

DELECTRIC HEATING PRETREATMENT OF ORGANIC SLURRIES

by

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Abstract

This study reports on the research findings from the investigations of three studies conducted on dielectric heating treatments of separated dairy manure and sewage sludge for the purpose of solids disintegration and nutrients release were carried out under batch operation. The treatment processes investigated included; radiofrequency/hydrogen peroxide advanced oxidation process (RF/H₂O₂-AOP), microwave/hydrogen peroxide advanced oxidation process (MW/H₂O₂-AOP) and combination of conventional heating (CH) and MW/H₂O₂-AOP. The broad objectives were to investigate the effects and factors affecting these processes. Significant factors affecting the RF/H₂O₂-AOP process; hydrogen peroxide dosage, heating time and input power were optimized using surface response methodology. The optimized operating conditions were determined to be an input power of 63%, holding time 60 min and H₂O₂ dose of 1.1% for orthophosphate release, and an input power of 71%, holding time 5 min and H₂O₂ dose of 2.4% for soluble chemical oxygen demand.

The second study was to examine the effects of organic acids (acetic, oxalic and citric) and mineral acids (sulfuric and hydrochloric acid) as acidifying reagents in MW/H₂O₂-AOP. The results showed that organic acids were good acidifying reagents comparable to mineral acids. The MW/H₂O₂-AOP and oxalic acid treatment could be combined into a single-stage process which could release phosphates, solubilize solids and remove calcium from dairy manure at the same time. A mixture of oxalic and mineral acids could produce the maximum volume of clear supernatant.

A combination of CH and MW/H₂O₂-AOP was applied for the treatment of aerobic sewage sludge and dairy manure in the final study. The substrates were preheated by CH method (40°C, 50°C and 60°C) followed by MW/H₂O₂-AOP (100°C and 120°C). The maximum SCOD/TCOD ratio obtained for sewage sludge and dairy manure were 60% and 22%, respectively. The best treatment conditions for COD solubilization for both sewage sludge and dairy manure was obtained for the treatment set conducted at CH temperature of 60°C followed by MW temperature 120°C with hydrogen peroxide. A maximum ortho-P/TP ratio of 50% and 98% was obtained for sludge and dairy manure, respectively. The overall results suggest that dielectric heating was effective in the treatment of dairy manure and sewage.

Preface

This research project would not have been completed without the invaluable support from my research advisors. The supervisory team greatly assisted in the overall completeness of the research scope, identification of the broad research needs, examination and interpretation of the data, revisions of the chapters and manuscripts.

The chapters 3 - 6 have been revised into three manuscripts for publication. The manuscripts prepared for publication have been strengthened by contribution by the supervisory team, Dr. Victor K. Lo, Dr. Ping H. Liao and Dr. Asha Srinivasan. I conducted laboratory analysis, analyzed the data, critically reviewed relevant literature, organized and presented the results and preparation of manuscripts. The experimental designs were originally done by Drs Ping H Liao and Asha Srinivasan.

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List of Abbreviations

AD	anaerobic digestion
AC	activated carbon
ADF	acid detergent fiber
ADL	acid detergent lignin
AOP	advanced oxidation process
BOD	biochemical oxygen demand
Ca	calcium
CH	conventional heating
COD	chemical oxygen demand
DNA	deoxyribonucleic acids
EPS	extracellular polymeric substances
HRT	hydraulic retention time
Mg	magnesium
MW	microwave
MW/H ₂ O ₂ -AOP	microwave / hydrogen peroxide advanced oxidation process
NDF	neutral detergent fiber
OH.	hydroxyl radicals
Ortho-P	ortho-phosphate
PO ₄ -P	ortho-phosphate
Poly-P	poly-phosphate
RF	radio frequency
RF/ H ₂ O ₂ -AOP	radio frequency / hydrogen peroxide advanced oxidation process

SCOD	soluble chemical demand
SRT	solids retention time
TCOD	total chemical oxygen demand
TKN	total kjehldahl nitrogen
TP	total phosphorus
TS	total solids
UBC	University of British Columbia
VFA	volatile fatty acids
VS	volatile solids
WAS	waste activated sludge
WWTP	wastewater treatment plant

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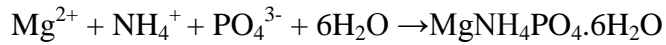
Chapter 1 : Introduction

1.1 Background

The management of dairy manure and sewage sludge is one of the challenges facing many countries in the world. Large quantities of these wastes are produced from many large and concentrated farms and wastewater treatment plants if it is not properly managed, because of the high organic matter and nutrients (nitrogen and phosphorous), can cause severe environmental pollution problems. Conventional method for the disposal of these wastes has largely centered on land application, with small amount being composted (Wen et al., 2004). However, due to the increasing stringent regulatory requirements combined with decreasing land availability, there is the need to develop new innovative management strategies and alternatives. A more sustainable alternative is a paradigm shift from perceiving manure and sewage sludge as wastes for disposal to a bioresource for the recovery of nutrients, energy and other bio-based products (Van Horn et al., 1994; Rico et al., 2007). Dairy manure contains nutrients, proteins, carbohydrates, fats, inorganic residue, minerals and lignin which can be harnessed through appropriate processing.

Recovering nutrients in the form of phosphorus (P) from manure and sewage sludge could be a more sustainable strategy to conserve P resources because there is a growing concern that global reserves of high quality mined phosphate deposits are being gradually depleted. It is predicted that the resource could be exhausted in 100-250 years if the current consumption patterns of phosphate rock is not changed (Shu et al., 2006). In recent years, much research efforts have been directed towards phosphorus recovery from organic slurries through struvite crystallization.

Struvite, (magnesium ammonium phosphate, $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) is a crystalline solid which can serve as a slow releasing fertilizer due to its lower solubility (Nelson et al., 2003). The technology has proven to be an effective process for the recovery of nitrogen and phosphorus from organic slurries including dairy manure and sewage sludge. The reaction equation for the formation of struvite is given by (Uludag-Demirer et al., 2005).



The effectiveness of the above reaction is affected by several factors, including the availability of orthophosphate and ammonium as well as the presence of an ideal Ca:Mg ratio (0.25 and below) (Shen et al., 2010; Zhang et al., 2010) in solution. The presence of Ca^{2+} ions is detrimental to struvite formation; either by competing for phosphorus ions or by interfering with struvite crystallization. Dairy manure is an excellent source because they contain high levels of nutrients including nitrogen and phosphorus. It is also a rich source of minerals such as magnesium and calcium. Recovering nutrients reduces the quantity of sludge to be disposed of as well as phosphorus discharge into ecological systems.

However, the higher suspended solids content and composition of organic slurries such as dairy manure limit their biodegradability and nutrients solubilization (Schuiling and Andrade, 1999). Therefore, pretreatment is required to solubilize the nutrients, and to disintegrate solids before subsequent processing for nutrients and energy recovery. With this goal in mind, a dielectric heating assisted pretreatment processes have been successfully developed by researchers in the Civil Engineering department at the University of British Columbia. The process consists of exposing the organic slurries, to dielectric heat (microwave or radiofrequency irradiation) for a

short period of time after the addition of mineral acids and hydrogen peroxide to alter the structure of the solid materials; this disintegrates the solids and solubilizes nutrients in the process. It has been found that dielectric heating oxidation process that combines with oxidants had higher treatment efficiency than dielectric heat alone possibly due to the increased synergy between the oxidants and dielectric heat. The microwave-enhanced hydrogen peroxide advanced oxidation process (MW/H₂O₂-AOP) has been well studied in recent years compared to radio frequency enhanced advanced oxidation process.

Previous research found that when MW/H₂O₂-AOP was used in dairy manure treatment, high phosphorus release was obtained only under acidic condition. Metals such as calcium and magnesium were also released during the treatment process (Pan et al., 2006; Qureshi et al., 2008; Kenge et al., 2009a; Jin et al., 2009; Lo et al., 2011). These compounds are known to enhance the subsequent struvite crystallization process. However, when mineral acid, especially sulphuric acid is used as acidifying reagent in MW/H₂O₂-AOP, there is the possibility of formation of undesirable products such as sulfite inhibition during acid hydrolysis which has been found to affect the subsequent anaerobic digestion process (Jin et al., 2009). There is the need to investigate acidifying reagents which will provide the ideal Ca:Mg ratio suitable for struvite crystallization whilst reducing the formation of undesirable products. My research seeks to investigate the use of organic acids (oxalic, acetic and citric acids) and mixtures of organic and mineral acids (sulfuric and mineral acids) as acidifying reagents in the MW/H₂O₂-AOP. The purpose was to develop a single-stage treatment process that could simultaneously reduce calcium concentration, improve settling whilst maximizing ammonium and orthophosphates release from dairy manure to enhance the subsequent struvite crystallization and anaerobic

digestion process. Previous researches carried out on MW/H₂O₂-AOP pretreatment of dairy manure for struvite recovery have largely focused on two-stage process.

Although the MW/H₂O₂-AOP treatment process have been investigated for enhancing nutrients release and solids disintegration from separated dairy manure, no study exist focusing on the radiofrequency (RF) advanced oxidation process (RF/H₂O₂-AOP). However, radiofrequency (RF) heating have been applied in other environmental technology areas such as soil remediation by soil vapour extraction or biodegradation, adsorptive-catalytic off-gas treatment, thermal regeneration of drying agents in biogas or natural gas treatment, and disinfection of dairy and animal facility wastewater (Price et al., 1999; Lagunas-Solar, et al., 2005). Considering the higher penetration depth which means that it can treat large volumes of waste with higher solids, it is important to investigate this treatment process. Srinivasan et al., (2013) reported that the application of RF/H₂O₂-AOP for the treatment of un-separated (whole) dairy manure was effective. The factors affecting the process were identified as; hydrogen peroxide dosage, power intensity, reaction time and acid addition. It has also been found that the treatment efficiency of RF heating was comparable to MW heating process (Kenge et al., 2009a; Lo and Liao, 2011).

The application of conventional heating for the treatment of sewage sludge has been investigated at several temperatures. It has been found that the efficiency increases with increased temperature however, at very high temperatures (>200°C) efficiency decreases due to the formation of refractory compounds (Stucky and McCarty, 1984). Low thermal temperature (< 100°C) has been found to be an effective treatment for increasing biogas production from both primary and secondary sludge and is becoming more attractive because of its lower energy

requirements (Gavala et al., 2003). Lo and Liao (2011) suggested an optimum MW temperature of 120°C for best nutrient recovery and solids disintegration from sludge and dairy manure in a batch mode MW/H₂O₂-AOP. However, studies by Yu et al., (2010) and Zhang et al., (2013) found that high treatment efficiency could be achieved at 100°C MW temperature for continuous mode treatment process which is comparable to the batch mode under similar conditions. Hence, it will be of great interest to study in detailed MW/H₂O₂-AOP at 100°C using sewage sludge and dairy manure in batch mode and compare it with that at 120°C. Also information on thermal pretreatment of dairy manure is limited.

Comparative studies on the performance of conventional heating (CH) and microwave and/or hydrogen peroxide have been well investigated (Eskicioglu et al., 2007; Chang et al., 2011; Mehdizaleh et al., 2013). However, there has not been any study to combine the two processes to understand the combined effects. The combination of CH and MW/H₂O₂-AOP processes could be more efficient compared to the individual treatment processes because of the possibility of synergy between the two processes and the potential for real time industrial applications. Based on the fact that no studies exists focusing on the dielectric electric heating treatment processes; RF/H₂O₂-AOP, MW/H₂O₂-AOP with organic acids as acidifying reagents and combined conventional heating and MW/H₂O₂-AOP treatment of organic slurries for the purpose of nutrients solubilization and solids disintegration, therefore, the investigation into the effects and the factors affecting these processes is of great interest and will significantly contribute to the progress of nutrients recovery from organic slurries research field. The results obtained suggest that these processes were effective for the treatment of organic slurries.

1.2 Research objectives

The purpose of this research project was to investigate three dielectric heating treatment processes for the purpose of nutrients release and solids disintegration from separated dairy manure and sewage sludge slurries. These treatment processes included; radio frequency and microwave-enhanced thermo-chemical pretreatment (MW/H₂O₂-AOP) process using mineral acids, organic acids (oxalic, acetic and citric acids), and mixtures of mineral and organic acids as acidifying reagents in MW/H₂O₂-AOP. Also, the combined effects of conventional heating and MW/H₂O₂-AOP processes were investigated.

1.2.1 Specific objectives

Specifically, the research objectives were;

- To optimize the RF/H₂O₂-AOP process for treating solids portion of dairy manure after solids/liquid separation.
- To investigate the effects of organic acids (oxalic, acetic and citric acids), and mixtures of mineral acid and inorganic acid as acidifying reagents for treating dairy manure slurry in MW/H₂O₂-AOP.
- To investigate the combined effects of conventional heating (CH) and MW/H₂O₂-AOP on nutrients release and solids disintegration from dairy manure slurry and sewage sludge.

1.3 Structure of the thesis

The structure of this dissertation followed the research objectives, and consisted of the five chapters: Chapter 1 introduces the research background, objectives and review of relevant literature on animal wastes management perspectives, principles, theory and mechanism of dielectric heating, comparison between dielectric and conventional heating, advantages and disadvantages of dielectric heating, acid hydrolysis. Account of previous research and the applications of microwave/ radiofrequency enhanced dielectric heating processes are presented.

Chapter 2 reports on the investigations of the factors affecting radio frequency/ hydrogen peroxide advanced oxidation process (RF/H₂O₂-AOP) treatment of separated dairy manure slurry for the purpose of nutrients solubilization and solids disintegration. The significant factors (temperature, hydrogen peroxide dosage and input power) affecting the RF/H₂O₂-AOP were optimized using response surface design methodology. A comparative study of RF/H₂O₂-AOP for the treatment of separated and un-separated manure as well as comparison between RF/H₂O₂-AOP and MW/ H₂O₂-AOP were discussed in details.

Chapter 3 reports on the investigation into combined effects of conventional heating (CH) and MW/H₂O₂-AOP on nutrients release and solids disintegration from enhanced biological phosphorus removal (EBPR) aerobic sewage sludge.

Chapter 4 reports on the investigation into combined effects of conventional heating (CH) and MW/H₂O₂-AOP on nutrients release and solids disintegration from dairy manure slurry.

Chapter 5 reports on the effects of organic acids (oxalic, acetic and citric acid) and mixtures of mineral and organic acids as acidifying reagents for the pretreatment of dairy manure to release nutrients, disintegrate solids and remove calcium from pretreated dairy manure slurry in MW/H₂O₂-AOP.

1.4 Literature review

1.4.1 The resource potential of dairy manure and sewage sludge

Dairy manure is a valuable bioresource which contains proteins 16%, cellulose 22%, hemicelluloses 12%, lignin 13% (Liao et al., 2007b) and inorganic residues (Table 1.1). It is also a rich source of nutrients (nitrogen and phosphorus) and minerals such as K, Ca, Mg, Fe, Cu, Mn, Zn etc. (Fontenot et al., 1983; Møller et al., 2002). The nutrients (N and P) and metals in the manure could be recovered through struvite crystallization which have been developed and implemented on full scale in some parts of the world (Tyagi and Lo, 2013). The major components of manure (cellulose and hemicelluloses) are polymers of sugar which can be converted through acid and enzymatic hydrolysis to fermentable saccharides, which can further be converted to bio-ethanol and other value - added products (Sun and Cheng, 2002). Wood and Layzell, (2003) estimated that livestock manure could produce over 3 billion m³/ year of biogas which translates into 0.065 EJ/year of energy use in Canada an equivalence of 0.8% of fossil fuel energy use (Table 1.2).

However, the lignocelluloses component (lignin, cellulose and hemicelluloses) still remains underutilized resource because the nitrogen content (3%) is high compared to that of wood and straw, which contains less than 1% nitrogen (Reinertsen et al., 1984). This negatively affects the

final sugar yield because of side reactions during hydrolysis. The source of nitrogen in dairy manure is from indigestible forage proteins, urine and/or ammonia (Liao et al., 2007b). These differences in the nitrogen composition affect the type and extents of pretreatments required to biodegrade and solubilize lignin and hemicelluloses. This will enable efficient hydrolysis and facilitate the resource recovery from dairy manure depending on the final objectives. For example, it has been found that under the treatment conditions; 6 M HCl and 24 h proteins can be completely hydrolyzed to soluble peptides and amino acids and the degree of protein hydrolysis increases with an increase in reaction condition severity (Liao et al., 2007b). Each individual component in dairy manure has a different sensitivity to acid and consequently behaves differently during acid treatment.

Sewage sludge is comprised of different groups of microorganism, organic and inorganic matter agglomerated together in a polymeric network formed by microbial extracellular polymeric substances (EPS) and cations (Eskicioglu et al., 2006). Sewage sludge, especially from enhanced biological phosphorus removal process (EBPR) contains higher levels of phosphorus (up to 12%) compared to (2-3.5%) those from waste activated sludge. As much as 80% of phosphorus contained in the EBPR sludge can be released back to the supernatant by various processes (Mudhoo and Sharma, 2011). Generally conventional or microwave treatment could disrupt the structure of sewage sludge and dairy manure to increase the solubilization and eventually the biodegradability of these wastes.

Table 1-1: Composition of raw dairy manure (Liao et al., 2007b)

Dry matter (%)	13.42 ± 0.10
<i>Composition (% of dry matter)</i>	
Crude protein, % dry matter	18.11 ± 0.27
Crude fiber (NDF), % dry matter	45.89 ± 0.35
Cellulose (ADF – ADL), % dry matter	23.13 ± 0.26
Hemicellulose (NDF – ADF), % dry matter	10.64 ± 0.10
Lignin (ADL), % dry matter	12.11 ± 0.19
Nitrogen, % dry matter	2.90 ± 0.045
Carbon, % dry matter	45.35 ± 0.52

Table 1-2: Livestock manure production, and biogas and heating potential in Canada (Wood and Layzell, 2003)

	Animal manure production (Mt)	Recoverable fraction (%)	Recoverable manure (Mt/year)	Biogas potential (Mm³/year)	Methane fraction (%)	Energetic heating (EJ/year)
Dairy (mature cows)	19	75	14	549	54	0.011
Beef (large animals)	81	25	20	1,701	53	0.034
Poultry	2	85	2	188	60	0.004
Swine	72	85	22	731	58	0.016
Total	128		58	3169		0.065

1.4.2 Structure and physical properties of lignocellulosics biomass

The major components found in manure and other lignocellulosics materials are cellulose, hemicelluloses and lignin. They are connected to each other by chemical bonds, such as ether/ester and glycosidic bonds, forming a very stable matrix structure (Sjostrom, 1993). Manure is considered a special type of lignocellulosics because it is more heterogeneous and very recalcitrant during hydrolysis because the easily hydrolyzed part has already been digested by the cattle (Chen et al., 2005; Jin et al., 2009). The following section gives basic information about cellulose, hemicellulose and lignin.

1.4.2.1 Cellulose

Cellulose is a homogeneous polymer of glucose connected by β -1,4-glycosidic bonds with strands of cellulose polymers associated through hydrogen bonds to form a crystal structure (Hendriks and Zeeman, 2009). This structure makes cellulose very strong and resistant to degradation, therefore severe conditions, such as use of concentrated acid, or long reaction time and high temperature are needed to break down the hydrogen and glycosidic bonds and degrade the cellulose (Sjostrom, 1993). Several of polymer strands (20-300) come together to form microfibrils which in turn are united to form cellulose fibers (Agbor et al., 2011). The cellulose consists of crystalline (organized) structure and an amorphous part (Hendriks and Zeeman, 2009). During enzymatic hydrolysis, cellulase favors amorphous part rather than the crystalline portion making cellulose with greater crystalline portion more resistant to hydrolysis (Taherzadeh and Karimi, 2008). The chemical formula of cellulose is $(C_6H_{10}O_5)_n$ and the structure of single chain of the polymer is presented in Figure 1.1

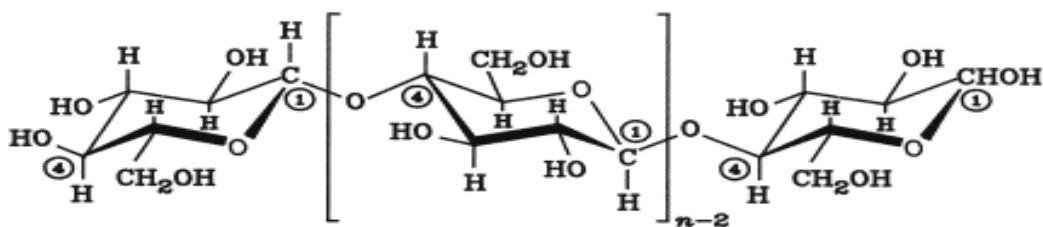


Figure 1-1: Structure of single chain of cellulose molecule (Harmsen et al., 2010).

1.4.2.2 Hemicellulose

Hemicellulose is a type of branched heterogeneous polymer consisting of pentoses (xylose, arabinose), hexoses (mannose, glucose and galactose) and sugar acids. Hemicellulose has a random, amorphous structure with little strength allowing it to be relatively easily hydrolyzed by acid (Hendriks and Zeeman, 2009). Hemicellulose serves as a connection between lignin and cellulose fibers and also serves as a physical protector of cellulose (Laureano-Perez et al., 2005). Hence removal of hemicelluloses through pretreatment can increase the surface area of cellulose for enzymatic attack and subsequently improve hydrolysis rate (Taherzadeh and Karimi, 2008). This is the main objective of acid hydrolysis of lignocellulosic materials.

The solubility of the different hemicelluloses compounds decreases in the following order: mannose, xylose, glucose, arabinose, and galactose. This trend increases with increasing temperature. The solubilization of hemicellulose not only depends on temperature, but also on other factors like moisture content, pH, acid concentration and reaction time. Bobleter (1994) found that the solubilization of hemicellulose compounds in water starts around 180°C under neutral conditions whilst Garrote et al., (1999) observed that from 150°C, already parts of the hemicellulose begin to solubilize. Liao et al., (2005a) reported that reaction temperature of 120°C

and sulfuric acid concentration of 2% was able to completely solubilize hemicelluloses. During thermo-chemical pretreatment, firstly the side groups of hemicellulose react, followed by the hemicelluloses backbone (Sweet and Winandy, 1999).

1.4.2.3 Lignin

Lignin is, after cellulose and hemicelluloses, one of the most abundant polymers in nature and is present in the cellular wall. Lignin is a polymer of phenolics, especially phenylpropanoids in plants. It is an amorphous heteropolymer consisting of three different phenylpropane units (p-coumaryl, coniferyl and sinapyl alcohol) that are held together by different kind of linkages (Hendriks and Zeeman, 2009). The structures of the phenylpropanoids are shown in Figure 1.2. Lignin is known as the “cement” which binds cellulose and hemicelluloses together; thus delignification processes of lignocellulosic organic substances can increase enzymatic hydrolysis (Taherzadeh and Karimi, 2008).

The amorphous heteropolymer is also non-water soluble and optically active; all these properties make the degradation of lignin very difficult (Hendriks and Zeeman, 2009). Lignin, just like hemicelluloses, normally starts to dissolve into water around 180°C under neutral conditions (Bobleter, 1994). The solubility of the lignin in acid, neutral or alkaline environments depends however on the precursor (p-coumaryl, coniferyl, sinapyl alcohol or combinations of them) of the lignin (Grabber, 2005). Lignins are very sensitive to mineral acids such as sulfuric acid and hydrochloric acid, even under quite mild treatments (Sjostrom, 1993).

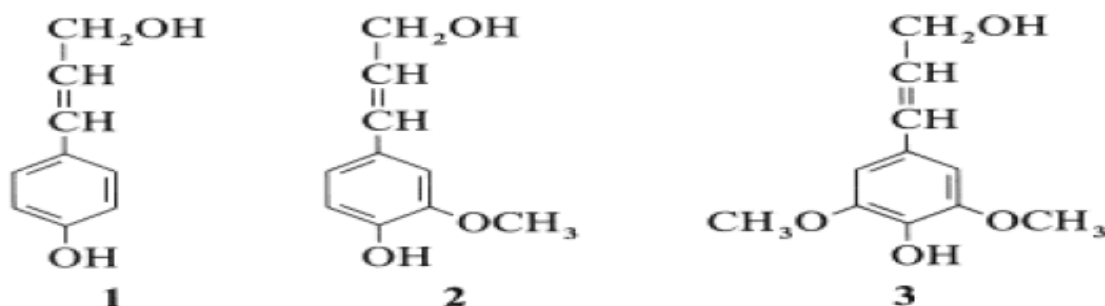


Figure 1-2: P-coumaryl-coniferyl-and sinapyl alcohol: dominant building blocks of the three - dimensional polymer lignin (Harmsen et al., 2010).

1.4.3 Pretreatment processes to enhance resource recovery from lignocellulosics biomass

As discussed in the previous section, the tight structure of lignocellulosics makes it difficult to biodegrade. Hence, pretreatment is very necessary for its bio-conversion to desired value-added products (e.g bio-ethanol). Pretreatment is required to alter the structure of lignocellulosics biomass to make cellulose more accessible to the enzymes that convert carbohydrate polymers to fermentable sugars (Mosier et al., 2005). An effective pretreatment process disrupts cell wall physical barriers as well as cellulose crystallinity and association with lignin so that hydrolytic enzymes can assess the biomass macrostructure (Vlasenko et al., 1997; Liao et al., 2005a; Zhao et al., 2009).

Various methods involving physical, chemical, biological, oxidative processes and different combinations have been developed including organosolv (Zhao et al., 2009), thermo-chemical (Jackowiak et al., 2011), dilute acid (Liao et al., 2007b), steam explosion (CO₂), ammonia fiber expansion, ammonia recycle percolation (ARP) (Mosier et al., 2005; Wyman et al., 2005; Yang and Wyman, 2008). Review articles on biomass pretreatment have been published by the following authors (Sun and Cheng, 2002; Mosier et al., 2005; Yang and Wyman, 2008;

Taherzadeh and Karimi, 2008; Hendriks and Zeeman, 2009). The choice depends on several factors including costs, type of lignocelluloses material, desired product etc.

This research project uses the thermo-chemical process which is the combination of thermal and chemical (hydrogen peroxide with organic acid and/or mineral acids as acidifying reagents) processes. Currently, this process appears to be an attractive alternative due to their higher efficacy over the individual chemical and thermal treatments as a result of the synergy between the two processes (Tyagi and Lo, 2013). However, the conventional thermal or thermo-chemical treatments are time-consuming. Therefore, dielectric heat combined with chemical treatments was developed to provide alternative treatment methods. Dielectric heat is used to provide the heating source and as well as the generator of hydroxyl ions (OH.) where hydrogen peroxide is added, which reacts with the biomass to disintegrate and solubilize solids to release nutrients. The addition of hydrogen peroxide also helps to improve the seattleability of dairy manure. The significant factors affecting thermo-chemical treatment processes include; temperature, input power, hydrogen peroxide dosage and reaction time (Tyagi and Lo, 2013).

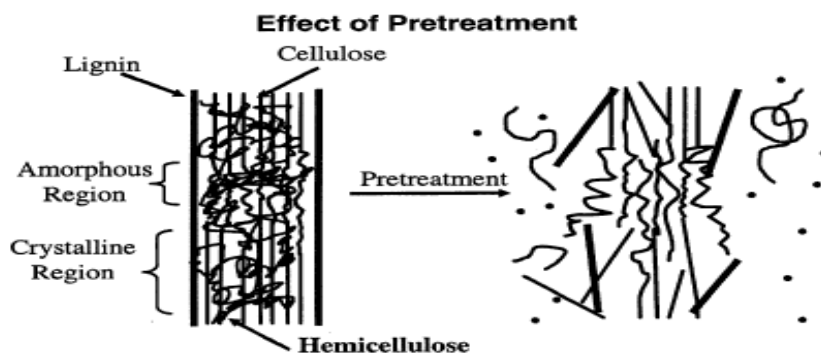


Figure 1-3: Schematic presentation of effects of pretreatment on lignocellulosic biomass (Harmsen et al., 2010).

1.4.4 Microwave and radio frequency dielectric heating

1.4.4.1 Theory of microwave heating

The microwave region of the electromagnetic spectrum (Figure 1.5) corresponds to waves of wavelength 1mm to 1 m (frequencies of 300 MHz to 300 GHz respectively) (Jacob et al., 1995 and Remya and Lin 2011). In order not to interfere with radar and telecommunication frequencies, domestic and industrial microwave ovens generally operate at a frequency range of either 2.45 GHz or 900 MHz unless the apparatus is shielded in way that radiation loss do not occur (Michael et al., 1991). Domestic microwave ovens generally operate at frequency of 2.45 GHz corresponding to a wavelength of 12.2 cm and energy of 1.02×10^{-5} eV (Jacob et al., 1995). Microwaves (MW) are a form of electromagnetic energy that can be transferred to the subject material by the interaction of the electric-field component of the wave with charged particles in the material. Microwave energy absorbed by the subject material will be converted into heat within the material, resulting in an increase in temperature. However, not all materials can be heated by microwaves. Materials which absorb microwave radiation are termed dielectrics and are characterized by possessing very few free charge carriers and exhibiting a dipole movement (Jones et al., 2002). Hence microwave heating are termed dielectric heating. When the microwaves are applied to dielectric materials with an oscillating electric field, the dipoles within the material attempt to realign themselves and flip around the applied field. The dipole movement generates friction inside dielectric materials and the internal energy is dissipated as heat within the volume (or bulk) of the material. This bulk heating increases the temperature of the materials such that the interior portion becomes hotter than the surface. The reverse is the process of conventional heating, in which heat from an external source is supplied to the exterior

surface and diffuses towards the cooler interior regions. Figure 1.4 illustrates the difference between conventional and microwave heating.

Compared to conventional heating techniques, microwave heating has the following advantages; higher volumetric heating rates, highly specific and non-contact heating especially in materials with low thermal conductivity, selective heating, greater control of the heating process, energy efficiency, reduced surface degradation during the drying of wet materials, reduced equipment size and waste, capacity to enhance yield and quality of product (Jones et al., 2002; Tyagi and Lo, 2013).

The dielectric constant is a measure of the material's capability to retard microwave energy as it passes through, whilst the dielectric loss factor is a measure of the material's capability to convert electromagnetic radiation into heat. The ratio of the dielectric loss and dielectric constant define the loss tangent (Michael et al., 1991). This depends on the relaxation times of the molecules in the material, which in turn, depends on the nature of the functional groups and the volume of the molecule (Gabriel et al., 1998).

Microwave dielectric heating has been applied in the following environmental technology fields; contaminated soil remediation, mineral processing, sewage sludge treatment, medical waste management, waste water treatment, activated carbon regeneration, extraction of metals etc (Wu, 2008; Remya and Lin, 2011). This is achieved through either MW heating alone or combined with oxidants, catalysts or advanced oxidation process. In the area on sludge treatment, MW radiation have been applied as pretreatment process to enhance; solids solubilization, nutrients

recovery, dewaterability, anaerobic digestion, heavy metals stabilization and inactivate pathogens (Menendez et al., 2002; Liao et al., 2005b; Wojciechowaska, 2005; Hong et al., 2006; Eskicioglu et al., 2007; Hsieh et al., 2007; Yu et al., 2009). In the field of chemistry, MW dielectric heating has been applied in the synthesis and extraction of wide range of organic compounds (Michael et al., 1991; Gabriel et al., 1998; Mudhoo and Sharma, 2011).

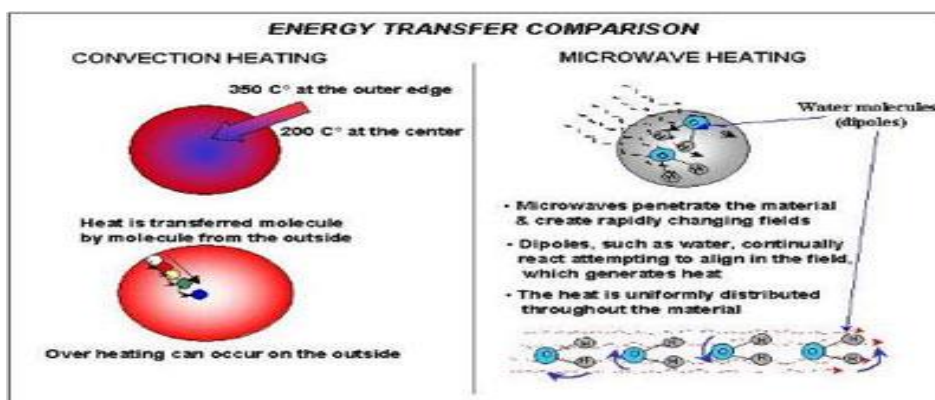


Figure 1-4: Difference between conventional and microwave heating (source: <http://ewi.ca/technology/microwave-information>).

1.4.4.2 Theory and mechanism of radiofrequency heating

Radiofrequency (RF) is somehow similar to microwave in terms of heating behavior are of higher frequency range, between 300 MHz and 300 000 MHz (Ryynanen, 1995). In order to avoid interference with communication systems, only selected frequencies are permitted for domestic, industrial, scientific and medical applications. These frequencies are 13.56, 27.12 and 40.68 MHz (RF), and 915 MHz, 2,450 MHz, 5.8 GHz and 24.124 GHz (MW) (Piyasena et al., 2003). Both microwave and radiofrequency are considered to be part of non-ionizing radiation because they do not have enough energy (less than 10eV) to ionize biologically important atoms and are subsets of several electromagnetic-based heating (ohmic, infrared, and microwave)

methods. Table 1.3 lists the most common electromagnetic-based heating methods, the critical parameters that most affect heating and the common frequency range of application (Zhao et al., 2000).

RF heating is also known as high frequency dielectric heating because it generates heat within a product due to frictional interaction of dipole molecules that reorient themselves continuously in response to an applied electric field (Nijhuis et al., 1998; Awuah et al., 2002). The higher the frequency of the alternating electric field, the greater the energy imparted to the heating medium until the frequency becomes so high that rotating molecules fail to keep up with the external field due to lattice limitations (Zhao et al., 2000). Although identical to MW heating in terms of heating behavior, radiofrequency has the added advantage of uniform heating in homogeneous materials and most important of all, high penetration depth. During RF heating, the product to be heated forms a “dielectric” between two metal capacitor plates, which are alternatively charged positively and negatively by a high frequency alternating electric field (Piyasena et al., 2003).

The advantages of RF heating include; better for large, thick sample, high energy efficiency, short residence time, lower investment cost, easier to control. Whilst the advantages of MW include higher heating rate, design flexibility and availability of much research work on its applications in the literature. The disadvantages of RF heating include; higher risk of arcing, larger floor space, narrow frequency bands and limited research available in the literature (Piyasena et al., 2003). Because RF uses longer wavelengths than MW, electromagnetic waves in the RF spectrum can penetrate deeper into the products so there is no surface overheating or hot or cold spots which are a common problem with MW heating. The RF heating also offers

simple uniform field patterns as opposed to the complex non-uniform, standing wave patterns in microwave heating (Piyasena et al., 2003).

For almost 50 years, extensive research has been carried out on the application of RF heating especially in the food industry and non-food industry including paper, lumber, plastic, contaminated sites remediation. RF heating has been applied in the pasteurization, sterilization and disinfection, drying, enhanced reaction kinetics, selective heating in the food industry (Awuah et al., 2002; Piyasena et al., 2003; Awuah et al., 2005; Ramaswamy and Tang, 2008).

In the field of environmental technology RF heating has been successfully applied in areas such as soil remediation by soil vapor extraction or biodegradation, adsorptive-catalytic off-gas treatment, thermal regeneration of drying agents in biogas or natural gas treatment, and disinfection of dairy and animal facility wastewater (USEPA, 1995; Price et al., 1999; Lagunas-Solar et al., 2005; Roland et al., 2007). However, the applications of RF technology for the purpose of nutrient release and recovery from organic waste streams have yet been fully examined.

The RF heating with or without H_2O_2 was employed in the treatment of dairy manure by Srinivasan et al., (2013). The RF heating-oxidation (RF/ H_2O_2), which uses a combination of RF heating with hydrogen peroxide, had higher treatment efficiency than RF heating alone. The factors affecting the performance of the RF/ H_2O_2 were: hydrogen peroxide dosage, power intensity, reaction time, and acid addition. The treatment efficiency of RF heating was comparable to MW heating process (Kenge et al., 2009a; Lo and Liao, 2011). The study also

concluded that there is significant potential for RF technology to be used for effective nutrient release and solids destruction from dairy manure, as well as organic waste streams.

Table 1-3: Electromagnetic-based heating methods (Zhao et al., 2000)

Heating method	Key parameter	Frequency range	Common frequency
Ohmic (lower f) (Electric field)	σ , E	$f < 1\text{mHz}$	50Hz, 60 Hz
Capacitive dielectric (Medium f) (Electric field)	f, ϵ'' , E	$100\text{ kHz} < f < 100\text{mHz}$ or wavelength \gg sample size	10 mHz 27mHz 39 mHz and others
Radiative dielectric (Higher f) (Electric field)	f, ϵ'' , E	$100\text{ mHz} < f < 100\text{GHz}$ or wavelength \leq sample size	915 mHz, 24.5 GHz, 5.8 GHz, 24.124 GHz and others
Inductive/ohmic combination (Lower f) (Magnetic field)	Hysteresis losses f (B-H curves, f) and Eddy current losses f (H σ)	$50\text{ Hz} < f < 1\text{ mHz}$	50 Hz, 60 Hz 1-50 kHz, 450kHz and others
Inductive (Medium f) (Magnetic field)	f, μ'' , H	$1\text{ mHz} < f < 100\text{ MHz}$ or wavelength \gg sample size	50 mHz and others
Radiative magnetic (Higher f) (Magnetic field)	f, μ'' , H	$100\text{ mHz} < f < 100\text{ GHz}$ or wavelength \leq sample size	915 mHz, 24.5 GHz, 5.8 GHz, 24.124 GHz and others

Note: σ = Electrical conductivity (s/m)
 ϵ = Electrical permittivity
 μ = Magnetic permeability
f = Electric field frequency (Hz)

E = RMS Electric field intensity (V/M)
H = RMS Magnetic field intensity (A/M)
B = Magnetic flux density (W/M^2)

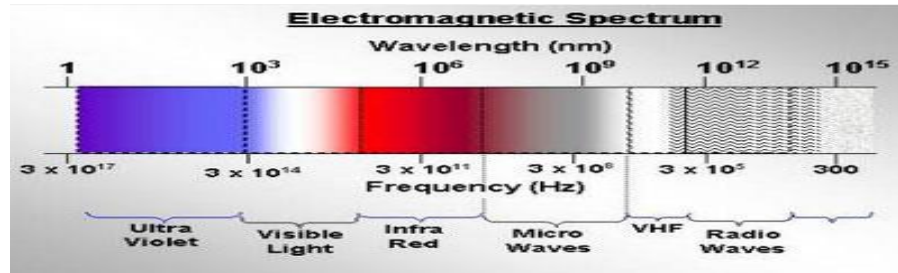


Figure 1-5: Electromagnetic spectrum (source: <http://ewi.ca/>)

1.4.5 Mechanism of matter interaction with microwave radiation

A material can be heated by applying energy to it in the form of high frequency electromagnetic waves. The origin of the heating effect produced by the high frequency electromagnetic radiation arises from the ability of an electric field to exert a force on charged particles, if the particles present in the substance can move freely through it, then a current has been induced. However, if the charge carriers are bound in the compound and restricted in their movements, they merely re-orient themselves in phase with the electric field. This is term dielectric polarization and is made up of four components based on the different types of the charged particles in matter: electrons, nuclei, permanent dipoles and charges at interfaces (Jacob et al., 1995).

$$\alpha_t = \alpha_e + \alpha_a + \alpha_d + \alpha_i$$

α_t = total dielectric polarization

α_e = electronic polarization due to polarization of electrons surrounding the nuclei

α_a = atomic polarization due to polarization of the nuclei

α_d = dipolar polarization due to polarization of permanent dipole in the material

α_i = interfacial polarization due to polarization of charges at interfaces

The electric field reversal of the microwave radiation causes the reversal of the dielectric polarization. The atomic and electronic polarizations occur at a faster time scale than the electric field reversal of a microwave and therefore do not contribute to the dielectric heating effect. The time scale of orientation and disorientation of permanent dipoles in a molecule is similar to the timescale of electric field reversal in the microwave region. Therefore the principal heating mechanisms of microwave are dipolar polarization, conduction and interfacial polarization (Jacob et al., 1995; Jones et al., 2002; Wu et al., 2008; Remya and Lin, 2011). In the case of dipolar polarization which is responsible for the majority of MW heating in solvent systems, when the dipole is subjected to a high-frequency alternating electric field of the MW, rotation (reversing) of the dipole cannot adequately follow the rate of change of direction of the electric field. This leads to a time delay, causing a substantial quantity of energy to be spent that turns into heat. The extent of this dipolar polarization depends on the power of the electric field, strength of the dipole moment, and the mobility of the dipole (Jones et al., 1995).

The conduction mechanism happens when an electrical conductor is irradiated with MW. At that time, the charge carriers (electrons, ions, etc) move through the material under the influence of the electric field resulting in a polarization. The combination of conduction and dipolar polarization produces interfacial polarization which contributes to dielectric heating when conducting particles are suspended in a non-conducting medium in a heterogeneous material (Jones et al., 1995; Remya and Lin, 2011). The interfacial polarization is responsible for the phenomenon of ‘hotspot’ formation, an important characteristic of microwave heating whereby regions of very high temperature form due to non-uniform heating (Hill and Marchant, 1996). This thermal instability arises because of the non-linear dependence of the electromagnetic

radiation and thermal properties of the material on temperature (Reimbert et al., 1996). The formation of standing waves within the microwave cavity results in some regions being exposed to higher energy than others. This results in an increased rate of heating in these higher energy areas due to the non-linear dependence. The hotspot mechanism is responsible for the rapid pollutant degradation in the MW system with adsorbent, for example activated carbon (AC). Cavity design is an important factor in the control, or the utilization of this hotspot phenomenon (Wu, 2008; Remya and Lin, 2011).

In terms of interaction of microwave irradiation with material, materials can be classified as conductors, insulators and absorbers (Church, 1993; Wu et al., 2008). The microwave is reflected from the surface of conductors such as metals, insulators are transparent to microwave and they possess a property to partially reflect and transmit the incident waves travelling through the material, but not store microwave energy in the form of heat. Insulators are often used in microwave oven to support the material to be heated. Absorbers absorb microwave radiation, direct energy transfer, and thus effectively heated at room temperature.

1.4.6 Microwave effects in sludge treatments

Microwave heating is highly effective for the treatment of sludge compared to the traditional thermal heat source. MW effects cannot be achieved by conventional heating. The MW effects are mainly classified as thermal or non-thermal effects. The thermal effects result from MW heating, which generates heat as a result of the absorption of MW energy whereas non-thermal effects are specific effects that are not associated with an increase in temperature when MW interacts with the substrate (Remya and Li, 2011). Thus, thermal effects are due to rapid heating,

volumetric heating, superheating, hotspots and selective heating which are distinct characteristics of MW heating. From sludge treatment perspectives, non-thermal effect occurs when the alternating electric field of electromagnetic field is able to force the polarized side chains of the cell wall macromolecules to break their hydrogen bonds and thus alter their structure (Woo et al., 2000; Loupy et al., 2002; Hong et al., 2004; Park et al., 2004). However, the existence of non-thermal effects has generated controversies within the scientific research community probably due to conflicting results obtained by different researchers. For example, biogas production of MW treated samples was found to be lower in some cases (Eskicioglu et al., 2006 ; Climent et al., 2007) in another case higher (Beszedes et al., 2011) and remained unchanged in (Eskicioglu et al., 2007; Solyom et al., 2011). This trend is same as that observed by other researchers who studied MW pretreatment of grass (Wang et al., 1997; Laser et al., 2002; Li et al., 2012; Jackowiak et al., 2012). However, Solynom et al., (2011) found that the reason for the contradictory results obtained from microwave experiments may be due to the different treatment conditions used. When microwave power is applied to heat a sample material, only a fraction is absorbed and this depend on several factors such as dielectric properties, size and geometry of sample, MW frequency and intensity process time and oven cavity characteristics (Swain and James, 2005; Camponone and Zaritzky, 2005; Gunasekaran and Yang, 2007; Zhu et al., 2007).

However, the formation of thermal gradient and the non-thermal effects of MW are relevant only for solvent-free or dry media reactions and for very viscous or biphasic reaction systems without effective stirring (Jacob et al., 1995).

1.4.7 Microwave enhanced thermo-chemical pretreatment

The heating for microwave assisted pretreatment process is provided by microwave irradiation and because of the advantages of microwave heating such as rapid and focused heating, it can provide a more favorable alternative compared to conventional heating. It has been found that pretreatment processes that combine microwave and chemicals i.e thermo-chemical could achieve higher treatment efficiency of sludge compared to individual chemical and thermal treatments due to synergistic effects (Kennedy et al., 2007; Eskicioglu et al., 2008; Qiao et al., 2008; Chi et al., 2010; Chang et al., 2011). Jin et al., (2009) conducted studies on microwave heating combined with different chemicals (NaOH, CaO, H₂SO₄ or HCl) for the pretreatment of dairy manure. The results show that these thermo-chemical pretreatment processes released 20-40% soluble phosphates and 9-14% ammonium as well as an increased in biogas production compared to conventional pretreatments. However, sulphuric acid pretreatment resulted in low anaerobic digestibility due to sulphur inhibition and side reactions. MW pretreatment alone has been found to be energy intensive (Tyagi and Lo, 2013).

MW assisted pretreatment processes comprise either, using MW alone or combined with; catalysts, Fenton's reagent, oxidants, photolysis, photocatalysis and acids/enzymes (Remya and Lin, 2011). These processes have been applied successfully for a wide range of environmental engineering applications to degrade pollutants, solubilize nutrients, disintegrate solids, enhance biogas yield or for the conversion of lignocelluloses biomass to monosaccharides and bio-ethanol (Van Horn, et al., 1994; Rico et al., 2007). This is achieved through thermal and non-thermal mechanism as discussed in the previous section.

Zhu et al., (2006a, b) reported that microwave-assisted pretreatment had proven effective in the breakdown of the structure of lignocellulosic materials such as switch grass and rice straw. Jin et al., (2009) reported that MW assisted processes can effectively disrupt the physical structure of heterogeneous lignocellulosics such as dairy manure compared conventional heating. According to Jin et al., (2009), when lignocelluloses biomass is microwave irradiated, the polar molecule is heated more rapidly than the non-polar substances causing a thermal gradient at the microscopic level. This eventually causes an “explosion” effect among the particles, and improves the disruption of the physical structure of lignocelluloses biomass particles. This is in contrast with conventional heating where heating is slow and transferred from the surface to the sample particles, resulting in less structural change.

The following sections gives an account of current research on the application domains of microwave assisted thermo-chemical pretreatment of organic slurries for the purpose of COD solubilization and disintegration of solids, nutrients recovery and enhancement of anaerobic digestion. The MW/H₂O₂-AOP which was developed as a novel process for treatment sewage sludge and dairy manure is discussed in details as well.

1.4.7.1 Enhancement of anaerobic digestion

Anaerobic digestion is a biochemical degradation process by which complex organic matter (animal manure or biomass) is decomposed by microbial population in the absence of oxygen into biogas and other by-products (Lusk, 1998). Anaerobic digestion of organic material follows three stages to convert insoluble particulate organic material to two final chemical products (70% CH₄ and 30% CO₂). It includes; hydrolysis (by hydrolytic bacteria), acidogenesis (by acidogenic

bacteria), acetogenesis (by acetogenic hydrogenating and dehydrogenating bacteria) and methanogenesis (by hydrogenotropic and acetoclastic bacteria). The hydrolysis stage is generally considered as rate limiting stage due to slowly bacterial breakdown of several organic compounds (hemicelluloses and lignin) resulting in long retention times (20-50 days) and low degradation efficiency (Tyagi and Lo, 2013).

The benefits of enhancing anaerobic digestion include; increase biogas production, reduction in digester footprints, reduction of biosolids volume for end disposal or beneficial use, production of high quality biosolids, high quality effluent discharge into receiving waters or reused as illustrated in Figure 1.6. When proven with enough data, MW pretreatment of dairy manure combined with struvite crystallization could provide a more effective and sustainable means of treating animal wastes.

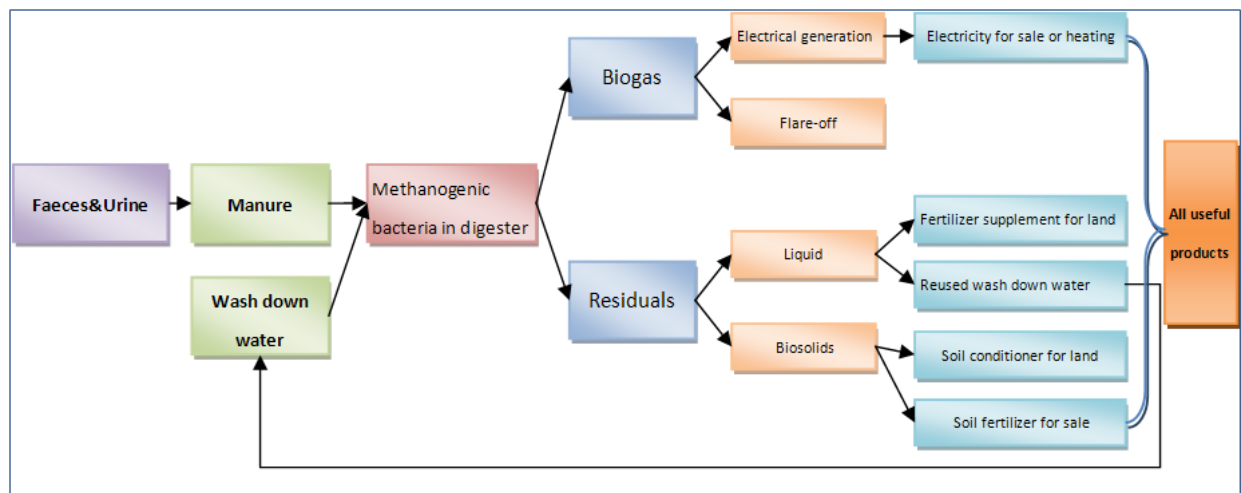


Figure 1-6 : Anaerobic digestion process for dairy manure (Tie and Sivakumar, 2006).

The application of MW pretreatment of sewage sludge for the enhancement of anaerobic digestion have been well studied by several authors (Park et al., 2004; Pino-Jelicic et al., 2006; Eskicioglu et al., 2007, 2008; Kennedy et al., 2007; Park and Ahn, 2010). However, in the case of pretreatment of dairy manure, extensive studies are limiting (Angelidaki and Ahring, 2000; Qureshi et al., 2008; Jin et al., 2009). Significant improvements in anaerobic digestion and/or biogas production is directly linked to the production of more digestible compounds such as volatile fatty acids in the pretreated manure as a result of the MW irradiation breaking down the complex structure of manure components. Other factors known to influence the enhancement of anaerobic digestion is the general COD solubilization and formation of toxic compounds and side reactions which could inhibit enzymatic activity especially when chemicals are combined with MW irradiation.

Eskicioglu et al., (2008) reported that anaerobic digestion of WAS (TS-5.4%) that was microwave treated at 96°C (50% MW intensity) enhanced its ultimate degradability and produced the highest amount of biogas with 21% increases over the controls after 19 days of digestion. Furthermore, Eskicioglu et al., (2007) observed that MW-acclimated inoculums treated at 95°C produced 16% more biogas compared to the control after 15 days of mesophilic batch digestion of pretreated sludge. Kennedy et al., (2007) also reported a 16% improvement in methane production during anaerobic digestion of MW pretreated sludge. Pino-Jelicic et al., (2006) reported a 53.9% volatile solids reduction for MW pretreated sludge followed by anaerobic digestion, which was higher than the control (49%). The volatile solids represent the organic part of total solids (TS). The MW-digested sludge showed higher biogas production by 16.4 and 6.3% as compared to control and conventionally heated-digested sludge, respectively.

Park and Ahn, (2010) investigated the effectiveness of MW-pretreatment at temperature of 80°C over the conventional thermal pretreatment at 80°C. They reported 60.6% improvement in biogas yield for MW pretreatment compared to conventional thermal pretreatment at a hydraulic retention time (HRT) of 5 days. Park and Ahn (2010) reported 79% increase in methane production, from mesophilic digestion of MW-pretreated sludge. Hong et al., (2006) reported 68% increase in biogas production at solids retention time (SRT) of 5 days for the reactor digesting MW-pretreated sludge compared with the control reactors operating at 11 days SRT. Qureshi et al., (2008) observed an increase in short chain volatile fatty acids (acetic acid) when dairy manure was MW pretreated at 170°C with a reaction time of 5 mins. These short chain volatile fatty acids are known to boost methane production in the subsequent anaerobic digestion process.

However, for plant based lignocellulosic conflicting results have been reported; Jakowiak et al., (2012) reported that microwave pretreatment has no significant effect on the ultimate volume of methane produced from switch grass. However methane yield increased by about 4.5% after thermal pretreatment. But the time required to achieve 80% of the ultimate volume was reduced by 4.5 days. Li et al., (2012) reported that thermal pretreatment of grass increased methane production by 8% whilst MW pretreatment decreased methane production by 12%.

1.4.8 Acid hydrolysis of lignocellulosic biomass

Acid hydrolysis of lignocelluloses biomass has been applied to enhance resource recovery processes such as biogas production and production of monosaccharides for value added products. During acid hydrolysis, acid is used to breakdown the matrix structure of

lignocelluloses biomass into fermentable sugars for subsequent conversion to value added products. The whole process can be carried out solely with the acid or acid pretreatment is combined with enzymatic hydrolysis to produce fermentable sugars (Iranmahboob et al., 2002; Wen et al., 2004). Conventional or dielectric heating provides the heating source. The acid normally used is mineral acids (HCl or H₂SO₄) and the process conditions are either concentrated acids at low temperature or dilute acid at high temperature (Sun and Cheng, 2002; Liao, et al., 2007b). Thus, temperature has profound influence on the acid hydrolysis process. However, dilute acid pretreatment is commonly used because of the significant reduction in the production of undesired products. Factors that affect the yield of lignocelluloses to monomeric sugars and by-products include particle size, liquid-to-solid ratio, type and concentration of acid used, temperature, reaction time and type of lignocelluloses material (Hendriks and Zeeman, 2009). During acid hydrolysis, the main objective is to solubilize the hemicellulose, especially xylan as glucomannan is relatively acid stable and by this, making the cellulose better accessible for further conversion to the desired product (Liao et al., 2007b; Hendriks and Zeeman, 2009).

Too severe pretreatment conditions such as high temperatures of 160°C and above causes the production of inhibitory substances such as furfural and hydroxymethylfurfural (HMF) in acidic environments which affects the downstream enzymatic hydrolytic processes (Ramos, 2003). At these higher temperatures, lignin is likely to be solubilized which also produces inhibitory compounds known to have effects on bacteria, yeast and methanogens/archae (Gossett et al., 1982). These soluble lignin compounds are very reactive and will, if not removed quickly, re-condensate and precipitate on the biomass (Shevchenko et al., 1999; Liu and Wyman, 2003).

Brownell et al., (1986) reported that temperatures of 250°C and higher causes unwanted pyrolysis reactions to take place.

Acid hydrolysis of lignocellulosics biomass is normally carried out in two stages; the first stage is carried out by higher concentrated acid during which the hemicellulose is hydrolyzed and then followed by dilute acid or enzymatic hydrolysis which minimizes the production of inhibitory substances. Liao et al., (2006) investigated a two stage hydrolysis of pretreated dairy manure with low nitrogen content (1.3%) dairy by combining concentrated and dilute acids. The conditions were 75% acid concentration, 3:5 sample to acid ratio, and 30 mins for the first stage and 12.5% acid, 10% dry sample at 135°C for 10 mins for the second stage which yielded 84% glucose and 80% hemicelluloses sugar. Yawson et al., (2011) reported that microwave-assisted thermo-chemical pretreatment of dairy manure was accomplished in one stage at a temperature of 160°C and heating time of 20 mins and the yield for reducing sugar was 15.5%. Liao et al., (2007b) observed that dilute acid (1%) and reaction time of 2.8 hours and temperature of 140°C yielded 31% cellulose, 3.2% hemicelluloses and 20.8% lignin.

Because of the negative environmental impacts and other disadvantages of mineral acid hydrolysis such as; tendency to produce inhibitory or toxic substances, corrosion of equipment and difficulty with regard to acid recovery after treatment, research efforts have been made on the use of organic acids such as oxalic acid (Ramos, 2003; Liu and Wyman, 2003; Negro et al., 2003; Lee et al., 2013). Besides, Lee et al., (2013) reported that, oxalic acid used in pretreatment could be recovered and reuse without any effect on the yield of the final product (fermentable

sugar). Oxalic acid pretreatment of dairy manure also has the advantage of removing calcium ions which interferes with the subsequent struvite crystallization process.

1.4.9 Microwave enhanced advanced oxidation process (MW/H₂O₂-AOP)

Advanced oxidation processes (AOPs) are highly efficient and novel methods that involves the generation of highly reactive free radicals especially (OH \cdot) for rapid oxidation/degradation of many organic and inorganic substances. With the aid of a catalyst or irradiation, hydrogen peroxide can be converted to hydroxyl free radical which is a highly powerful oxidizing agent with an oxidation potential of 2.80V which is second highest after fluorine (Table 1.4). This can undergo rapid and non-selective reaction with many organic and inorganic solutes.

A mixture of iron (II) salts and hydrogen peroxide is called Fenton's reagent and is one of the widely applied AOPs because of its ability to degrade high loading of organic compounds (Lo et al., 2008). The most widely adopted AOPs include photodegradation, Fenton, photo-Fenton, ultrasonication and ozonation (O₃). Unlike conventional physicochemical processes, AOPs provide faster reaction rate; at the same time, AOPs are effective in the removal of various bio-refractory organics present in water and wastewater. In recent years, AOPs are considered as a green technology because of the ability to reduce hazardous product formation and emissions (Tyagi and Lo et al., 2013).

Table 1-4: Oxidation potential of several oxidants

Species	Oxidation potential (V)
Fluorine	3.03
Hydroxyl radical	2.80
Atomic oxygen	2.42
Ozone	2.07
Hydrogen peroxide	1.78
Perhydroxyl radical	1.70
Permanganate	1.68
Hypobromous acid	1.59
Chlorine dioxide	1.57
Hyperchlorous acid	1.49
Chlorine	1.36

The mechanism responsible for enhancing the degradation of various pollutants in thermochemical systems combining MW and H_2O_2 is the dipolar polarization (Remya and Lin, 2011). The mechanism creates higher temperatures within a shorter span compared to conventional heating methods, which provokes the increased decomposition of H_2O_2 into (OH.) free radicals (1) - (3). Subsequently, (OH.) free radicals generated in the system undergoes adduction reaction with the target pollutants and the resulting intermediates as shown in (4) - (6) below. As a result, rapid and improved degradation rates are observed. On the other hand, H_2O_2 can act as (OH.) quencher at high concentrations, consequently lowering the (OH.) concentration as shown in (4).

This decreases the degradation rate. The mechanism for free radical formation is given as follows;

Irradiation (MW or UV)



Iron salts and hydrogen peroxide



Ozone and hydrogen peroxide



Once the hydroxyl radical is generated it undergoes series of complex reaction as shown below:



Researchers at Civil Engineering department at University of British Columbia (UBC) have developed MW/H₂O₂-AOP as a novel and highly efficient pretreatment technology for the purpose of nutrient solubilization, solids destruction and disintegration of organic particles from sewage sludge and dairy manure. The process has been examined in a temperature range of 40°C to 200°C. Various amounts of H₂O₂ (0.05-1wt %) and different heating times (1.5-20 mins) have been tested. Other researchers have applied MW/H₂O₂-AOPs for enhanced pollutant degradation (Prasannakumar et al., 2009; Yu et al., 2009; Ravera et al., 2009; Lee et al., 2009; Shiyong et al., 2009). Lo et al., (2008) compared microwave enhanced oxidation processes with and without

ferrous sulfate addition in the pretreatment of secondary sewage sludge for the purpose of solids reduction and nutrients solubilization. The results indicated that MW/H₂O₂-AOP was more effective than MW/H₂O₂-AOP with ferrous sulfate solution. A similar result was obtained by Sanz et al., (2003) when they did a comparative study between MW/H₂O₂-AOP and Fenton processes for the treatment of synthetic phenol solution. A comprehensive literature review of up to date research on the application of MW/H₂O₂-AOP for sludge treatment and resource recovery has been provided by Lo and Tyagi, (2013). It has been found that the MW/H₂O₂-AOP technology is more effective in the solubilization of ortho-phosphates from dairy manure than from sewage sludge. Liao et al., (2005b) reported that sewage sludge treated with microwave at 120°C for 17 mins released 36.3% ortho-P whilst manure treated by microwave heating released 12.91% ortho-P at a much higher heating time of 30 mins. Similar trends were reported by Pan et al., (2006) and Jin et al., (2009). This is because sewage sludge contains essentially microbial cells which are relatively easy to disintegrate through microwave irradiation leading to cell lysis with the consequent release of biodegradable organic materials, whereas dairy manure contains much higher proportion of dissolved organic compounds compared to microbial cells. For example, dairy manure contains many forms of phosphorus including inorganic-P, acid soluble organic-P, lipid-P and nucleic acid-type P which are more difficult to solubilize (Barnett, 1994). The major drawback of MW/H₂O₂-AOP is the relatively higher operational cost (Remya and Lin, 2011). Detailed literature review on the application of MW/H₂O₂-AOP treatment of organic slurries for COD solubilization and nutrients recovery are discussed below.

1.9.1.1 COD Solubilization

The primary organic compounds found in organic slurries are carbohydrates, proteins and lipids. When MW treated, carbohydrates are hydrolyzed into lower molecular weight polysaccharides and possibly simple sugars. Proteins are hydrolyzed into a series of saturated and unsaturated acids, ammonia and carbon dioxide. Lipids are hydrolyzed to palmitic acid, stearic acid, and oleic acid. The factors that affect sludge solubilization include water content, solids concentration, sludge type (primary, secondary, mixed), treatment temperature, power intensity and reaction time (Tyagyi and Lo, 2013).

Liao et al., (2007a) reported that up to 96% of TCOD was solubilized after MW pretreatment of WAS at a MW heating time of 5 mins. Jin et al., (2009) reported that thermo-chemical pretreatment of dairy manure using microwave and HCl led to higher performance in terms of COD solubilization, anaerobic digestibility and phosphorus recovery. The optimal temperature and heating time reported were 147°C and 25.3 mins for methane production, and 135°C and 26 mins for orthophosphate release, respectively. Beszedes et al., (2011) applied MW heating (5 W/g and 30 mins) to treat dairy manure and they observed a significant enhancement in COD solubilization (up to 57%) and VS/TS ratio (up to 32%). Wong et al., (2006) also reported the effect of MW/H₂O₂-AOP on sludge COD, with up to a complete solubilization at temperature of 80°C and above. The study showed that with regards to struvite recovery, ammonia was the limiting factor without H₂O₂ and ortho-P was limiting with H₂O₂ dosage. In addition, sludge pasteurization or sterilization was enhanced with MW/H₂O₂-AOP. Chan et al., (2007) reported that all of COD in sewage sludge was solubilized at 80°C with a 34 ml/L H₂O₂ and 17 mL/L H₂SO₄ dose indicating that all of the organic material was solubilized. Kenge et al., (2008)

reported a 25% increase in SCOD upon pretreatment of WAS (2.9% TS) at 80°C with 5 mins heating time with 1-mL H₂O₂ (30% per 1% TS dosage). Lo et al., (2008) reported that 18% increase in COD solubilization after pretreatment of WAS by MW/H₂O₂-AOP at 80°C for 3mins. Eskicioglu et al., (2008) reported that for hydrogen peroxide dosage of 1g H₂O₂ (30% v/v)/g TS, COD solubilization increased from 3% (control) to 24% after MW/H₂O₂ treatment for 10 mins at 120°C. They concluded that higher temperatures (>80°C) increased the decomposition of H₂O₂ into (OH.) radicals and enhanced both the oxidation and the particulate COD disintegration of WAS samples. Wang et al., (2009) applied MW heating at (80°C) for the treatment of WAS, followed by the addition of H₂O₂ and then continuous heating to 100°C. They observed that the higher the H₂O₂ dosing ratio, the more the SCOD was released into the supernatant.

Liao et al. (2007a) investigated the relationship of COD solubilization, VFA formation and final oxidation with MW/H₂O₂-AOP in acid condition. They found that over 96% of the total COD was solubilized and up to 25% of this soluble COD was acetic acid. The conditions were MW (20°C/ min) for 5mins with a 7-ml/L H₂O₂ dose (30% by wt.). The presence of an inorganic acid was a stability factor in retaining the SCOD in solution, instead of the formation of carbon dioxide, resulting in reduced total COD in solutions. By controlling the amounts of H₂O₂ and acid addition, MW/H₂O₂-H⁺AOP process could solubilize and/or reduce the sludge mass. Qureshi et al., (2008) reported that over 36% of total chemical oxygen demand was reduced when dairy manure was treated with MW/H₂O₂-AOP at temperature of 170°C and heating time of 5mins.

1.9.1.2 Nutrient recovery

Organic slurries contain considerable amounts of nutrients (nitrogen and phosphorus). These nutrients exist mainly in the form of proteinaceous compounds. The breakdown and solubilization of waste biomass and its subsequent conversion to phosphates and ammonia could potentially be recovered as calcium phosphate and magnesium ammonium phosphate (struvite). Calcium phosphate is the same chemical as that in mined phosphate ore, and is readily recycled in the phosphate industries (Mudhoo and Sharma, 2011). Struvite is an excellent plant fertilizer because of its slow release properties, and can be used directly. Struvite precipitation occurs naturally in waste streams with the right environmental conditions. Historically, much of the literature and research efforts on struvite had focused on the prevention of its formation in the piping and pumps of waste water treatment plants and agricultural waste treatment systems. In order to resolve the dilemma of nutrients removal from municipal and agricultural wastewaters and the dwindling natural phosphates deposits, much research efforts have been directed towards controlled struvite crystallization on both batch and field scales. The Netherlands, Australia and Japan are among the first countries where significant research work on struvite crystallization has been developed and implemented on the full-scale. In order to precipitate phosphorus, it must be available as soluble phosphates (ortho-P). Organically bound phosphorus must be converted to phosphates through pretreatment process. This is achieved through chemical, biological or conventional thermo-chemical processes. In search for a rapid, efficient phosphorus solubilization process, MW technology was developed for the treatment of sewage sludge (Liao et al., 2005b, c). After the successful application of MW enhanced technology to sewage sludge pretreatment, it was successfully extended for the pretreatment of dairy manure (Pan et al., 2006; Qureshi et al., 2008).

Pan et al., (2006) reported that 80% of total phosphate could be release from liquid dairy manure into solution at microwave heating time of 5 mins at 170°C. They observed that when microwave heating was combined with hydrogen peroxide, 85% of total phosphate could be released at lower temperature (120°C). Liao et al., (2005c) reported that at the same heating time and temperature, up to 76% of total phosphorus (TP) could be released from sewage sludge, when microwave radiation was combined with hydrogen peroxide and same heating time, 84% of total phosphorus could be released at 170°C. Wong et al., (2006) reported that MW/H₂O₂-AOP released up to 61% of total phosphorus and 36% of TKN released into solution at 100°C and 120°C respectively with 5 mins exposure time. Chan et al., (2007) reported that about 70% phosphorus and 47% of ammonia as TKN was solubilized after treatment of WAS in a single-stage MW/H₂O₂-AOP at temperature of 120°C, H₂O₂ dosage 35 mL/L, and H₂SO₄ concentration of 17 mL/L. Wong et al., (2007) reported that maximum quantity of ammonia (217 mg/L) which represented 52.6% TKN was solubilized at 200°C with H₂O₂ dosage of 2 mL whilst under same conditions, 95.5% of the initial TP was solubilized with 0.5 ml H₂SO₄ dose. Detailed review of results obtained by several researchers reveal that, MW treatment alone could solubilize up to 76% TP and 36% TKN at temperature of 100°C and reaction time of 5 mins. However MW/H₂O₂-AOP could increase TP and TKN solubilization up to 95.5% and 53%, respectively after pretreatment of WAS at a high temperature (200°C) with 2 mL H₂O₂ and 0.5 mL H₂SO₄ chemical dosages. When proven with enough performance data, MW/H₂O₂-AOP pretreatment of organic waste slurries combine with struvite crystallization could provide efficient and sustainable treatment of organic slurries wastes.

Chapter 2 : Radiofrequency pretreatment of dairy manure

2.1 Introduction

Dielectric heating using radiofrequency (RF) has been widely used in drying of food products in food processing industry applications (Ramaswamy and Tang, 2008). It has also been applied in the environmental technology areas such as soil remediation by soil vapour extraction or biodegradation, adsorptive-catalytic off-gas treatment, thermal regeneration of drying agents in biogas or natural gas treatment, and disinfection of dairy and animal facility wastewater (Price et al., 1999; Lagunas-Solar et al., 2005). However, the applications of RF technology for the purpose of nutrient release and recovery from organic waste streams have yet been fully examined.

The RF heating with or without H_2O_2 was employed in the treatment of dairy manure by Srinivasan et al., (2013). The RF heating-oxidation (RF/ H_2O_2), which uses a combination of RF heating with hydrogen peroxide, had higher treatment efficiency than RF heating alone. The factors affecting the performance of the RF/ H_2O_2 were: hydrogen peroxide dosage, power intensity, reaction time, and acid addition. The treatment efficiency of RF heating was comparable to MW heating process (Kenge et al., 2009a; Lo and Liao, 2011). The study also concluded that there is significant potential for RF technology to be used for effective nutrient release and solids destruction from dairy manure, as well as organic waste streams.

The objective of this study was to optimize the RF/ H_2O_2 process for treating solids portion of dairy manure after solids/liquid separation. Dairy manure contains fats, proteins, lignin,

carbohydrates and inorganic residue, and is rich in a variety of nutrients including nitrogen, phosphorus, and minerals. It can be converted into valuable products, instead of a waste material to be disposed. Carbonaceous matters such as lignocellulosic components in dairy manure can be transformed into fermentable saccharides, and then they can further be converted into ethanol and other useful organic products (Sun and Cheng, 2002; Cantrell et al., 2008). Nutrients and metals, such as phosphorus, nitrogen, and potassium can be recovered via crystallization process to produce struvite and/or K-struvite. The solids fraction of dairy manure after liquid-solids separation process results in higher lignocellulosic and phosphorus content than that of un-separated manure. The separated solids dairy manure is considered to be a better substrate for nutrient and energy recovery than dairy manure itself (Barnett, 1994; Rico et al., 2007; Hjorth et al., 2010).

2.2 Materials and methods

2.2.1 Apparatus

A 6 kW radiofrequency unit (RF specialists Ltd., Vancouver, Canada) was used to heat the dairy manure. The RF oven is an aluminum box with doors on one side and an electrode suspended on polypropylene insulators. A transmission line connects the generator output to the oven electrode. The system has a capacity of accommodating up to 9 L of sample in a single run at an operating temperature of up to 95°C. Commercially available microwave safe plastic containers were used as reaction vessels, with aluminum plates moulded to their bottom surface. The top surface of the vessels was covered with an aluminum cap with two 0.8 cm rods including Teflon spacers and locking nuts to mount the plate. The temperature was measured using a Neoptix fiber

optic probe inserted into the container through a hole in the cap. The aluminum cap can be removed from the container, without removing the rods, when experiments are not performed.

2.2.2 Substrate

Dairy manure was obtained from the Dairy Education & Research Centre, University of British Columbia in Agassiz, British Columbia, Canada. Once collected from the farm, the dairy manure was stored in closed containers at 4°C. Dairy manure used in this study was the solids portion obtained after solid-liquid separation. The separated dairy manure contained large amounts of sand, bedding material, as well as undigested lignocellulosic materials. Distilled water was added to the samples and subsequently decanted to remove the sand. The resulting separated dairy manure had 4.4% total solids (TS).

2.3 Experimental design

The experimental design was following the same design protocols in the earlier study conducted by Srinivasan et al., (2013). Acidified dairy manure samples were subjected to RF/H₂O₂ advanced oxidation (RF/H₂O₂-AOP) process to investigate the effects of various factors contributing to solids disintegration and nutrients release from separated dairy manure samples. These factors include input power, hydrogen peroxide dosage and holding time. The separated solids manure samples were acidified using sulphuric acid (certified ACS plus, Fischer chemical) to pH 4.0. The samples were acidified because previous research work by Kenge, et al., (2009a) and Lo and Liao, (2011) show that substantial amounts of ortho-phosphate were released into solution only in acidic condition, preferable below pH 4.0.

Three litres of dairy manure was used for the RF/AOP process with or without hydrogen peroxide. The runs were carried out in three 1L vessels and a sample volume of 600 mL was used. After addition of acid, the samples were subjected to RF heating held at 90°C for 20, 30 or 50 mins. Initially, the power control was set to a desired setting level until the manure samples reach 90°C after which they were held at that temperature for the desired holding time.

2.3.1 Surface response design

Response surface methodology (RSM) is one of the most popular statistical experimental designs widely used to find improved or optimal process settings. It has the advantages of rotatability and is less complex in terms of optimization compared to full factorial designs. Box-Benken design for response surface design was chosen for this experiment to develop a mathematical model which was able to predict responses (ortho-P, ammonium, SCOD and VFA) as a function of holding time, input power and hydrogen peroxide dosage. The model was able to predict the optimal conditions for the responses.

The response surface designs are used for modeling a curved surface (quadratic) to continuous factors. These designs are capable of fitting a second order prediction equation for the response. The quadratic terms in these equations model the curvature in the true response function. Using a statistical program, MINITAB, version 16.0, an experimental design consisting of 15 trials was selected. The experiment design is presented in Table 2.1. The three factor levels chosen for input power setting were 50, 60 and 70%, holding time were 20, 50 and 80 min and hydrogen peroxide dosage were 0.5, 1.0 and 1.5% (v/v). The input power was directly related to heating ramp rate. The model equation can be written as follows:

$$E(Y) = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_1 X_2 + \beta_5 X_1 X_3 + \beta_6 X_2 X_3 + \beta_7 X_1^2 + \beta_8 X_2^2 + \beta_9 X_3^2 \quad (1)$$

Where $E(Y)$ is the response (nutrient concentration or solids disintegration), X_1 , X_2 , X_3 are the main variables (holding time, input power and H_2O_2 dosage), and β_0 , β_1 , β_2 , β_3 , β_4 , β_5 , β_6 , β_7 , β_8 , β_9 are statistical coefficients. The response and variables were analyzed by the response surface analysis function of the MINITAB software to obtain the values of the coefficients of equation (1).

Table 2-1: Summary of experimental conditions

Set	Input power (%)	Holding Time (Min)	H_2O_2 Dosage (%) v/v
1	60	20	0.5
2	50	50	0.5
3	60	80	0.5
4	70	50	0.5
5	60	50	1
6	50	80	1
7	70	20	1
8	60	50	1
9	70	80	1
10	50	20	1
11	60	50	1
12	60	80	1.5
13	70	50	1.5
14	50	50	1.5
15	60	20	1.5

2.3.2 Sampling, chemical and statistical analysis

Sampling was carried out immediately after the RF treatment and treated manure slurry was diluted in 1:1 ratio with distilled water and centrifuged at 3500 rpm for 15 min through Beckman centrifuge. The liquid portion from the centrifuge tubes were filtered through 0.45µm whatman No.4 filter papers. The filtrate was collected for chemical analysis. The dairy manure samples, both untreated and treated, were analyzed for TS, total COD (TCOD), total phosphorus (TP) and total Kjeldahl nitrogen (TKN). Table 2.2 shows the characteristics of raw separated dairy manure used over the course of this study.

The soluble COD (SCOD), ortho-phosphate, soluble ammonia, volatile fatty acids (VFA) and metals in the soluble portion of the dairy manure were measured. All of the chemical analyses were carried out following the procedures outlined in Standard Methods (APHA, 1998). For orthophosphate analysis, dairy manure samples were determined at 0.5% TS to ensure correct measurement (Wolf et al., 2005). The treated dairy manure samples were also analyzed for total solids (TS), total COD (TCOD), total phosphorus (TP) and total Kjeldahl nitrogen (TKN). Ortho-phosphate, soluble ammonia, TP and TKN were determined by a flow injection system (Lachat Quik-Chem 8000 Automatic Ion Analyzer, Lachat Instruments, USA). A Hewlett Packard 6890 Series II gas chromatograph, equipped with a flame ionization detector (FID), was used to measure VFA. Volatile separation was accomplished with a HP free fatty acid phase (FFAP) column. Calcium (Ca), magnesium (Mg), sodium (Na) and potassium (K) were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Control samples were used in a similar manner throughout the experiments to affirm the calibration curve and to ensure the accuracy of measurements.

Table 2-2: Characteristics of raw separated manure slurry

Parameters	Values
pH	7.11
TS (%)	4.1 – 4.4
VS (%)	24.47±1.24
Total COD (g/L)	30 – 41
Total Phosphorus (mg-P/L)	211.96±24.05
VFA	0.7 – 3
TKN (mg-N/L)	1264±93.49
Soluble COD (g/L)	2.3 – 6.5
Ortho-P (mg-P/L)	42 – 76
Ammonia Nitrogen (mg-N/L)	348 – 613
Ca (mg/L)	1076±236
Mg (mg/L)	517±288.18

2.4 Results and discussion

The initial characteristics of the liquid manure slurry are given in Table 2.2. Three different starting materials were used to cover all the fifteen trials and the characteristics varied which may be due to ageing of the manure. The effects of hydrogen peroxide dosage, input power and holding time on nutrient release and solids disintegration were studied based on the concentrations of the soluble parameters; ortho-P, ammonia, COD and VFA. Response surface plots which display a three-dimensional view was used to determine the appropriate response values and operating conditions. The results obtained before and after treatment which was used in the surface response model are provided in Table 2.3.

2.4.1 Nutrient release

2.4.1.1 Orthophosphate release

Orthophosphate concentrations for untreated separated solids varied from 42 to 76 mg/L. This was caused by anaerobic decomposition during storage of the manure; longer the ageing, higher the orthophosphate content was in the raw separated solids manure. Orthophosphate concentrations also varied from 52 to 155 mg/L after acidification with sulfuric acid.

After RF/H₂O₂ treatment, orthophosphate concentration ranged from 62 to 160 mg/L, and the yield of orthophosphate was between 39 to 75% of TP. In the previous study using un-separated manure, the yield of orthophosphate after the treatment was between 58 to 91% of TP (Srinivasan et al., 2013). The ratio of ortho-P/TP was higher for un-separated dairy manure than separated manure. Albeit different substrates, from Table 2.5, it was obvious that percent of orthophosphate in TP increased significantly after RF/H₂O₂ for whole manure and separated solids fraction of dairy manure. For both types of manure, the % ortho-P as TP was the highest from trial 13 (70% power intensity, 50 min holding time and 1.5% H₂O₂ dose), 91% and 75% for un-separated and separated dairy manure, respectively. This could be because the operating conditions used in trial 13 were very close to the optimum conditions predicted for both manure types.

The results of RF/H₂O₂ were comparable to the results reported by other researchers using microwave-enhanced advanced oxidation process (MW/H₂O₂-AOP); percent TP released as orthophosphate increased from 21 to 47% at 80°C (Kenge et al., 2008). Notwithstanding, the different substrates and environmental conditions, the results were quite comparable. The %TP

release as ortho-P from dairy manure was lower than sewage, this was because dairy manure contains many forms of phosphorus including, inorganic, acid soluble organic-P, lipid-P and nucleic-P, which are difficult to solubilize. Compared to sewage sludge, which is essentially microbial cells, and therefore relatively easy to release phosphorus when the cells are disrupted (Barnett, 1994; Liao et al, 2005c; Jin et al., 2009).

Based on the surface response design analysis, a model was proposed based on the regression coefficients for the concentration of orthophosphate remaining in the treated manure. The regression model proposed is as follows:

$$Y = 781.19 - 6.95T - 116.00D - 14.27P + 0.007 T^2 + 17.97 D^2 + 0.08P^2 + 1.40DT + 0.091 PT - 0.180PD. \quad (1)$$

Where, Y is orthophosphate (mg/L), P is input power (%), T is holding time (min) and D is H₂O₂ dose (%). The equation is valid within the range of parameters used in the study: input power of 50, 60 and 70%, holding time 20, 50 and 80 mins, and, H₂O₂ dosage of 0.5, 1 and 1.5%. The correlation coefficient (R²) was 0.52; the low R² value may be due to the fact that different starting materials were used to cover all the fifteen trials and the orthophosphate content in the untreated manure samples varied widely (Table 2.2& 2.3). According to the statistical parameter estimate from equation (1), an increase in hydrogen peroxide dosage would decrease the release of orthophosphate. Input power and holding time had negative effect on orthophosphate concentration, indicating that as these parameters increased, orthophosphate concentration decreased. The results were similar to the previous RF/H₂O₂ treatment of un-separated manure (Srinivasan et al., 2013). The interaction between hydrogen peroxide dosage with input power

and holding time with input power were also found to be significant factors for orthophosphate release. For the concentration of orthophosphate in treated solution, the magnitude of factor affecting orthophosphate was found to increase in the following order: H_2O_2 dose > second order effect of H_2O_2 dose > input power > holding time. A response surface profile for orthophosphate release is shown in Figure 2.1 & 2.2. The optimized operating conditions for orthophosphate were an input power level at 62.9%, holding time of 55.9 min and H_2O_2 dose of 1.1%.

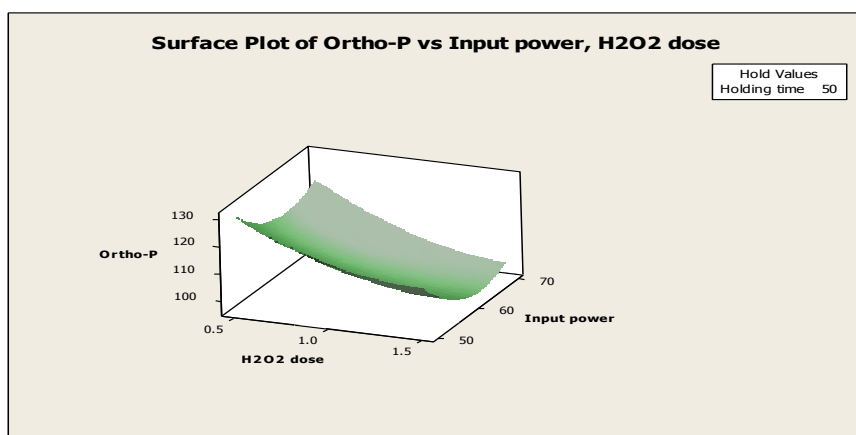


Figure 2-1: Response surface profile showing ortho-P with respect to input power and H_2O_2 dosage

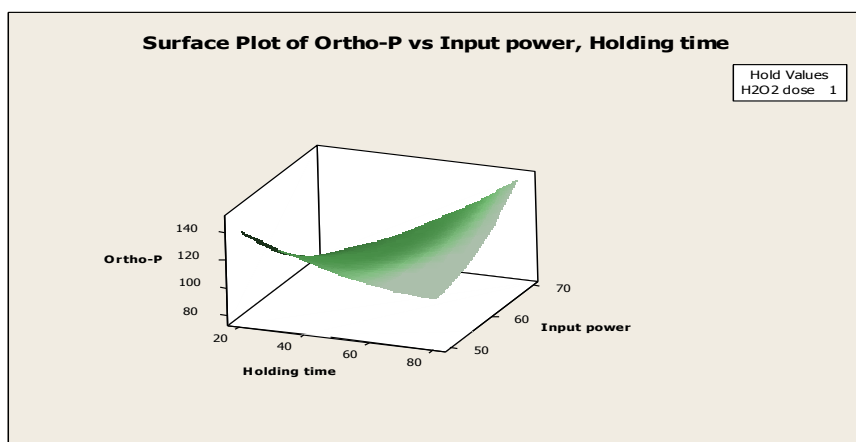


Figure 2-2: Response surface profile showing ortho-P with respect to input power and holding time.

Table 2-3: Experimental results from the surface response study

Trial no.	TS	Ortho-P	Ammonia	SCOD	TCOD	VFA
	%	mg/L	mg/L	g/L	g/L	g/L
Raw	4.1 – 4.4	42 – 76	348 – 613	2.3 – 6.5	30 - 41	0.7 – 3
Acidified	4.2 – 5.0	52 – 155	412 – 731	1.7 – 8.4	28 - 40	1.1 – 3
1	5.4±1.6	134±11	673±31	6.6±0.7	28±2.2	2.8±0.1
2	5.4±1.6	128±5.6	689±47	6.8±0.2	31±0	2.9±0.1
3	4.7±1.4	101±6.9	631±11	6.6±0.5	36±14	2.8±0.1
4	5.9±3.3	142±21	706±116	7.4±0.3	38±0.9	2.8±0.1
5	4.2±0.1	160±3.9	756±17	4.0±0.2	44±22	2.1±0.1
6	4.8±3.4	122±13	680±47	9.6±0.2	35±10	2.8±0.1
7	4.2±0	62±4.4	613±11	2.6±0.2	47±6.9	1.8±0.1
8	4.2±0.2	74±6.3	610±27	3.5±0.1	59±11	1.9±0
9	5.9±3.3	140±25	769±118	11±1.0	38±2.5	2.9±0.1
10	4.4±0.2	147±17	781±76	4.7±0	48±12	2±0.2
11	4.2±0.2	77±1.9	622±40	3.7±0.1	57±6.6	1.8±0.1
12	5.4±1.5	139±13	687±36	11±0.9	36±5.5	2.7±0
13	3.7±0.2	103±2.4	452±7.5	2.4±0.3	49±15	1.4±0.1
14	3.7±0.1	92±3.5	459±7.8	2.0±0.1	57±7.5	1.4±0
15	3.9±0.1	86±13	655±14	3.5±0.6	54±8.5	1.9±0.1

Note: All samples were acidified to pH 4.0 before RF/ H₂O₂ treatment.

2.3.1.2 Ammonia release

Ammonia to TKN ratio was in the range of 0.26 to 0.51 for untreated separated solids while it was 0.11 for untreated whole manure. Ammonia is produced as one of soluble products from the RF/H₂O₂ process, which is a major constituent of the slow releasing fertilizer, struvite (magnesium ammonium phosphates). After RF/H₂O₂ treatment, ammonia concentration ranged from 452±7.5 mg/L to 781±76 mg/L and the percentage TKN released as ammonia concentration ranged from 35% to 57%. For both whole manure and separated solids, trial 13 resulted in higher ammonia/TKN ratio and trial 1 resulted in the lowest ratio; similar trend was observed for ortho-P/TP for these cases indicating the effect was similar to that of phosphate solubilization. The regression model proposed for the concentration of ammonia in solution is:

$$Y = 775.10 - 20.17T + 509.67D + 6.88P + 0.07T^2 - 286.58D^2 - 0.14P^2 + 0.69DT + 0.21PT - 1.24DP \quad (2)$$

Where, Y is ammonia (mg/L), P is input power (%), T is holding time (min) and D is H₂O₂ dose (%). From the surface response analysis, in order to achieve a high degree of nitrogen solubilization, the process should be conducted at a higher hydrogen peroxide dosage, shorter holding time and high input power intensity. The magnitude of factor affecting ammonia concentration was found to increase in the following order: H₂O₂ dose > secondary effect of H₂O₂ dose > holding time > input power. Holding time had negative influence on ammonia. This was also similar to previous studies on RF and MW treatment of dairy manure; hydrogen peroxide dosage was a significant factor affecting ammonia solubilization (Yawson et al., 2011, Srinivasan et al., 2013). The optimum conditions predicted for ammonia concentration were 59.2% power intensity, 51.5 mins of holding time and 0.8% of H₂O₂ dosage.

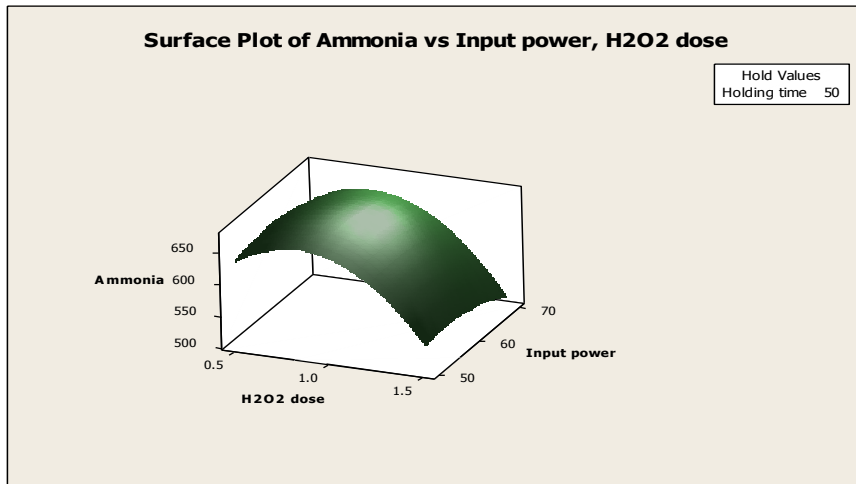


Figure 2-3: Response surface profile showing ammonia with respect to input power and hydrogen peroxide dosage.

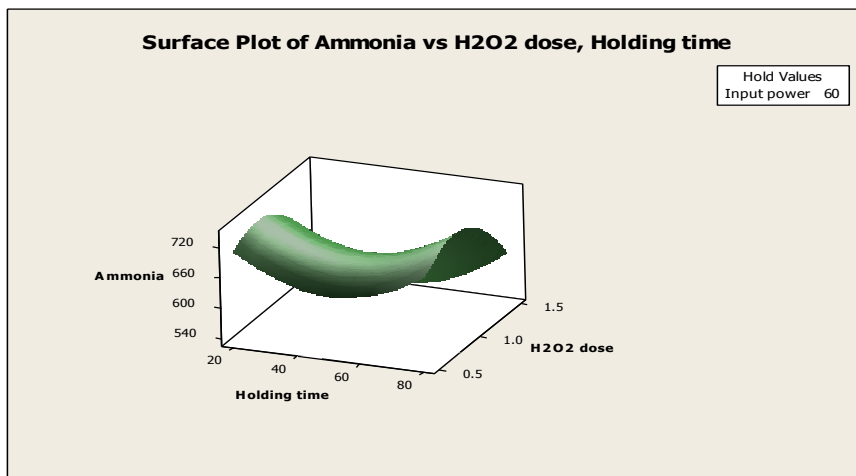


Figure 2-4: Response surface profile showing ammonia with respect to holding time and hydrogen peroxide dosage

2.4.2 Solids disintegration

Solids disintegration can be represented in terms of SCOD and VFA concentration in the resulting solution. Disintegration process occurs when particulate organic substances in the manure are further disrupted and solubilize. As a result, more readily biodegradable portion of

the substrate would be expected to be in solution. SCOD concentration levels represent the solubilization of total organic substances in manure. VFA are intermediate products in the RF/H₂O₂ treatment process. Therefore, it is expected that an increased SCOD concentration and hydrogen peroxide will result in increased VFA production. The regression model equation obtained for SCOD concentration in the treated manure is given as follows:

$$\text{SCOD concentration (mg/L)} = 49124.2 - 513 T - 12588 D - 942 P + 3.2 T^2 + 2715 D^2 + 6.9P^2 + 118TD + 2.9PT - 14.3PD \quad (3)$$

Where, P is input power (%), T is holding time (min) and D is H₂O₂ dose (%). The predicted values for SCOD from equation (3) were comparable to that of the experimental values. A correlation coefficient (R^2) of 84% was obtained. A sample response surface profile for SCOD is shown in Figure 2.5&2.6. All the three factors, hydrogen peroxide dosage, holding time and input power had a negative statistical coefficient; however the statistical coefficient for the interaction effects were all positive except that for input power and hydrogen peroxide dosage. A low input power means that longer time will be required to reach the desired temperature. However, holding time had a negative effect on SCOD concentration; this may be due to significantly longer reaction times used in the RF/H₂O₂ process.

The interaction effect of holding time and H₂O₂ dosage was found to be statistically significant ($p < 0.05$). The magnitude of the statistical coefficients of hydrogen peroxide and its interaction with itself was higher than all of the rest suggesting that hydrogen peroxide dosage was a significant factor in COD solubilization. Previous research by Wong et al., (2007) on MW/H₂O₂-AOP shows that the significant factors affecting SCOD, from most to least were: microwave

heating temperature, hydrogen peroxide dosage and heating time. However, the statistical coefficient for H_2O_2 dosage was negative in this study. It is likely that the hydrogen peroxide dosage used in the study was not sufficient enough to react with manure particles or to generate hydroxyl free radicals that would further aid in solids disintegration. This was also supported by the fact that the optimum conditions predicted for SCOD concentration were 70.6% of power intensity, 4.5 mins of holding time and 2.4% of H_2O_2 dosage. A value of high H_2O_2 dosage, outside the range studied, suggest that the effect of H_2O_2 dosage with varying levels on solids disintegration further needs to be investigated for RF heating oxidation process.

The SCOD/TCOD ratio for separated solids and whole manure is depicted in Table 2.5. The percentage of SCOD/TCOD in the treated solution indicates the process efficiency of solubilization. SCOD/TCOD ratio was highest resulting from trials 9 and 12 for separated solids and for trials 7 and 12 for whole manure. This confirm that the interaction effect of holding time and H_2O_2 dosage resulted in higher SCOD release; the effect was found to be statistically significant ($p < 0.05$) for both the types of manure (Srinivasan et al., 2013). The highest SCOD/TCOD ratio for separated manure is 30% while it was only 26% for whole manure. It should be noted that ramp times and rates were different as the two manures had different composition and separated solids underwent liquid-solids separation unlike whole manure; hence, the dielectric properties of the two manures might be different from each other. Ramp rate was different for the two manures for the same power input set during RF heating process. RF heating of separated manure had a ramp rate of approximately 2.7, 4 and 5.8°C/min, respectively for input power levels 50, 60 and 70%, respectively, whereas, for whole manure it was 7, 9 and 11°C/min, respectively. Furthermore, whole dairy manure had TS of 12.2%, the H_2O_2 dose added

per gram of TS may not be sufficient enough to break down the solids. Lowest SCOD/TCOD ratio for whole manure resulted from trials 1 and 3. As indicated earlier, 0.5% of H_2O_2 used in these trials were not sufficient enough to break down the solids. However, for separated manure, trials 1-4 had comparatively higher SCOD/TCOD ratio in spite of a lower H_2O_2 dosage. This could be due to the fact for these trials fresh batch of separated solids was used unlike the rest of the trials. Similarly, trials 7, 8, 13, 14 and 15 resulted in poor SCOD/TCOD ratio, which was far lower than the rest (20 to 67%). These trials, came from the separated solids batches that was stored longer over time, therefore, the effect of ageing was more pronounced.

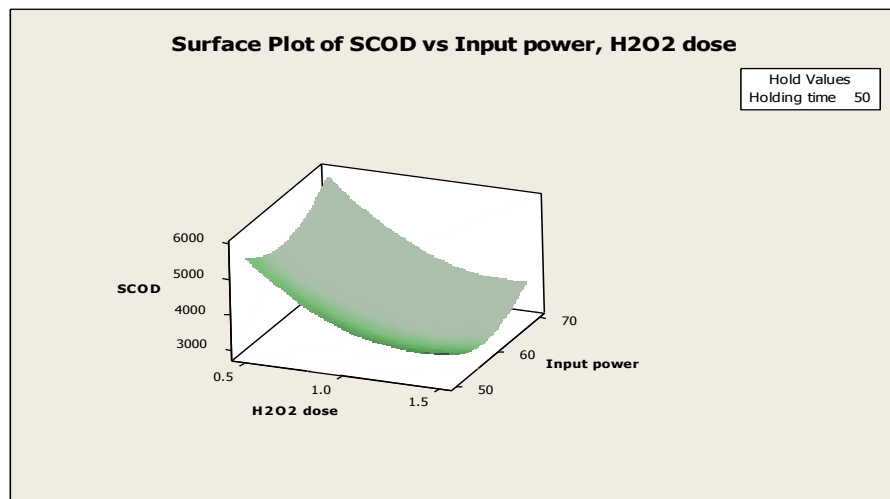


Figure 2-5: Response surface profile showing SCOD with respect to input power and hydrogen peroxide dosage.

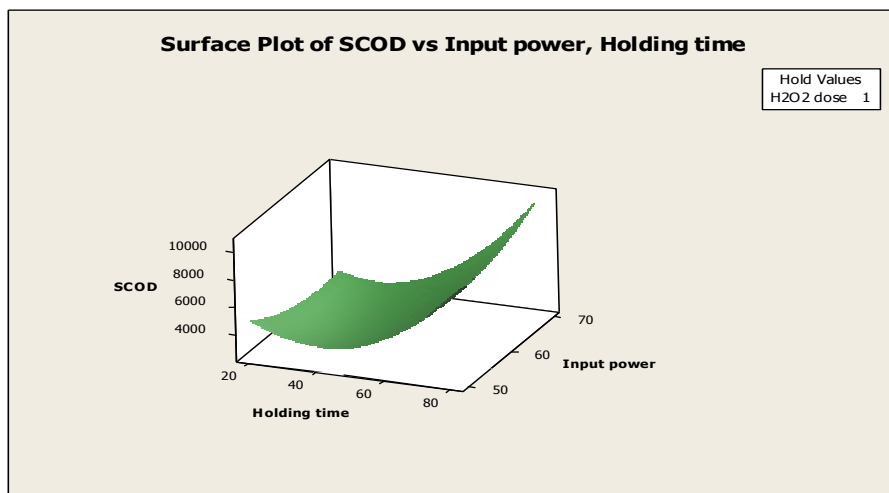


Figure 2-6: Response surface profile showing SCOD with respect to input power and holding time.

2.3.2.2 VFA Solubilization

RF/H₂O₂ treatment resulted in high TVFA concentration in the treated solution. Acetic acid was generally found to be more than 80% of the TVFA in most of the trials. The TVFA concentration ranges from 1389±33mg/L in the treated samples to the maximum at 2941±82 mg/L. The maximum TVFA concentration occurred in trial 9, (input power 70%, holding time of 80 mins and 1% hydrogen peroxide). This represented about 92% increase over the initial TVFA concentration suggesting that the RF/H₂O₂-AOP resulted in an increased TVFA production. However, for trials 13 and 14, no increase in the TVFA concentration in the treated manure were observed; the concentrations of all other parameters for these trials were among the lowest, suggesting that ageing was more pronounced in the untreated manure used for these trials. The regression model proposed for TVFA concentration is given as:

$$\text{TVFA concentration} = 5814 - 26.77T - 3165.77 D - 18.81P + 0.48T^2 + 763.75D^2 + 0.02P^2 + 10.53DT + 0.27PT + 3.09 DP \quad (4)$$

Where, P is input power (%), T is holding time (min) and D is H₂O₂ dose (%). A correlation coefficient (R^2) of 84% was obtained. The statistical coefficients of the four factors were negative, meaning that as they increase, TVFA production decreases. However, hydrogen peroxide dosage had a higher influence on TVFA concentration than all the other factors. Similar trend was observed in COD solubilization. The interaction effects were all positive with the interaction effects of hydrogen peroxide dosage and holding time having a higher influence on TVFA production than the rest of the factors. Lo et al., (2012) reported that higher TVFA production was obtained at higher temperature and hydrogen peroxide dosage. The reasons for the disparity in the results obtained may be due to lower dosages of H₂O₂ used in this study. The H₂O₂ dosage (0.5-1.5%) used in this experiment was lower than what was used by the other researchers (1-8.5%) using the MW/H₂O₂-AOP. The optimum conditions predicted for TVFA were 43.8% of power intensity, 33.9 min of holding time and 1.8% of H₂O₂ dose.

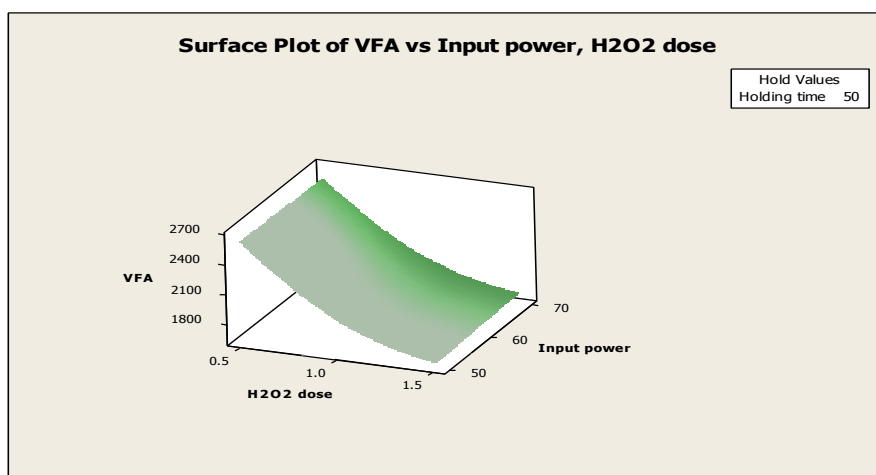


Figure 2-7: Response surface profile showing VFA with respect to input power and hydrogen peroxide dosage.

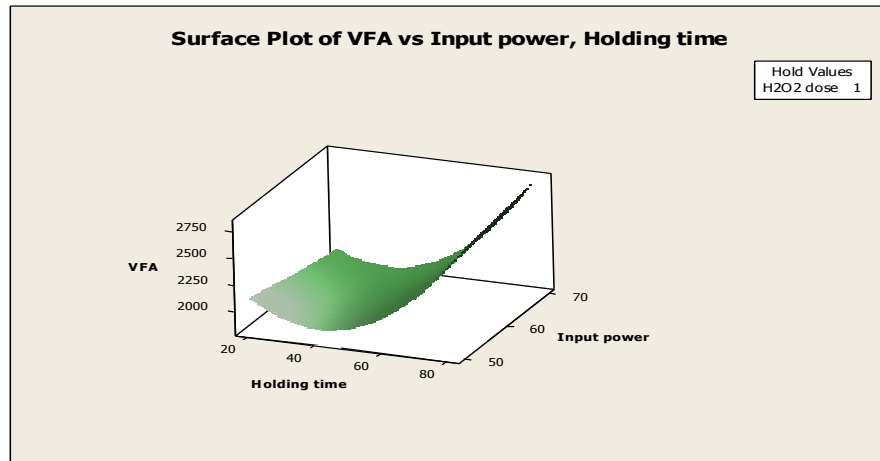


Figure 2-8: Response surface profile showing VFA with respect to input power and hydrogen peroxide dosage

2.4.3 Optimization

The model was used to find the optimal values of input power, hydrogen peroxide and holding time for nutrients release and solids disintegration. The optimization was conducted using the optimization function of Minitab based on the model equations. The optimal values of the three factors for all the four parameters; ortho-P, ammonia, COD and VFA are listed in Table 2.4

Table 2-4: Summary of optimal values

Parameters	Optimal values		
	P (%)	D (%)	T (mins)
Ortho-P	62.9	1.1	55.9
Ammonia	59.2	0.8	51.5
SCOD	70.6	2.4	4.5
VFA	43.8	1.8	33.9

Note: P – Input power, D – Hydrogen peroxide dosage, T – Holding time.

Table 2-5: Comparison of separated solids with un-separated manure

Sample	Ortho-P / TP		SCOD / TCOD		Ammonia / TKN	
	SS	WM	SS	WM	SS	WM
Raw	0.32-0.37	0.24	0.05-0.21	0.11	0.26-0.51	0.11
Acidified	0.34-0.62	0.73-0.75	0.04-0.21	0.08-0.1	0.29-0.41	0.12-0.14
1	0.29	0.58	0.23	0.15	0.25	0.12
2	0.60	0.72	0.21	0.21	0.57	0.15
3	0.32	0.63	0.18	0.17	0.35	0.13
4	0.43	0.60	0.20	0.21	0.39	0.13
5	0.72	0.67	0.09	0.22	0.44	0.15
6	0.39	0.66	0.27	0.22	0.43	0.15
7	0.32	0.68	0.05	0.26	0.37	0.14
8	0.36	0.75	0.06	0.24	0.38	0.15
9	0.51	0.75	0.30	0.23	0.52	0.14
10	0.59	0.75	0.1	0.23	0.46	0.14
11	0.38	0.76	0.07	0.23	0.40	0.16
12	0.38	0.69	0.30	0.26	0.35	0.15
13	0.75	0.91	0.05	0.24	0.54	0.18
14	0.56	0.68	0.04	0.21	0.39	0.16
15	0.42	0.70	0.06	0.24	0.42	0.14

Note: SS – separated solids and WM – whole (un-separated) manure

2.4.4 Comparison of RF/H₂O₂-AOP and MW/H₂O₂-AOP

A comparison of the RF and MW processes in terms of ortho-phosphate and SCOD release at various operating temperature regimes is shown in Table 2.6; higher ortho-phosphate and SCOD concentrations were observed in the treated manure. The RF/H₂O₂-AOP results were comparable to MW/H₂O₂-AOP studies at similar operating temperature regions. Temperature was one of significant factors affecting treatment efficiency of MW/H₂O₂-AOP; the process was most effective at 120°C, as evident from Table 2.6. However, RF/H₂O₂-AOP was studied only at one temperature; a detailed study of the process at different operating temperatures may be needed.

H₂O₂ dosage was the most significant factor besides temperature for treating dairy manure using both RF/H₂O₂-AOP and MW/H₂O₂-AOP. For RF/H₂O₂-AOP the magnitude of effect of H₂O₂ dosage was the highest among the three factors, increase in H₂O₂ dosage aided in release of SCOD, ammonia and VFA, similar to MW/H₂O₂-AOP (Lo et al., 2010). However, for RF/H₂O₂-AOP process, H₂O₂ dose had a negative effect on ortho-phosphate similar to what was reported by Srinivasan et al., (2013). They studied RF/H₂O₂-AOP process for the treatment of whole manure (TS 12.2%) under similar experimental conditions. Yu et al., (2010) suggested that a high H₂O₂ dosage was not necessary for the solubilization of phosphate in lower temperature regimes.

MW/H₂O₂-AOP results have indicated that treatment time and ramp rates play a significant role, as important as H₂O₂ dosage and temperature (Chan et al., 2010; Lo et al., 2010); all constituent parameters solubilized better with longer reaction times. Similar observations were made with RF/H₂O₂-AOP process. For all four constituent parameters, treatment time was found to have a

positive coefficient in the regression equation (e.g., equations 1 and 2), indicating that the parameters solubilized better with an increase in treatment time. However, the effect of magnitude of treatment time on the RF/H₂O₂-AOP process was less compared to other two factors used. This could be due to the fact that three levels of holding times chosen (20, 50 and 80 mins) were significantly longer than the conditions used in MW/H₂O₂-AOP studies (1.5 to 20 mins) (Lo et al., 2012; Chan et al., 2010). Hence the effect may not appear as significant as found in MW/H₂O₂-AOP.

Irradiation power level was also found to affect the degree of nutrient release and solids destruction of dairy manure (Chan et al., 2010; Lo et al., 2010). Using a MW irradiation power level of 1000 W, highest ortho-phosphate concentration was obtained at a ramp rate of 20°C/min while SCOD concentration was higher at 30°C/min. However, for RF/H₂O₂-AOP, power intensity had a negative effect on the three constituent parameters except ammonia although its magnitude was higher than holding time. This could be because ramp times associated with power intensity levels significantly varied in the case of RF/H₂O₂-AOP, unlike MW (2.5 to 5 mins). The average ramp times associated with 50, 60 and 70% power input levels were approximately, 10, 8 and 6.5 mins, respectively. Hence, the process at lower power setting may operate for a longer time, thus releasing higher concentration of nutrients. Also, the total reaction time, which includes ramp time required to reach the desired temperature in addition to the holding time, was significantly longer in RF/H₂O₂-AOP process compared to MW/H₂O₂-AOP. The total reaction time used in MW/H₂O₂-AOP is listed in Table 2.6. This may also be the reason for observing a smaller extent of effect by holding time on the nutrient release and COD solubilization.

From Table 2.6, it was obvious that percentage of ortho-phosphate in TP increased significantly after both RF/H₂O₂-AOP and MW/H₂O₂-AOP. For MW/H₂O₂-AOP, ortho-phosphate percent in TP increased from 20.5% to 46.8% for a 5.1% TS manure at 80°C, while it increased from 24% to as high as 69.8% at 90°C for a 12.2% TS and 39% to 75% of TP for 4.4% TS manure samples after RF/H₂O₂-AOP for study conducted by Srinivasan et al., (2013) and this study respectively; albeit different substrates, the results were comparable. For MW/H₂O₂-AOP studies on dairy manure, H₂O₂ addition helped in increase of phosphate release, however, it was not necessarily required as shown in chapter 4 of this thesis and (Table 2.6) as most of ortho-phosphate was solubilized upon acid addition (Lo et al., 2010). Ortho-phosphate content in the separated manure varied widely (Table 2.3). The same trend was observed by Srinivasan et al., (2013). This is could be because of ageing of the manure; longer the ageing, higher the ortho-phosphate content in the untreated dairy manure. As shown in Table 2.6, ortho-phosphate release in the treated manure increases with operating temperature and time. Similarly, higher percent of SCOD was observed at higher operating temperatures and longer heating times. H₂O₂ dosage played an important role in solids disintegration; increase in dosage of H₂O₂ aided in increase of SCOD/TCOD ratio at 120°C (Table 2.6). On the whole, MW and RF processes resulted in similar treatment benefits.

The advantage of RF process is that it can treat higher sample volume than MW batch systems. RF/H₂O₂-AOP process could handle higher total solids content due to longer penetration depth of RF waves. RF/H₂O₂-AOP process resulted in significant release of ortho-phosphate and SCOD comparable to MW/H₂O₂-AOP even at lower temperature regimes (85-95°C). On the other hand, RF process requires longer heating times (20 to 80 min) when compared to MW processes (10

min). Ramp rate is also lower for RF than MW; RF has a ramp rate of approximately 7, 9 and 11 °C/min and 2.7, 4 and 5.8°C/min for input power levels 50, 60 and 70%, for un-separated and separated manures respectively, whereas, MW has a typical rate of 20 °C/min. However, energy required by the RF batch system used during this study was in the range of 71 to 85 kJ/ g TS whilst that for whole manure was 25.6 to 28.5 kJ/g TS. Thus, the energy required for RF heating of separated manure was very comparable to that of MW/H₂O₂-AOP batch systems which was within the range of 76 to 128 kJ/g TS.

Table 2-6: Comparison of RF and MW results for dairy manure

H ₂ O ₂ dose	Temperature	Heating time	Total solids	Initial ortho-P as TP	Final ortho-P as TP	Initial SCOD as TCOD	Final SCOD as TCOD	Reference
% (v/v)	°C	Min	%	%	%	%	%	
Microwave heating ^a								
1	70	10	0.5	7.7	17.9	1.5	2.2	Kenge et al., 2009a
5	70	10	1.6	33.3	108.7	17.1	8.9	
5	80	7.5	5.1	20.5	46.8		N/A	Kenge 2008
8.5	80	7.5	4.3	17.5	35.4			
7	80	10	4.7	19.0	45.6			
1	120	10	0.5	14.4	22.8	1.2	2.1	Kenge et al., 2009a
3	120	10	1.6	10.4	88.5	7.1	9.9	
6	120	10	3.4	37.5	162.5	8.6	17.7	
1.5	60	10	1.5	10.0	71		N/A	Pan et al., 2006
1.5	90	10	1.5	10.0	72			
1.5	120	10	1.5	10.0	85			
1.5	170	10	1.5	10.0	85			
3	120	30	6.6	8.4	38.8		N/A	Jin et al., 2009
3	120	30	6.6	8.4	22.8	5.0	9.57 ^b	
Radiofrequency heating ^c								
0.5, 1, 1.5	90	20, 50, 80 ^d	12.2	24.0	58 - 91	11.3	14.6 - 26.5	Srinivasan et al., 2013
0.5, 1, 1.5	90	20, 50, 80 ^d	4.47	0.37	39 – 75	8.53	8.71 - 24.33	This study

Note: pH for all cases is 4.0 acidified using sulphuric acid. ^a Substrate used in MW studies is solid dairy manure (obtained after solid-liquid separation); ^b manure was acidified using HCl; ^c un-separated dairy manure was used for RF study; and ^d refers to holding time only (ramp time is not included).

2.4.5 Energy estimation

Energy required for the RF/H₂O₂ process was estimated using the method used by Danesh et al., (2008). The energy required by the RF batch system for separated manure used in this study was in the range of 71 to 85 kJ/ g TS while it was 25.6 to 28.5 kJ/g TS for the whole manure; the energy required is lower for whole manure due to its higher TS content of 12.2% compared to 4.4% TS for the separated manure. However, the energy required for RF heating of separated manure was comparable to that of MW batch systems; it was 76 to 128 kJ/g TS for MW batch systems (Srinivasan et al., 2013).

2.5 Conclusion

The RF/H₂O₂ process was as effective for release nutrient release and solids disintegration from separated solid fraction of dairy manure. The RF system was capable of handling different types of dairy manure with varying solids content. The RF/H₂O₂-AOP treatment of separated dairy manure released up to 72% of TP as orthophosphate along with 30% of SCOD/TCOD. The RF/H₂O₂-AOP process was as effective as MW/H₂O₂-AOP for release nutrient release and solids disintegration from dairy manure. The RF system was capable of handling higher volumes of manure with higher solids content. The energy required per gram of total solids was lower for RF/H₂O₂-AOP process compared to MW/H₂O₂-AOP.

Chapter 3 : Combined effects of conventional and microwave heating on nutrient release and solids disintegration from sewage sludge.

3.1 Introduction

Waste water treatment plants generate large quantities of sludge which require proper treatment and disposal. Increasing stringent regulations on sludge disposal combined with decreasing land availability has generated research interest on innovative treatment processes. These treatment processes are also known to enhance sludge solids disintegration and organic matter solubilization from these wastes.

Waste activated sludge is comprised of different groups of microorganism, organic and inorganic matter agglomerated together in a polymeric network formed by microbial extracellular polymeric substances (EPS) and cations (Eskicioglu et al., 2006). Thermal-chemical treatment could disrupt the extracellular polymeric substances (EPS) and the divalent cation network and therefore, increases the solubilization and eventually the biodegradability of the sludge.

Thermal treatment is suitable for stabilization and to enhance dewatering of the sludge and sludge sanitation (Müller, 2001). Several researchers have studied thermal pretreatment of sewage sludge for a wide range of temperatures from 60°C to 270°C but the most common optimum treatment temperatures reported are between 160°C and 180°C (Li and Noike, 1992; Haug et al., 1978; Sawayama et al., 1995; Kepp et al., 2000). It has been reported that COD solubilization and biodegradability of sewage sludge increases with increasing temperature whereas treatment time have less effect if higher than 30mins (Valo et al., 2004). Temperatures above 200°C have been found to be responsible for the formation of refractory/inhibitory

compounds such as dioxins (Stucky and McCarty, 1984). Low thermal temperature ($<100^{\circ}\text{C}$) has been found to be an effective treatment for increasing biogas production from both primary and secondary sludge and is becoming more attractive because of its lower energy requirements (Gavala et al., 2003).

Microwave enhanced advanced oxidation process (MW/ H_2O_2 -AOP) was developed as a novel process for sewage sludge treatment and enhanced nutrients recovery. Significant factors affecting the MW/ H_2O_2 -AOP have been identified: microwave heating temperature, hydrogen peroxide dosage, microwave heating time and amount of acid addition (Wong et al., 2007; Lo et al., 2010; Chan et al., 2010). MW/ H_2O_2 -AOP has been successfully used at higher temperatures to increase nutrient solubilization and solids disintegration in order to enhanced anaerobic digestion and nutrients recovery via struvite crystallization (Qureshi et al., 2008; Jin et al., 2009 Kenge et al., 2009b; Lo et al., 2012). When the MW/ H_2O_2 -AOP is operated at higher temperatures, the synergistic effect of microwave irradiation and H_2O_2 is enhanced. Elevated microwave temperatures ($>80^{\circ}\text{C}$) increase the decomposition of H_2O_2 into OH radicals, and therefore increase the oxidation rate; this results in a higher degree of solubilization of substrate (Liao et al., 2007a; Eskicioglu et al., 2008).

Several researchers have done a comparative study on the performance of the two thermal treatment processes; conventional and microwave and/or hydrogen peroxide (Eskicioglu et al., 2007; Chang et al., 2011; Mehdizaleh et al., 2013). However, there has not been any study to combine the two processes to take advantage of conventional heating at lower temperature and the synergistic effects of MW/ H_2O_2 -AOP. The objective of this study was to investigate the

combined effect of conventional heating and MW/H₂O₂-AOP on nutrients release and solids disintegration from dairy manure and sewage sludge.

Lo and Liao (2011) suggested an optimum MW temperature of 120°C for best nutrient recovery and solids disintegration from sludge and dairy manure for MW/H₂O₂-AOP in a batch mode. However, continuous-flow 2,450 MHz microwave systems, both laboratory-scale and pilot-scale, was tested at 100°C for further development of the MW/H₂O₂-AOP technology; the continuous process resulted in higher treatment efficiency, under similar conditions compared to the batch mode (Yu et al., 2010; Zhang et al., 2013). Hence, there is the need to study in detail the MW/H₂O₂-AOP at 100°C and compare it with that at 120°C. The focus of this research was to test the effects of the combination of these two processes on the overall treatment efficiency of sewage sludge and dairy manure.

3.2 Materials and methods

3.2.1 Substrate

Secondary aerobic sewage sludge (0.6% TS) was collected from the pilot-scale wastewater treatment plant located at the south campus of the University of British Columbia (UBC). The pilot scale wastewater treatment plant utilizes the membrane-enhanced biological phosphorus removal (MEBPR) process; it consists of three stages, which utilizes anaerobic, anoxic and aerobic zones to remove carbonaceous materials and nitrogenous compounds, as well as phosphorus from the wastewater. A recycle line allows flow from the aerobic zone back to the anoxic zone for increased denitrification efficiency and enhanced phosphorus uptake by bacteria.

Sludge retention time (SRT) during the study was maintained at approximately 25 days and the process was operating with a hydraulic retention time (HRT) of 10 hours.

3.2.2 Experimental design

The aerobic sludge samples were preheated by conventional heating (CH) method in a water bath (Precision, microprocessor controlled 280 series water bath) to reach the desired temperature. Three CH temperatures were studied, 40, 50 and 60 °C. The water bath was maintained at the temperature desired for CH for each experimental set. The preheated sample was immediately subjected to microwave heating upon addition of hydrogen peroxide. The MW experiments, each with triplicates, were conducted at two MW temperatures, 100 and 120°C with a ramp rate of 20°C/min and held for 5 minutes. After heating on the water bath, 0.25mL per 30 mL of sample H₂O₂ was added. The details of the experimental design are provided in Table 3.1.

Table 3-1: Summary of experimental conditions

Set	Conventional heating		Sludge mL	H ₂ O ₂ mL	Microwave heating			Tot. time/ mins	pH
	Temp/°C	Time/mins			Temp/°C	Ramp time /mins	Holding time/mins		
1	40	27	30	0.25	100	3	5	35	6.7
2	40	35	30	0.25	120	4	5	44	6.7
3	50	33	30	0.25	100	2.5	5	40.5	6.7
4	50	35	30	0.25	120	3.5	5	43.5	6.7
5	60	31	30	0.25	100	2	5	38	6.7
6	60	36	30	0.25	120	3	5	44	6.7

^aRT represents ramp time and ^bHT represents holding time

3.2.3 Microwave treatment

A closed vessel microwave digestion system (Ethos TC Digestion Labstation 5000, Milestone Inc., Monroe, CT, USA) with a maximum power output of 1000 W was used in this study. The system operates at 2,450 MHz and consists of dual independent magnetrons with a rotating microwave diffuser for homogeneous microwave distribution. The MW system can attain a maximum operating temperature of 220 °C and can handle a pressure of up to 3,000 kPa. A total of 12 vessels of 100 mL capacity each, including one reference vessel equipped with a thermocouple, are provided in the system. An independent system controller provides real-time temperature control. The microwave treatment consisted of three stages as follows: the ramp time to reach the targeted temperature, ii) the holding time at targeted temperature and iii) the time to cool down in order to allow safe open of the vessels.

3.2.4 Analytical methods

Both the MW/H₂O₂-AOP treated samples and the initial untreated sewage samples were centrifuged at 3500 rpm for 10 mins. The resulting supernatant was filtered through 4.5 µm fiber glass filters. The filtered samples (treated and untreated) were analyzed for SCOD, soluble ammonia, orthophosphate, volatile fatty acids (VFA) and metals. All chemical analyses followed the procedures outlined in Standard Methods (APHA, 1998). Both the raw and untreated samples were analyzed for total chemical oxygen demand (TCOD), total phosphate (TP), total Kjeldahl nitrogen (TKN) and SCOD. All chemical analyses, except for the determination of total solids (TS) and COD were made using flow injection analysis (Lachat Quick-Chem 8000 Automated Ion Analyser, Lachat Instruments, Milwaukee, WI, USA).

An HP 5890 Series II gas chromatograph (Hewlett Packard, Palo Alto, CA, USA) equipped with a flame ionization detector (FID) was used to measure volatile fatty acids. Volatile separation was accomplished with an HP free fatty acid phase (FFAP) column (0.25 m x 0.31 mm, 0.52 μ m film thickness). The injection temperature was set at 175°C and the FID temperature at 250°C. Helium was used as the carrier gas at a head pressure of 69 kPa. The characteristics of the secondary sludge used for this study are summarized in Table 3.2.

Table 3-2: Characteristics of raw sample

Parameter	Concentration
Ortho-Phosphates	0.10 ± 0.12
Ammonia	1.55 ± 2.07
Total Phosphorus (TP)	155.25 ± 9.47
Total Kjeldhal Nitrogen (TKN)	727.9 ± 20.8
SCOD	53.54 ± 4.24
TCOD	7056.10 ± 598.1
VFA	1.33 ± 0.27

3.3 Results and discussion

The organic fraction of sewage sludge contains both intracellular (within the bacterial cell) and extracellular (within the polymeric matrix) biopolymers, such as proteins, sugars, lipids and nuclei acids. It was hypothesized that thermal treatment would disrupt the complex structure of waste activated sludge (WAS) and release the extracellular and intracellular biopolymers into the soluble phase as well as the solubilization of particulate (microbial) COD. Six treatments

conditions were investigated: conventional thermal heating to 40°C followed by microwave heating to 100°C (40°C CH-100°C MW) and 120°C (40°C CH-120°C MW); conventional heating to 50°C followed by microwave heating to 100°C (50°C CH-100°C MW) and 120°C (50°C CH-120°C MW); conventional heating to 60°C followed by microwave heating to 100°C (60°C CH-100°C MW) and 120°C (60°C CH-120°C MW).

3.3.1 COD solubilization

SCOD concentration, SCOD/TCOD ratio and TVFA were used to measure the extent of solids destruction. The initial SCOD concentration in the untreated sewage sludge was only 54 ± 4.2 mg/L. The SCOD concentration increased with CH heating; however, the concentration at 40°C was very low compared to that at 50°C and 60°C (Figure 3.1). Subsequent MW treatment further improved COD solubilization; significant increase in COD solubilization was observed at 120°C when compared to that at 100°C irrespective of H₂O₂ usage. This was approximately 82 times the initial SCOD concentration and 60% of the total COD. The results indicate a near linear correlation of COD solubilization profile with the applied temperature, which is consistent with that reported in the literature. (Li and Noike, 1992; Bougrier et al., 2006; Eskicioglu et al., 2008; Wang et al., 2009; Mehdizadeh et al., 2013).

With the use of hydrogen peroxide, subsequent MW heating to the desired temperatures (100 and 120°C) resulted in significant COD solubilization. A maximum concentration of 4401 ± 176 mg/L was observed when the sludge was subjected to a CH temperature of 60°C followed by MW heating at 120°C with H₂O₂. With the same volume of H₂O₂ (0.25 ml) added to the samples, microwave pretreatments resulted in higher COD solubilization compared to those without

hydrogen peroxide. This result is consistent with that reported in the literature where the effect of microwave irradiation on organic matter solubilization from waste activated sludge was investigated within a temperature range of 50°C CH-200°C MW. SCOD/TCOD ratio increased from 0.75% in the untreated sewage sample to a maximum of 60% for the treated ones. This indicated that the combination of CH and MW/H₂O₂-AOP treatments strongly increased sludge solubilization. Other researchers have reported a similar trend in increase of SCOD with addition of hydrogen peroxide (Liao et al., 2007a; Kenge et al., 2008). The reason for the increase may be due to synergistic effect between microwave temperature and H₂O₂ treatment. At elevated MW temperatures (>80°C) there is a possibility for increased decomposition of H₂O₂ into OH free radicals, which enhance COD disintegration of waste activated sludge (Eskicioglu et al., 2008).

In this study, total reaction time ranged from 35 to 44 mins. The maximum treatment time of 44 mins occurred at three different treatment conditions; 40°C CH-120°C MW, 50°C CH-120°C MW and 60°C CH-120°C MW. It was observed that there was no linear relationship between the total treatment time and COD solubilization. This is consistent with what other researchers reported that treatment time has little effect on COD solubilization especially if higher than 30 mins (Carrere et al., 2004; Valo et al., 2004; Bougrier et al., 2006).

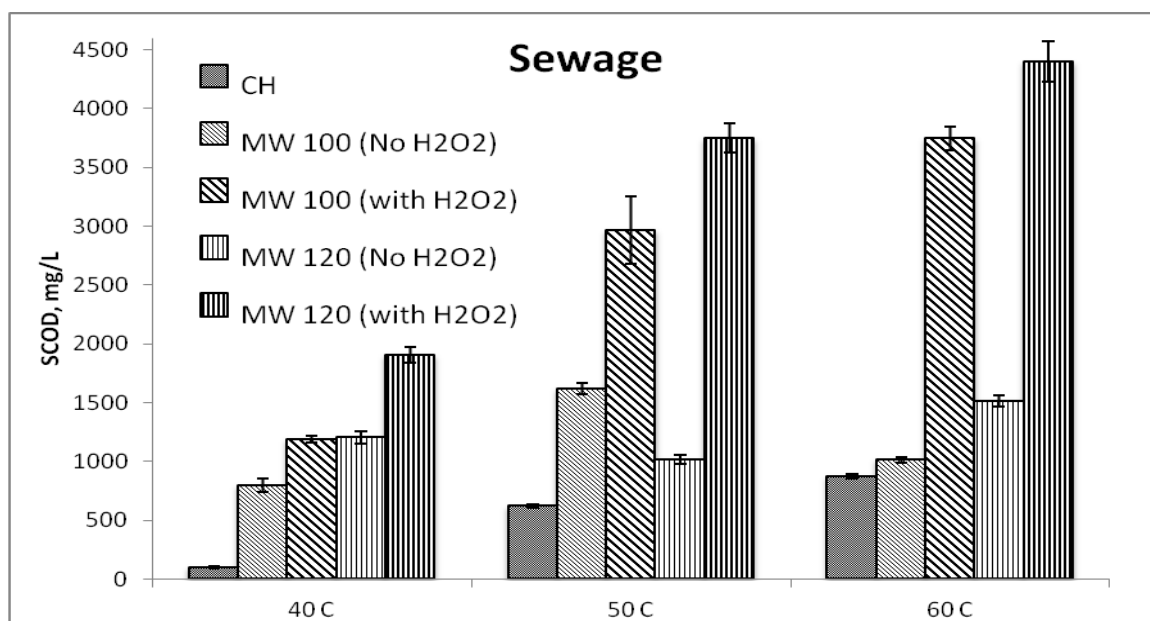


Figure 3-1: Comparison of SCOD at different conventional treatment conditions

3.3.2. Volatile fatty acids production

VFA is a valuable product which could be utilized not only in anaerobic digestion but also in the biological nutrient removal process. VFA formation during thermo-chemical treatment of organic slurries occurs through two processes: first is the breakdown of large particulate organic matter and hydrolysis into soluble organic substance, resulting in the accumulation of SCOD. The second involved oxidation, which consumes and transforms the soluble organic substance into oxygenated organic intermediates and eventually inorganic end-products. It is expected that VFA formation increases with increased SCOD concentration and oxidant dosage.

In this study, acetic acid, propionic acid, butyric, iso-butyric, iso-valeric acid and valeric acid were identified. The total VFA was calculated as acetic acid equivalence. Acetic acid was found to be more than 80% in most of the experiments. Total VFA concentration for the various

treatment sets are given in Figure 3.2. The total VFA concentration ranged from 1.33mg/L in the untreated sewage samples to 108 mg/L for the treated ones. The maximum TVFA concentration occurred at the treatment condition: 60°C CH-120°C MW with addition of H₂O₂ which is the same as that observed for SCOD results. For the same hydrogen peroxide added, VFA formation increased with increased MW temperature which is consistent with the results reported by other researchers that temperature and hydrogen peroxide dosage significantly affect VFA formation (Liao et al., 2005c; Liao et al., 2007a; Lo et al., 2008; Kenge et al., 2009b). VFA was found to be 1-2% of SCOD for the CH and MW temperatures sets without H₂O₂, while the ratio increased to 3% with the addition of H₂O₂. VFA concentration increased from 1.6 to 9.3 times when H₂O₂ was added compared to no H₂O₂ sets. VFA increased with increase in CH and MW temperatures. VFA concentration increased 10 times with the addition of H₂O₂ after CH at 60°C and MW heating at 120°C compared to that at same treatment conditions without H₂O₂. The results indicate that synergistic effect between H₂O₂ and MW temperature played a significant role in the reaction. The low VFA concentration might be due to the pH which was constant at 6.7 (near neutral) this is because Liao et al., (2007a) and Lo et al., (2008) reported a higher accumulation of VFA at low pH.

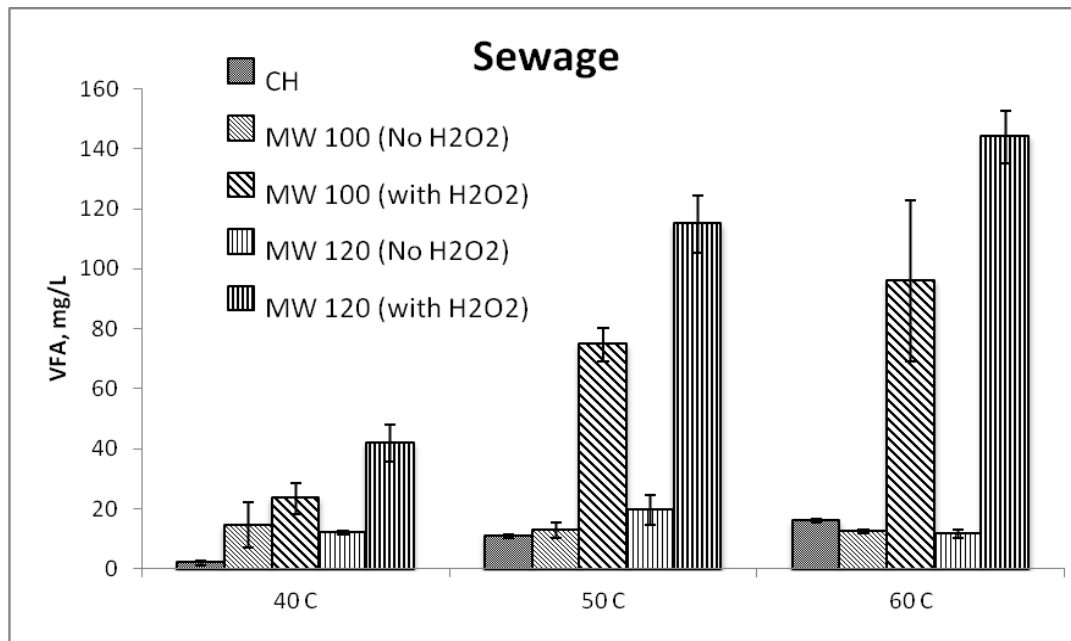


Figure 3-2: Comparison of VFA production between treatments

3.3.4 Nutrient release

The results of solubilization of phosphates and ammonia are presented in Table 3.4. For this experiment, sludge from enhanced biological phosphorus removal (EBPR) process was used which is known to have high content of stored phosphates in the sludge biomass. The hypothesis is that thermal pretreatment destroys bacterial cells and difficult-to-degrade organic compounds which ultimately cause the release of stored polyphosphate and phosphorus trapped in extracellular polymeric material into solution. Ammonia is also released with phosphate (Mavinic et al., 1995). The breakdown and solubilization of sludge biomass and its subsequent conversion to ammonia and phosphorus could potentially be used to produce plant fertilizers such as struvite. Even though many P-solubilization processes have been developed (Ray et al., 1990; Mavinic et al., 1995 and Mavinic et al., 1998; Liao et al., 2003), however, these processes

require either the addition of chemicals to initiate the reaction or a longer reaction time. MW was introduced for rapid and efficient nutrient recovery.

The ortho-P concentrations ranged from 0.1 mg/L for the untreated sludge to 78mg/L for the treated ones; these represented 0.07% to 50% of total phosphate (TP). The initial ortho-P content was very low. CH treatment at 40°C did not result in any significant ortho-P release compared to that at 50°C and 60°C (Table 3.4). The low soluble phosphate level at CH temperature of 40°C may be due to the presence of intermediate products of soluble polyphosphates (poly-P) at that low temperature. According to the findings by Kuroda et al., (2002), the initial release of phosphorus from EBPR sludge was entirely poly-P, which was then degraded to ortho-P. The breakdown of poly-P to ortho-P is largely dependent on temperature.

Of all the trials, the maximum ortho-P release occurred under the treatment conditions; 60°C CH-120°C MW with hydrogen peroxide. This trend is consistent with the findings from other authors that microwave treatment temperature was the most significant factor for ortho-P release from sewage sludge (Liao et al., 2005c; Wong et al., 2006; Lo et al., 2008). Total treatment time ranged from 38 to 44 mins with the highest occurring at the treatment conditions; 40°C CH-120°C MW, 50°C CH-120°C MW and 60°C CH-120°C MW. Sewage sludge treated at a MW temperature of 120°C with hydrogen peroxide resulted in the highest ortho-P release at each conventional treatment temperature (Table 3.4). This shows that treatment time and MW temperature had significant effect on ortho-P solubilization.

Ammonia concentration ranged from 1.55 mg/L to 26.57 mg/L with the maximum release occurring at the treatment condition; 60°C CH-120°C with H₂O₂ addition. This represented 0.21% to 3.65% of TKN. Treatment with hydrogen peroxide resulted in significantly higher ammonia concentrations at both MW temperatures 100°C and 120°C. Generally, increasing MW temperature resulted in an increased in ammonia solubilization. The results indicate that hydrogen peroxide dosage and MW temperature were significant factors for ammonia solubilization which is consistent with the results obtained by other researchers (Wong et al., 2006; Lo et al., 2008).

Mehdizadeh et al., (2013) conducted CH and MW treatments, separately on dewatered municipal sludge cake with TS of 17%. At 120°C the SCOD/TCOD ratio increased from approximately 7.5% to 17.5% and 15% for CH and MW treatments, respectively. While Valo et al., (2004) compared the treatment efficiency of CH alone, CH at pH 12 and CH with hydrogen peroxide (150 mmol/dm³), individually, on waste activated sludge; at 130°C the SCOD increased from 2.7% to 25.3, 30.7, and 35%, respectively for CH alone, CH at pH 12 and CH with H₂O₂. Comparing these results with that of the present study on sewage sludge, the combined CH and MW/H₂O₂-AOP proved to be efficient than the individual treatment methods.

Table 3-3: Ortho-P and ammonia release from sewage sludge

	Ortho-P mg/L	TP mg/L	Ammonia mg/L	TKN mg/L
Raw	0.1±0.1	155±9.5	1.6±2.7	728±21
Preheated to 40 °C				
CH 40	9.6±0.3	162±12	6.3±3.8	680±17.8
MW 100 (No H ₂ O ₂)	24±8.5	168±2.2	7.8±3.9	752±8.1
MW 100	20±1	162±1.5	6.6±0.6	709±19
MW 120 (No H ₂ O ₂)	30±2.0	180±3.8	6.6±2.9	799±15
MW 120	30±0.8	189±37	10±1.1	973±292
Preheated to 50 °C				
CH 50	71±0.8	184±56	10±0.2	667±84.4
MW 100 (No H ₂ O ₂)	68±5.5	192±15	5.9±0.6	855±110
MW 100	62±3.9	182±53	15±0.7	664±86
MW 120 (No H ₂ O ₂)	64±2.7	158±13	6.2±0.6	734±169
MW 120	76±1.5	144±5.4	24±0.5	778±50
Preheated to 60 °C				
CH 60	69±2.3	142±1.4	8.8±0.1	786±22.2
MW 100 (No H ₂ O ₂)	63±2.2	148±2.1	6±0.3	830±22
MW 100	67±0.6	146±8.1	17±0.9	818±16
MW 120 (No H ₂ O ₂)	60±2.2	149±3.8	5.9±0.7	831±9
MW 120	78±1.8	142±4.6	27±2.1	733±78

3.4 Conclusion

This study applied the combination of CH and MW/AOP for treatment of secondary aerobic sludge for the purpose of nutrients recovery and solids disintegration. The focus of this research was to test the effects of the combination of these two processes at different CH 40°C, 50°C, 60°C and MW 100°C, 120°C heating temperatures. The results indicated that, combination of CH and MW/H₂O₂-AOP was very effective in the treatment of sewage sludge for nutrient release and solids disintegration. CH and MW heating temperatures and the addition of hydrogen peroxide resulted in an increased in COD solubilization for sewage sludge which represented 60% removal of the total COD. There was no clear linear relationship between the treatment times and

COD solubilization for the various treatment conditions. For orthophosphates release, temperature played a significant role and the maximum ortho-P release occurred at 60°C CH-120°C MW with hydrogen peroxide addition which represented 50% of TP. The combined CH and MW heating method proved to be more efficient compared to the CH and MW/H₂O₂-AOP methods separately. This might offer energy saving alternatives in real time industrial applications.

Chapter 4 : Combined effects of conventional and microwave heating on nutrient release and solids disintegration from dairy manure

4.1 Introduction

Animal manure management is a major challenge facing the dairy industry. Currently land application which is the traditional method of manure management is no longer a sustainable practice because of limited land availability and pollution of surface and ground water bodies by nutrients found in the manure. However, manure contains nutrients, proteins, carbohydrates, fats, inorganic residue, minerals and lignin and thus represents a valuable resource potential which can be harnessed through appropriate processing technology to fertilizer, methane, bioethanol and others (Van Horn et al., 1994 and Rico et al., 2007). Significant fraction of the nutrients and organic matter are contained in the form of fibers and particles which are non-biodegradable or difficult to degrade. Hartmann et al., (2000) reported that 25% of the unused biogas potential was found to be bound in the particulate organic matter. Also 65% of the phosphorus in dairy manure is in organic form, which is tied up in the solids (Barnett, 1994). The biodegradability of dairy manure is typically in the range of 30-43% yielding 150-240 l CH₄ kg VS⁻¹ (Møller et al., 2004; Nielsen et al., 2004). One of the possibilities to enhance resource recovery from manure is to implement a pretreatment step for increasing the solubilization of organic matter prior to struvite crystallization and conventional anaerobic digestion.

Whereas a lot of work have focused on the enhancement of anaerobic digestion (Valo et al., 2004; Bougrier et al., 2006; Eskicioglu et al., 2006, 2007) and nutrient solubilization (Liao et al., 2005c; Wong et al., 2006; Lo et al., 2008) of sewage sludge by thermal or thermo-chemical treatments. Information about pretreatment of dairy manure is limited. Mechanical pretreatment

of dairy manure by maceration was reported to increase the methane potential up to 25% (Angelidaki and Ahring, 2000; Hartmann et al., 2000); chemical alkali pretreatment of fibers resulted in a varying increase of the methane yield from 0 to 20% (Angelidaki and Ahring, 2000). Pretreatment by thermal hydrolysis at 160°C-200°C and pressure up to 40 bar was demonstrated to enhance solubilization, as well as to improve the performance of biogas process in terms of volatile solids (VS) removal, biogas yield and dewaterability of the residues. 60°C and 80°C treatments were applied to pig manure (Bonmati et al., 2001), 100°C treatments to chicken manure (Ardic and Taner, 2005), 100°C to 140°C treatments to a mixture of cattle and swine manure (Mladenovska et al., 2006) and 140°C-180°C treatments to cow manure (Yoneyama et al., 2006).

Recently, microwave-enhanced thermo-chemical sulfuric acid and/or hydrogen peroxide pretreatment has been successfully used at high temperatures (>80°C) to increase solubilization in order to enhance anaerobic digestion and nutrients recovery via struvite crystallization (Qureshi et al., 2008; Kenge et al., 2009b; Jin et al., 2009; Lo et al., 2012). High temperatures have been found to increase the decomposition of H₂O₂ into OH· radicals, and therefore increase the oxidation rate which results in a higher degree of solubilization of substrate (Liao et al., 2007a; Eskicioglu et al., 2008). To build upon the successes of MW enhanced thermo-chemical pretreatment process at higher temperatures (>80°C), there is the need to consider its application in continuous flow systems which is more suitable for industrial operations. Continuous-flow 2,450 MHz microwave systems, both laboratory-scale and pilot-scale, tested for further development of the MW-AOP technology, resulted in much better yields of resources than from a batch operation mode, under similar conditions (Yu et al., 2010, Zhang et al., 2013).

In the previous study, the combined effect of CH and MW processes for the treatment of sewage sludge was successfully investigated. The results indicated that combined CH and MW treatments were very efficient in the treatment of sewage sludge. With increasing CH and MW temperatures, synergistic effects of CH and MW were very pronounced which facilitated COD solubilization and nutrients release. This study is a direct application of both processes to the treatment of separated dairy manure with the same experimental conditions. The MW/H₂O₂-AOP was first developed for the treatment of sewage sludge and following the success, was applied for the treatment of dairy manure (Pan et al., 2006). It was in this same concept that this experimental study on dairy manure was designed and carried out. The purpose of this study was to examine the effects of the combination of CH and MW/H₂O₂-AOP processes on the treatment efficiency of dairy manure and then compare it with sewage sludge.

4.2 Materials and methods

4.2.1 Substrate

Dairy manure used in this study was obtained from the University of British Columbia (UBC) Dairy Education & Research Centre in Agassiz, British Columbia, Canada. The solids portion after solid-liquid separation was collected from the farm, and was stored in closed containers at 4°C. Separated dairy manure contained large amounts of sand, bedding material, as well as undigested lignocellulosic materials. Distilled water was added to the manure samples and subsequently decanted to remove the sand. The resulting manure had a total solids (TS) content of 4.7%.

4.2.2 Apparatus

The Milestone Ethos TC microwave oven digestion system (Milestone Inc., Monroe, CT, USA) was used in this study. The system operates at a frequency of 2,450 MHz with a maximum power output of 1000 W. The MW system can attain a maximum operating temperature of 220 °C and can handle a pressure of up to 3,000 kPa. A total of 12 vessels of 100 mL capacity each, including one reference vessel equipped with a thermocouple, are provided in the system. An independent system controller provides real-time temperature control.

4.2.3 Experimental design

Dairy manure was acidified with sulfuric acid to a pH of 4.0. It has been known that substantial amounts of orthophosphate were released into solution only in acidic condition, preferably below pH 4.0 (Kenge et al., 2009b, Lo and Liao, 2011). Acidified dairy manure was preheated by conventional heating (CH) method in a water bath (Precision, microprocessor controlled 280 series water bath) to reach the desired temperature. Three CH temperatures were studied, 40°C, 50°C and 60°C. The water bath was maintained at the temperature desired for CH for each experimental set. The preheated sample was immediately subjected to microwave heating upon addition of hydrogen peroxide.

The MW experiments, each with triplicates, were conducted at two MW temperatures, 100 and 120°C with a ramp rate of 20°C/min and held for 5 mins. 1 mL of 30% of H₂O₂ was added into 30 mL of sample. The detailed experimental design is provided in Table 4.1.

Table 4-1: Summary of experimental conditions

Set	Conventional heating		Sludge mL	H ₂ O ₂ mL	Microwave heating			Tot. time/mins	pH
	Temp/°C	Time (mins)			Temp/°C	Ramp time/ mins	Holding time/ mins		
1	40	31	30	1	100	3	5	39	4
2	40	37	30	1	120	4	5	46	4
3	50	31	30	1	100	3.5	5	39.5	4.1
4	50	37	30	1	120	3.5	5	45.5	4.1
5	60	29	30	1	100	2	5	36	4.1
6	60	31	30	1	120	3	5	39	4.1

4.2.4 Analytical methods

Both the MW/H₂O₂-AOP treated samples and the initial untreated sewage samples were centrifuged at 3500 rpm for 10 mins. The resulting supernatant was filtered through 4.5 µm fiber glass filters. The filtered samples (treated and untreated) were analyzed for SCOD, soluble ammonia, orthophosphate, volatile fatty acids (VFA) and metals. All chemical analyses followed the procedures outlined in Standard Methods (APHA, 1998). It has been reported that in the orthophosphate (o-PO₄) analysis of dairy manure samples, different dilution ratios could cause interference; the initial dairy manure sample was diluted to TS of 0.5% for ensuring accurate orthophosphate measurement (Wolf et al., 2005). Both the raw and untreated samples were analyzed for total chemical oxygen demand (TCOD), total phosphate (TP), total Kjeldahl nitrogen (TKN) and SCOD. All chemical analyses, except for the determination of TS and COD, were made using flow injection analysis (Lachat Quick-Chem 8000 Automated Ion Analyser, Lachat Instruments, Milwaukee, WI, USA).

An HP 5890 Series II gas chromatograph (Hewlett Packard, Palo Alto, CA, USA) equipped with a flame ionization detector (FID) was used to measure volatile fatty acids. Volatile separation was accomplished with an HP free fatty acid phase (FFAP) column (0.25 m x 0.31 mm, 0.52 µm film thickness). The injection temperature was set at 175°C and the FID temperature at 250°C. Helium was used as the carrier gas at a head pressure of 69 kPa.

Table 4-2: Characteristics of raw sample

Parameter	Concentration
Ortho-phosphates, mg/L	4.9 ± 0
Ammonia, mg/L	256.30 ± 5.3
Total Phosphorus (TP), mg/L	149.9 ± 4.6
Total Kjeldhal Nitrogen (TKN), mg/L	1155.40 ± 35.9
SCOD, g/L	4.80 ± 0.04
TCOD, g/L	46.40 ± 0.09
SCOD/TCOD	0.10
VFA	0.05 ± 0.01

4.3 Results and discussion

The results of the previous experiments on the combined conventional heating (CH) and MW/H₂O₂-AOP treatments of sewage sludge had proven successful to enhance nutrients solubilization and disintegration of sludge biomass. It was hypothesized that these treatment processes could disrupt the complex structure of waste activated sludge floc and release extracellular polymer substances, proteins, lipids and sugars into a soluble phase as well as the solubilization of particulate (microbial) COD. The results obtained in this study showed that the combination of CH and MW/H₂O₂-AOP treatments at the same experimental conditions was also effective in the solubilization of the complex manure particles.

4.3.1 Solubilization

SCOD, TVFA and SCOD/TCOD ratio were used to measure the extent of solubilization and disintegration of organic matter as used for the previous experiments. The COD solubilization results in the release of more digestible compounds such as volatile fatty acids in pretreated dairy manure slurry. These compounds are known to boost methane production (Jin et al., 2009).

The SCOD concentration ranged from 4.80 g/L for raw sample to a maximum concentration of 10 g/L for the treated ones. When raw manure was acidified using H_2SO_4 to pH 4, SCOD concentration increased from that of untreated manure; SCOD concentrations did not change significantly during the subsequent CH treatments. This shows that pH played major role in COD solubilization. With addition of hydrogen peroxide added, the MW treatment (100°C and 120°C) of the CH treated samples resulted in significant COD solubilization. Generally, COD solubilization increased with increasing temperature even though the extent was not as high as that observed for sewage sludge. This is because at higher temperatures, there is increased synergistic effect between MW and hydrogen peroxide, which results in the decomposition of H_2O_2 into OH free radicals and enhanced both the oxidation and the particulate COD disintegration. However, the MW heating temperatures did not affect SCOD release as shown in Figure 4.1. The hydrogen peroxide dosage added may not be sufficient enough to result in high COD solubilization so that the difference in its concentration is not obvious between the two MW temperatures; only 0.2% H_2O_2 /%TS was added. However, the COD solubilization after MW treatment increased with CH temperatures indicating that beginning the MW process at an elevated temperature improved SCOD. Upon MW treatment with H_2O_2 , the maximum COD solubilization occurred at the treatment condition; 60°C CH- 120°C MW and total reaction time

of 39 mins. This was approximately 2 times the SCOD concentration of the untreated dairy manure and 22% of the total COD solubilization which was far lower than what was obtained for secondary sludge (82 times) under similar pretreatment conditions. This is because sewage sludge is essentially microbial cells, which are relatively easy to disrupt compared to the complex manure particles. This is consistent with what was reported by other researchers (Quereshi et al., 2008; Kenge et al., 2009b; Lo et al., 2012). As expected, the same trend was observed for sewage sludge under the same experimental conditions. SCOD/TCOD ratio, which gives a general indication of the extent of hydrolysis ranged from 0.009 to 0.13 for the untreated samples and from 0.18 to 0.22 for the treated samples. This shows that CH and MW treatment resulted in increased solubilization of complex manure organic components.

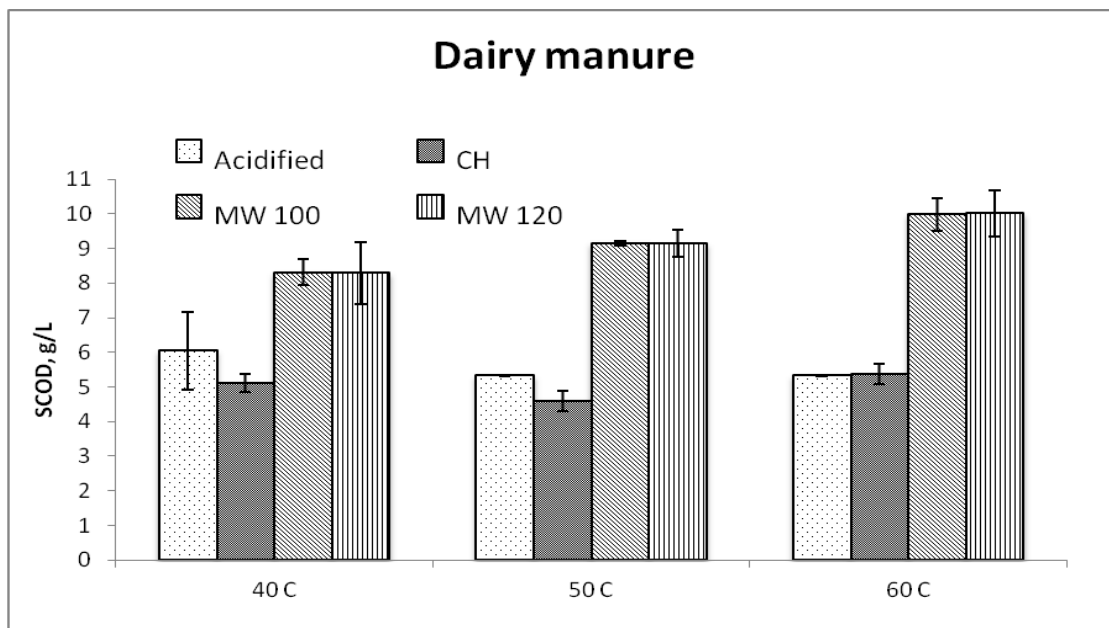


Figure 4-1: Comparison of COD solubilization from dairy manure at various temperatures

4.3.2 Volatile fatty acids

The results for VFA formation is shown in Figure 4.2. As expected short-chain fatty acids, such as acetic acid, propionic acid, butyric, iso-butyric, and to a lesser extent iso-valeric acid and valeric acid were identified after pretreatment of the raw manure. The total VFA was calculated as acetic acid equivalence. Acetic acid was found to be more than 80% of the TVFA in most of the experiments.

The initial concentration of VFA in raw manure was only 0.05 mg/L but increased significantly to 2.65 mg/L after acid treatment. No significant change in VFA concentration was observed after CH treatment. VFA concentration increased during the subsequent MW/H₂O₂-AOP treatment at both temperatures. The increase in VFA after MW/H₂O₂-AOP treatment shows that hydrogen peroxide and MW temperature play significant roles in VFA formation. With H₂O₂ addition, the maximum TVFA concentration (3.26 ± 0.14 g/L) occurred at the treatment condition; 50°C CH-120°C MW at total treatment time of approximately 46 mins. This was approximately 65 times the value of the untreated samples which means that the combination of both CH and MW treatments resulted in significant production of short chain fatty acids. By the mechanism for VFA formation which is the same as that for wet oxidation process; the biodegradable organics will be transformed to VFA at high temperatures with H₂O₂ dosage during thermal treatment process. The pH after each treatment condition remained constant at 4.1.

Generally, the VFA concentration of microwave treated samples was higher than the untreated samples. However, MW/H₂O₂-AOP treatment at MW temperature 100°C and 120°C did not result in varying VFA concentration. This trend is the same as that observed for SCOD results.

The VFA concentration was generally found to be less than 60% of SCOD for the pretreated samples with most of the concentration levels below 50% whilst that for the microwave treated samples had TVFA concentration less than 40% of SCOD with most of them less than 35%. The reactions between the manure organic particles and hydrogen peroxide did not only result in the disintegration of organic particles but significant secondary oxidation to form oxygenated compounds like VFA.

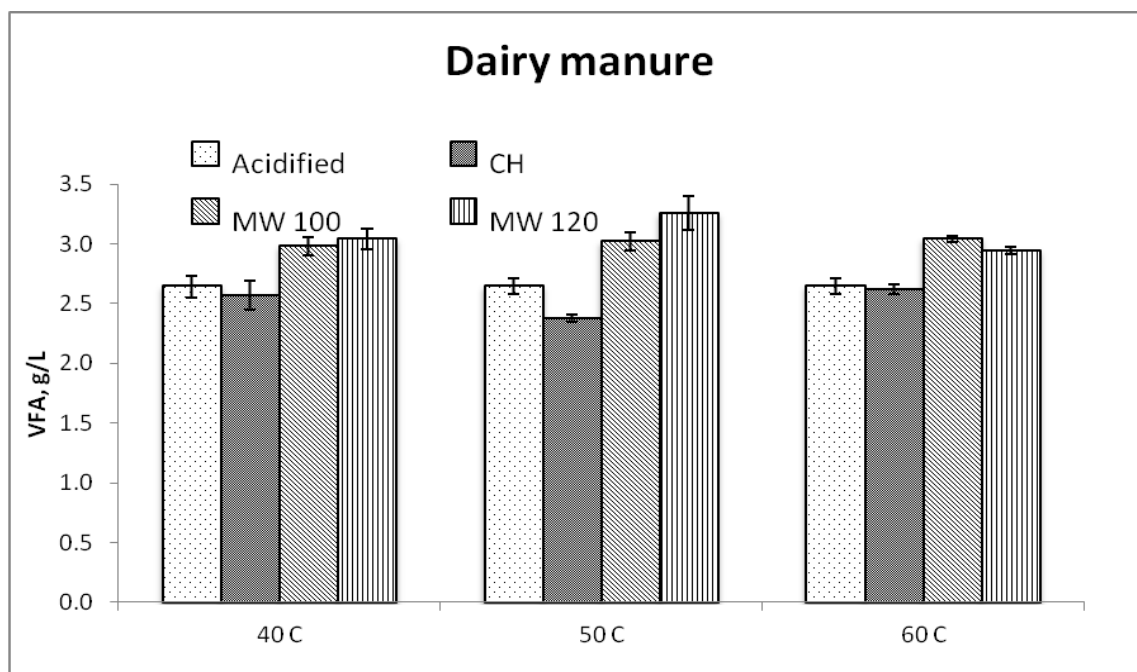


Figure 4-2: VFA production from dairy manure

4.3.3 Nutrient release

The combination of CH and MW/H₂O₂-AOP treatments increased the solubilization of organic phosphorus and proteins, as indicated by the release of soluble-P, ortho-P, and ammonium from treated dairy manure (Table 4.4). The breakdown and solubilization of sludge biomass and its

subsequent conversion to ammonia and phosphorus could potentially be used to produce plant fertilizers such as struvite.

For this experiment, ortho-P concentration of the untreated sample was 4.9 mg/L and the treated ones were in the range of 107 to 148 mg/L. This represented percentage ortho-P release, which ranged from 3% of TP for raw sample to 98% of TP for treated samples. The TP for the initial sample was 150 ± 4.6 mg/L. However, the TP values for all other cases were all lower than the ortho-P for the triplicates, which is possibly due to analytical issues.

The maximum ortho-P release occurred at treatment condition: (40°C CH-120°C MW) with a total treatment time of 46 mins. Total treatment time ranged from 36 to 46 mins and it was observed that longer treatment time resulted in increased ortho-P solubilization. Highest ortho-P concentration was obtained for the treatment set with longest reaction time. The results obtained from this study are within the range of values reported by other researchers even though the experimental conditions were different (Pan et al., 2006; Kenge et al., 2008; Jin et al., 2009; Lo et al., 2012).

The ortho-P release from the raw manure samples ranged from 3% to 75% of TP whilst that for the treated samples ranged from 74% to 98% of TP. This result is significantly lower than what was obtained from the previous study with sewage sludge under the same experimental conditions which had percentage ortho-P release within the range of 0.07% to 50.31%. The reason for the lower release efficiency of ortho-P could be attributed to the complex structure of dairy manure. Sewage sludge is essentially comprised of microbial cells, which are relatively

easy to release phosphorus when the cells are disrupted, while dairy manure particles contained many forms of phosphorus including inorganic-P, acid soluble organic-P, lipid-P and nucleic acid-type P which are difficult to solubilize (Barnett, 1994; Pan et al., 2006).

It was observed that significant ortho-P release occurred after acid treatment of the raw sample with concentrated H_2SO_4 to pH 4. This is consistent with other studies that reported liquid manure samples had to be acidified to obtain ortho-P release (Kenge et al., 2009b). However for sewage sludge, ortho-P release occurred irrespective of the pH. CH treatment of the acidified samples at three temperatures 40°C, 50°C and 60°C did not affect ortho-P release probably due to the presence of high levels of polyphosphates at lower temperatures (>60°C). However, the subsequent MW/ H_2O_2 -AOP treatment at 100°C and 120°C resulted in release of ortho-P which increased with increasing MW temperature. The results indicate that MW heating with H_2O_2 played significant role in ortho-P solubilization.

It can be observed that the conventional thermal preheating before MW/ H_2O_2 -AOP treatment resulted in the reduction of the ramp time (less than 4). Usually MW assisted pretreatment processes are conducted at higher temperatures with short heating time or low temperature with longer heating time to obtain the optimum ortho-P release. However the results obtained from this study indicates that excellent ortho-P yield could be obtained by the combination of conventional and MW/ H_2O_2 -AOP treatment at moderate heating times and temperature. This could have a very useful industrial application.

Ammonia is also released with phosphate during the treatment of organic waste material (Mavinic et al., 1995). Ammonium concentration ranged from 256.3 ± 5.3 mg/L for untreated sample to 624 ± 6.3 mg/L for the acidified samples. This range of values corresponds to 22% to 54% of TKN, respectively. As was observed for ortho-P release, substantial ammonia release occurred when raw sample was acidified. Kenge et al., (2009b) reported that, acid addition helps to retain ammonia in solution because it prevents its volatilization at the high microwave temperature. It was observed that conventional thermal heating of the acidified samples at temperatures 40°C, 50°C and 60° C did not result in further ammonia release similar to what was observed for ortho-P.

MW/H₂O₂-AOP treatment at the desired MW temperature resulted in further ammonia release. For the MW treated samples, ammonium release ranged from 928 ± 23 mg/L to 1101 ± 128 mg/L which corresponds to 80% to 95% of TKN. Maximum ammonium release was obtained for the treatment condition; 60°C CH-120°C MW with the total treatment time of 39 min. This results shows that MW heating temperature and H₂O₂ significantly affect ammonium release. This is consistent with the results reported by other researchers (Lo et al., 2012). Upon MW/H₂O₂-AOP treatment, ammonium release increased with CH temperature; this could be because 120°C had a higher treatment time than 100°C, which may have caused increased ammonia volatilization.

Pan et al., (2006) treated dairy manure with MW/H₂O₂-AOP with 1.5% hydrogen peroxide that resulted in an increase of ortho-P/TP ratio from 10 to 85% at 90°C. Kenge et al., (2009b) treated dairy manure slurry with MW/H₂O₂-AOP system at 120°C with varying hydrogen peroxide dosage; ortho-P/TP ratio increased from 14.4% to 22.8% while SCOD/TCOD ratio increased

from 1.2 to 2.1% for a 1% H₂O₂ set. Higher efficiency was observed only in the case with 6% H₂O₂ dosage that resulted in an ortho-P/TP to increase from 37.5 to 162.5% and SCOD/TCOD to increase from 8.6 to 17.7%. However, the present study combining CH and MW/H₂O₂-AOP with only 1% H₂O₂ resulted in releasing over 90% TP as ortho-P.

Table 4-3: Ortho-P and ammonia release from dairy manure

Sample	Ortho-P/ mg/L	Sol TP/ mg/L	TP/ mg/L	Ammonia/ mg/L	Sol TKN/ mg/L	TKN/ mg/L
Raw	4.9±0	26±18	150±4.6	440	623	1430
Acidified	108±1.3	123±4.4	164±22	868±223	838±21	1600±64
Preheated to 40 °C						
CH 40	105±12	120±2.7	160±12	913±39	825±54	1643±44
MW 100	139±7.2	101±2.3	93±20	1075±138	1213±90	1753±59
MW 120	148±12	114±17	108±19	928±23	1128±53	1585±21
Preheated to 50 °C						
CH 50	103±1.5	115±4.4	154±15	773±166	847±66	1639±60
MW 100	133±3.8	127±9	73±18	1028±174	1168±183	1663±63
MW 120	145±6	128±10	86±14	945±87	1288±59	1541±88
Preheated to 60 °C						
CH 60	111±2	124±3	156±7	913±32	897±52	1577±33
MW 100	112±7	107±2.7	88±7.9	1043±99	1192±98	1652±65
MW 120	126±8.4	116±6	91±13	1102±128	1373±267	1619±92

4.3.4 Comparison of CH and MW/H₂O₂-AOP treatments of sewage sludge and dairy manure

The overall treatment results can be summarized as follows: A maximum COD solubilization for both sewage and dairy manure occurred at 60°C CH-120°C MW with hydrogen peroxide. For sewage, the role of synergistic effect was prominent at high CH and MW temperatures with hydrogen peroxide. However, unlike sewage, there was no difference between the SCOD levels for dairy manure at the two microwave heating temperatures (100°C and 120°C). This could be

due to complex nature of dairy manure compared to sewage and lower dosage of hydrogen peroxide being used for dairy manure. 0.2% of H_2O_2 / % TS was used for dairy manure while 1.7% of H_2O_2 / % TS was used for sewage. Similar to COD solubilization, the VFA levels increased following the same trend.

For orthophosphates release, temperature and treatment time played a significant role. For sewage, significant ortho-P release occurred at higher CH temperature (i.e at 50°C and 60 °C) and subsequent MW/ H_2O_2 -AOP treatment resulted in substantial increase. The maximum ortho-P release occurred at 60°C CH-120°C MW with hydrogen peroxide addition. For dairy manure, the maximum ortho-P release occurred at treatment condition: 40°C CH-120°C MW, which represented approximately 98% of TP. The treatments also resulted in ammonia release, with a maximum release representing 95% TKN; MW temperature played significant role similar to ortho-P release.

A one-factor analysis of variance (ANOVA) was conducted to study the effect of CH and MW temperature, individually, on Ortho-P and SCOD release. The effect of CH and MW temperature, individually, on both Ortho-P and SCOD release were significant ($P < 0.05$) for sewage sludge and dairy manure. However, a two-way ANOVA involving both temperatures were not significant on Ortho-P and SCOD release. Irrespective of temperatures studied, combined CH and MW heating achieved statistically similar outcomes.

In general, CH treatment before MW/ H_2O_2 -AOP reduces the duration of MW heating. This step helps in saving energy used by the MW unit, consumed otherwise. Applying the combined

method in real time application may prove to be advantageous. The heat from the MW treated sludge and manure can be recovered and used in the pre-heating/CH step. Using the heat available in the treated material, which leaves the MW unit at approximately 100°C, to pre-heat the untreated slurry may reduce the energy requirements of the pre-heater.

4.4 Conclusion

This study applied the combination of CH and MW/AOP for the pretreatment of dairy manure for the purpose of nutrients recovery and disintegration of solids. The results indicated that, increased CH and MW temperatures and the addition of hydrogen peroxide resulted in an increased in COD solubilization of dairy manure and 22% of the total COD was solubilized. This was lower than sewage sludge probably because of the low hydrogen peroxide dosage used for dairy manure. The maximum ortho-P release occurred at treatment condition; (40°C CH-120°C MW) which represented approximately 98% of TP suggesting that the combination of conventional heating and MW/H₂O₂-AOP was very effective in the pretreatment of dairy manure for orthophosphates release. The overall results of the two experiments indicated that, the combination of CH and MW/H₂O₂-AOP was very effective in the treatment of dairy manure and sewage for nutrient release and solids disintegration.

Chapter 5 : Effects of organic acid treatment of dairy manure

5.1 Introduction

Dairy manure can be considered as a valuable bioresource rather than a waste material as it contains fats, proteins, lignin, carbohydrates and inorganic residues, and is rich in a variety of nutrients including nitrogen, phosphorus, and minerals. Through conversion processes, these elements can be recovered as useful products such as struvite, bioenergy, ethanol and others (Van Horn et al., 1994; Rico et al., 2007). The conversion processes can be facilitated by various pretreatment methods such as thermal, chemical, physical or combination (Mosier et al., 2005). A microwave enhanced advanced oxidation process (MW/H₂O₂-AOP) has been shown to be efficient treatment for solids solubilization and nutrient release from various organic wastes. The MW/H₂O₂-AOP utilizes the unique advantages of microwave (MW) dielectric heating and hydrogen peroxide to produce hydroxyl free radicals to react with organic compounds (Liao et al., 2007a; Eskicioglu et al., 2008). Microwave heating technology is advantageous because the heating is rapid and is carried out within the whole object. Studies by Zhu et al., (2005); (2006a), (2006b) have shown that microwave radiation can change the supermolecular structure of lignocellulosic material to improve reactivity.

Based on previous research on MW/H₂O₂-AOP in dairy manure treatment, large amounts of phosphorus and carbonaceous compounds which are reflected in soluble chemical oxygen demand concentration were released into solution only under acidic condition (Kenge et al., 2009a; Jin et al., 2009; Lo and Liao, 2011). When dairy manure samples were subjected to an addition of acid at pH below 4, fine suspended particles in dairy manure agglomerated, resulting

in decreased SCOD concentrations. When these acid treated samples were further treated with the MW process, the agglomerates were destroyed, resulting in an overall increase in SCOD (Lo and Liao, 2011). However, anaerobic bacteria could not utilize some of degradation products constituted in SCOD; Methane production from the MW/H₂O₂-AOP treated solution was found to be lower than from the untreated dairy manure filtrate (Chan et al., 2013). The biodegradability of dairy manure is typically in the range of 30-43% yielding 150-2401 CH₄kg VS⁻¹ (Møller et al., 2004; Nielsen et al., 2004). When sulfuric acid is used for pH adjustment, the sulfate reducing bacteria (SRB) during anaerobic digestion would produce sulfite which can be toxic to various bacterial groups; SRB may also compete with methanogens for common organic and inorganic substrates, thereby suppressing methane production (Koster et al., 1986). Jin et al., (2009) reported that MW heating, combined with different chemicals (NaOH, CaO, H₂SO₄ or HCl) enhanced solubilization of manure particulates and degradation of glucan/xylan in dairy manure. A higher SCOD/TCOD ratio was observed for dairy manure treated under acidic condition than under basic condition, and for MW treatment without H₂O₂ than with H₂O₂ in their studies. Lesser methane was produced with acidified MW treated solution than that with raw manure: methane production was lower with the use of sulphuric acid than to that of hydrochloric acid.

The majority of total phosphorus in dairy manure is in the form of inorganic phosphorus, is predominantly bound to particulate organic matter (Barnett, 1994; Gungor and Karthikeyan, 2008) or inorganic (precipitate) matter (Vanotti et al., 2002; Masse et al., 2005). Cooperband and Good, (2002) and He et al., (2003) have shown that a major fraction of the phosphorus in animal manure is associated with Ca and Mg present in the manure. With a decrease in pH significant

amounts of phosphorus were released into solution resulting in an increase of orthophosphates concentration (Lo and Liao, 2011). More phosphorus release from acidified dairy manure was obtained by using the MW/H₂O₂-AOP. The addition of hydrogen peroxide also helped the breakdown of particulates to release phosphorus. Furthermore, hydrogen peroxide not only aids release of nutrients and solubilizes dairy manure solids; it also improves settleability of dairy manure.

Most of magnesium and calcium were also released into solution upon MW/H₂O₂-AOP treatment in acidic condition (Kenge et al., 2009a; Lo and Liao, 2011). The presence of Ca²⁺ ions is detrimental to struvite formation; either by competing for phosphorus ions or by interfering with the crystallization of struvite. A high Ca²⁺ concentration would favor the formation of calcium-phosphorus compounds, and affect struvite crystal size, shape and purity. Le Corre et al., (2005) reported that at higher Ca:Mg molar ratios of 0.5:1 and 1:1, the preferential reaction of Ca²⁺ was with carbonate or phosphate. At a Ca:Mg molar ratio of 1:1 and above, no more crystalline compound was formed. The ideal molar ratio of calcium to magnesium for struvite recovery is around 0.25:1 (Shen et al., 2010; Zhang et al., 2010). It has been reported that ethylenediaminetetraacetic acid (EDTA) and oxalic acid can effectively remove calcium ion from the solution: they were able to reduce Ca²⁺ by 90%, while no more than 10% of Mg²⁺ was removed (Shen et al., 2010). Suspended solids (SS) concentration at more than 1000 ppm (mg/L) interfered with struvite crystallization (Schuiling and Andrade, 1999). Therefore, excess amounts of calcium and SS in MW/H₂O₂-AOP treated solution need to be removed, prior to struvite crystallization (Zhang et al., 2013).

There is a need to find reagents that can acidify and disintegrate dairy manure simultaneously, without producing undesirable products unsuitable for anaerobic digestion. Various organic acids have been used in treatment processes as alternatives to inorganic acids. Fumaric, maleic, and sulfuric acids were used for pretreatment of wheat straw for enzymatic hydrolysis (Kootstra et al., 2009). Oxalic and maleic acids proved to be very effective to depolymerize cellulose, producing oligomers and glucose; under mild reaction conditions of 100-125°C for hydrolysis (Von Stein et al., 2010). The low-molecular weight organic acids were used for release of phosphorus from phosphate rocks: there were two monocarboxylic acids (pyruvic & glycolic), nine di-carboxylic acids (oxalic, tartaric, malonic, fumaric, malic, ketoglutaric, maleic, oxalacetic, and succinic acids), two aliphatic tri-carboxylic acids (citric and cis-aconitic acids), and six aromatic acids. Oxalic acid was most effective for releasing phosphorus from phosphate rock among organic acids; its effectiveness was comparable to sulfuric acid (Kpoblekou and Tabatabai, 1994). In recent times, oxalic acid has been proposed as an alternative to sulphuric acid for lignocellulosic pretreatment because it has higher efficiency for hydrolysis of lignocellulosic biomass than sulphuric acid (Mosier et al., 2005; Lee et al., 2009; Kim et al., 2011). Since the development of MW/H₂O₂-AOP for the enhancement of nutrient recovery from dairy manure via struvite precipitation and to improve anaerobic digestion, there has not been any study on the use of organic acids as acidifying reagents, even though it has been reported to be effective in the hydrolysis of other lignocellulosic biomass. The use of oxalic acid unlike sulfuric acid has the advantages of the production of less inhibitory compounds, noxious odours, corrosion of equipment but also the ability to remove Ca ions which interferes with struvite precipitation process. It is also possible to recover the oxalic acid after the pretreatment process (Yang and Wyman, 2008; Lee et al., 2013).

With this goal in mind, the purpose of this study was to develop an efficient single stage MW/H₂O₂-AOP that could release phosphate, solubilize solids and remove calcium from dairy manure. This research was thus to investigate the effects of three organic acids (mono-, di- and tri-carboxylic acid), and mixtures of mineral acid and organic acid as acidifying reagents for treating dairy manure in MW/H₂O₂-AOP.

5.2 Materials and methods

5.2.1 Sample preparation

Dairy manure used in this study was obtained from the University of British Columbia (UBC) Dairy Education & Research Centre in Agassiz, British Columbia, Canada. The solid portion obtained after solid-liquid separation, was used. Once collected from the farm, the dairy manure was stored in closed containers at 4°C. Separated dairy manure contained large amounts of sand, bedding material, as well as undigested lignocellulosic materials. Distilled water was added to the manure samples and subsequently decanted to remove the sand.

5.2.2 Microwave pretreatment

The Milestone Ethos TC microwave oven digestion system (Milestone Inc., Monroe, CT, USA) was used in this study. The system operates at a frequency of 2,450 MHz with a maximum power output of 1000 W. The MW system can attain a maximum operating temperature of 220 °C and can handle a pressure of up to 3,000 kPa. A total of 12 vessels of 100 mL capacity each, including one reference vessel equipped with a thermocouple, are provided in the system. An independent system controller provides real-time temperature control.

5.2.3 Experimental design

The experiments, each with triplicate, were conducted at MW temperature of 120°C with a ramp time of 5 min (20°C/min), and held for 5 minutes. If hydrogen peroxide was needed, then 1 mL of 30% H₂O₂ was added into 30 mL of sample. The study was divided into four phases: manure was subjected to MW treatment without hydrogen peroxide in the first phase; MW treatment with hydrogen peroxide was used in the second phase; the effects of pH on the MW/H₂O₂-AOP were examined in the third phase; calcium removal efficiency using various dosage of oxalic acid was evaluated in the final phase. All of the samples were adjusted to desired pH by using various organic (acetic, oxalic & citric) and inorganic acids (hydrochloric and sulfuric), wherever applicable. The detailed experimental conditions are presented in Table 5.1.

Table 5-1: Summary of experimental conditions

	Set	pH	Acid	Acid added in 30ml	H ₂ O ₂ (%)
Phase 1	1.1	4.1	Acetic	21 mmol	0
	1.2	4.4	Oxalic	3.2 mmol	0
	1.3	4.2	Citric	2.7 mmol	0
	1.4	4.1	Sulfuric	3.8 mmol	0
Phase 2	2.1	7.1	No		1
	2.2	4.2	Acetic	21 mmol	1
	2.3	4.2	Oxalic	3.2 mmol	1
	2.4	4.6	Citric	1.9 mmol	1
	2.5	4.1	Sulfuric	3.8 mmol	1
Phase 3	3.1	6.0	Oxalic	1.3 mmol	1
	3.2	5.0	Oxalic	2.8 mmol	1
	3.3	4.1	Oxalic	3.5 mmol	1
	3.4	6.2	Sulfuric	1.9 mmol	1
	3.5	5.2	Sulfuric	2.8 mmol	1
	3.6	3.8	Sulfuric	3.8 mmol	1
	3.7	2.7	Oxalic + sulfuric	0.7 mmol + 3.8 mmol	1
	3.8	2.6	Oxalic + HCl	0.7 mmol + 6 mmol	1
Phase 4	4.1	4.0	Oxalic + sulfuric	0.98 mmol + 1.69 mmol	1
	4.2	4.1	Oxalic + HCl	0.98 mmol + 2.39 mmol	1
	4.3	2.7	Oxalic + sulfuric	0.84 mmol + 1.69 mmol	2
	4.4	2.7	Oxalic + HCl	0.84 mol + 2.39 mmol	2

5.2.4 Sample and data analysis

Both the MW/H₂O₂-AOP treated samples and the initial untreated dairy manure samples were centrifuged at 3500 rpm for 10 minutes, and then filtered using a 4.5 µm fiberglass filter. The filtered samples (treated and untreated) were analyzed for SCOD, orthophosphate, soluble ammonia, volatile fatty acids (VFA) and metals. All of the chemical analyses followed the procedures outlined in Standard Methods (1998). It has been reported that in the orthophosphate (o-PO₄) analysis of dairy manure samples, different dilution ratios could cause interference; the initial dairy manure sample was diluted to total solids (TS) of 0.5% for ensuring accurate orthophosphate measurement (Wolf, et al., 2005). The initial dairy manure samples were also analyzed for TS, total chemical oxygen demand (TCOD), total phosphate (TP) and total Kjeldahl nitrogen (TKN). All chemical analyses were determined by a flow injection system, except determinations of TS and COD (Lachat Quik-Chem 8000 Automatic Ion Analyzer, Lachat Instruments, USA). A Hewlett Packard 5890 Series II gas chromatograph, equipped with a flame ionization detector (FID), was used to measure VFA. Volatile separation was accomplished with an HP FFAP (free fatty acid phase) column (0.25 m × 0.31 mm with 0.52 µ film thickness). The injection temperature and the detector temperatures were set at 175 and 250 °C, respectively. Helium gas was used as the carrier at a head pressure of 69 kPa. Metals were determined using a Varian Spectra 220 Fast Sequential Atomic Absorption Spectrometer.

5.3 Results and discussion

In earlier studies conducted by Jin et al., (2009) and Lo and Liao, (2011) large quantities of phosphorus and degradation products were released from dairy manure in acidic condition under MW treatment. Many non-biodegradable products were also formed using mineral acids as acidified reagents (Chen et al., 2008; Chan et al., 2013) which affect the yield of the downstream value added processes. The effects of three organic acids (acetic acid, oxalic acid and citric acid) instead of mineral acids as acidified reagents were studied. They are weak acids, compared to sulfuric acid or hydrochloric acid (Table 5.1). Using organic acids, instead of mineral acids was to prevent or reduce the formation of undesirable sulfite products from the MW treatment.

5.3.1 The effects of organic acids with or without hydrogen peroxide treatment

From this study, it was found that orthophosphate was released into solution upon addition of organic acids prior to MW treatment (Figure 5.1). The extent of orthophosphates release was comparable to sulfuric acid treatment (Lo and Liao, 2011). Soluble magnesium and calcium ions increased with addition of acetic acid, citric acid and sulfuric acid (Sets 1.1, 1.3 & 1.4). Oxalic acid addition (Set 1.2) slightly decreased magnesium ions, but completely removed calcium ions from dairy manure (Table 5.2). The total chemical oxygen demand (TCOD) concentrations of acidified dairy manure increased with addition of organic acids. As expected, there was no increase in TCOD concentration with the addition of sulfuric acid. This is because of the contribution of carbon from the organic acids which increased with the amount of organic acid added. The SCOD concentrations which measured the extent of solubilization of biodegradable organics components increased with additions of acetic and citric acid; however, with oxalic acid addition the SCOD concentration remained more or less the same as in raw manure. The

explanation may be due to the fact that some of oxalic acid being a good binding agent for metals was binding with calcium and magnesium ions to form precipitates that were filtered out of solution. Acidified dairy manure was then subjected to MW treatment without hydrogen peroxide (Phase 1). Orthophosphate concentration in solution after MW treatment was similar to the acidified set, regardless of organic acids or sulfuric acid used (Figure 5.1). All other parameters such as, TCOD, SCOD concentration and pH for each set were similar to the initial manure (Table 5.2). The results suggested that integrity of molecular structure of organic acids was retained after MW irradiation and heating. The results proved that organic acids were effective acidified reagents, and oxalic acid was an excellent reagent to acidify manure and remove calcium ion at the same time. MW heating alone was unable to disintegrate dairy manure particulate or release nutrient in a large quantity. The settling of MW treated dairy manure was not improved either. The settling occurred in MW treatment only in the presence of hydrogen peroxide (Kenge et al., 2009a; Lo et al., 2012). As evidenced in phase 1, there was little solids disintegration and settling happening in the MW process without H₂O₂. Therefore, hydrogen peroxide was used in MW process in phase 2. It was to examine the effects of hydrogen peroxide on organic acids, as well as on treatment efficiency of the process. The resulting solutions retained pH for the treated solutions, except dairy manure without pH adjustment (set 2.1), and acetic acid (set 2.2). It was not clear why pH increased in the case of dairy manure without pH adjustment (set 2.1). Ammonia, SCOD, TCOD and VFA concentrations remained more or less the same as the initial values in this set; however, a decrease of calcium and magnesium concentrations was observed. At a high pH of 8.6 in the MW treated set 2.1, less free magnesium and calcium ions would be in solution, and various calcium and magnesium phosphate products could be formed (Le Corre et al., 2005; Shen et al., 2010; Zhang et al., 2013). In the case of

acetic acid (set 2.2), pH increased from 4.2 to 6.5 after MW and H₂O₂ treatment. With an increase in pH, orthophosphate concentration decreased from 104 to 40.8 mg/L. SCOD, TCOD and VFA concentrations were also decreased in the resulting solution (Table 5.2). It was assumed that either acetic acid reacted with H₂O₂ to produce final oxidation product of CO₂ or it evaporated and escaped into headspace during the process. Due to an increase in pH, magnesium and calcium ion concentrations also decreased; both free magnesium and calcium ions are pH dependent.

It was assumed that oxalic acid and citric acid (sets 2.3 and 2.4) retained their molecular integrity as indicated by no change of pH value; they neither reacted with hydrogen peroxide, nor decomposed under MW irradiation and heating. There were slight increase in orthophosphate, ammonia, COD, and VFA for sets 2.3 and 2.4. Calcium was completely removed from the solution when oxalic acid was used as an acidified agent (set 2.3); after MW/H₂O₂-AOP, magnesium concentration increased slightly. Magnesium concentrations remained the same as the initial, while calcium concentration decreased in citric acid set (set 2.4). The results confirmed previous findings that oxalic acid can effectively remove calcium ion from the solution (Shen et al., 2010; Zhang et al., 2013). TKN, soluble TKN and ammonia for phases 1 and 2 are showed in Figure 5.2. In general, ammonia concentration increased slightly with MW treatment with or without H₂O₂. However, for all three organic acid sets, much more soluble TKN were released with the MW/H₂O₂-AOP than with MW treatment alone. Under similar conditions, Protein and amino acid were liberated from particulate into soluble form. However, they were not converted into ammonia (Yi, 2012). A paired t-test was applied to test the

difference in the concentrations of ammonia and soluble TKN; the difference was found to be statistically similar ($p < 0.05$) for each set in phases 1 and 2 at 95% confidence interval.

The results indicated that very low treatment efficiency was obtained in terms of solids disintegration for MW/H₂O₂-AOP using organic acids. Hydrogen peroxide dosage was the most significant factor affecting solids disintegration in MW/H₂O₂-AOP. The SCOD concentration increased with an increase of H₂O₂ dosage (Wong et al., 2007; Kenge et al., 2009a). This might be due to the low hydrogen peroxide dosage (approximately 0.2% H₂O₂ per 1% TS) and a shorter reaction period (5 min) used in this study may not have aided in solids disintegration. A much high treatment efficiency was reported in the previous studies, because they were conducted at much higher hydrogen peroxide dosage (1-2.4% H₂O₂ per 1% TS), and longer held heating time of 7.5 to 10 mins (Kenge, 2008; Kenge et al., 2009a). It should be noted that sulfuric acid was used in these studies; it was a strong acid which could also react with dairy manure which resulted in high solids reduction.

Sludge settling occurs in the presence of both H₂O₂ and mineral acids in the MW treatment of dairy manure (Yu et al., 2010; Zhang et al., 2013). In this study, a clear solution, which occupied 30% of test volume, was obtained after MW and H₂O₂ treatment from samples acidified only with oxalic acid. In previous studies, dairy manure acidified with sulfuric acid had a good settling property after H₂O₂ and MW treatment: about 40-60% of supernatant was obtained from the treated solution (Yu et al., 2010; Zhang et al., 2013). As noted earlier, sulfuric acid was not only an acidified reagent, but also a reactant in the MW/H₂O₂-AOP. When sulfuric acid was mixed with hydrogen peroxide, an aqueous solution of peroxymonosulfuric acid (H₂SO₅) was

produced, which rapidly destroyed most organic materials. As a result, a higher yield of soluble materials was attained with addition of sulfuric acid than with organic acids. While organic acids are less reactive, they do not destroy organic materials; thus, as expected they would produce less undesirable side products for anaerobic digestion when compared to using sulfuric acid. Due to these non-reactive characteristics, organic acids were used for the purpose of phosphate release, acid hydrolysis of organic waste materials, and others (Kpoblekou and Tabatabai, 1994; Kootstra, et al., 2009; Von Stein, et al., 2010).

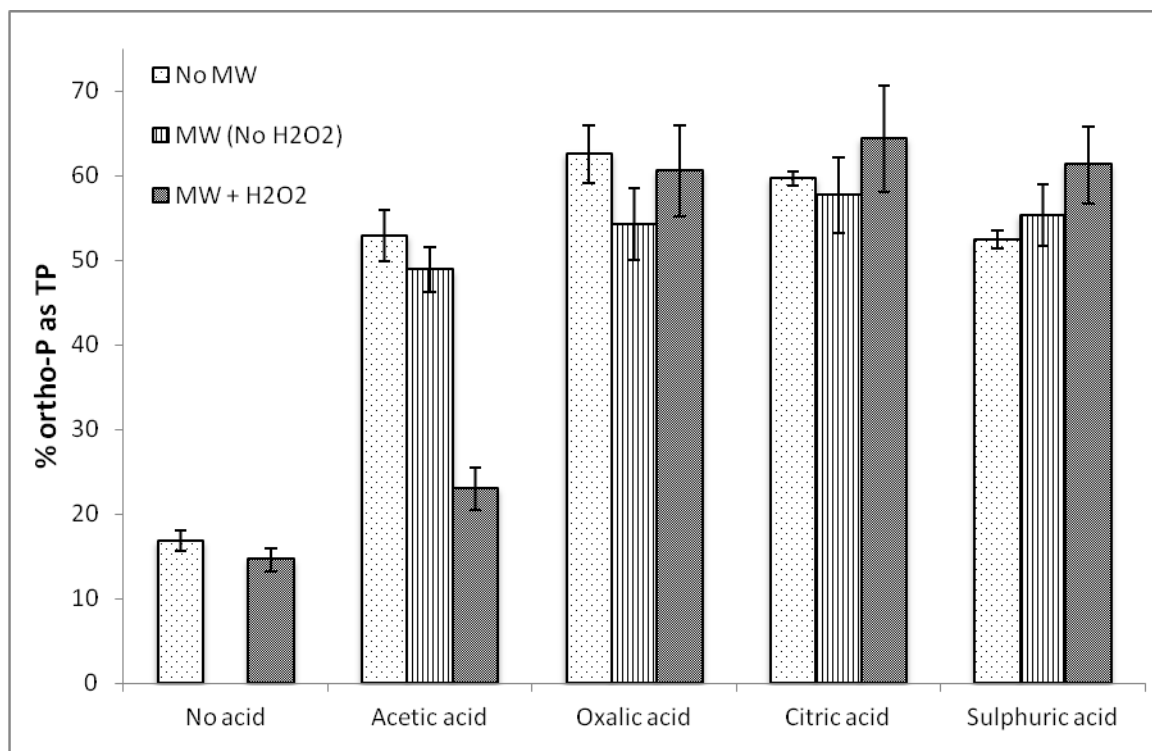


Figure 5-1: Ortho-P release for phase 1 and 2

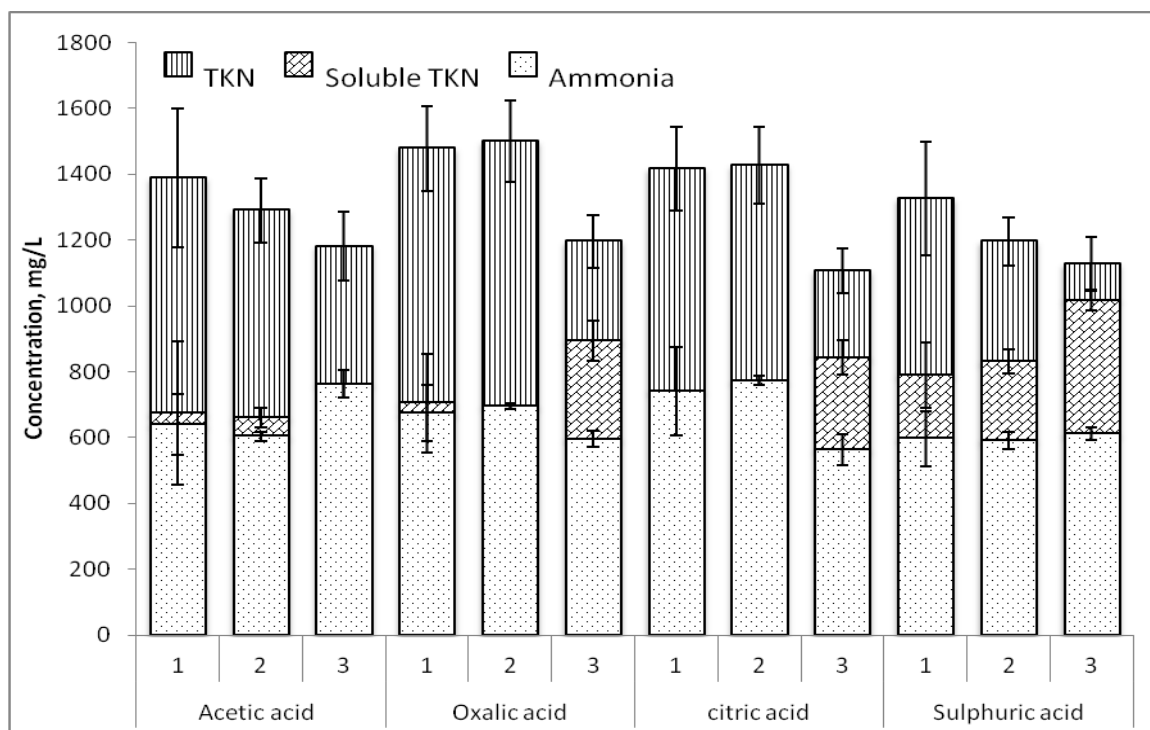


Figure 5-2: Ammonia and TKN release for phase 1 and 2; 1 is acidified manure, 2 is acid + MW (No H₂O₂) and 3 is acid + H₂O₂ + MW.

5.3.2 Effects of oxalic acid treatment at different pH

The results showed that the MW/H₂O₂-AOP using oxalic acid could release phosphorus, reduce calcium concentration in liquid dairy manure, and produce a clear supernatant. Thus, oxalic acid was chosen for further study and compared to sulfuric acid; the effects of pH on the MW/H₂O₂-AOP were examined in Phase 3. There was little orthophosphate release at pH 6, regardless of oxalic acid or sulfuric acid added (Figure 5.3). It appeared that orthophosphate concentration in the solution increased slightly with a decrease in pH. Under MW/H₂O₂-AOP at pH 5, orthophosphate concentration increased with oxalic acid, while it decreased with sulfuric acid (Figure 5.3). No explanation could be given for the decrease of orthophosphate. Substantial amounts of orthophosphate were produced at pH 4; 82% and 90% of TP were released in the

oxalic acid and sulfuric acid treated sets, respectively. As discussed earlier, oxalic acid does not react or destroy organic matter; an increase of SCOD concentration was attributed to H_2O_2 and MW irradiation (Table 5.3). Due to the reactive nature of sulfuric acid, it was not only an acidifying agent, but also an active reactant. The SCOD concentration in the MW/ H_2O_2 -AOP solution for sulfuric acid set was higher than that of oxalic acid. It was evident that sulfuric acid did help break down organic matter; a higher soluble TKN concentration was also obtained for samples acidified with sulfuric acid than with oxalic acid (Figure 5.2). Also, only about 30% of clear solution was obtained after MW/ H_2O_2 -AOP with the use of oxalic acid at pH 4.0.

5.3.3 Effects of combinations of oxalic acid and mineral acids

To further improve settleability of treated solution and solids disintegration, a mixture of mineral acids (HCl and H_2SO_4) and oxalic acid at pH 4 were selected in phase 3 (Table 5.1). Among all of treatment sets in phase 3, much higher SCOD, VFA, ortho- PO_4 , and soluble TKN were obtained in the sets with a mixture of oxalic and sulfuric acid (set 3.7) and a mixture of oxalic and HCl (set 3.8).

The initial Ca:Mg molar ratio of dairy manure was calculated to be approximately 1.5 in phase 3. For sulfuric acid (sets 3.4, 3.5 and 3.5), the molar ratio of Ca:Mg were 1, 1.59, and 1.72 at pH 6, 5, and 4, respectively. As noted earlier, calcium and magnesium were pH dependent. After the MW/ H_2O_2 -AOP, they were 0.6, 1.58, and 1.45, at pH 6, 5 and 4, respectively. Molar ratio of Ca:Mg for sulfuric acid solution was similar to that of the initial. In order to adjust pH to 6, 5, and 4, amounts of required oxalic acid were 1.3, 2.8 and 3.5 mmol in 30 mL. Due to very high

oxalic acid dosage, free calcium ion was near undetectable in sets 3.1, 3.2 and 3.3 prior or after MW/H₂O₂-AOP (Table 5.2 and Figure 5.4).

Table 5-2: Organic matters and metals for Phase 1 – 2

Set	pH	SCOD (g/L)	TCOD (g/L)	VFA (g/L)	Ca (mg/L)	Mg (mg/L)
Raw	7.3	4.6±0.5	65.6±10.6	0.84±0	107	149
1.1 ^a	4.1	42.8±0.9	81.3±3.7	42.9±0.6	755	252
1.1 ^b	4.1	43±0.9	81.4±8.1	37.2±1.8	744±11	247±3.4
1.2 ^a	4.5	4.6±0.5	74±11.7	1.9±0.01	0	101
1.2 ^b	4.4	4.7±0.3	35.5±2.3	1.8±0	0	120±7.9
1.3 ^a	4.2	17±1.2	67.7±6.7	2.1±0.2	710	224
1.3 ^b	4.2	16.5±0.6	60.9±4.5	1.9±0.1	743±27	245±10
1.4 ^a	4.2	6±0.4	47.1±0.77	2.5±0.04	697	249
1.4 ^b	4.1	5.9± 0.3	46.5±3.1	2.4±0. 1	729± 40	249 ±14
Raw	7.1	6.9±0.2	41.8±3.1	1.7±0.05	156	162
2.1 [*]	8.6	7.3±0.3	44.4±2.5	2.4± 0.07	91.4 ±2.8	127± 2.7
2.2 ^a	4.3	39.6±0.8	86.2±7.8	38.2±0.6	465	215
2.2 ^b	6.6	39.0±1.4	74.7±2.5	35.6±1.1	363±11	199 ± 9.4
2.3 ^a	4.2	7.2±0.09	42.5±9.6	2.6±0	0	110
2.3 ^b	3.9	8.7±0.5	40.6±3.1	2.4±0.09	0.8 ± 0.4	135 ± 12
2.4 ^a	4.6	14.7±0.8	62.9±6.1	2.5±0.1	711	244
2.4 ^b	4.3	15.2±0.1	52.9±4.1	2.4±0.1	682 ±17	241 ± 6.1
2.5 ^a	4.1	6.7±0.5	53.8±13.7	2.8	737	255
2.5 ^b	4.1	6.7±0.2	48.5±2.5	2.6±0.4	687±15	254± 3.8

Note: ^a is only acidified and ^b is acidified + microwave treated.

Table 5-3: Organic matters and metals for Phase 3

Set	pH	SCOD (g/L)	TCOD (g/L)	VFA (g/L)	Ca (mg/L)	Mg (mg/L)
Raw	7.3	6.5±0.03	59.7±7.8	2.64	652.00	266
3.1 ^a	6.0	6.9±0.08	47.3±4.5	2.08	4.1	153
3.1 ^b	7.4	7.5±0.3	43.5±10.2	2.64 ±0.22	2.8±0.3	161±4
3.2 ^a	5.0	6.9±0.1	57.0±20.1	2.82±0.1	0.7	272
3.2 ^b	5.3	7.6±0.3	41.1±4.6	2.8 ±0.03	1.6±0.4	261±2
3.3 ^a	4.1	6.6±0.1	54.9±6.4	2.8±0.04	0	255
3.3 ^b	4.5	7.9±0.5	45.8±0.8	2.81 ±0.09	0.3±0.1	265±99
3.4 ^a	6.2	5.4±0.03	55.8±0.3	2.58	324	194
3.4 ^b	7.5	7.0±0.1	39.2±1.5	2.69 ±0.05	232±62	241±32
3.5 ^a	5.2	5.9±0.3	43.1±3.4	2.87±0.03	748	282
3.5 ^b	5.5	6.7±0.1	50.0±3.7	2.73 ±0.10	657±7	249±12
3.6 ^a	3.8	5.1±0.1	46.8±3.9	2.55±0.1	785	275
3.6 ^b	3.3	9.6±0.2	52.4±4.2	2.98 ±0.29	694±40	288±21
3.7 ^a	3.1	4.6±0.08	60.1±1.7	2.38±0.03	175	237
3.7 ^b	2.7	10.5±0.5	39.9±1.9	3.02 ±0.25	266±19	285±19
3.8 ^a	3.1	4.7±0.04	52.9±6.0	2.33±0.1	137	244
3.8 ^b	2.6	11.9±0.1	50.2±2.9	3.32 ±0.09	250±4	283±2

Note: ^a is only acidified and ^b is acidified + microwave treated.

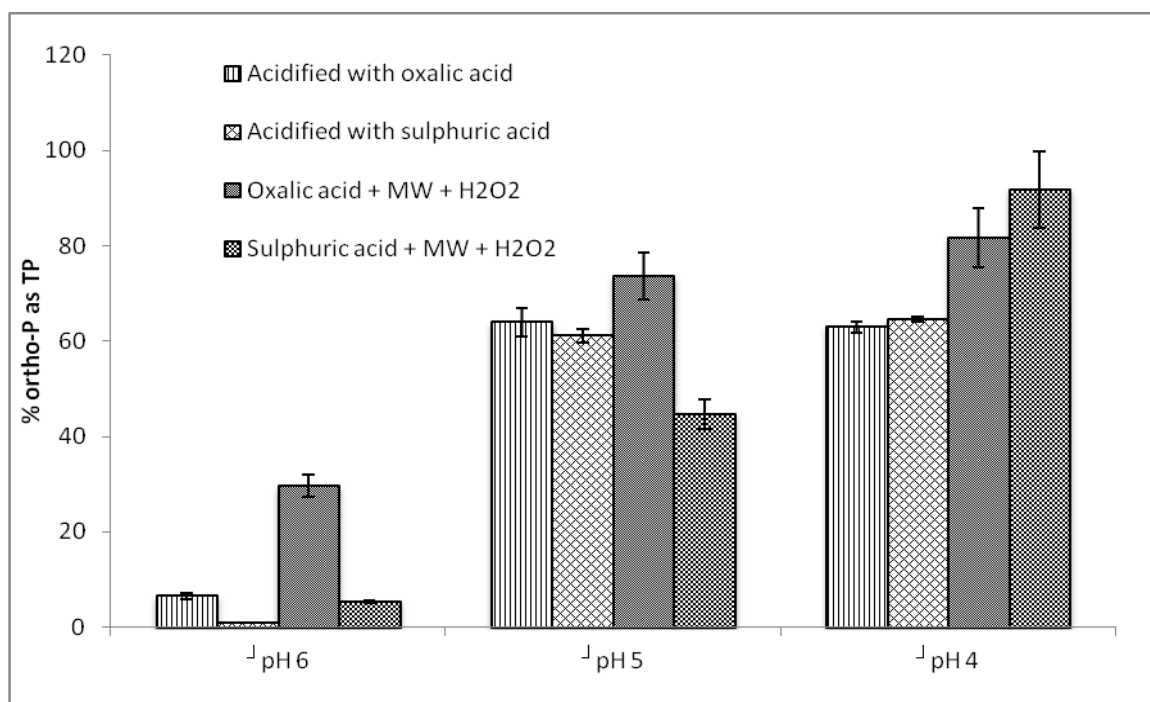


Figure 5-3: Ortho-P release for phase 3.

With mixtures of mineral acid and oxalic acid, about 266 to 250 mg/L of Ca^{2+} ion were in the MW/ H_2O_2 -AOP treated solutions (sets 3.7 and 3.8). The relative high calcium ion in the treated solutions was due to a low dosage of oxalic acid. There was no difference on removal efficiency of calcium between sulfuric acid and hydrochloric acid. The resulting solutions had a Ca:Mg molar ratio of 0.5, which was still too high for struvite crystallization. The ideal Ca:Mg molar for struvite crystallization shall be approximately 0.25 or below (Shen et al., 2010, Zhang et al., 2010). However, sludge settling was improved in these two sets. Zhang et al., (2013) reported that a clarified solution of dairy manure was obtained using sulfuric acid and MW/ H_2O_2 -AOP, followed by addition of oxalic acid to the supernatant to remove calcium. In their study, calcium ion was reduced to a Ca:Mg molar ratio below 0.17 by using 2 moles of oxalic acid per mole of Ca^{2+} . As a result, a large quantity of struvite crystals was obtained. Thus, the results obtained

from this study indicate that MW/H₂O₂-AOP and oxalic acid treatment could be combined into a single-stage process, instead of two-stage process. A higher oxalic acid dosage (0.98 and 0.84 mmole in 30 mL) was used in the mixtures of oxalic acid and mineral acid in Phase 4. A higher hydrogen peroxide dosage (2% v/v) was also used in the sets (4.3 and 4.4). The results are shown in Table 5.4 and Figure 5.4. The resulting solution had a Ca:Mg molar ratio of approximately 0.25 for sets 4.3 and 4.4. For sets 4.1 and 4.2, free calcium ion in the treated solution was about 20 mg/L, with a Ca:Mg molar ratio of 0.03. The resulting solution had an ideal Ca:Mg molar ratio, which was most suitable for struvite crystallization. A higher SCOD concentration was obtained with 2% H₂O₂ dosage than with 1% H₂O₂ dosage. The results confirmed that hydrogen peroxide was the most significant factor affecting solids disintegration in the MW/H₂O₂-AOP. A low yield of SCOD concentration in the earlier phases was due to insufficient hydrogen peroxide dosage in this study.

Table 5-4: Phase 4 experimental results

Sample	Ortho-P (mg/L)	Ammonia (mg/L)	TP (mg/L)	TKN (g/L)	SCOD (g/L)	TCOD (g/L)	Ca (mg/L)	Mg (mg/L)
Raw	2±0.02	699±14.4	270±6	1.9±0.1	7.5±0.8	74±4	152±10	221±3
4.1 ^a	121±0.7	748±10.6	299±6	2.0±0.1	7.3±0.9	81±3	20±1.9	318±0
4.1 ^b	122±1.2	763±7.6	291±20	2.1±0.1	9.0±0.6	68±4	3.3±1.9	299±4
4.2 ^a	117±0	748±10.6	297±17	2.0±0	7.9±0.4	69±0	3.6±2.2	306±2
4.2 ^b	114±2.7	735±0	277±5	2.0±0	9.0±0.2	62±7	19±5.7	307±32
4.3 ^a	124±0.7	765±7.1	291±1	2.1±0	7.0±0	66±5	74±1.9	358±7
4.3 ^b	191±12	850±5	285±1	2.0±0	19.6±1	63±5	172±5	377±6
4.4 ^a	119±0.7	743±39	305±16	2.2±0.1	6.6±0.1	72±5	62±2.9	322±18
4.4 ^b	176±2.	823±10.4	272±1	1.9±0	17.4±4	67±5	129±14	339±43

Note: ^a is only acidified and ^b is acidified + microwave treated.

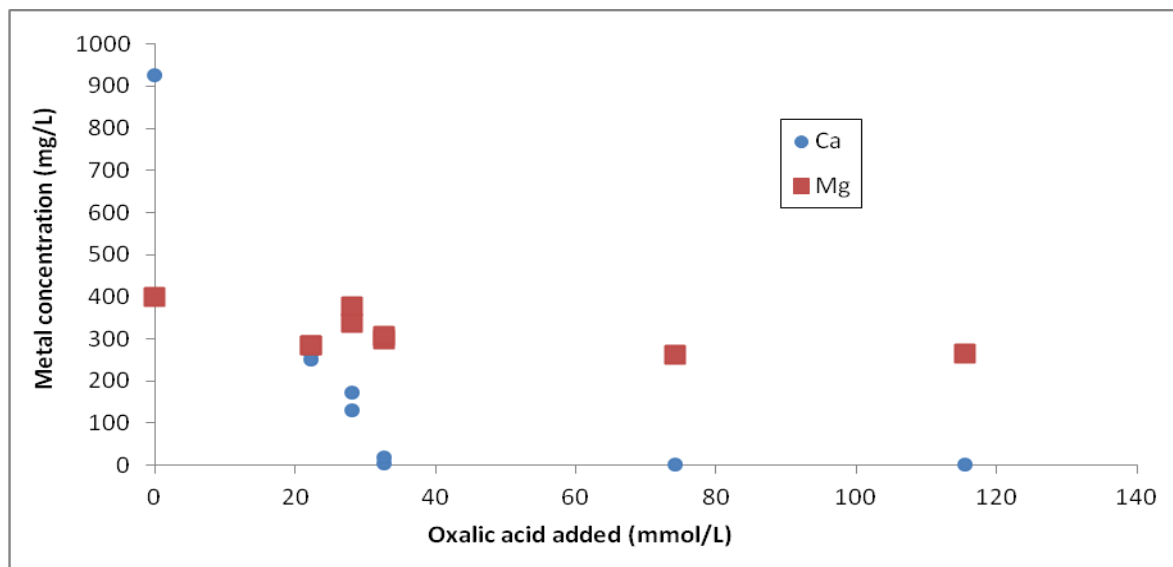


Figure 5-4: Ca and Mg release.

5.4 Conclusion

The MW/H₂O₂-AOP and oxalic acid treatment could be combined into a single-stage process, which could release phosphate, solubilize solids and remove calcium from dairy manure at the same time. A mixture of oxalic acid and mineral acids could improve sludge settling, and produce a clear supernatant having an ideal Ca:Mg molar ratio for subsequent struvite crystallization.

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