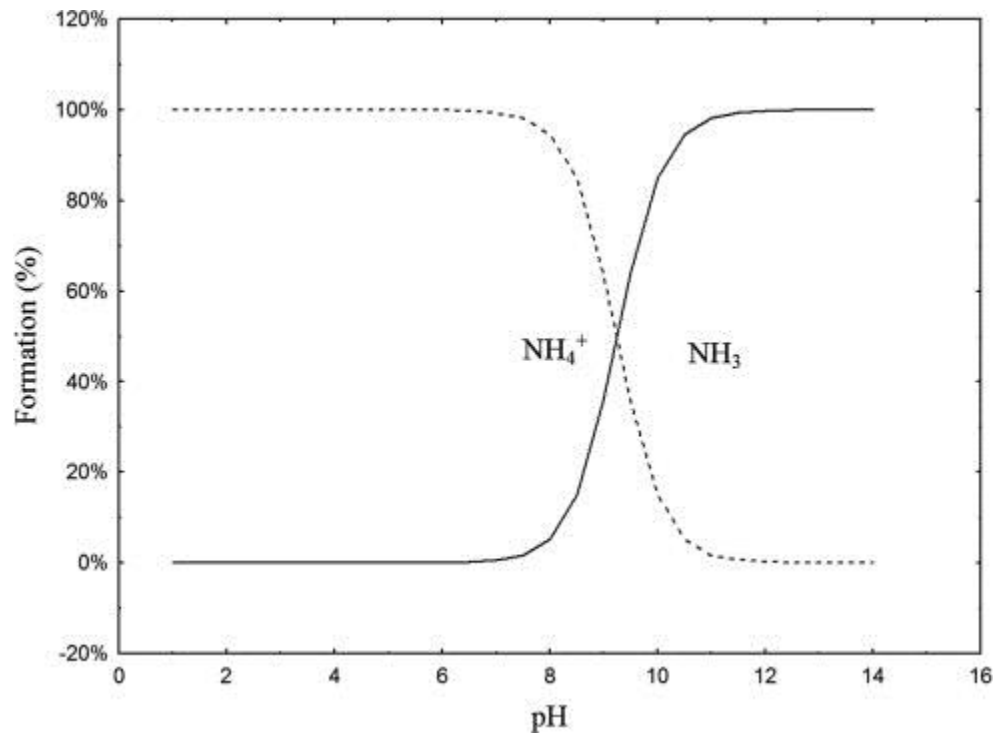
The reactor used for this study is an upflow, fluidized bed reactor. Fluidized bed reactors, by definition, contain two distinct phases. Inside the reactor used for this study, the liquid phase flows through the reactor where they come into contact with the solid phase. The surfaces of the solid phase are where the desired reaction occurs. In past studies, various seed materials have been used as the solid phase for struvite to grow upon (e.g. Battistoni *et al.*, 2000; Perez-

Rodriguez *et al.*, 1992; Stratful *et al.*, 1999; Greaves *et al.*, 1999). In the current study, the struvite crystallization reactor (CY), developed and patented at UBC, was used. The said reactor consists of a column reactor, as depicted in Figure 2.3, with four different cross sectional areas that increases from bottom to top. The seed material chosen for this study was struvite itself. Using struvite as a media for new struvite to grow not only produces a product that is more pure, but should theoretically make struvite crystallization easier, since the energy required for struvite to grow on like crystals is less than growing on a foreign substance.

As described in previous chapters, struvite is more soluble in acidic pH and highly insoluble in basic pH conditions. By exploiting this property, struvite can be forced to precipitate. Adnan *et al.* (2003) found that the P removal efficiency can be controlled by merely adjusting the reactor operating pH. It is likely that as pH changes, the speciation of both ammonium and phosphate will change, as shown in Figure 5.1 (a) and (b). Therefore, by changing the operating pH in the reactor, the degree of struvite saturation will change. The operating pH must be constantly monitored and adjusted since pH of the solution is expected to decrease due to the crystallization reaction. At the operating pH values used during this study, majority of the phosphate species existed as  $\text{HPO}_4^{2-}$  and  $\text{H}_2\text{PO}_4^{1-}$ . As the  $\text{HPO}_4^{2-}$  becomes incorporated into the struvite crystalline structure, a free proton is expected to form and thus decrease the solution pH (Schuiling and Andrade, 1999). In order to adjust the pH back to operating values, caustic soda has been used with success (*e.g.* Yaffer *et al.*, 2002; Ueno and Fujii 2001; Celen and Turker, 2001) and will be the method used for this study.

In order for struvite to precipitate out of solution, the product of the mineral's constituent concentrations must be equal or greater than the  $K_{sp}$  value. Selection of the correct  $K_{sp}$  to use is important, since recorded and published values have a range as wide as 5 orders of magnitude.

a)



b)

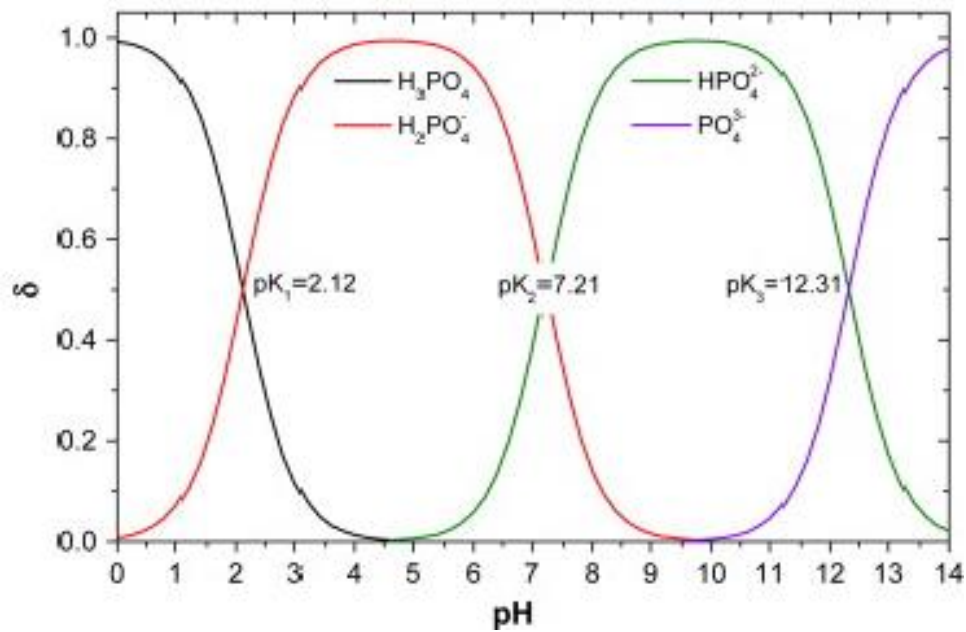


Figure 5.1. a) Speciation of ammonium and ammonia as a function of pH (Markou and Georgakakis, 2011). b) Species of phosphate as a function of pH (Pan *et al.*, 2009)

The  $pK_{sp}$  chosen for this study was 13.26 (Ohlinger *et al.*, 1998) since it considers ionic strength effects and availability of the struvite constituents.

The efficiency of phosphate recovery not only depends on struvite solubility, but also on the stoichiometrical quantities of struvite's component ions in solution. Using a CY reactor similar to the one in the current study, Adnan *et al.* (2003) found a linear relation ( $R^2 = 0.9955$ ) between phosphate removal percentage and Mg:P molar ratio when treating synthetic wastewater. In order to maximize phosphate recovery as struvite, the molar ratio of  $PO_4$  to either  $NH_4$  or Mg should both be less than 1, so that  $PO_4$  remains as the limiting reagent in the reaction. In a study conducted to find the effect of Mg on phosphorus recovery, it was found that a molar ratio of Mg to P was optimal at 1.3:1 (Adnan, 2002). Mg was often lacking in previous studies completed for wastewater treatment; however, dairy manure has more than sufficient Mg in solution for complete P removal by struvite crystallization.

An effective method for describing struvite's precipitation potential is by a value termed the supersaturation ratio (SSR). SSR can be defined as the quotient of the ion product (Q) to the conditional solubility product  $K_{so}$ . In this case, Q and the SSR can be calculated using equations (17) and (18) respectively.

$$Q = [NH_4 - N][PO_4 - P][Mg] \quad (17)$$

Where the values in [ ] are the molar concentrations of the dissolved substance.

$$SSR = \frac{Q}{K_{so}} \quad (18)$$

Therefore, struvite precipitation should occur when the solution is supersaturated and  $SSR > 1$ ; vice versa when  $SSR < 1$ . When the  $SSR = 1$ , then  $Q = K_{so}$  and equilibrium conditions are reached. In a supersaturated solution, the degree of supersaturation will determine the

spontaneity of nucleation. The region of supersaturation, where crystal growth outweighs nucleation, is called the metastable zone. Knowing the upper limit of the metastable zone will determine whether the existing struvite will grow or new fine crystal nuclei will form. To maintain metastable conditions within the reactor, the influent solution is diluted by the recycled effluent. The recycle also plays a role in increasing the upflow velocity, and turbulence of the liquid phase, since it was hypothesized that crystal growth is limited by low mixing energy (Ohlinger 1999).

## **5.2 Materials and Methods**

### **5.2.1 Influent Material**

The influent material that entered the CY reactor was dairy manure slurry that had been treated using  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP, cleared of solids, and finally treated with OA for soluble Ca removal (as described in previous chapters). To minimize the use of sulphuric acid, while solubilising a respectable percentage of P, raw manure was acidified to pH3.5 only. This manure was combined with 0.3%  $\text{H}_2\text{O}_2$  for the  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP process. Batches of  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP effluent were collected daily and solids were allowed to settle, for a minimum of 8 hours to a maximum of 14 hours, in a clarifier. The clarified liquid fraction of the  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP effluent was then transferred to a second clarifier where OA (technical grade 99.6%, Univar) was added for Ca precipitation. Using the total Ca concentration found in the raw manure slurry, OA was added at a molar concentration that was 2 times that of Ca.

Now devoid of suspended solids and Ca, the liquid material was termed CY influent. All CY influent was transferred to a storage tank until ready for the struvite crystallization experiments. In most cases, approximately 1000 L of CY influent was collected for each CY run.

The pH of the CY influent was slightly below 2.0, which allowed us to assume that the solution would remain sterile for the duration before it was used in the CY process.

One positive aspect of recovering P from dairy manure, via struvite crystallization, is that the material was Mg rich. In many previous works on struvite crystallization, soluble Mg was a limiting reagent (e.g. Wu and Bishop, 2004; Bhuiyan *et al.*, 2009) in the influent materials. In previous studies using similar reactors, the Mg would be added through an injection port near the bottom of the CY reactor. As described earlier, the soluble Mg concentration after  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP and OA treatment was stoichiometrically greater than soluble  $\text{PO}_4$ . Mg addition was not necessary in these experiments, hence a potential cost savings for a full scale application.

### 5.2.2 Chemicals

The only chemical addition made to the reaction was technical grade sodium hydroxide (98.5% purity, Univar). The appropriate concentration of the NaOH stock solution depends on the pH of the influent material and the recycle ratio. Due to limitations of the pH controller, only a certain range of [NaOH] stock solution will provide the appropriate operation pH. With that said, it was found that 0.5 – 0.7 molar solution of NaOH worked well in the experiments conducted.

The pH within the bottom section of the CY reactor was monitored by a pH controller. When the reactor pH reached below that prescribed by the crystallizer model (described in chapter 5.2.3), it would pump NaOH solution via a port close to the bottom of the CY reactor.



### 5.2.3 Crystallizer Model

Struvite crystallization chemistry, and its potential for phosphate recovery, were modeled with success. Selection of the correct  $K_{sp}$  value is critical for determining the SSR. The  $pK_{sp}$  chosen for the crystallizer model was 13.26. As mentioned previously, Doyle and Parsons (2002) compiled a list of measured struvite  $K_{sp}$  values that are found in literature. The  $K_{sp}$  and their corresponding  $pK_{sp}$  values range from  $3.98 \times 10^{-10}$  to  $5.50 \times 10^{-14}$  and 9.4 to 13.26, respectively. Since this study was meant as a preliminary look at whether the  $H_2O_2/MW/H^+$ -AOP and OA pretreatment of dairy manure is suitable for producing an influent material of the CY reactor, the crystallizer model was not contested for its validity.

The input parameters for the crystallizer model include soluble [Mg], soluble [NH<sub>3</sub>-N], soluble [PO<sub>4</sub>-P], conductivity, reactor geometry, temperature, recycle ratio, desired SSR, and upflow velocity. The model uses these parameters to establish the desired pH for the reactor, as well as predict the constituent concentrations in the effluent.

Three reactor conditions that were interesting for discussion are listed in Table 5.1. Recycle ratio and SSR were two important reactor conditions that were varied in the experiments conducted. The reactor pH values were calculated using the crystallizer model.

Table 5.1. Description of experimental crystallization reactor conditions used.

Experiment	PO <sub>4</sub> -P (mg/L)	NH <sub>3</sub> -N (mg/L)	Mg (mg/L)	SSR	Upflow Velocity (cm/min)	Recycle Ratio	pH
1	63.5	627	139	5	400	5	7.49
2	197	1002	398	5	575	10	7.26
3	245	1233	387	3	580	12.7	6.77

#### 5.2.4 Experimental Reactor Conditions

The current study, like many experiments at a pilot scale, is nearly impossible to replicate. The content of dairy manure has a high degree of variation, thus causing deviation in the concentrations of struvite constituents in the CY influent from batch to batch. Temperature within the reactor varied constantly. Since the reactor temperature could not be controlled, constant reaction conditions were impossible to maintain.

Self-seeding in the CY reactor, to produce crystals large enough for harvest, is very time intensive. With the volume of CY influent material accumulated for each experiments, there was not enough to grow crystals to the desired size for harvest. Therefore, previously formed struvite pellets were used as seed material. Crystal seed was first graded using a standard number 10 and 18 sieve (2 mm and 1 mm opening, respectively). The seed added to the reactor all had a diameter between 2 and 1 mm. When harvesting, the solid phase from the reactor that were used for analysis was greater than 2 mm in diameter.

During the period of time when struvite crystallization was studied, the variation in manure nutrient content was greater than during  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP experiments. Manure TP in this period was observed to be as low as around 60 mg/L and as high as about 250 mg/L; TKN to TP ratio varied more than early experiment and ranged between roughly 5 and 10. For this reason, crystallization experiments were conducted in batches, so that constant constituent monitoring was not required. CY influent material was collected until about 1000 L was accumulated. Each batch of CY influent was manually stirred before samples were taken and analysed for their soluble struvite constituents. Due to the pretreatment processes used for the manure, pH of the CY influent was always below 2.0. Therefore, the solution remained relatively sterile and biochemical effects were not expected. The low pH also caused the solution to be undersaturated

for struvite. For both these reasons, changes in soluble nutrients for each batch were not observed over long periods of time.

The CY reactor was placed outdoors and, thus, temperatures would fluctuate throughout the day. Temperature of the reactor solution was an input parameter in the reactor model used to determine appropriate operating pH. During the day, the fluid temperature reached as high as 15°C, and dropped to 5°C at night. The temperature change was, unfortunately, not constantly monitored. Due to the temperature changes, the thermodynamics and equilibrium of the crystallization reaction were expected to change. In this case, the reactor SSR will not be the predetermined value. For example, under one of the struvite crystallization experiments with a desired SSR of 5, the operating pH differed by as much as 0.46, when temperature decreased by 10°C. In this case, if the operating pH was not corrected, the reactor solution would be more supersaturated than what was desired. With the solution being too supersaturated, it is possible the SSR had reached beyond the upper limit of the metastable zone. If so, nucleation is likely to occur, more than crystal growth, and cause struvite formation to increase while its recovery yield would decrease.

### 5.2.5 Analysis of Effluent and Crystals

Analysis of the CY effluent was conducted for residual  $\text{NH}_3\text{-N}$  (Standard Methods 4500- $\text{NH}_3\text{ H}$ ) and  $\text{PO}_4\text{-P}$  (Standard Methods 4500-P G) according to Standard Methods. Samples were taken at designated times after start of the reactor. Since crystallization optimization, *per se*, was not one of the scopes of this study, struvite recovery yield was not examined in detail. Instead, the formation of new struvite crystals in the reactor was measured by growth in crystal size, increase in crystal mass, and changes in crystal morphology.

X-ray crystallography and chemical analysis methods were also used to determine the existence of struvite crystals in the harvested material. X-ray diffraction crystallography was conducted on the Bruker D8 Advanced X-ray Diffractometer, using  $\text{CuK}\alpha$  radiation. Power Diffraction File database PDF-2 was used for peak identification. Measured quantities of harvested crystals were dissolved in known volumes of 5% HCl solution for chemical analysis.  $\text{NH}_3\text{-N}$  and  $\text{PO}_4\text{-P}$  were conducted as described in earlier chapters. Metals were analyzed by either ICP or flame-AA, as described in earlier chapters.

It should be noted that large amounts of precipitate accumulated inside the external clarifier of the CY reactor. The accumulation of fine precipitate in the external clarifier may have occurred for two reasons. Firstly, it is possible that the upflow velocity was too large and CY reactor's internal clarifier was not able to trap the fine struvite nuclei. The second reason may be due to the rate of struvite nucleation being too slow, and supersaturated liquid was entering the external clarifier. Since the HRT of the external clarifier was long, nuclei would form inside the clarifier. Complete harvest of the fine material was not possible. However, a sample was taken and cleaned for analysis by X-ray crystallography.

## **5.3 Results and Discussion**

### **5.3.1 Experiment 1**

The soluble struvite constituent concentrations in the CY influent material used for experiment 1 were 63.5 mg/L  $\text{PO}_4\text{-P}$ , 627 mg/L  $\text{NH}_3\text{-N}$ , and 139 mg/L Mg. The strength of the CY influent in experiment 1 was relatively weak compared to most dairy manures observed at DERC. Other input parameters used for the crystallizer model were 115 000  $\mu\text{S/cm}$  for conductivity; desired SSR of 5.00; a  $Q_i$  of 340 mL/min and RR of 5.00; the upflow velocity was

400 cm/min at the reactor section with lowest diameter. The liquid temperature was monitored at random times throughout the experiment. The majority of the observed temperatures during day time was roughly 15°C. Therefore, using the crystallizer model, the solution pH 7.49 was calculated. The temperature at night reached as low 11°C, and operating pH was adjusted accordingly.

Samples of the CY effluent material were taken at predetermined time intervals after the operating pH stabilized. The samples were preserved and analyzed for soluble  $\text{NH}_3\text{-N}$  and  $\text{PO}_4\text{-P}$ . Results of the analysis were plotted against the post-pH stabilized times that the samples were taken (see Figure 5.2). The highest observed  $\text{PO}_4\text{-P}$  and  $\text{NH}_3\text{-N}$  removal was approximately 69% and 27%, respectively. Interestingly enough, the highest  $\text{PO}_4\text{-P}$  removal did not coincide with the highest  $\text{NH}_3\text{-N}$  removal. In fact the observed ratio of  $\text{NH}_3\text{-N} / \text{PO}_4\text{-P}$  removed had a range between 2.4 - 9.9 mmol/mmol. Theoretically, struvite removes one ammonia for every phosphate. The higher than expected removal of ammonia could be attributed to volatilization or impurities in the solid phase.

To the surprise of this researcher, the harvested solid phase from the CY reactor under these reaction conditions produced a solid with three distinct morphologies. The substances were manually separated, based on colour and were labelled white, medium, and brown. A known quantity of each crystal type was dissolved in a known volume of 5% hydrochloric acid before being analyzed for its chemical composition. The actual amounts of each sample used and the predicted concentrations of struvite constituents, if the sample were pure struvite, are recorded in Table 5.2. Two different dilutions of each sample were made and each dilution was analyzed 3 times for  $\text{PO}_4\text{-P}$  and  $\text{NH}_3\text{-N}$ ; each dilution was analyzed for metals twice, using ICP.

Each sample was analyzed for total organic carbon (TOC) in triplet. The resulting concentrations of each analyte are shown in Table 5.3.

Table 5.2. Pellet samples used for analysis from experiment 1. Quantities dissolved and concentrations expected.

	Mass used (g)	Vol of 5% Nitric Acid (mL)	Expected N (mg/L)	Expected P (mg/L)	Expected Mg (mg/L)
Brown	0.1875	100	107	237	186
Medium	0.2062	100	118	261	204
White	0.1904	100	109	241	189

Table 5.3. Chemical composition of each pellet type generated from experiment 1.

		Brown		Medium		White	
		Mean	Std error	Mean	Std error	Mean	Std error
NH <sub>3</sub> -N	(mg/L)	40.22	0.239	65.30	1.88	57.24	0.269
	(mmol/L)	2.87	0.0171	4.66	0.134	4.09	0.0192
PO <sub>4</sub> -P	(mg/L)	57.75	0.814	120.01	0.295	115.40	0.134
	(mmol/L)	1.86	0.0262	3.87	0.00953	3.72	0.00432
Ca	(mg/L)	224.21	22.0	1.99	1.15	0.48	0.279
	(mmol/L)	5.594	0.549	0.0497	0.0287	0.012	0.00696
Fe	(mg/L)	43.28	2.27	1.22	0.719	0.71	0.410
	(mmol/L)	0.775	0.0406	0.0218	0.0129	0.0127	0.00734
Mg	(mg/L)	69.76	3.73	179.62	6.73	152.66	4.74
	(mmol/L)	2.87	0.153	7.39	0.277	6.28	0.195
Mn	(mg/L)	3.30	1.91	*	*	*	*
	(mmol/L)	0.0601	0.0347	*	*	*	*
Zn	(mg/L)	8.99	4.98	*	*	*	*
	(mmol/L)	0.137	0.0762	*	*	*	*
Li	(mg/L)	0.31	0.0961	0.16	0.0659	0.169	0.0713
	(mmol/L)	0.0447	0.0138	0.0236	0.00950	0.0244	0.0103
Sr	(mg/L)	1.46	0.124	0.027	0.00509	0.00472	0.00278
	(mmol/L)	0.0167	0.00142	3.05x10 <sup>-4</sup>	5.81x10 <sup>-5</sup>	5.39 x10 <sup>-5</sup>	3.17 x10 <sup>-5</sup>
K	(mg/L)	40.96	14. 7	51.87	15.9	49.20	19.78
	(mmol/L)	1.05	0.375	1.33	0.408	1.26	0.506
Na	(mg/L)	58.14	20.465	132.51	40.1	206.85	78.7
	(mmol/L)	2.53	0.890	5.76	1.74	9.00	3.42
TOC	(mg/L)	71.30	0.872	2.10	0.308	9.50	0.571

\* Represent values that were below detection limit.

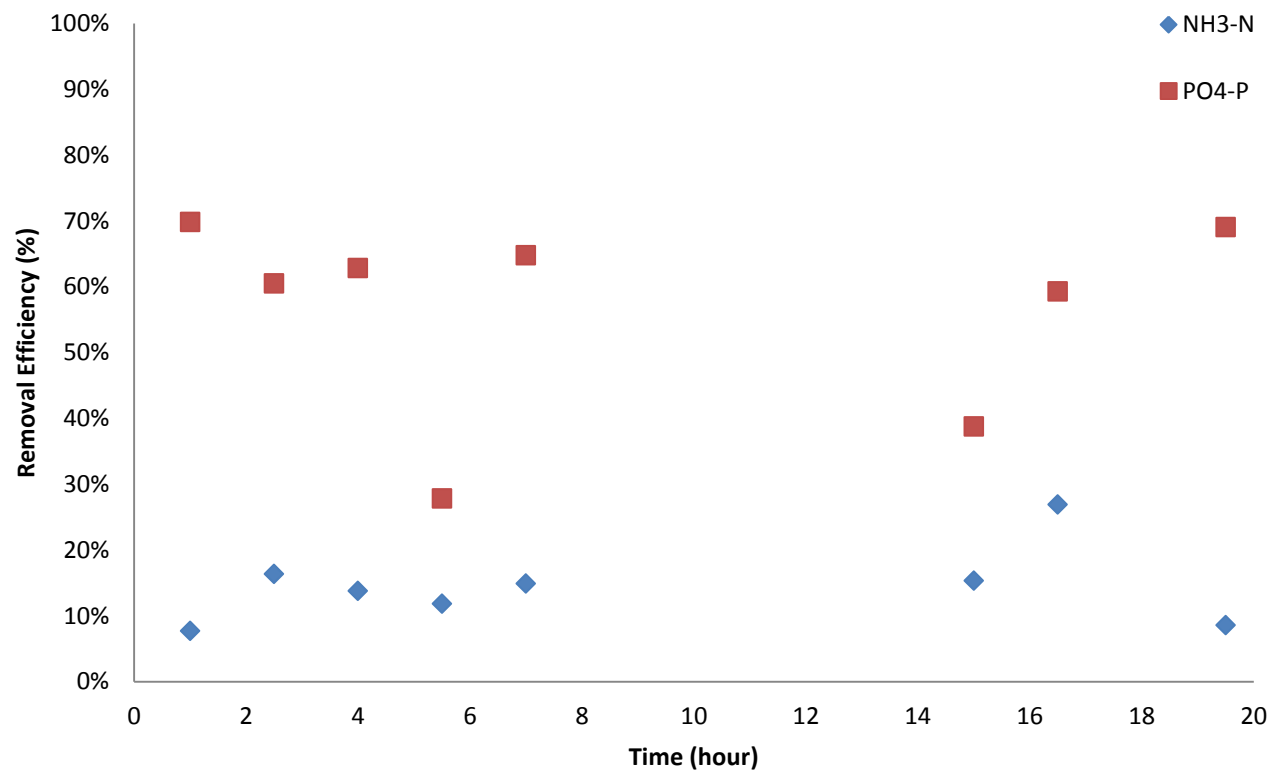


Figure 5.2. A plot of the removal efficiencies for soluble  $\text{PO}_4\text{-P}$  and  $\text{NH}_3\text{-N}$  in experiment 1.

It was very clear from first glance that the amount of struvite constituents in the samples were, especially for nitrogen and phosphorus, much less than the expected values. The obvious explanation for the low yield is the presence of impurities. Therefore, various constituents that held significant quantities in the three crystal types were normalized against the molar quantity of  $\text{PO}_4\text{-P}$ , and are presented in Figure 5.3. The ideal and pure struvite crystal would contain Mg,  $\text{NH}_3$ , and  $\text{PO}_4$  in equimolar ratios with one another. Any deviation from equimolar ratios will help identify contaminants, as well as the type of compounds being formed inside the CY reactor.

Through this analysis, it becomes noticeable that the medium and white coloured crystals were, more or less, of consistent composition. The only significant difference between the medium and white coloured crystals appears to be the larger proportion of Na in the white. The brown crystals appear to contain much more contaminants, including Fe and Ca that were not found in noticeable quantities elsewhere. It may be possible that the brown appearance is a result of oxidation of the Fe contaminant.

What was curious to see was the existence of K in each of the sample types. Dairy manure is a fairly rich source of K. More often than not, dairy manure is used locally as soil amendments, to grow feedstuffs for on-site consumption. Prolonged dairy effluent irrigation has led to K accumulation in the fields and higher K concentration in the feed. Increased K consumption for dairy cattle has been shown to cause increased incidences of milk fever (Goff and Horst, 1997). Removing K from the dairy waste stream will be an ideal way to decrease K accumulation, without interrupting crop production patterns and methods.

Both the morphology and composition of the three crystal types were distinct from one another. The white crystals had a pearly lustre and smooth appearance, with the shape being spherical to oval. The smooth appearance suggests that the crystals formed by crystal growth



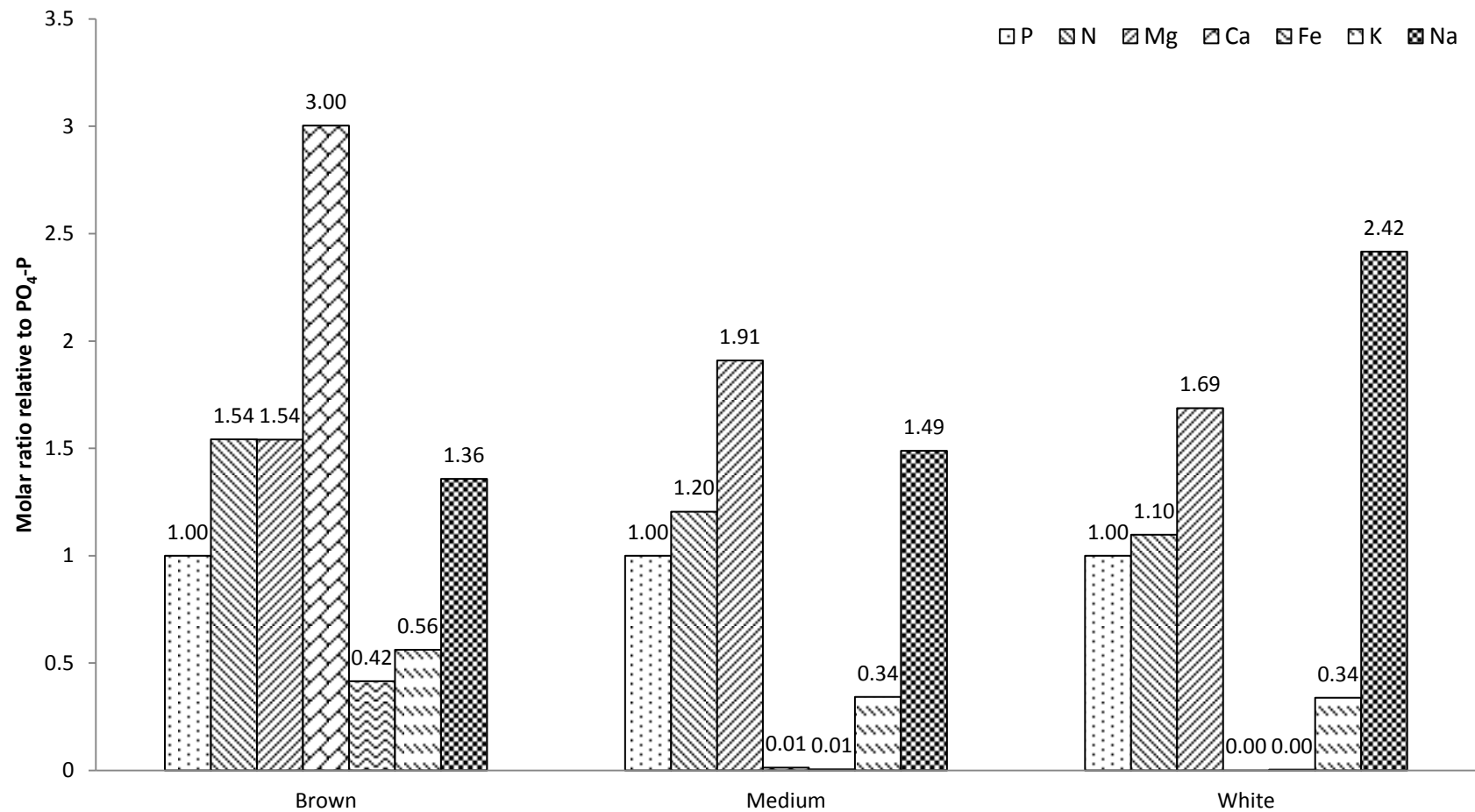


Figure 5.3. Molar ratios, relative to  $\text{PO}_4\text{-P}$ , of each detected element from each of the dissolved pellet types.

then rounded due to abrasion and shear from their surroundings. The medium coloured solids were more porous on the surface compared to the white. There also appear to be spherical lumps on the medium coloured pellets, suggesting that it formed through agglomeration of smaller pellets. The brown pellets had very few rounded edges and corners. In fact, the majority were platelet shaped with jagged edges. The microscopic images reveal the brown pellet to be an agglomeration of many small crystalline particles.

From the microscopic appearances of each coloured pellet, the possibility of each pellet to be composed of more than one crystal type and even amorphous compounds are likely. A relatively simple method of identifying crystalline substances is through X-ray crystallography. X-ray crystallography is a technique that uses a crystal's ability to create unique diffraction patterns for identification. Therefore, each colour type was pulverized using a mortar and pestle before analyzed by X-ray diffraction crystallography. Both microscopic photos and X-ray diffraction patterns of the white, medium, and brown crystals are shown in Figure 5.4 a), b), and c) respectively.

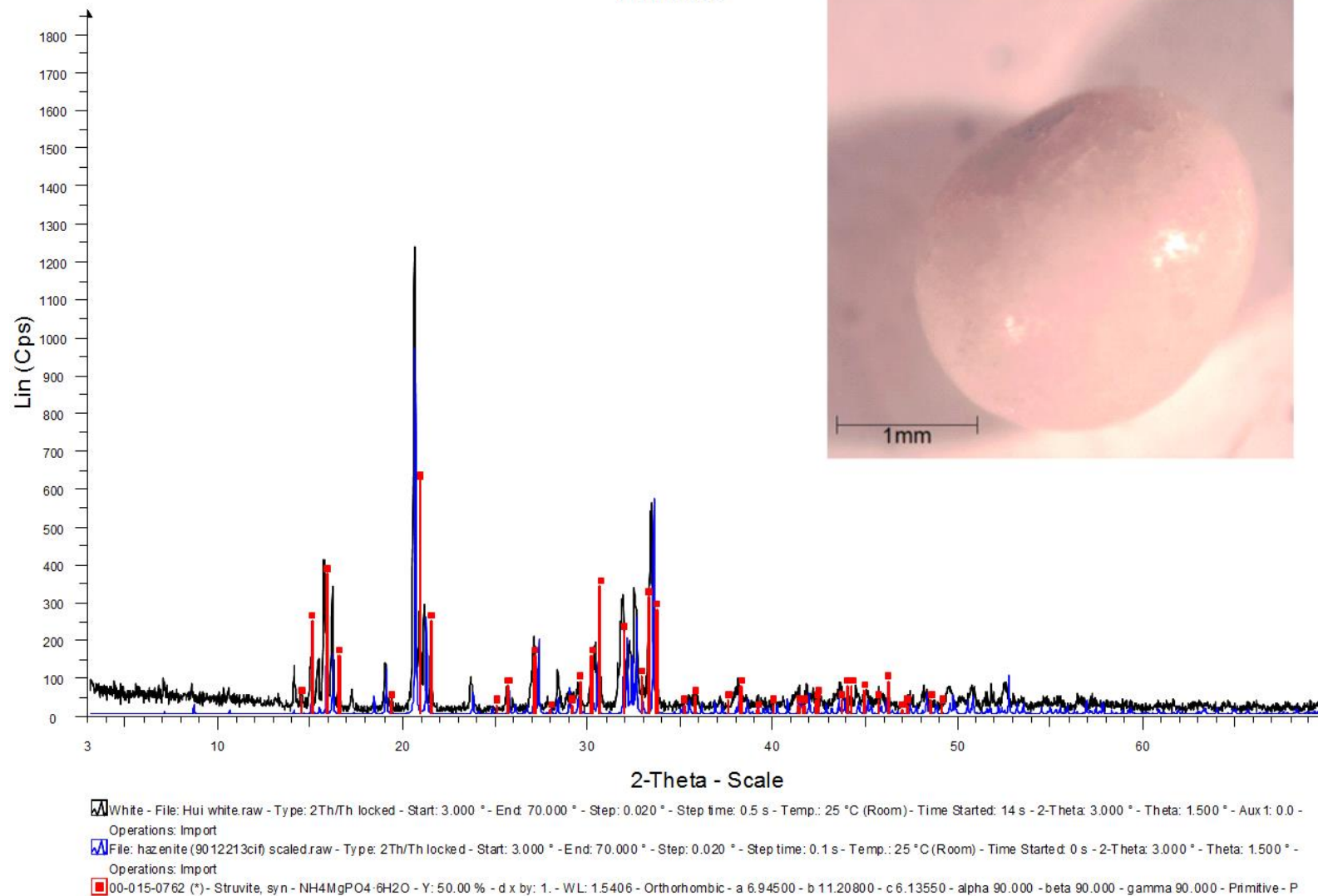
Plots of the diffracted X-ray intensity versus the incident angle  $2\theta$  of the white and brown crystals contained the pattern produced by the crystals themselves, peaks shown in black line; those peaks generated by struvite as provided by the database Powder Diffraction File (PDF-2) for peak identification, shown in red bars; the bars shown in blue are those produced by the potassium containing mineral  $\text{KNaMg}_2(\text{PO}_4)_2 \cdot 14\text{H}_2\text{O}$  (hazenite) and was generated from the work of Yang *et al.*, 2011. Hazenite is a hydrous, alkali, magnesium phosphate mineral that is a member of struvite group of minerals. Due to its recent discovery, the diffraction pattern for hazenite was not found in PDF-2 database.

Hazenite was specifically chosen since it was the only mineral containing K and Na that had diffraction patterns which matched that of the pellets produced in the CY process. The diffraction patterns of both white and brown crystals show the presence of both struvite and hazenite in the samples.

Figure 5.4 c) shows the microscopic photograph and X-ray diffraction pattern of the brown coloured pellets. In the diffraction pattern chart, the black peaks are those produced by the pellet itself. The green, blue, and red peaks are those produced by struvite, potassium struvite, and weddelite, respectively, as found in PDF-2. The sample patterns matched well with those of struvite and weddelite; K-struvite peaks did not match sufficiently to identify its presence in the sample. For K-struvite to form in theory, the influent material should be devoid of ammonia/ammonium ions, since K-struvite has slightly higher solubility than its ammonium counterpart. Nitrification and denitrification treatment has been previously shown to aid in K-struvite formation from calf manures (Schuiling and Andrade, 1999). Hazenite peaks also did not match with those produced by the sample. Therefore, the K and Na containing minerals were not identifiable for the brown coloured pellets. It should be noted that X-ray diffraction background noise produced by the brown pellets were relatively large, compared to those of the white and medium samples. The background noise may be a sign of amorphous compounds in the sample that is unidentifiable by X-ray diffraction analysis.

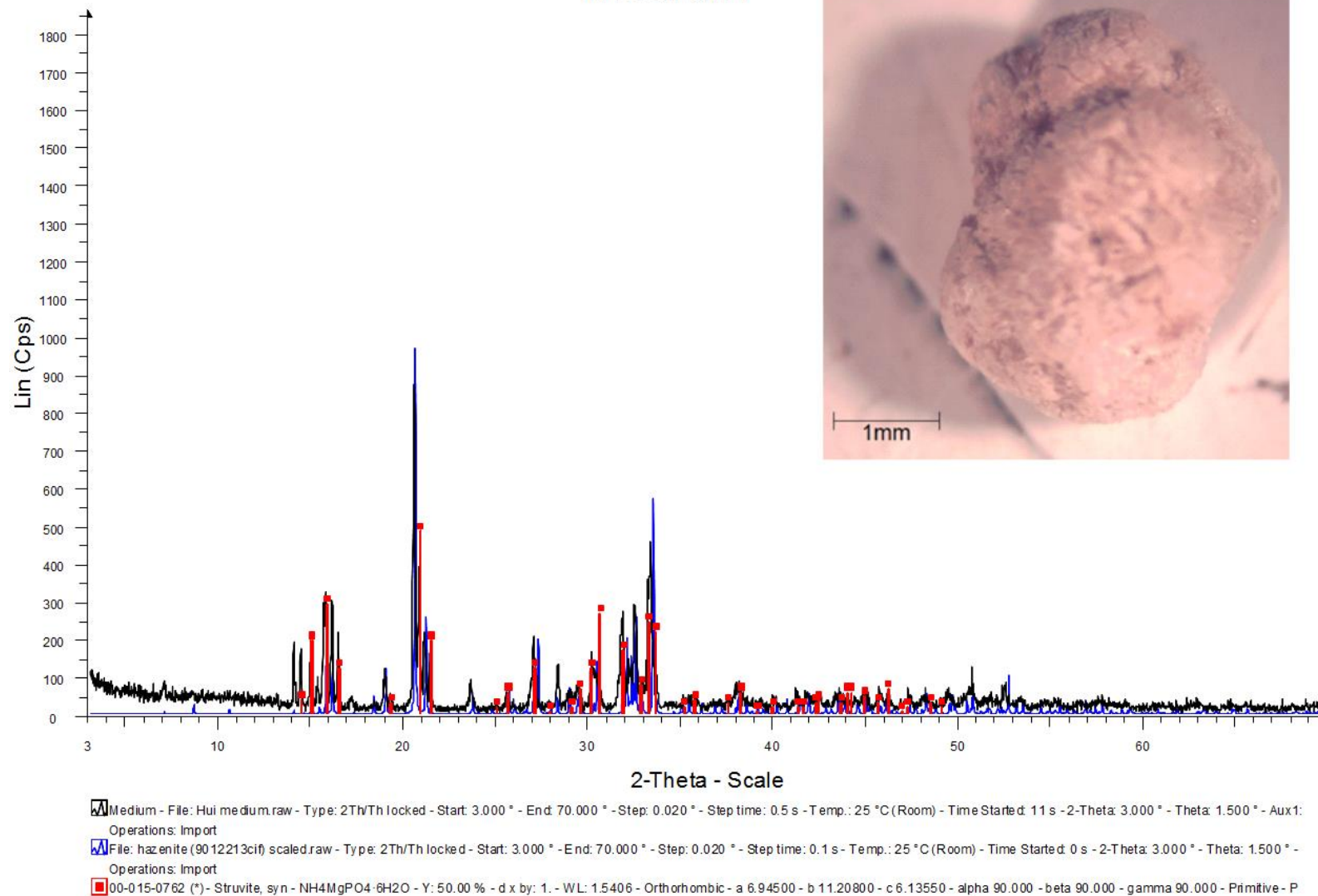
a)

White



b)

## Medium



c)

Brown

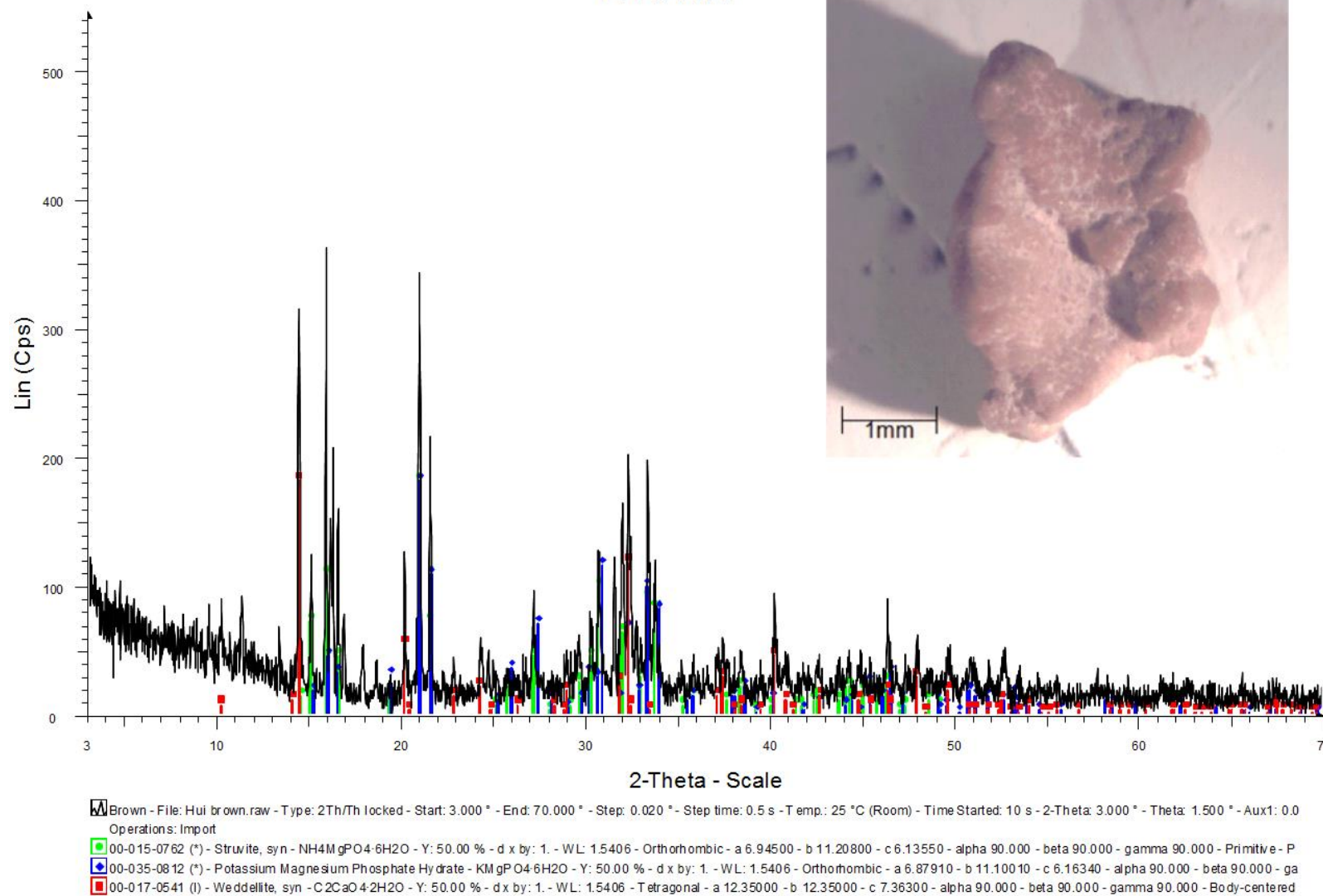


Figure 5.4. Representative microscopic images and X-ray diffraction patterns of the three pellet morphologies observed in the solid phase of the CY reactor in experiment 1. Plots a), b) and c) are those of the white, medium, and brown pellets respectively.

### 5.3.2 Experiment 2

The lower than expected  $\text{PO}_4\text{-P}$  removal, compared to previous studies at UBC, was thought to be due to reaction time. Therefore, the second CY experiment was conducted with a smaller  $Q_i$  and greater RR, in order to increase the HRT of the reactor. Water temperature reached as high as  $20^\circ\text{C}$  in the external clarifier in the duration of the experiment. The desired SSR was kept consistent with that of experiment 1. The  $Q_i$  and  $Q_R$  flow rates were measured to be 250 ml/min and 2450 ml/min respectively, making the RR about 9.8 and an upflow velocity of 533 cm/min. The influent material was characterized to be 197 mg/L  $\text{PO}_4\text{-P}$ , 1002 mg/L  $\text{NH}_3\text{-N}$  and 398 mg/L Mg. Using above parameters for the crystallizer model, it was determined that the operating pH should be 7.26. The seed pellets used for this experiment was struvite. The size of the seed material was reduced to less than 1 mm, in order to increase time between harvests.

At the time that reactor pH began to stabilize at the desired operating pH, grab samples of the CY effluent was taken at specific times of 1, 2, 4, 6, 8, 10, 12 hours. The influent was sampled at 1, 4, and 8 hours after pH stabilisation as well to better determine the efficiency of the reactor. Both the influent and effluent samples were analyzed for soluble Mg,  $\text{NH}_3\text{-N}$ , and  $\text{PO}_4\text{-P}$ . The effluent values were paired, time wise, to the influent values and the removal efficiency is presented in Figure 5.5.

The increased RR has led to increased  $\text{PO}_4\text{-P}$  removal, compared to the conditions used in experiment 1, once the reaction reached its steady state. It is interesting to note that the observed removal efficiencies decreased in the first 2 hours for  $\text{PO}_4\text{-P}$  and first 4 hours for Mg and  $\text{NH}_3\text{-N}$ . The initial drop in observed removal efficiency may be due to the operation pH having yet to reach a stable value. The pH controller would first inject caustic into the reactor at a higher rate

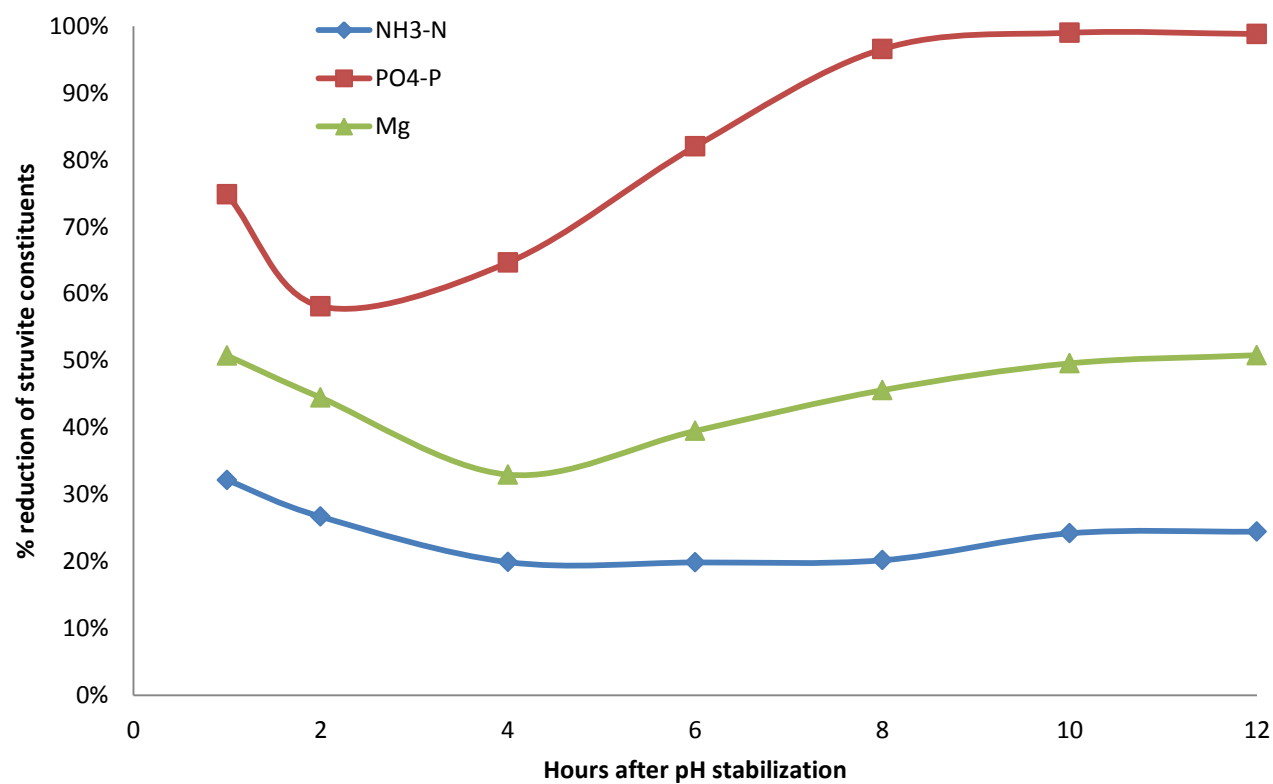


Figure 5.5. Removal efficiency for each struvite constituent in experiment 2. The red, green, and blue lines are the percent removal of PO<sub>4</sub>-P, NH<sub>3</sub>-N and Mg respectively.



than it would under stabilized conditions, thus increasing the reactor pH beyond that of the desired. The higher pH will lead to a greater struvite SSR in the reactor causing increased removal of struvite constituent ions from solution. The decrease in caustic flow from the pH controller would most likely be the cause for the removal efficiency to decrease.

PO<sub>4</sub>-P removal began to stabilize roughly 8 hours after reactor pH stabilized. The highest PO<sub>4</sub>-P removal efficiency reached 99% at steady state. The PO<sub>4</sub>-P removal seen in this experiment was higher than that observed in previous studies at UBC, and was higher than the 96% removal efficiency projected by the crystallizer model. NH<sub>3</sub>-N and Mg removal reached steady state at a later time compared to PO<sub>4</sub>-P, which was roughly 10 hours after reactor pH stabilization. Final NH<sub>3</sub>-N and Mg removal efficiencies were 24% and 51%, respectively.

The seed pellets in the CY reactor in experiment 2 were allowed to grow, with reactor on continuous mode, for 36 hours after the final effluent sample was taken. Harvested pellets in experiment 2 had different morphologies compared to that of experiment 1. Although both experiments produced white to medium coloured pellets in the harvested material, the plate shaped brown pellets found in experiment 1 were not observed to form in experiment 2. Instead, a new pellet type that appears smooth and round but near black in colour was found. A representative photo of what was harvested from experiment 2 is shown in Figure 5.6.

Since it was determined in experiment 1 that the medium to white coloured pellets had consistent constitution, these two pellet varieties were treated as such for their analysis and was labelled white, to differentiate it from the observed black pellets. Two samples weighing 0.2 g each of the white coloured pellets were pulverized, dissolved in 200 mL of 5% HCl, and analyzed for NH<sub>3</sub>-N, PO<sub>4</sub>-P, and Mg content. Analysis of each sample was carried out in

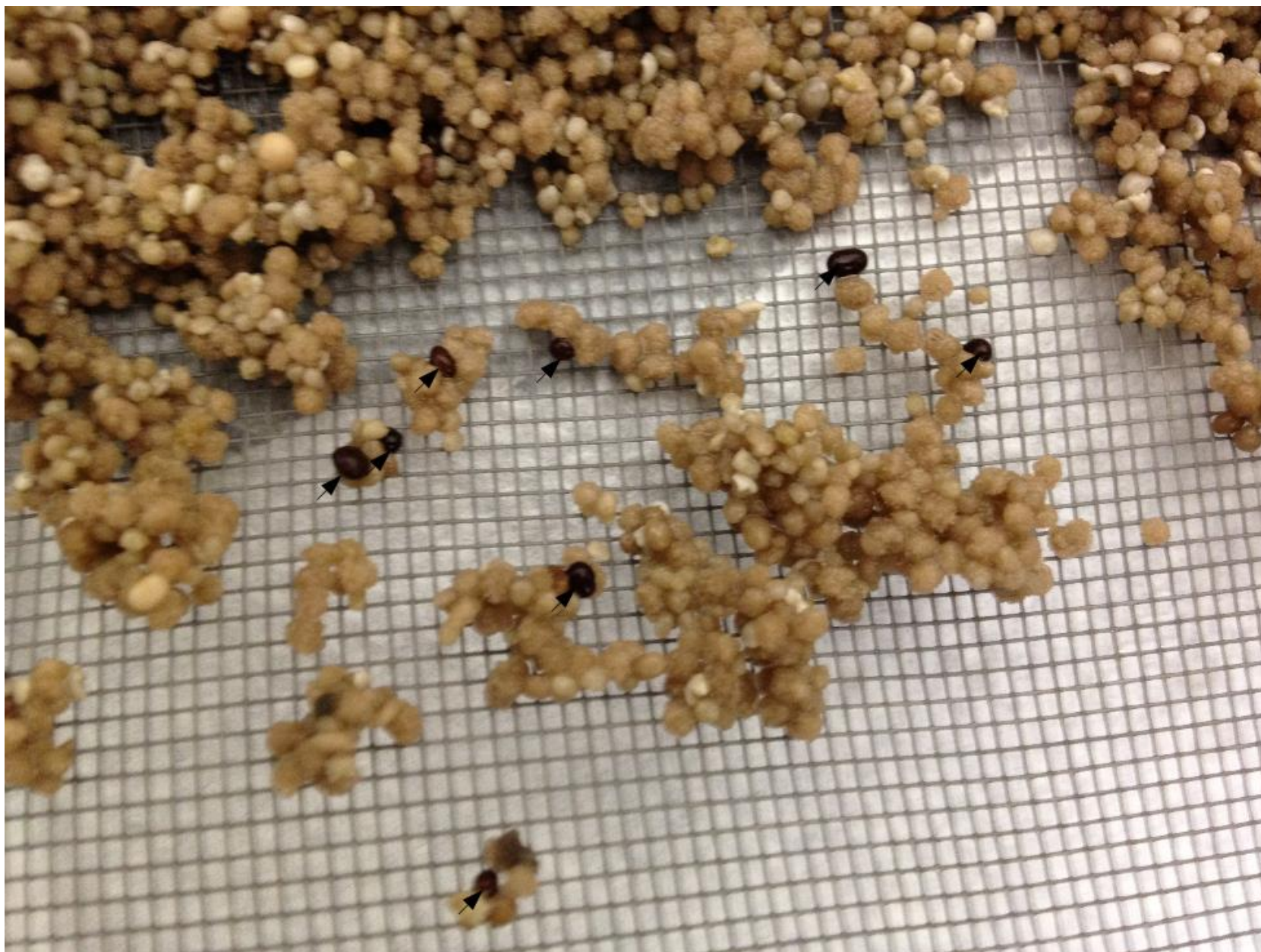


Figure 5.6. A representative photograph of the harvest from experiment 2. The black arrows point to the pellets considered to be “black”. The remaining pellets were, for the purposes of this study, termed “white”.

triplicates making a total of 6 measurements per analyte per sample. The expected versus measured quantities of each analyte is recorded in Table 5.4.

Table 5.4. Expected versus actual concentrations of each struvite constituent from dissolving 0.2 g of harvested white pellet material.

	NH <sub>3</sub> -N	PO <sub>4</sub> -P	Mg	Ca	Na	K
	(mg/L)					
Expected	57.0	126	99.0	n/a	n/a	n/a
Observed	55.7±1.38	127±3.75	89.2±0.350	8.40±0.039	1.29	2.16

The uncertainties are the standard errors about the mean.

The observed NH<sub>3</sub>-N and PO<sub>4</sub>-P values were in reasonable range to the expected concentrations. However, Mg was observed to be about 10 mg/L less than expected. ICP analysis also identified trace amounts of Ca, Na, and K, which indicates the presence of impurities in the struvite pellets. In comparison to the pellets harvested from experiment 1 however, those pellets produced in experiment 2 show much higher purity for struvite.

For more in-depth examination of the harvested materials, a plot is shown in Figure 5.7 for each struvite constituent removed from the influent and that which exist in the harvested white pellets. Each value was presented as a value normalized to the molar concentration for PO<sub>4</sub>-P. As shown, for each mole of PO<sub>4</sub>-P removed from the CY influent, 2.72 mole of NH<sub>3</sub>-N and 1.09 moles of Mg were removed. The large loss of NH<sub>3</sub>-N from the influent may be due to the formation of other ammonium containing minerals and salt, or it could be due to volatilization. In the case of experiment 2, the likelihood of ammonium salts to form were small, since they are highly soluble in aqueous environments. Another reason supporting volatilisation as the main mechanism for NH<sub>3</sub>-N loss is the strong scent of ammonia observed in the vicinities of the CY reactor. The loss of nitrogen in the crystallization process is not small, and may be

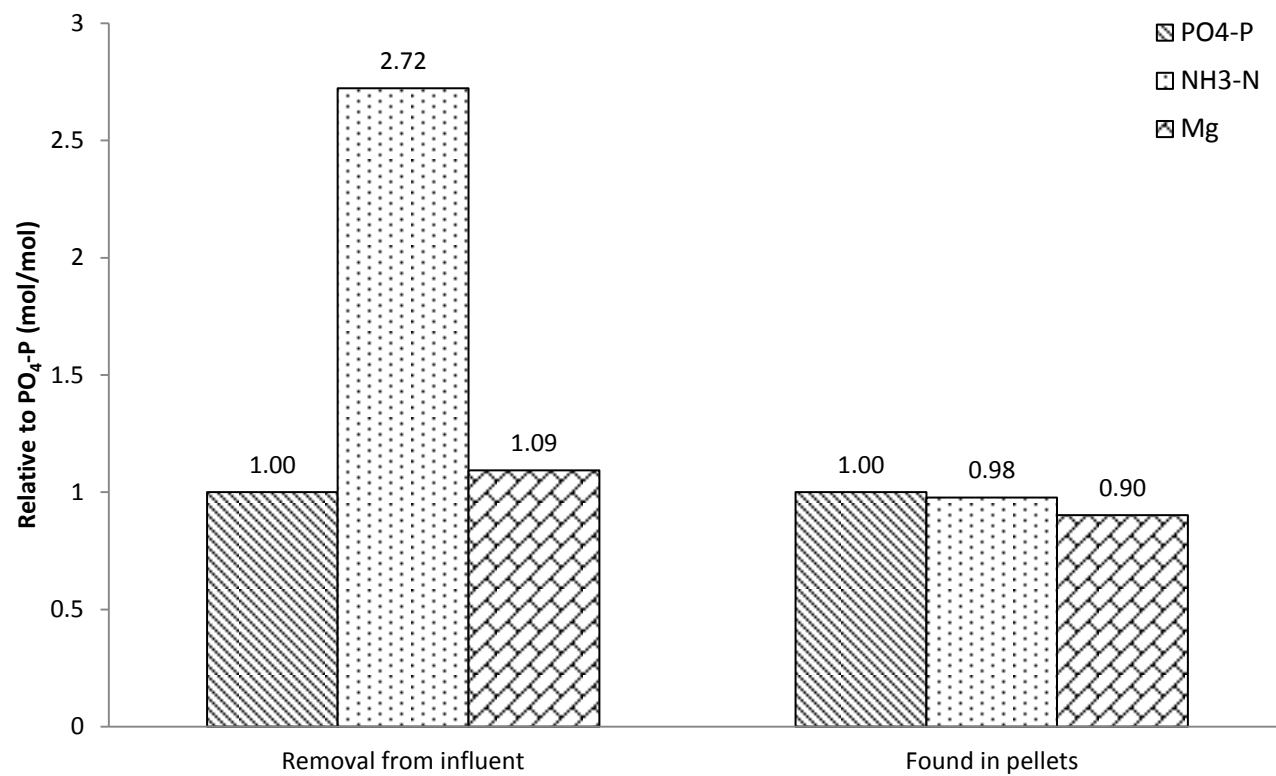


Figure 5.7. Molar ratios, relative to that of PO<sub>4</sub>-P, for the amounts of each struvite constituent removed from the influent and those found in the harvested pellets.

detrimental if the effluent should be used as soil amendments. However, the amount of nitrogen lost is comparable to the current storage conditions. It has been well documented that roughly 70% urine N and up to 13% of feces N is lost in slurry storage lagoons, which brings total average N loss to about 20% (Bussnik and Oenema, 1998).

Some possible solutions to reduce the rate of  $\text{NH}_3\text{-N}$  loss could be by technical means. If  $\text{NH}_3\text{-N}$  loss is indeed by volatilization, then it is possible to cover any openings of the CY reactor to reduce volatilization and isolate it from the environment. Acidification and covering of the effluent storage after treatment is also a possibility. These techniques have been known for a long time and now become available on large scale in practice.

In the pellets, however, molar quantities of both  $\text{NH}_3\text{-N}$  and Mg were found to be slightly less than that of  $\text{PO}_4\text{-P}$ . Such findings also give reason to believe that  $\text{PO}_4\text{-P}$  is being removed by means other than struvite crystallization. For this reason, X-ray diffraction crystallography was conducted on the two pellet types harvested from the experiment and the diffraction intensities is shown in Figure 5.8 a) and b) for the white and black pellets, respectively. Chemical analysis for the black pellets was not conducted due to the insignificance of its quantity in the harvested pellet.

In both charts, showing the diffraction intensities versus the incident angles, the black line is the actual produced by the pellets. The red intensities are those produced by struvite as identified by the PDF-2 database. In both pellet types, struvite was the only crystal identified by PDF-2, leaving the cause for the black colour a mystery. All peaks produced in the diffraction pattern were matched with those of struvite and all peaks were identified. Therefore, there is strong evidence for the crystalline material of the pellets to be pure struvite. It should be noted

that hazenite diffraction patterns did not match with either of the pellet types. Therefore, the Na and K contaminant is unknown, and could be a part of amorphous substances.

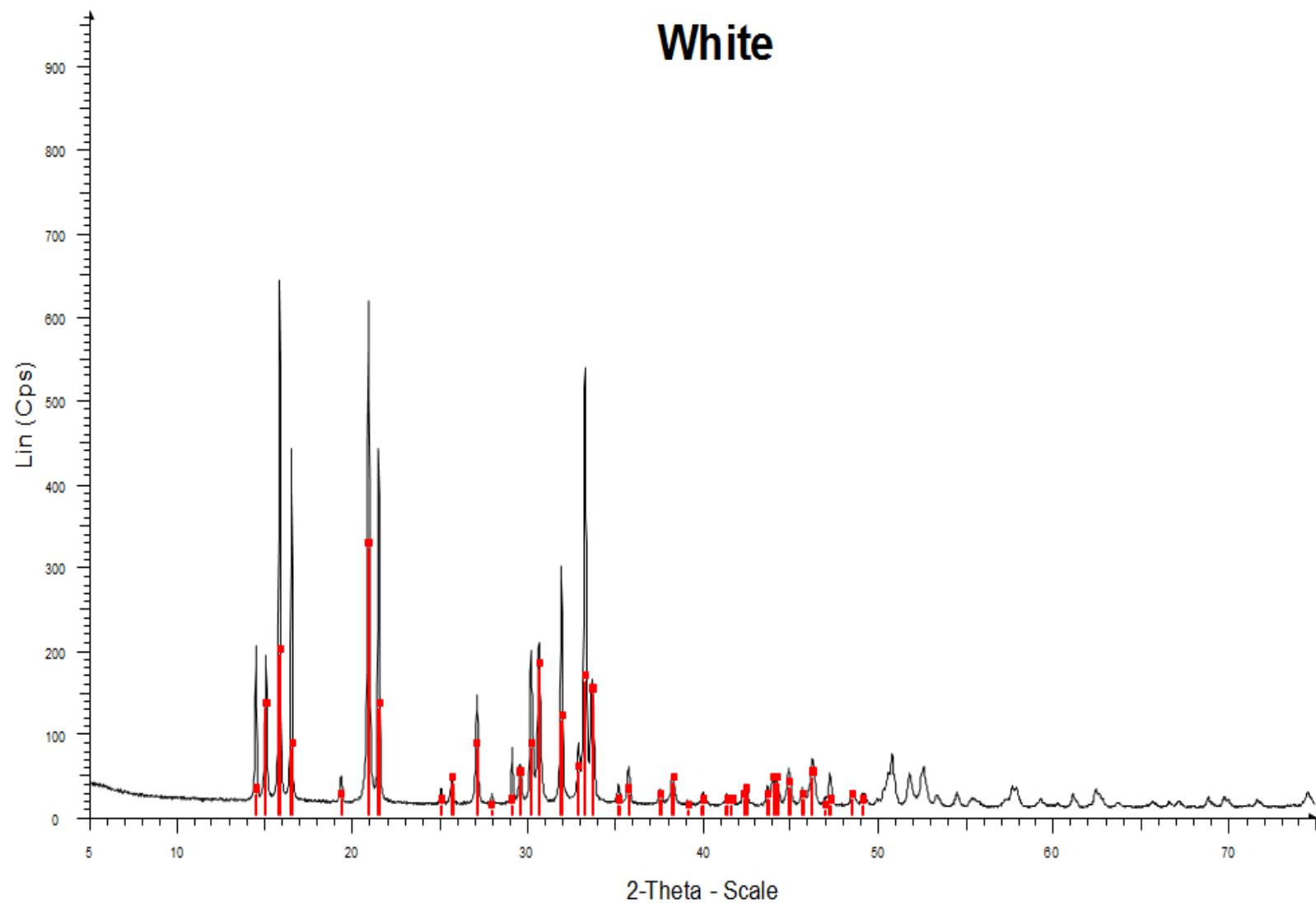
### 5.3.3 Experiment 3

Experiments 1 and 2 both used an in-reactor SSR of 5, hoping that the seeded pellets would grow at a more rapid rate. However, previous struvite crystallization experiments using a similar reactor, Adnan (2002) found that system performance, both in terms of process efficiency and product quality was at its best when the SSR was between 2 and 3.

Experiment 3 was then conducted to determine whether or not a better struvite pellet, in terms of pellet strength and morphology, can be produced in the manure treatment process, by reducing the SSR. Since it is intuitive that the crystallization/nucleation rate would be slowed due to the lower SSR, the reaction time required for similar  $\text{PO}_4\text{-P}$  removal would increase. Due to equipment constraints, the volume of each CY influent batch was restricted. The  $Q_R$  was increased and the  $Q_i$  was decreased in order to increase the HRT, without changing the upflow velocity compared to experiment 2.

The strength of the influent used for experiment 3 had  $\text{PO}_4\text{-P}$ ,  $\text{NH}_3\text{-N}$  and Mg concentrations of 245 mg/L, 1233 mg/L, and 387 mg/L, respectively. Other crystallizer model input variables such as conductivity of the influent was measured to be 13000  $\mu\text{S/cm}$ . The upflow velocity was adjusted to 580 cm/min so that it closely resembles that of experiment 2. Of the total flow,  $Q_i$  and  $Q_R$  were measured to be 0.215 L/min and 2.72 L/min respectively, providing a RR of 12.7. Under these conditions, and a desired SSR of 3.0, the crystallizer model determined the operation pH to be 6.77.

a)



☒ Hui struvite(w) run3 - File: Hui struvite(w) run3.raw - Type: 2Th/Th locked - Start: 5.000 ° - End: 75.007 ° - Step: 0.019 ° - Step time: 38.4 s - Temp.: 25 °C (Room) - Time Started: 25 s - 2-Theta: 5.000 ° - T  
 Operations: Import  
☒ 00-015-0762 (\*) - Struvite, syn - NH<sub>4</sub>MgPO<sub>4</sub>·6H<sub>2</sub>O - Y: 50.00 % - d x by: 1. - WL: 1.5406 - Orthorhombic - a 6.94500 - b 11.20800 - c 6.13550 - alpha 90.000 - beta 90.000 - gamma 90.000 - Primitive - P

b)

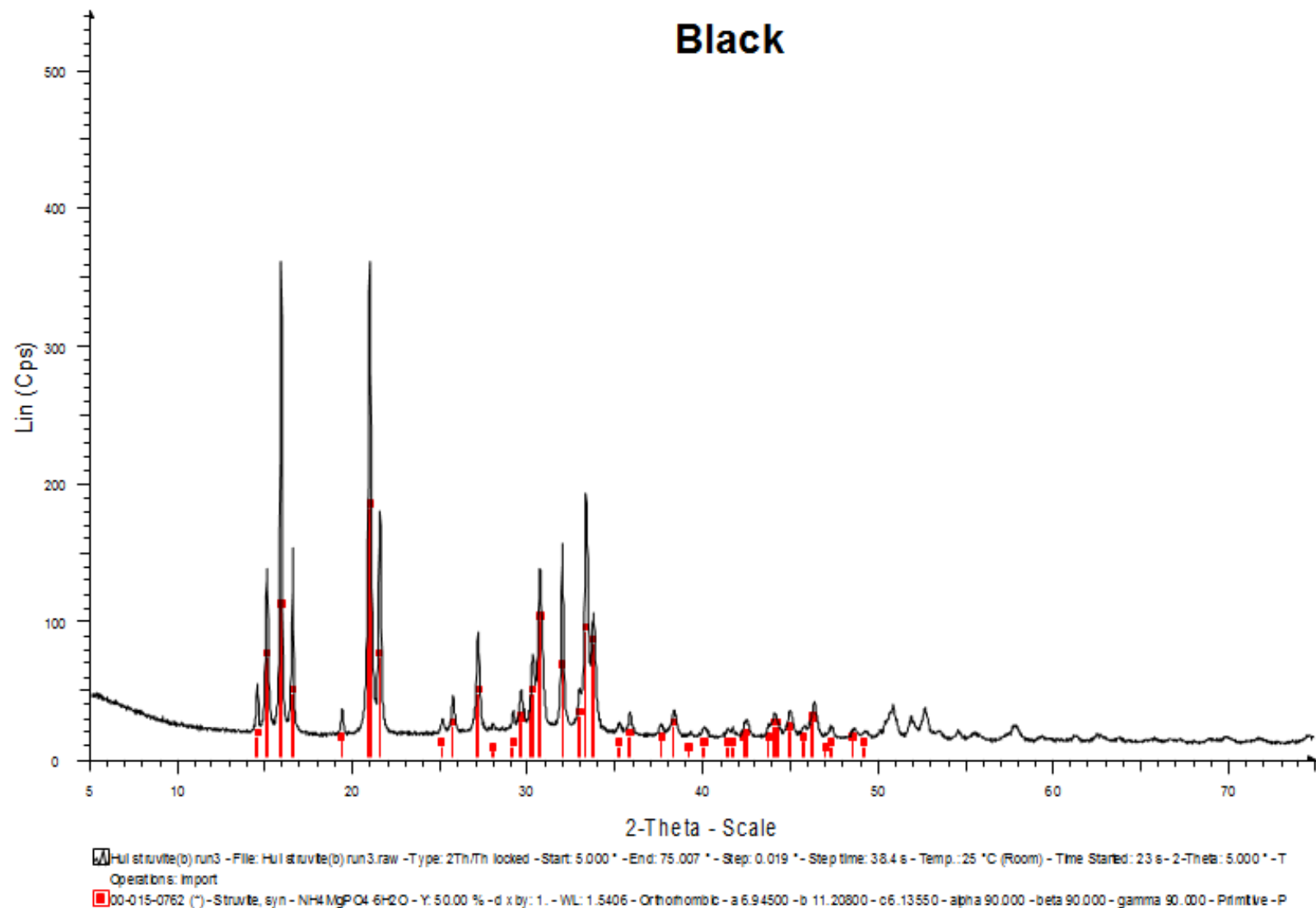


Figure 5.8. X-ray diffraction patterns for the pellets harvested in Experiment 3. Graph a) is a representative of the pattern produced by the white pellets and b) is that produced by the black pellets. In both graphs, the black peaks are those generated by the pellets and the red peaks are those struvite would generate as taken from PDF-2 database.



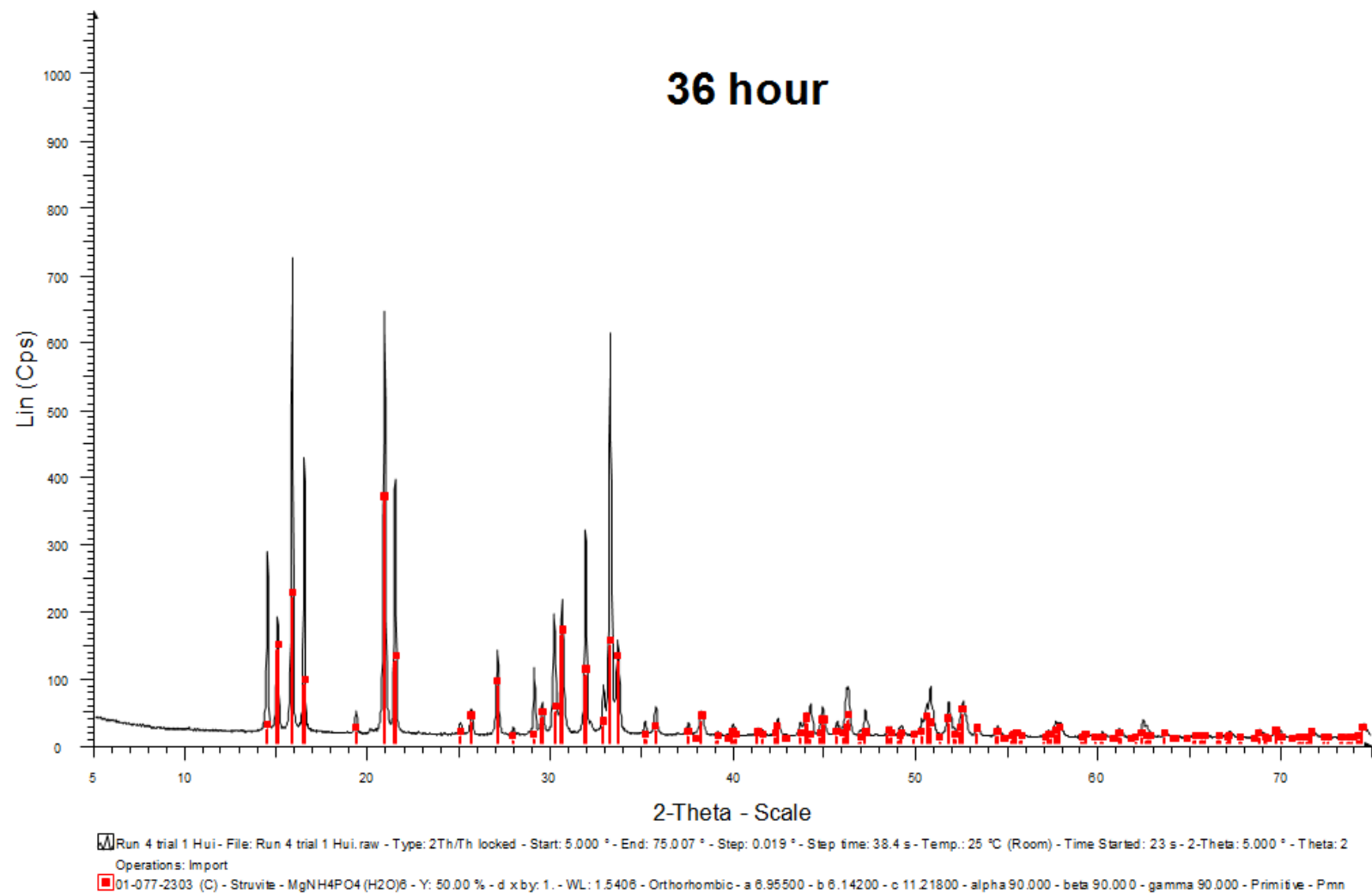
Since the goal of this experiment was to improve crystal morphology, the effluent was not sampled. Instead, the CY reactor was run continuously for 48 hours, with the flow stopped every 12 hours to harvest crystals that grew too large to remain fluidized in the crystallization portion of the reactor.

It was surprising to find that the pellets grown under experiment 3 conditions were holistically different from what was observed in experiments 1 and 2. Despite the uniformity of the pellets' appearances and growth in pellet sizes, the pellet surfaces were not at all smooth, but had a fuzzy appearance. The strength of the pellets was also less than those harvested in the first two experiments. In fact the pellets could be crumbled by simply pressing them against fingertips.

X-ray diffraction crystallography was conducted to examine the content of the pellets produced in experiment 3. A sample was taken from the later 2 harvests at 36 and 48 hours for analysis. The first 2, harvest at 12 and 24 hours, were excluded since the content would mostly be seeded struvite. A representative of the resulting diffraction intensity patterns from both 36 hours and 48 hours harvests, are shown in Figure 5.9 a) and b), respectively. Again, the black line shows the diffraction peaks generated by the pulverized pellet samples and the red peaks are those of struvite, as identified by the PDF-2 database. To our surprise, the pellets produced in experiment 3 showed no signs of having crystalline substances other than struvite. The low level of background noise in the diffraction intensities is also indicative of low quantities of amorphous substances.

One conclusion that could be drawn from the data is that the pellets likely formed through agglomeration of fine crystalline struvite particles, rather than through crystal growth. It is

a)



b)

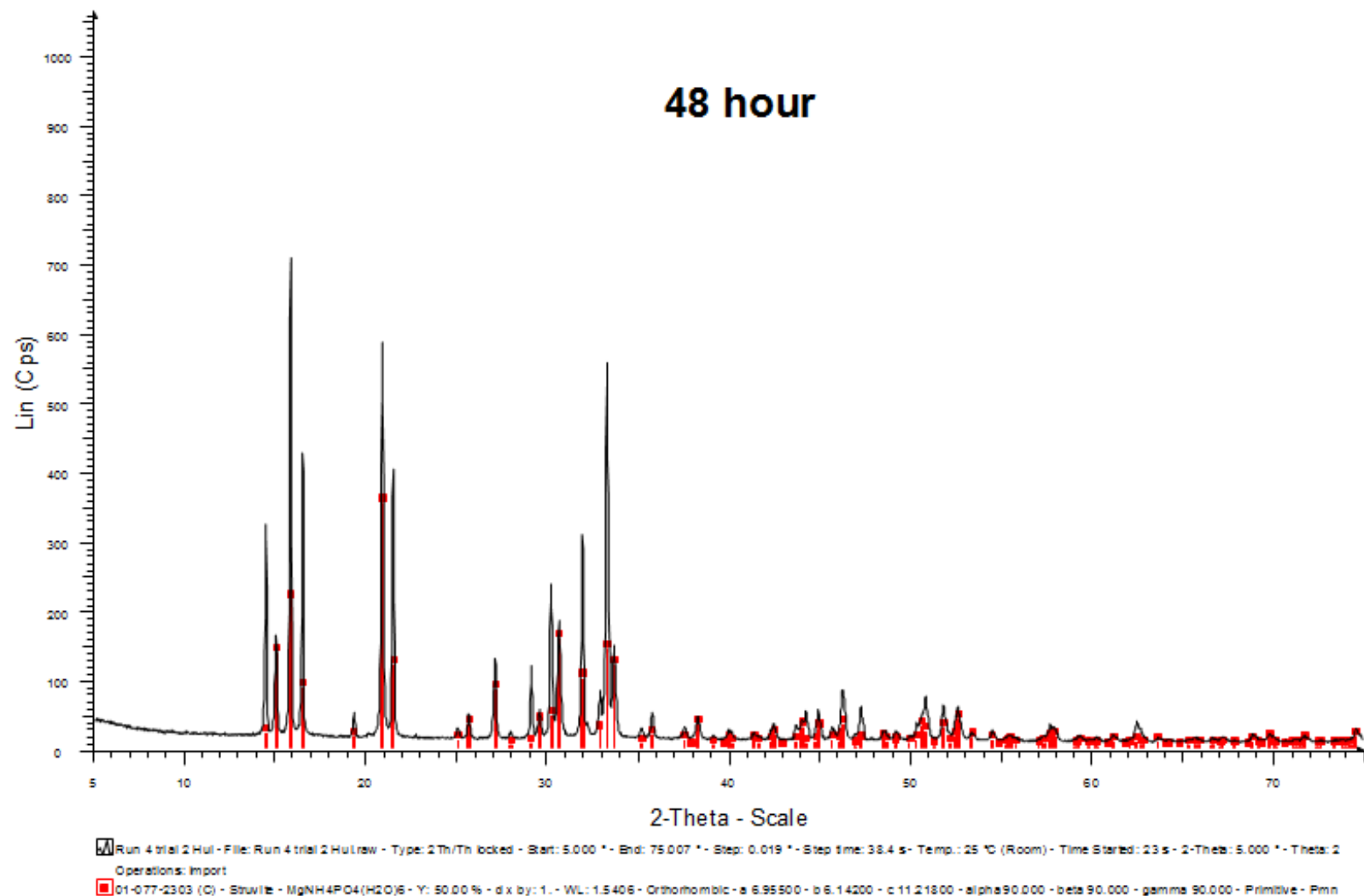


Figure 5.9. X-ray diffraction patterns for the pellets harvested in experiment 3. Graphs a) and b) are the pellets harvested at 36 and 48 hours respectively. The black intensity peaks are those generated by the pellets and the red peaks are those of struvite as derived from the PDF-2 database.

possible that nucleation was occurring at higher rate in the bottom section of the reactor where it receives caustic in pulses. It should be noted that the Reynold's number (Re) in this pipe section is not too large. Using the upflow velocity of the current experiment, and assuming the fluid has viscosity and density similar to that of water, Re was calculated according to equation (19) to be 1878. If the flow is not turbulent and mixing is insufficient in this region, plug flow condition may occur with sections of the pipe having high pH fluid, which induces nucleation to occur rapidly.

$$R_e = \frac{\rho v D_H}{\mu} \quad (19)$$

Where:

- $\rho$  is the density of water ( $\text{kg}\cdot\text{m}^{-3}$ );
- $v$  is the average velocity of the fluid ( $\text{m}\cdot\text{s}^{-1}$ );
- $D_H$  is the hydraulic diameter (m);
- $\mu$  is the dynamic viscosity of the fluid ( $\text{kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}$ )

Assuming the fluid had similar characteristic to water

- $\rho \approx 1000 \text{ kg}\cdot\text{m}^{-3}$
- $v = 0.09667 \text{ m}\cdot\text{s}^{-1}$
- $D_H = 0.0254 \text{ m}$
- $\mu = 0.001307 \text{ kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}$

$$R_e = \frac{1000 \frac{\text{kg}}{\text{m}^3} \cdot 0.09667 \frac{\text{m}}{\text{s}} \cdot 0.0254 \text{ m}}{0.001307 \frac{\text{kg}}{\text{m}\cdot\text{s}}}$$

$$R_e = 1878$$

To mitigate this problem, a less concentrated NaOH solution could have been used. In this way, the pH controller would add caustic solution more consistently, rather than having pauses between pulses. However, more frequent doses of caustic will also dilute the CY fluid. Under current conditions, the volume of caustic added is less than 2% of  $Q_i$ , making the additional

volume insignificant. However, more frequent pulses of caustic will dilute the overall content of the reactor and may need to be considered when calculating for SSR and other reactor conditions.

## 5.4 Conclusions

The current chapter discussed pilot scale experiments that showed the  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP process, followed by liquid/solid separation and OA treatment for Ca removal, produced a material suitable for struvite crystallization using the CY reactor. It was clearly shown in experiments 1 and 2 that the degree of  $\text{PO}_4\text{-P}$  removal can be optimized by altering reactor conditions.  $\text{PO}_4\text{-P}$  removal was elevated from 69% to about 99% by increasing RR from 5 to 9.8. However, more experiments should be conducted to determine the actual trend between the reactor RR and percentage  $\text{PO}_4\text{-P}$  removal. The ability to select the level of P removal becomes important, if the manure were to be used as soil amendments. Experiments 1 and 2 also showed that roughly 25% of N is also removed in the crystallization process. It was thought that a large fraction of the removal was due to ammonia volatilization, since struvite alone is not capable of N extraction to the observed amount. Controlling N removal will also be a factor to consider for the manure's eventual use as a soil amendment, since growth of feedstuffs require an N : P ratio to be roughly 9 : 1.

One interesting and unexpected observation was the recovery of K in experiment 1. The discovery of hazenite within the pellets of struvite was exciting, since K removal from dairy manure is desired in most cases. However, since the occurrence of hazenite was not observed in experiments 2 and 3, it is an indication that very specific reaction conditions are required for this mineral to form. This author conducted some further experiments using synthetic water, made to resemble the CY influent of experiment 1, with the attempt to crystallize hazenite. However, the

attempt was not successful. The side experiment also generated data that suggested the possibility for struvite to absorb  $K^+$  into its crystal matrix, possibly by displacing  $NH_4^+$ , forming a crystal solution.

The pellets generated in experiment 2, for the most part, were similar to those described by Adnan *et al.*(2004). However, small amounts of smooth black pellets were also produced. X-ray crystallography did not find the presence of crystalline material other than struvite in the black pellets.

Experiment 3 produced pellets that were contradictory to previous studies at UBC, where struvite pellet quality was at its best when reactor SSR was between 2 – 3 (Adnan, 2002). The pellets produced from pre-treated dairy manure, when SSR was set to 3.0, were relatively fragile and rough. The fuzzy appearance of the pellets is likely to be the product of small struvite crystals agglomerating, rather than by crystal growth.

Overall, we have conclusive evidence suggesting successful phosphorus extraction from dairy manure by means of struvite crystallization. Further research, however, should be conducted to improve the system in terms of process efficiency and struvite pellet quality.

## **Chapter 6: Summary and Recommendations**

The current study provided sufficient evidence supporting a possible novel method for sequestering phosphorus from dairy cow manure. The manure treatment process involved  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP for nutrient solubilisation and solids destabilisation, gravity clarification for liquid/solid separation, OA treatment for calcium removal, as well as struvite crystallization for phosphorus recovery. The treatment study was done at a pilot scale and it was found, for  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP treatment, that up to 94.9% of total nitrogen was solubilised as ammonia and 101.7% of TP was solubilised as orthophosphate.  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP treatment also displayed a “never before seen” phenomenon, where suspended solids in the slurry became destabilized. Gravity clarification of the  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP effluent attained solids removal by as high as almost 2 log. The sludge volume, as a percentage of total effluent volume, can be highly variable and depends on the solids content of the initial manure slurry used. Calcium removal of up to 97.2% was accomplished by calcium oxalate precipitation, while all other substances analyzed were unchanged.

The leftover sludge from liquid/solid separation of the  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP effluent is mainly of organic composition. It is logical to believe that the sludge volume can be decreased if more hydrogen peroxide was used for increased oxidation of the organics. Perhaps future studies could be conducted to examine the effects of a wider range of  $\text{H}_2\text{O}_2$  concentrations. It should be noted however, that the oxidation effects of  $\text{H}_2\text{O}_2$  is expected to plateau after a certain point, due to the nature of the radical formation reaction. Increased solids destruction could potentially lead to a greater percentage volume of the  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP effluent recoverable after liquid solid separation, which, in turn, increases the amount of phosphorus recoverable in the struvite crystallization process.

Having removed the solids and calcium, the treated manure was thought to be suitable for use as the influent material of the struvite crystallization reactor. Struvite crystallization studies were then conducted for three different reaction conditions. It was surprising to find that the morphologies and constitutions of the struvite pellets changed with different conditions. One fascinating observation was the presence of the potassium-containing, mineral hazenite amongst the pellets produced. Hazenite crystallization may be a viable method for K removal from dairy manure. However, hanzenite was only observed under one of the experimental conditions, which suggests that it will form under strict and narrow circumstances. More experiments should be conducted, using conditions similar to struvite crystallization experiment 1, to verify the reproducibility of the findings.

The pilot plant itself was constructed in such a way that each process in the process train can be rearranged. Therefore, different combinations and the order of the treatment process become versatile and variable. All the equipment used in each of the treatment processes can also be easily modified. There would be many benefits to modifying the current MW setup, since a number of clogging events occurred during its operation for this study. Clogging was more likely to occur during events where liquid/solid separation or the manure at the dairy facility was less effective and the slurry had high quantities of solids. During these events, large quantities of undigested fibrous feed material were present in the slurry. Therefore, the best solution is to monitor the manure, or even having a screening process, to limit the amount of fibres entering the system. To further reduce clogging, the options could be to increase the diameter of the piping or to increase the velocity of the flow. Increase in pipe diameter has limitations, since the MW frequency from the generator is set to 2450 MHz. The penetration of the MW in fluids is restricted and dependent on the wave frequency. Increasing the flow also



has restrictions, since sufficient time is required for the slurry to be irradiated by the MW to reach desired temperatures. A possible solution is to allow the manure to pass through the MW chamber multiple times.

Having the slurry entering the MW chamber multiple times may become energy intensive. Energy usage by the MW generator also contributes to a large fraction of the operating costs and is a hurdle to overcome, if ever full-scale operations are considered. Since the amount of MW exposure was not previously observed to be a significant factor for nutrient solubilisation, a system for heat exchange would be installed to preheat the influent slurry. This can easily be accomplished by having the  $\text{H}_2\text{O}_2/\text{MW}/\text{H}^+$ -AOP effluent run through a system of pipes submerged inside the MW influent tank.

Another modification to the MW could be to increase operating temperatures. Although all TP can be solubilised under our experimental conditions, volatile fatty acid concentrations were not observed to increase. In previous studies, where secondary municipal wastewater sludge was treated with  $\text{H}_2\text{O}_2/\text{MW}$ -AOP, there was an observed increase in soluble short chained fatty acids, when temperature exceeded  $120^\circ\text{C}$ . It was suggested that the increase in soluble VFA would be beneficial, if used as an influent material for anaerobic digestion and biogas production. The current MW system would need to be pressurized, in order for temperatures to rise higher than those used for this study. A system for harvesting steam for the hot manure slurry can augment a pressurized system. In full scale operations, the steam may be useful for offsetting some of the energy costs of operating the MW.

Overall, the pellets generated in some of the struvite crystallization experiments were shown to be struvite of high purity, through both chemical and X-ray diffraction analysis. The degree of phosphorus removal was observed to range between 69 and 99%, simply by increasing

the recycle ratio. Nitrogen removal, on the other hand, remained a steady 25%, the majority of which was thought to be lost due to volatilization. More experiments should be conducted in order to establish the actual trend between recycle ratio and phosphorus recovery yield. The amount of phosphorus removal should be established, if the final effluent were to be used as soil amendments.

The quantity of fine struvite particles observed in the external clarifier of the crystallization reactor should not be ignored. The build up of fine struvite crystals in the external clarifier is most likely because of escape from the reactor column. The upflow velocity should be decreased, to avoid fine particles being suspended. The best way is to slightly alter the dimensions in the top two sections of the crystallizer reactor by increasing the inside diameter. Keeping the diameter of the bottom section allows for the high velocity required to induce turbulence necessary for mixing and enhanced pellet growth. The increase in diameter in the top two sections would then slow the upflow velocity enough to trap more of the newly-formed, fine struvite particles.

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**Appendix A.** T-tests for H<sub>2</sub>O<sub>2</sub>/MW/H<sup>+</sup>-AOP effluent soluble nutrients (confidence interval of 95% was deemed statistically significant).

Treatment condition	T-test against raw manure		T-test against acidified manure	
	PO <sub>4</sub> -P	NH <sub>3</sub> -N	PO <sub>4</sub> -P	NH <sub>3</sub> -N
pH4.0 (no MW)	0.021473981	0.090334729	---	---
pH4.0 + 0.1% H <sub>2</sub> O <sub>2</sub>	1.41846E-05	0.000670451	0.001354466	0.011023297
pH4.0 + 0.3% H <sub>2</sub> O <sub>2</sub>	3.15396E-06	0.000523488	0.001784755	0.007229702
pH4.0 + 0.5% H <sub>2</sub> O <sub>2</sub>	9.78766E-05	0.000552748	0.00136429	0.006757646
pH3.5 + 0.1% H <sub>2</sub> O <sub>2</sub>	1.7052E-05	0.000748476	0.001886897	0.009695204
pH3.5 + 0.3% H <sub>2</sub> O <sub>2</sub>	8.15404E-06	0.000317212	0.001366101	0.008531224
pH3.5 + 0.5% H <sub>2</sub> O <sub>2</sub>	5.27554E-05	0.000141124	0.000277275	0.002923624
pH3.0 + 0.1% H <sub>2</sub> O <sub>2</sub>	3.56307E-05	0.011245967	0.000221723	0.036867435
pH3.0 + 0.3% H <sub>2</sub> O <sub>2</sub>	0.000714819	0.04424135	0.001394997	0.099857549
pH3.0 + 0.5% H <sub>2</sub> O <sub>2</sub>	7.71066E-05	0.004034917	0.000161718	0.007267731

Same pH different [H <sub>2</sub> O <sub>2</sub> ]				
T-Tests for PO <sub>4</sub> -P			T-Tests for NH <sub>3</sub> -N	
pH4.0			pH4.0	
[H <sub>2</sub> O <sub>2</sub> ]	0.30%	0.50%	[H <sub>2</sub> O <sub>2</sub> ]	0.30% 0.50%
0.10%	0.0682025	0.102308379	0.10%	0.004672101 0.000935553
0.30%	---	0.010550591	0.30%	--- 0.268472167
pH3.5			pH3.5	
[H <sub>2</sub> O <sub>2</sub> ]	0.30%	0.50%	[H <sub>2</sub> O <sub>2</sub> ]	0.30% 0.50%
0.10%	0.247495509	0.037706409	0.10%	0.371851347 0.001619676
0.30%	---	0.055497271	0.30%	--- 0.001779841
pH3.0			pH3.0	
[H <sub>2</sub> O <sub>2</sub> ]	0.30%	0.50%	[H <sub>2</sub> O <sub>2</sub> ]	0.30% 0.50%
0.10%	0.37353776	0.230865076	0.10%	0.49426221 0.137162096
0.30%	---	0.191674852	0.30%	--- 0.197921998



Same H<sub>2</sub>O<sub>2</sub> different pH

T-Tests for PO <sub>4</sub> -P			T-Tests for NH <sub>3</sub> -N		
0.1% H H <sub>2</sub> O <sub>2</sub>	pH3.5	pH3.0	0.1% H <sub>2</sub> O <sub>2</sub>	pH3.5	pH3.0
pH4.0	0.091810772	0.05187644	pH4.0	0.142445	0.479942
pH3.5	---	0.02641741	pH3.5	---	0.477088
0.3% H H <sub>2</sub> O <sub>2</sub>	pH3.5	pH3.0	0.3% H <sub>2</sub> O <sub>2</sub>	pH3.5	pH3.0
pH4.0	0.183644583	0.10182145	pH4.0	0.160602	0.424596
pH3.5	---	0.15333404	pH3.5	---	0.466534
0.5% H H <sub>2</sub> O <sub>2</sub>	pH3.5	pH3.0	0.5% H <sub>2</sub> O <sub>2</sub>	pH3.5	pH3.0
pH4.0	0.118488425	0.040977	pH4.0	0.004908	0.140775
pH3.5	---	0.19166196	pH3.5	---	0.287602

**Appendix B.** Mean sludge volume of the H<sub>2</sub>O<sub>2</sub>/MW/H<sup>+</sup>-AOP effluents.

			Time (min)									
	n		0	10	20	30	40	50	60	80	100	120
Untreated manure	2	Mean	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
		Std error	0	0	0	0	0	0	0	0	0	0
			<b>180</b>	<b>210</b>	<b>240</b>	<b>270</b>	<b>300</b>	<b>330</b>	<b>360</b>	<b>390</b>	<b>1440</b>	
Untreated manure	2	Mean	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	
		Std error	0	0	0	0	0	0	0	0	0	

			Time (min)										
pH3.0	n		0	10	20	30	40	50	60	80	100	120	140
0% H <sub>2</sub> O <sub>2</sub>	4	Mean	100.00	100.00	100.00	100.00	100.00	100.00	99.50	99.50	99.00	99.00	98.88
		Std error	0.00	0.00	0.00	0.00	0.00	0.00	0.50	0.50	0.00	0.00	0.13
0.1% H <sub>2</sub> O <sub>2</sub>	4	Mean	100.00	98.13	96.63	95.19	93.44	92.00	90.13	86.50	82.94	79.44	76.69
		Std error	0.00	0.13	0.38	0.51	0.65	0.91	1.26	2.04	2.57	3.26	3.33
0.3% H <sub>2</sub> O <sub>2</sub>	4	Mean	100.00	97.31	94.19	90.25	86.44	82.81	79.44	74.75	70.69	67.19	64.00
		Std error	0.00	0.12	0.77	1.78	2.79	3.73	4.51	5.20	5.38	5.09	4.91
0.5% H <sub>2</sub> O <sub>2</sub>	4	Mean	100.00	96.88	94.38	89.75	86.31	83.75	81.13	76.81	72.69	69.06	65.56
		Std error	0.00	0.63	1.29	4.09	5.52	6.10	6.56	6.73	6.57	6.18	5.62
			160	180	200	220	240	270	300	330	360	390	420
0% H <sub>2</sub> O <sub>2</sub>	4	Mean	98.88	98.25	98.25	97.75	97.75	96.75	95.75	93.88	92.00	90.63	89.63
		Std error	0.13	0.25	0.25	0.25	0.25	0.75	0.75	0.63	0.25	0.38	0.38
0.1% H <sub>2</sub> O <sub>2</sub>	4	Mean	74.00	71.13	68.50	65.88	64.44	61.63	58.94	57.13	55.25	53.63	52.25
		Std error	3.45	3.73	3.97	4.27	4.56	4.28	4.00	3.90	3.57	3.42	3.27
0.3% H <sub>2</sub> O <sub>2</sub>	4	Mean	61.31	58.63	56.25	54.25	52.38	49.88	47.88	46.50	45.31	44.31	43.06
		Std error	4.44	3.97	3.47	2.89	2.38	1.81	1.52	1.15	0.69	0.69	0.40
0.5% H <sub>2</sub> O <sub>2</sub>	4	Mean	62.00	58.81	56.38	54.06	52.00	49.81	48.13	46.44	45.00	44.25	43.44
		Std error	5.02	4.58	4.08	3.63	3.17	2.67	2.30	2.07	1.83	1.65	1.45

			Time (min)							
pH 3.5	n		0	10	20	30	40	60	80	100
no MW			100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
0% H <sub>2</sub> O <sub>2</sub>	2	Mean	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
		Std error	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.1% H <sub>2</sub> O <sub>2</sub>	8	Mean	100.00	83.88	68.88	63.69	60.88	57.25	54.56	52.63
		Std error	0.00	5.47	7.06	7.75	8.12	8.46	8.61	8.58
0.3% H <sub>2</sub> O <sub>2</sub>	6	Mean	100.00	77.00	67.08	62.63	59.75	56.08	53.50	50.92
		Std error	0.00	8.64	10.38	11.10	11.49	11.89	11.89	11.60
0.5% H <sub>2</sub> O <sub>2</sub>	6	Mean	100.00	83.75	71.21	63.42	59.50	51.21	46.33	43.29
		Std error	0.00	7.05	8.95	9.59	10.03	8.08	7.00	6.60
			120	140	160	180	240	300	360	1440
no MW			100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
0% H <sub>2</sub> O <sub>2</sub>	2	Mean	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
		Std error	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.1% H <sub>2</sub> O <sub>2</sub>	8	Mean	51.03	49.75	48.38	47.25	44.81	42.13	40.88	46.50
		Std error	8.57	8.40	8.26	8.11	7.45	6.31	6.11	0.50
0.3% H <sub>2</sub> O <sub>2</sub>	6	Mean	49.13	47.21	45.67	44.46	42.21	40.50	38.92	45.50
		Std error	11.36	11.05	10.74	10.54	10.03	9.75	9.19	1.00
0.5% H <sub>2</sub> O <sub>2</sub>	6	Mean	41.42	40.04	38.83	37.83	37.67	36.25	35.33	43.00
		Std error	6.46	6.32	6.15	6.13	5.67	5.49	5.35	2.00

pH 4.0	n		Time (min)										
			0	10	20	30	40	50	60	80	100	120	140
no MW	2		100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	-
0% H <sub>2</sub> O <sub>2</sub>	4	Mean	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
		Std error	0	0.000	0	0	0	0	0	0	0	0	0
0.1% H <sub>2</sub> O <sub>2</sub>	6	Mean	100.00	98.92	98.17	97.54	96.88	96.25	95.54	93.96	92.21	89.92	88.08
		Std error	0.00	0.05	0.08	0.16	0.18	0.26	0.31	0.57	0.98	1.69	2.18
0.3% H <sub>2</sub> O <sub>2</sub>	6	Mean	100.00	98.75	94.92	91.13	86.83	84.42	82.67	77.54	74.54	72.33	69.46
		Std error	0.00	0.11	1.72	3.14	4.42	5.06	5.17	5.72	5.66	5.17	5.12
0.5% H <sub>2</sub> O <sub>2</sub>	6	Mean	100.00	96.50	92.13	89.08	86.75	84.79	83.25	80.13	78.08	76.04	74.29
		Std error	0.00	2.01	5.13	6.42	7.03	7.44	7.72	8.07	7.96	7.73	7.55
			<b>160</b>	<b>180</b>	<b>210</b>	<b>240</b>	<b>270</b>	<b>300</b>	<b>330</b>	<b>360</b>	<b>390</b>	<b>1440</b>	
no MW	2		-	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	
0% H <sub>2</sub> O <sub>2</sub>	4	Mean	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	
		Std error	0	0	0	0	0	0	0	0	0	0	
0.1% H <sub>2</sub> O <sub>2</sub>	6	Mean	86.17	84.88	82.58	80.50	78.54	76.71	75.13	73.58	72.13	51.25	
		Std error	2.44	2.58	2.81	2.99	3.10	3.09	3.13	3.10	2.97	0.25	
0.3% H <sub>2</sub> O <sub>2</sub>	6	Mean	67.33	65.46	63.25	61.67	60.00	58.83	57.63	56.54	55.75	47.00	
		Std error	5.01	4.79	4.53	4.32	4.08	3.86	3.70	3.51	3.37	4.00	
0.5% H <sub>2</sub> O <sub>2</sub>	6	Mean	72.54	71.00	68.71	66.38	64.17	62.08	60.38	58.54	57.04	41.50	
		Std error	7.16	6.78	6.34	5.91	5.38	4.88	4.51	4.13	3.73	3.50	

**Appendix C.** Concentrations of nutrients and various metals, before and after OA treatment.

Trial	Oxalic acid		Metals Concentration (mg/L)											
	mmol/L	OA:Ca ratio	Al	Ca	Fe	K	Mg	Na	S	P	NH <sub>4</sub> -N	PO <sub>4</sub> -P	Cu	Zn
1	0.00	0.00	0.89	798.46	2.02	1580	300.29	401.76	2902	179.47	1018	164.90	-	-
2	0.00	0.00	0.94	808.48	2.01	1601	302.97	406.12	2898	179.19	1036	171.85	-	-
3	0.00	0.00	6.36	709.57	6.61	2050	362.62	569.41	3327	257.81	788	104.94	7.03	23.48
4	0.00	0.00	6.18	724.60	6.26	2068	365.15	573.75	3377	250.36	788	94.73	6.99	22.79
3	3.74	0.21	7.62	701.29	7.96	2505	431.10	693.24	3950	307.47	733	90.60	8.63	27.75
4	3.74	0.21	7.23	703.81	8.02	2511	440.14	692.74	4029	312.22	736	85.86	8.61	28.12
3	7.49	0.42	7.76	573.95	8.03	2448	437.42	680.67	3992	312.16	731	90.34	8.19	27.85
4	7.49	0.41	7.80	563.61	8.09	2432	443.36	675.50	4022	318.02	745	91.20	8.49	28.41
3	11.23	0.63	7.16	409.20	7.74	2225	411.85	619.36	3751	297.55	759	87.58	7.73	26.58
4	11.23	0.62	7.61	459.12	8.24	2535	443.20	702.69	4048	315.64	765	91.16	8.49	28.49
1	15.00	0.75	1.23	395.90	3.70	1567	304.14	402.74	2933	181.82	1012	166.60	-	-
2	15.00	0.74	1.30	397.32	3.73	1608	306.29	411.96	2900	182.90	1060	169.05	-	-
3	14.97	0.85	8.07	322.61	8.74	2514	450.39	691.53	4044	312.26	747	87.00	10.58	28.39
4	14.97	0.83	7.97	328.01	8.69	2661	451.48	721.07	4135	321.42	744	87.76	10.83	29.17
3	18.71	1.06	8.07	258.24	8.53	2511	441.59	700.95	3993	325.76	751	90.22	8.11	28.90
4	18.71	1.04	8.10	274.03	9.02	2710	456.29	744.44	4098	320.72	750	94.62	11.19	29.05
3	26.20	1.48	7.83	209.08	8.69	2626	447.61	719.74	4018	318.53	737	87.28	7.31	28.16
4	26.20	1.45	7.88	211.04	9.07	2566	450.11	706.53	4084	317.37	738	88.00	8.29	28.15
1	30.15	1.51	1.33	115.11	4.01	1570	299.88	400.80	2822	181.08	1010	169.95	-	-
2	30.15	1.49	1.36	110.94	4.20	1556	300.62	399.23	2898	185.25	1018	173.35	-	-
3	29.94	1.69	8.08	188.04	8.58	2653	443.56	709.18	3976	317.68	738	91.22	6.82	28.00
4	29.94	1.66	8.04	187.43	8.60	2477	444.97	680.67	3979	320.62	738	92.04	6.93	28.29
1	45.46	2.28	1.62	85.05	4.57	1493	288.75	384.21	2781	175.63	966	160.50	-	-
2	45.46	2.25	1.61	84.72	4.28	1515	290.51	387.20	2771	176.67	988	164.85	-	-
1	60.92	3.06	1.44	70.33	4.38	1592	306.85	407.53	2992	187.79	1051	170.40	-	-
2	60.92	3.02	1.35	72.74	4.35	1616	310.18	410.76	2974	188.98	1050	179.00	-	-
1	76.54	3.84	1.65	58.02	4.69	1585	304.84	407.21	2965	185.81	1037	166.80	-	-
2	76.54	3.79	1.68	69.81	4.71	1592	306.08	409.60	3000	187.78	1048	170.30	-	-
1	92.33	4.63	1.50	64.58	4.39	1535	298.50	394.42	2902	182.48	1004	168.45	-	-
2	92.33	4.58	1.54	67.31	4.38	1543	298.05	395.38	2946	182.15	1020	169.30	-	-

Trial	<u>Oxalic acid</u>		<u>% remaining of each constituent after OA treatment</u>											
	mmol/L	OA:Ca ratio	% Al	% Ca	% Fe	% K	% Mg	% Na	% S	% P	%NH3-N	% PO4-P	% Cu	% Zn
1	0.00	0.00	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	-	-
2	0.00	0.00	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	-	-
3	0.00	0.00	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%
4	0.00	0.00	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%
3	3.74	0.21	119.7%	98.8%	120.4%	122.2%	118.9%	121.7%	118.7%	119.3%	93.1%	86.3%	122.8%	118.2%
4	3.74	0.21	117.1%	97.1%	128.1%	121.4%	120.5%	120.7%	119.3%	124.7%	93.3%	90.6%	123.3%	123.4%
3	7.49	0.42	122.0%	80.9%	121.5%	119.5%	120.6%	119.5%	120.0%	121.1%	92.8%	86.1%	116.6%	118.6%
4	7.49	0.41	126.3%	77.8%	129.2%	117.6%	121.4%	117.7%	119.1%	127.0%	94.5%	96.3%	121.5%	124.7%
3	11.23	0.63	112.6%	57.7%	117.2%	108.5%	113.6%	108.8%	112.8%	115.4%	96.4%	83.5%	110.1%	113.2%
4	11.23	0.62	123.2%	63.4%	131.7%	122.6%	121.4%	122.5%	119.9%	126.1%	97.0%	96.2%	121.5%	125.0%
1	15.00	0.75	137.8%	49.6%	182.8%	99.2%	101.3%	100.2%	101.1%	101.3%	99.4%	101.0%	-	-
2	15.00	0.74	138.1%	49.1%	186.0%	100.4%	101.1%	101.4%	100.1%	102.1%	102.3%	98.4%	-	-
3	14.97	0.85	126.9%	45.5%	132.3%	122.6%	124.2%	121.4%	121.6%	121.1%	94.8%	82.9%	150.6%	120.9%
4	14.97	0.83	129.1%	45.3%	138.9%	128.6%	123.6%	125.7%	122.5%	128.4%	94.3%	92.6%	154.9%	128.0%
3	18.71	1.06	126.8%	36.4%	129.1%	122.5%	121.8%	123.1%	120.0%	126.4%	95.4%	86.0%	115.4%	123.1%
4	18.71	1.04	131.2%	37.8%	144.1%	131.0%	125.0%	129.7%	121.4%	128.1%	95.1%	99.9%	160.1%	127.5%
3	26.20	1.48	123.0%	29.5%	131.5%	128.1%	123.4%	126.4%	120.8%	123.6%	93.5%	83.2%	104.1%	119.9%
4	26.20	1.45	127.5%	29.1%	145.0%	124.1%	123.3%	123.1%	120.9%	126.8%	93.6%	92.9%	118.6%	123.5%
1	30.15	1.51	149.5%	14.4%	197.9%	99.4%	99.9%	99.8%	97.2%	100.9%	99.2%	103.1%	-	-
2	30.15	1.49	144.8%	13.7%	209.0%	97.2%	99.2%	98.3%	100.0%	103.4%	98.2%	100.9%	-	-
3	29.94	1.69	127.1%	26.5%	129.9%	129.5%	122.3%	124.5%	119.5%	123.2%	93.7%	86.9%	97.0%	119.3%
4	29.94	1.66	130.2%	25.9%	137.3%	119.8%	121.9%	118.6%	117.8%	128.1%	93.6%	97.2%	99.2%	124.2%
1	45.46	2.28	181.9%	10.7%	225.8%	94.5%	96.2%	95.6%	95.8%	97.9%	94.9%	97.3%	-	-
2	45.46	2.25	171.6%	10.5%	213.2%	94.6%	95.9%	95.3%	95.6%	98.6%	95.3%	95.9%	-	-
1	60.92	3.06	162.3%	8.8%	216.3%	100.8%	102.2%	101.4%	103.1%	104.6%	103.2%	103.3%	-	-
2	60.92	3.02	144.4%	9.0%	216.8%	100.9%	102.4%	101.1%	102.6%	105.5%	101.3%	104.2%	-	-
1	76.54	3.84	186.0%	7.3%	231.5%	100.3%	101.5%	101.4%	102.2%	103.5%	101.9%	101.2%	-	-
2	76.54	3.79	179.5%	8.6%	234.8%	99.5%	101.0%	100.9%	103.5%	104.8%	101.1%	99.1%	-	-
1	92.33	4.63	169.1%	8.1%	216.9%	97.1%	99.4%	98.2%	100.0%	101.7%	98.7%	102.2%	-	-
2	92.33	4.58	164.2%	8.3%	218.0%	96.4%	98.4%	97.4%	101.6%	101.6%	98.5%	98.5%	-	-