APPLICATIONS OF THE MICROWAVE-ENHANCED ADVANCED OXIDATION PROCESS

by

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BASc., University of British Columbia, 2006

A THESIS SUBMITTED FOR THE PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF APPLIED SCIENCE

in

The Faculty of Graduate Studies

(Civil Engineering)

THE UNIVERSITY OF BRITISH COLUMBIA

(Vancouver)

October 2008

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Abstract

Municipal wastewater treatment using biological nutrient removal generates large amounts of waste sludge. An effort is made to solubilize nutrients from sludge and reuse them in subsequent processes. The microwave-enhanced advanced oxidation (MW/H2O2-AOP) process using hydrogen peroxide as the oxidant was applied to the treatment of different organic slurries including wasted sludge, blood meal, and fish silage.

The factors controlling phosphates, ammonia, and COD release into solution included inorganic acid addition, hydrogen peroxide dosage, treatment times and temperatures. Higher dosages and treatment temperatures yielded better solubilization of phosphates and ammonia. It was found that approximately all of the COD was solubilized at a treatment temperature of 80°C. Volatile fatty acid (VFA) concentrations were also found to have increased with the amount of inorganic acid added into treatment. Up to 25% of soluble COD was composed of acetic acid.

Higher irradiation levels tended to be more effective in the solubilization of nutrients. In terms of trends of particle size distribution, detectable particles increased in size in acidic conditions, with the largest fraction of larger particles in a given sample being the treatment with highest irradiation power. In neutral condition treatments, the higher the irradiation power provided to the samples, the more spread out the particle sizes range. In alkaline condition treatments, an increase in smaller particles were found after treatment; higher power irradiation yielded significantly higher numbers of smaller particles. This study provided an insight into the athermal effects of the MW/H2O2-AOP.

Blood meal solubilization for the purpose of its application as an organic ferilizer was investigated using the MW/H2O2-AOP. It was found that over the treatment temperature range of 60 to 120°C, solids particle reduction, ammonia and orthophosphate production were achieved. Maximum solubility of chemical oxygen demand (COD) occurred at 80°C.
Without the addition of acid, soluble COD decreased due to protein denaturation and coagulation out of the solution.

Fish silage is also a valuable fertilizer for organic greenhouse hydroponics operations, but a pretreatment step is required. It was found that up to 26 % of total Kjeldahl nitrogen could be released as ammonia with 6 % hydrogen peroxide dosage at 170°C. An increase of nitrate/nitrite concentration was observed with higher hydrogen peroxide dosage and higher microwave temperature.
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List of abbreviations

ATP – Adenosine triphosphate  
BC – British Columbia  
BOD – Biochemical oxygen demand  
CO\textsubscript{2} – Carbon dioxide  
COD – Chemical oxygen demand  
EBNR – Enhanced biological nutrient removal  
HCl – Hydrochloric acid  
MW/H\textsubscript{2}O\textsubscript{2}-AOP – Microwave-enhanced advanced oxidation process  
N – Nitrogen  
NO\textsubscript{x} – Nitrates and nitrites  
NH\textsubscript{3} – Ammonia  
Ortho-P – Ortho-phosphates  
PHA – Polyhydroxyalkanoates  
P – Phosphorous  
PO\textsubscript{4} – Phosphates  
Poly-P – Polyphosphorous  
TS – Total solids  
TP – Total phosphorous  
VFA – Volatile fatty acid  
WAS – Waste activated sludge
Acknowledgements

Over my two years of study in the Department of Civil Engineering, I have received much support and aid from various people, without whom, I would not have been able to work towards my masters degree.

I am extremely honoured to have Dr. Victor Lo as my supervisor, who provided me with guidance, and inspired me in many aspects of life. I thank him for first giving me the opportunity to work for him, performing research on the microwave enhanced advance oxidation process, then accepting me as his student, and continuing to believe in me.

I thank Dr. Ping Liao sincerely for all his selfless help and guidance. Dr. Liao has consistently provided me with ideas and challenged my speculations to further my thinking. He has also encouraged me in many ways to stay strong and focused, while supporting me unconditionally.

Dr. Donald Mavinic has been supportive of me over my two years at Civil Engineering. He has always welcomed my questions and concerns, and gave me answers with a smile on his face. I thank him for his patience, support, and his great leadership. I thank Dr. Eric Hall for his generous support. He has always been concerned with the progress of his students, and I appreciate his help very much. Prof. Jim Atwater and Dr. Pierre Berube have both been outstanding teachers to me. Not only are they great teachers, their standard of care for their students outside their courses are phenomenal and I thank them for teaching me so much in the field of Environmental Engineering.

Thanks to Mr. Fred Koch for his ideas and suggestions which helped my research. He always welcomed students and our questions with open arms and was ready to have discussions in order to help. Thanks to Paula Parkinson who continuously performed analyses for us in order for us to obtain results for our research. She provided me with excellent suggestions and support over the last two years, and I thank her greatly for that.
Thanks to Susan Harper who is always concerned with the students safety in the laboratory, and she kept the laboratories in an orderly manner, making them very comfortable to work in. Thanks to Leiz for her administrative help and patience.

Special thanks go to Dr. Sietan Chieng for his help in editing this thesis given a short period of time despite his very busy schedule.

A special thanks to my colleagues Yang Yu and Anju Kenge who collaborated with me on our projects together. Their support, help, and spirit made my time in Civil Engineering memorable and most definitely, enjoyable. We shared opinions, laughter and stress together and I appreciate their company. I give thanks to Wayne Lo for his patience and support whenever they are asked of him; he is intelligent and helpful to his peers. I'd like to mention my gratitude for my colleagues Ali Abedini, Zaki, Weigang Yi, James Yin, Andrea Miskelly, Wade Achambault, Blair Fulton, Calvin Lam, Steven Levesque, and Wayne Wong for their companionship and support.

I thank my mother Jennifer Lok for her continual support and undying love for me, asking nothing but my own success in return. Her willingness to help her family and others is unparallel. Thanks to my family and friends for their care and love. Thanks to Brian Suen for his continual support to me over my years of study.

I wish to acknowledge the research funding, in the form of a Discovery Grant, provided by the Natural Science and Engineering Research Council, Canada.
Co-authorship statement

The collaboration of many authors has contributed to the manuscripts used in this thesis. The following applies to all Chapters: Design of experimentation was performed by Winnie Weng I Chan, Dr. Ping Huang Liao, and Dr. Kwang Victor Lo. Research and data analysis was performed by Winnie Weng I Chan with input from Dr. Ping Huang Liao and Dr. Kwang Victor Lo. Manuscript preparation was performed by Winnie Weng I Chan. Research and data analyses by Mr. Wayne Wong were contributed to Chapters 2, 3 and 4.

Chapter 2: Exploring the role of hydrogen peroxide in the microwave advanced oxidation process: solubilization of ammonia and phosphates
Co-authored with: Wong, W.T., P.H. Liao, K.V. Lo and D.S. Mavinic

Chapter 3: Sewage sludge nutrient solubilization using a single stage microwave treatment.
Published in Journal of Environmental Science and Health, Part A-Environmental Science and Engineering. 2007, 42 (1): 59-63
Co-authored with: Wong, W.T., P.H. Liao, and K.V. Lo

Chapter 4: Use of a hydrogen peroxide/microwave advanced oxidation process for sewage sludge treatment.

Chapter 5: Sludge reduction and volatile fatty acid recovery using microwave advanced oxidation process.

Chapter 6: The effects of irradiation rates on sewage sludge using the microwave enhanced advanced oxidation process.
In preparation.
Co-authored with Liao, P.H., and Lo, K.V

Chapter 7: Solubilization of blood meal to be used as a liquid fertilizer.
Published in Journal of Environmental Science and Health, Part B-Pesticides Food Contaminants and Agricultural Wastes. 2007, 42 (4): 417-422
Co-authored with K.V. Lo and P.H. Liao
Chapter 8: Nutrient release for fish silage using microwave-enhanced advanced oxidation process
Accepted in Journal of Environmental Science and Health, Part B-Pesticides Food Contaminants and Agricultural Wastes.
Co-authored with K.V. Lo and P.H. Liao
1 Introduction

1.1 Preface

Many environmental concerns have risen in the last decades that require innovative means of treatment and reuse of materials. Soluble constituents from organic waste slurries are valuable resources which are recyclable, but when disposed of improperly, can become detrimental to the receiving environments. This includes the land application of agricultural wastes as well as sludge from wastewater treatment plants. When dairy waste is land-applied, surface runoff contaminates the storm water, causing an increased nitrogen and phosphorous content in the stormwater [15]; fecal coliforms can also contaminate the groundwater below [4]. In municipal wastewater, copious amounts of phosphorous find their way to the wastewater treatment plants, and if not treated properly, the released phosphorous can cause eutrophication in the receiving waters. Besides regulations requiring the removal of phosphorous from effluents, the recovery of phosphorous is also cost effective and alleviates the issue of phosphorous reserves becoming depleted. Approximately 80% of mined phosphorous is used in agriculture [5], so its recovery for agricultural use is suitable. Phosphorous recovery has been achieved by means of struvite crystallization; however, since phosphorous is entrapped in biological cells during the enhanced biological nutrient removal (EBNR), methods by which the breakdown of the biological cell need to be applied prior to its recovery. Nitrogen in the form of nitrates and ammonia can also be detrimental to fish in the receiving waters in low concentrations. It was reported that a lethal concentration where 50% of the fish dies (LC₅₀) for ammonia concentrations for Atlantic salmon smolts are as low as 0.15 mg/L in freshwater and 0.30 mg/L in 30% salt water [1]. The removal of nitrates and ammonia from the effluent is therefore critical and achieved by a nitrification/denitrification step of the biological nutrient removal process. Nitrates are formed by the conversion of nitrates which were converted by ammonia. The denitrification process involves the addition of a volatile fatty acid, where nitrates are converted into nitrogen gas [17]. High nitrogen content is held within the cell along with
phosphorous and metals. Chemical, thermal, and ultrasound treatments have been used in the breakdown of bacterial cells for the release of nutrients.

1.1.1 Microwave

Research on microwave technology has been ongoing since the Second World War. The microwave spectrum run between 300 MHz to 300 GHz, and its applications range broadly from telecommunications to chemical and textile industries, to household use. Heating from the microwave is generated by magnetrons. As electromagnetic waves are generated through alternate current provided to the magnetrons, these waves generate electrical dipole moments with any polar molecule present in the path of the electromagnetic waves. The sudden alignment and realignment of molecules as the field alternates creates friction, thereby providing heating. The microwave technology is used broadly in the food industry and is effective in the drying and pasteurization of food since it can apply heat directly to the food. The microwave frequency designated for heating, as in most household microwaves has been designated to be at 900 MHz or 2450 MHz (2.45 GHz), so not to interfere with other telecommunications bandwidth [16].

1.1.2 The Microwave-enhanced advanced oxidation process

The microwave-enhanced advanced oxidation process (MW/H₂O₂-AOP) was developed by the Civil Environmental Group led by Dr. Kwang Victor Lo. The process uses a powerful oxidant, namely, hydrogen peroxide, along with microwave heating to generate hydroxyl radicals, which are very powerful oxidizing agents. Hydrogen peroxide is one of the most powerful oxidants available, and was chosen for its ease to handle and relatively low toxicity. The process has been proven to be effective in treating a multitude of organic slurries. One of the slurries being treated and tested comprehensively was waste-activated sludge (WAS). The majorities of wastewater treatment plants around the world adopt biological treatment where WAS disposal can account for 25 to 65% of operation costs [14]. Waste-activated sludge was chosen as a substrate of interest since its disposal costs are high, generated in large volumes, and contain copious amounts of nutrients that are beneficial to other processes. In order to decrease the amount of disposed solids, while releasing nutrients from biological cells in the WAS, various
treatments can be adopted. Traditional methods of digestion include thermal disruption of bacterial cells in WAS, where the bacterial cell membranes become broken down, releasing nutrients from within the cell. Another common method for releasing nutrients from bacterial cells includes anaerobic digestion, but incorporates a rather high capital cost as well as labour-intensive maintenance. The MW/H₂O₂-AOP is a fast and effective alternative, using hydrogen peroxide as the oxidant and a direct heating of the substrate through microwave irradiation. The oxidant used in this process is 30% v/v high purity laboratory grade hydrogen peroxide.

The process can aid in the breakdown of large organic molecules and particles into more soluble forms. The soluble forms of these “nutrients” are then used in subsequent processes for a multitude of purposes. The majority of research has been performed for waste activated sludge (WAS) and liquid dairy manure in the past. Investigation of other organic slurries treatment such as fish silage and blood meal has also been performed. The results for solubilizing nutrients into solution for all these slurries by the MW/H₂O₂-AOP thus far from this research group appear promising. Many parameters affecting the solubilization of nutrients into solution were tested. These parameters included treatment temperature, treatment time, hydrogen peroxide dosage, pH adjustment, and per cent solids.

1.2 Objectives

1. Test the factors affecting the solubilization of nutrients from waste activated sludge (WAS);
2. Test the effects of irradiation, or athermal effects on WAS;
3. Test that the microwave-enhanced advanced oxidation process (MW/H₂O₂-AOP) is effective in solubilizing nutrients from fish silage and blood meal.

Chapters 2, 3, 4, and 5 will address objective 1, where factors including treatment temperature, treatment time, hydrogen peroxide dosage, pH adjustment, and total solids concentration will be investigated. Chapter 6 will address objective 2, while Chapters 7 and 8 will address objective 3.
1.3 Apparatus

A closed-vessel, microwave digestion system (Ethos TC Digestion Labstation 5000, Milestone Inc., USA) was used in the studies performed. It has a maximum output of 1000 W. The system operates at 2450 MHz and consists of dual independent magnetrons, with a rotating microwave diffuser for homogeneous microwave distribution. The system has the capacity of accommodating up to 12 vessels (each with a volume of approximately 100 mL with one reference vessel) in a single run (Figure 1), at operating temperatures and pressures of up to 220°C and 30 bar (435 psig), respectively. The material of construction for the vessels is PTFE Teflon. The microwave digestion system, using an independent system controller, provides real-time temperature control (Figure 2). Automatic feedback control is achieved with a thermo-well contacting the reference vessel, allowing the system to monitor and regulate the power output, given a pre-programmed temperature profile.

Figure 1 Ethos TC Digestion Labstation 5000
Figure 2 Real time temperature control
1.4 Microwave sampling and analyses

For the experiments involving waste-activated sludge, secondary aerobic sludge was obtained from the pilot-scale wastewater treatment facilities, located at the University of British Columbia (UBC) campus. Fresh sludge samples were collected daily for the duration of the experiments.

The heating time was kept constant at 5 min at the pre-determined heating temperatures for all experiments, except for Chapter 6, where various heating times were used. The ramp times were varied with respect to temperature, in order to maintain a uniform rate of heating (increase of ca. 20°C per minute of heating) up to the desired experimental temperatures.

Samples were taken from the microwave immediately upon cooling to approximately 60°C after treatment for all experiments, and again after acid hydrolysis in the block heater for Chapter 2. The mixed liquors from all samples were spun in a centrifuge at 4000 rpm for 15 min. The resulting supernatants were filtered through Whatman No. 4 glass-fiber filter papers (pore size of 1.6 μm) and analyzed. Total solids (TS), ammonia, nitrate and (or) nitrite, ortho-phosphate, total kjeldahl nitrogen (TKN), chemical oxygen demand (COD) and total phosphate (TP) were analyzed according to the procedures described in Standard Methods [2]. In Chapter 2, poly-P was determined by the hydrolysis of the mixed liquors after microwave treatment in 1 N HCl at 100°C for 7 min [9]. All analyses, except for the determination of TS, were analyzed using the flow injection analysis (Lachat Quik-Chem 8000 Automated Ion Analyzer, Lachat Instruments, USA). In Chapter 4, metals (Fe, Mg, Ca, K), were also determined according to the procedures described in Standard Methods [2] by inductively coupled plasma (ICP) optical emission spectroscopy (Liberty 100 ICP-OES Spectrometer, Varian Inc., USA). In Chapter 5, the measurement of the oxidation-reduction potential (ORP), as \( \text{Eh}_{(\text{measured})} \) in mv, was conducted by using an ORP probe. The corrected ORP value (Eh) was calculated as the follows: \( \text{Eh} = \text{Eh}_{(\text{measured})} - 0.0591 \pH \).[6] A Hewlett Packard 5890 Series II gas chromatograph equipped with a flame ionization detector (FID) was used to
measure volatile fatty acids (VFA). Volatile separation was accomplished with an HP free fatty acid phase (FFAP) column (0.25m×0.31mm with 0.52μm film thickness). The injection temperature was set at 175°C and the FID detector was at 250°C. Helium gas was used as the carrier at a head pressure of 10 psi (69 kPa).

For Chapter 6, Experiments A to F were used for the size distribution analyses. Duplicates of the initial substrate were analyzed for total chemical oxygen demand (TCOD). For the size distribution analyses, 10mL of samples from each replicate was collected without centrifugation. The Malvern Mastersizer 2000 Hydro S sample dispersion unit was used for the size distribution analyses.

Samples collected before treatments were also measured for TS, TP, TKN, orthophosphate, ammonia and total COD [2]. All supernatant samples were analyzed for orthophosphate, ammonia and soluble COD. The percentage soluble was defined as the amounts of the soluble in the resulting supernatant solution divided by the total concentrations of the starting materials.
1.5 Waste-activated sludge

Municipal wastewater treatment plants utilize bacteria to perform nutrient removal including biological phosphorous (P) removal, biochemical oxygen demand (BOD) reduction, nitrogen (N) removal, and solids removal to some extent. The biological nutrient removal process is adopted to meet release guidelines and alleviate environmental issues such as eutrophication. These bacteria uptake copious amounts of macronutrients necessary for their survival such as carbonaceous matter (lipids, carbohydrates), nitrogenous compounds such as ammonia, nitrates, or nitrites, oxygen, phosphorous, sulfur from sulfates, potassium and magnesium [3]. Micronutrients are also required, otherwise growth rate can be limited; micronutrients include iron, zinc, manganese, and iron [3]. Large organic molecules or solids are broken down by enzymes released by the bacteria to become smaller compounds, which the bacteria can use as a source of nutrient, hence contributing to partial solids reduction and nutrient removed from the process flow. Phosphorous is also taken up during the aerobic phase for adenosine triphosphate (ATP) storage energy. Through bacterial growth, nutrients are taken up from the wastewater while the effluent becomes clean. A large amount of bacteria is created during the wastewater treatment process, referred to as sewage sludge, or secondary treatment aerobic sludge.

Traditionally, sludge is dewatered by means of a chemical or polymer addition and is subsequently incinerated, composted or landfilled. Some of the energy from incineration of the sludge can be reclaimed, but the process in itself is not efficient. Landfill of sludge is also common, but the cost of transportation as well as the scarcity of landfill space in recent years makes this option also unappealing. In some cases, residual sludge is composted, but depending on the purity of the feed, the finished compost may contain heavy metals. Another typical way of treating sludge is to digest it anaerobically. Anaerobic digestion of sludge yields high concentrations of volatile fatty acids (VFA), generates energy via biogas, requires little energy and reduces solids. Anaerobic processes, however, require a high capital cost, and include intensive labour, maintenance and training as the process is known to become unstable with slight changes in operating
parameters [7]. The resulting solution can be used in subsequent processes to recovery energy; processes include biogas production, polyhydroxyalkanoates (pHAs), a biodegradable plastic production [10], as well as for nutrients recovery such as struvite production. Solubilized COD consisting of high VFA content can also be recycled to the enhanced biological nutrient removal (EBNR) process as an external carbon source, which is required. The MW/H₂O₂-AOP can be seen as a fast, effective and efficient alternative to treat sewage sludge. Research already performed on this process has already proven the treatment of sludge prospective. The combined effects of hydrogen peroxide and microwave heating and possibly athermal effects contribute to the destruction of sludge, releasing nutrients into solution, while reducing solids. Parameters affecting phosphates release has been investigated and found to be treatment temperature, time, sulfuric acid addition, and hydrogen peroxide dosage [19]. The parameters which govern the action of sludge disintegration and nutrient solubilization are not yet fully understood, so an effort is made to shed light on operating parameters.

1.6 Agricultural applications

1.6.1 Blood meal

As an effort to reduce waste generation as well as the costs associated with disposal, the treatment of agricultural wastes is investigated. The treatment of agricultural waste is beneficial to the environment, and at the same time, can be an economical process. The concept of waste-to-resource is also applied in this case. A major byproduct of animal slaughter houses includes blood meal. Blood meal from slaughter houses undergoes a process to form a dehydrated powder to ease handling and decrease transportation costs. Because of its powder form, it is also highly insoluble when mixed with water. The process of resolubilizing blood meal can potentially provide greenhouse operations with an organic liquid fertilizer. Since blood meal is rich in nitrogen, it can be a valuable addition to fertilizer. Approximately 13% of its mass is nitrogenous, while approximately 80% of blood meal mass consists of proteins; hence, blood meal can potentially be a good source of nitrogen, for use as a fertilizer. Blood meal is currently being used as a liquid fertilizer at organic greenhouses in British Columbia (BC), but the insoluble nature of
blood meal makes it hard for its distribution through pipes and nozzles. Insoluble particles not only clog the distribution system and reduce flow, but the nutrients within the substrate are not released effectively into solution, making blood meal less effective as an organic fertilizer. The MW/H₂O₂-AOP is applied to the treatment of blood meal as an attempt to solubilize its nutrients and to reduce solids to alleviate clogging process. This process will act as a pre-treatment process to reduce suspended solids and prepare the substrate to be used as an effective liquid fertilizer, so that nutrients are available for crop uptake. Enzymes are used traditionally to break down enzymes, but they are expensive and time consuming. The MW/H₂O₂-AOP can potentially reduce problems associated with its use in organic greenhouses and increase its efficiency as an organic fertilizer constituent for hydroponics operations. Factors affecting blood meal solubilization will be investigated.

### 1.6.2 Fish silage

Fish silage is a by-product of fish processes. It is rich in nitrogen and phosphorous, both of which are essential constituents to plant growth. In order to use fish silage in hydroponics operations, a pretreatment method must be applied to reduce suspended solids inherent in fish silage. This added pretreatment step will aid in decreasing the plugging of nozzles of the distribution pipes. A pretreatment step will also aid in the solubilization of nutrients such as ammonia and nitrates/nitrites from particles. Enzymatic breakdown of large particles are sometimes used, but the process is costly and time consuming. Anaerobic digestion is commonly used to destruct fish silage particles as well as solubilize some of its contained nutrients. There is; however, some drawbacks to using anaerobic digestion as a pretreatment method – a long reaction period, high capital costs and skilled operators are inherent to the process. The microwave enhanced advanced oxidation process (MW/H₂O₂-AOP) has been recognized for improving the release of nutrients and reducing suspended solids from wastewater sludge [11]. The MW/H₂O₂-AOP was proposed to occur by two major reaction processes, the breakdown of large particulate organic matters such as proteins into smaller and more soluble organic components such as amino acids, and further oxidation or gasification of the resulting
organic products [12] into ammonia or nitrates/nitrites, volatile fatty acids (VFAs) or carbon dioxide (CO₂). The resulting oxidation products can be in the form of proteins, amino acids [8], ammonia, VFAs and/or CO₂ depending on the reaction conditions. If carbonaceous materials can be decreased in the fish silage solution, then a reduction of biofilm growth in distribution pipes and nozzles can be achieved. As higher temperatures would more likely yield CO₂ as a final oxidation product, higher treatment temperatures can be desirable; given the energy input is worth the savings from cleaning clogged pipes and nozzles. Again, the MW/H₂O₂-AOP could be applied as a pretreatment process in order to use fish silage as a potent fertilizer constituent. The variations of treatment temperature and hydrogen peroxide dosage on treatment efficiency, based on solubilized nutrients, will be investigated.
1.7 References


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2 Exploring the role of hydrogen peroxide in the microwave advanced oxidation process: solubilization of ammonia and phosphates

2.1 Summary

Struvite is a by-product in wastewater treatment facilities, which causes fouling of pipes and equipment. Its application as a potent fertilizer with slow-release properties allow for direct land applications [20] and it is worthwhile for struvite to be produced and marketed. Before struvite can be formed, phosphorous must be available in the ortho-phosphates form in solution. Since the MW/H₂O₂-AOP was found to be effective in the solubilization of phosphates from EBPR or bio-P sludge while requiring a relatively short reaction time at low treatment temperatures [24, 25]. For the purpose of struvite crystallization, the MW/H₂O₂-AOP was adopted along with a subsequent acid hydrolysis step to investigate the extent of phosphates and ammonia release. The hydrogen peroxide concentration was varied to investigate the dependence of phosphates and ammonia release on dosage, while the acid hydrolysis step was included to explore its role in hydrolyzing poly-phosphorous released from bacterial cells into soluble phosphates. It was noticed that at treatment temperatures of 80 and 100°C, poly-phosphorous was being formed, but were broken down into phosphates upon acid hydrolysis. Up to 61% of TP was solubilized as phosphates, while 39% of TKN was solubilized as ammonia with the combination of the two steps of treatment. For the purpose of ammonia release, it appeared that a treatment temperature of 120°C with 3 wt% hydrogen peroxide dosage was most effective, while a 1.5 wt% dosage of hydrogen peroxide treated at 80°C was sufficient for maximum poly-phosphorous release followed by subsequent acid hydrolysis. From this study, one learned that acid hydrolysis helps to break down poly-phosphorous that is in solution, and that higher hydrogen peroxide dosage along with higher treatment temperatures can yield high ammonia solubilization.¹

2.2 Introduction

The recovery of nutrients such as phosphorus (P) from wastewaters has drawn much interest [26, 27, 28, 30] and has been studied in great detail in recent years with the emphasis on struvite (magnesium ammonium-phosphate, known as MAP) crystallization [32, 31]. Once thought of as an unwanted by-product in waste treatment facilities and causing process equipment fouling problems, struvite is, in fact, an excellent plant fertilizer with slow-release properties that can be used for direct application on land [20]. Since fertilizer use in agriculture represents 80% of total phosphorus rock consumption, the recovery of a useful product such as struvite from wastewaters is important in terms of maintaining a sustainable supply of phosphorus [21]. Struvite crystallization requires ortho-phosphate (ortho-P) in solution, and thus it is necessary to convert other forms of phosphorus to ortho-P, before a crystallization process can be applied. These conversion processes typically require the use of chemical agents to initiate reactions and require long periods of time for these reactions to reach completion [26].

Wastewaters containing phosphates are treated by either chemical precipitation with alum or lime, or more commonly through an enhanced biological phosphorus removal (EBPR) process, in which there is a net uptake of phosphorus by phosphate accumulating organisms [29] present in the activated sludge. The use of EBPR sludge, or bio-P sludge, is particularly amenable for struvite recovery because of the greater amount of stored P potentially available for crystallization. Recent studies from the University of British Columbia [24, 25] demonstrated that both a microwave thermal treatment process and a combined hydrogen peroxide—microwave treatment advanced oxidation process (AOP), were particularly suitable for P-solubilization from bio-P sludge, by breaking down the sludge and releasing the soluble phosphate. The benefits of these processes included high yields of soluble P, low operating temperature, and short reaction times. For example, it was found that, with microwave heating alone, up to 76% of the total phosphorus could be solubilized within 5 min of treatment at 170°C. The yield of soluble P was increased when microwave treatment was combined with hydrogen peroxide, where up to 84% of the total phosphorus could be released at the same temperature and treatment time [25]. Acid hydrolysis improved the amount of soluble P release by converting poly-phosphate (poly-P) present in solution into ortho-P. However, the combined effects of H2O2–
microwave treatment and acid hydrolysis have not been studied previously. The peroxide concentration was kept constant throughout each set of experiments. The focus of this study was to investigate the combined effects of hydrogen peroxide concentration and acid hydrolysis on P-solubilization. In particular, a lower microwave temperature regime between 60 and 120°C was of interest in this study because of the greater amount of polyphosphates found in the treated sludge at these temperatures [25]. Polyphosphates formed during the microwave treatments can be easily broken down by acid hydrolysis into ortho-P [22].

2.3 Experimental design

A set of 12 experiments was performed to investigate the effect of various hydrogen peroxide concentrations in the MW/H₂O₂-AOP. Experiments were carried out at temperatures of 60, 80, 100, and 120°C. Various concentrations of hydrogen peroxide were tested, with the objective of improving the yield of soluble phosphates from secondary sludge. Either 1 mL or 2 mL of hydrogen peroxide (30 wt%) was added to undiluted sludge to make up a total volume of 30 mL for each microwave sample. Table 1 summarizes the experimental conditions tested in this study. A total of 12 microwave vessels were used for each experimental run. In addition to the MW/H₂O₂-AOP process, a secondary step involving acid hydrolysis was also included. Samples were obtained after microwave treatment and placed in a block heater. Six of the 12 microwave-treated samples were transferred for acid hydrolysis according to the method outlined by Harold [22]. The objective of this secondary step was to explore the additional benefit of acid hydrolysis, after the MW/H₂O₂-AOP treatment, in terms of further enhancing the yield of soluble ortho-P from the sludge. Table 2 defines the characteristics of the secondary aerobic sludge over the course of the study.
Table 1 Summary of experimental conditions

<table>
<thead>
<tr>
<th>Set</th>
<th>Temp. (°C)</th>
<th>H₂O₂ (mL)</th>
<th>Sludge Ramptime (min)</th>
<th>Heating time (min)</th>
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Table 2 Aerobic sludge characteristics

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<td>pH</td>
<td>6.2–6.7</td>
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<td></td>
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<td>COD</td>
<td>3700–4100 mg/L</td>
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<td>Total P</td>
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<td>Initial ortho-P</td>
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<tr>
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<td>Initial NO₂/NO₃-N</td>
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<td>TKN</td>
<td>200–331 mg N/L</td>
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Table 3 Summary of experimental results

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<th>Temp. (°C)</th>
<th>H₂O₂ (mL)</th>
<th>Ortho-P (mg P/L)</th>
<th>NH₃ (mg N/L)</th>
<th>NO₂ (mg N/L)</th>
<th>PO₄:NH₃ molar ratio</th>
<th>Soluble N (%)</th>
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<tr>
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<td>MW BD</td>
<td>MW BD</td>
<td>MW BD</td>
<td>MW BD</td>
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<tr>
<td>60</td>
<td>0</td>
<td>75.6 93.7</td>
<td>3.5   5.3</td>
<td>30.3   13.0</td>
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<td>10.9   5.9</td>
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<td>1</td>
<td>59.0  89.7</td>
<td>29.3   26.9</td>
<td>16.1   7.6</td>
<td>0.4   0.6</td>
<td>14.6   11.1</td>
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<tr>
<td>60</td>
<td>2</td>
<td>54.1  89.1</td>
<td>66.0   64.0</td>
<td>13.6   5.0</td>
<td>0.1   0.2</td>
<td>25.6   22.1</td>
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<tr>
<td>80</td>
<td>0</td>
<td>39.3  89.8</td>
<td>2.1   4.9</td>
<td>3.8   7.5</td>
<td>3.3   3.3</td>
<td>1.9   4.0</td>
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<tr>
<td>80</td>
<td>1</td>
<td>27.5  94.4</td>
<td>29.5   33.5</td>
<td>12.3   12.7</td>
<td>0.2   0.5</td>
<td>13.4   14.8</td>
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<td>2</td>
<td>37.8  77.0</td>
<td>85.7   71.9</td>
<td>8.4   3.2</td>
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<td>30.2   24.1</td>
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<tr>
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<td>37.2  71.2</td>
<td>1.5   3.2</td>
<td>3.3   1.5</td>
<td>4.4   4.0</td>
<td>1.6   1.5</td>
</tr>
<tr>
<td>100</td>
<td>1</td>
<td>38.9  72.6</td>
<td>29.8   35.6</td>
<td>5.3   3.1</td>
<td>0.2   0.4</td>
<td>11.2   12.4</td>
</tr>
<tr>
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<td>2</td>
<td>39.7  81.3</td>
<td>66.2   88.0</td>
<td>9.6   4.6</td>
<td>0.1   0.2</td>
<td>34.0   29.7</td>
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<tr>
<td>120</td>
<td>0</td>
<td>55.6  91.7</td>
<td>1.2   2.9</td>
<td>10.3  1.7</td>
<td>8.1   5.7</td>
<td>3.7   1.5</td>
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<tr>
<td>120</td>
<td>1</td>
<td>60.3  94.3</td>
<td>52.6   70.5</td>
<td>12.0  6.1</td>
<td>0.2   0.2</td>
<td>20.8   24.6</td>
</tr>
<tr>
<td>120</td>
<td>2</td>
<td>63.3  98.3</td>
<td>108.4  105.5</td>
<td>12.6  5.9</td>
<td>0.1   0.2</td>
<td>38.8   35.8</td>
</tr>
</tbody>
</table>

Note: MW, microwave heating; BD, block heating.
2.4 Results and discussion

For all experiments, there was a significant release of ortho-P after microwave treatment, and an even greater amount released after acid hydrolysis (Table 3). The results after microwave treatment were consistent with those obtained previously [24, 25]. In these studies, much longer ramp times were used to reach the desired heating temperatures. In this study, a shorter ramp time with a uniform rate of heating (increase of ca. 20°C per minute of heating) produced comparable results. This indicates that ramp time, by itself is not a significant factor affecting P-solubilization. A decrease in ortho-P was observed with lower concentrations in solution, at the lowest and highest temperatures. After the acid hydrolysis step, additional ortho-P was found in solution, indicating that greater formation of poly-P was occurring at the intermediate temperatures. This is also consistent with the results previously obtained by our research group [25]. Kuroda et al. [23] investigated the heating of sludge at temperatures between 50 and 90°C and found that this process resulted in the release of poly-phosphates into solution. The results obtained by these authors demonstrated that more poly-P was being formed at intermediate temperatures between 70 and 80°C. This is consistent with the data obtained in this study. However, the thermal treatment process in their study required heating for 1 h to achieve poly-P breakdown. Therefore, the MW/H₂O₂-AOP is superior in terms of treatment time, where only 5 min of heating was required to achieve the same results. Figure 3 summarizes the results for both microwave treatment and acid hydrolysis, at various hydrogen peroxide concentrations. Before acid hydrolysis (Figure 4), the same trends were detected at all tested hydrogen peroxide concentrations. After acid hydrolysis (Figure 5), the lowest soluble ortho-P concentration occurred at a lower temperature, at the highest hydrogen peroxide concentration. This suggests that increasing the hydrogen peroxide concentration results in the formation of more polyphosphates at a lower temperature. At 60°C, higher hydrogen peroxide concentrations resulted in less soluble ortho-P, but resulted in more poly-P, since the ortho-P values were the same after the acid hydrolysis step. In terms of facilitating poly-P breakdown into ortho-P, hydrogen peroxide was found to be the most effective at 80°C and at a concentration of 1.5 wt% hydrogen peroxide, resulting in up to 61% of total P as soluble ortho-P. At temperatures of 100 and 120°C, the amount of soluble ortho-P after microwave treatment and after
block heating was found to increase with hydrogen peroxide concentration (Figure 6). Therefore, at temperatures of 80°C and below, the use of hydrogen peroxide inhibits the solubilization of ortho-P, whereas at temperatures of 100°C and greater, the addition of hydrogen peroxide was found to be beneficial for P solubilization.

Figure 3 Comparison of ortho-P solubilization after microwave and block heating stages

Figure 4 Soluble ortho-P after microwave heating
Figure 5 Soluble ortho-P after microwave heating and acid hydrolysis
Figure 6 Soluble phosphate fractions after microwave treatment

The ammonia concentration in solution was found to be very sensitive to hydrogen peroxide concentration. Figure 7 shows the relationship between ammonia released into solution and hydrogen peroxide concentration, at various microwave heating temperatures. At all experimental temperatures, it was found that the addition of hydrogen peroxide enhanced the release of ammonia. Up to 108 mgN/L (as ammonia) was found in solution after microwave treatment, compared to an initial value of between 0 and 2.3 mg N/L before treatment. At the lower hydrogen peroxide concentrations, the amount of ammonia found in solution remained constant with respect to temperature.
However, at the highest concentration of peroxide, it was found that increasing temperatures resulted in more ammonia in solution. This suggests that at greater hydrogen peroxide concentrations, there is a synergistic effect between hydrogen peroxide and microwave heating temperature, similar to that for ortho-P [25]. At the highest microwave heating temperature and hydrogen peroxide concentration, approximately 36% of the total Kjeldahl nitrogen was found to be present as ammonia in solution. The ammonia concentration remained constant after block heating. The addition of hydrogen peroxide resulted in a dramatic decrease in PO4:NH3 molar ratio (Figure 8). From the results shown in Table 3, the ortho-P concentrations remained approximately the same with increasing hydrogen peroxide concentrations, while the ammonia concentration increased. Therefore, the PO4:NH3 molar ratio decreased with increasing hydrogen peroxide concentration. Since the PO4:NH3 molar ratio is sensitive to the increasing hydrogen peroxide concentration, it is important to control the amount of hydrogen peroxide with respect to struvite formation, where the stoichiometric molar ratio is 1:1. The soluble nitrogen concentration in solution was found to increase with peroxide concentration at each of the experimental heating temperatures. These percentages may be affected by various factors such as denitrification of nitrates into nitrogen gas, or volatile loss of ammonia. Although these factors were not controlled, the results indicate that the highest percent soluble nitrogen was obtained at a microwave heating temperature of 120°C and a hydrogen peroxide concentration of 3 wt%. At these operating conditions, it is likely that the organic nitrogen present in the sludge is being converted to soluble nitrogen, in either ammonia or nitrate and (or) nitrite forms.
Figure 7 NH₃ concentration after microwave treatment

Figure 8 PO₄:NH₃ molar ratio at various hydrogen peroxide concentrations
2.5 Conclusions

The examination of the effect of hydrogen peroxide concentration on the solubilization of phosphates, over the microwave heating temperatures of 60–120°C, indicated that there is a beneficial effect on not only phosphorus solubilization, but also on ammonia solubilization. At higher microwave temperatures and a reaction time of only 5 min, the combination of hydrogen peroxide and acid hydrolysis resulted in up to 61% of total phosphorus and up to 36% of TKN released into solution, as soluble ortho-Ps and ammonia, respectively. The amount of soluble nitrogen in solution after microwave treatment was found to increase with hydrogen peroxide concentration. The highest percentage of soluble nitrogen was 39% at operating conditions of 120°C and a hydrogen peroxide concentration of 3 wt%. The addition of hydrogen peroxide resulted in a dramatic decrease in PO4:NH3 molar ratio, an important factor controlling struvite formation. In terms of facilitating poly-P breakdown into ortho-P after acid hydrolysis, hydrogen peroxide was found to be the most effective at 80°C and at a hydrogen peroxide concentration of 1.5 wt%. At temperatures of 100°C and 120°C, the amount of soluble ortho-P increased with hydrogen peroxide concentration.
2.6 References


3 Sewage sludge nutrient solubilization using a single-stage microwave treatment

3.1 Summary

Following effective phosphates solubilization with a subsequent acid hydrolysis step followed by the MW/H2O2-AOP, the following research investigated the combined treatment for sewage sludge, mainly focused for the crystallization of struvite. In addition, soluble COD was measured to study the extent of solids destruction and as a measure of organic matter breakdown after treatment. The MW/H2O2-AOP combined with acid hydrolysis in a single-stage treatment was investigated for its effectiveness in the treatment of and nutrient release from sewage sludge. It was found that the combination of MW/H2O2-AOP with the inorganic acid (sulfuric acid) was effective in achieving a higher soluble phosphate content compared to the MW/H2O2-AOP followed by acid hydrolysis. Without the addition of acid, polysphosphates were formed at a treatment temperature of 80°C. It was also noted that in higher temperature treatments, the combined MW/H2O2/H⁺-AOP was even more effective in the solubilization of phosphates into solution. Ammonia was also solubilized into solution, with the maximum solubilization taking place at 120°C. Temperature alone did not contribute much to ammonia solubilization up until a treatment temperature of 120°C, whereas solubilization can be seen with the addition of acid. The highest amounts of ammonia were found in the high temperature regimes along with hydrogen peroxide addition as well as acid addition in one single treatment. The solubilization of COD was also investigated in this project, where approximately all of the COD was solubilized at a treatment temperature of 80°C, after which, no improvement in further solubilization was found.

2

3.2 Introduction

Domestic wastewater contains significant amounts of nutrients including phosphorus, nitrogen, and organic carbon in non-soluble forms. The conventional activated sludge (AS) process in domestic wastewater treatment converts organic carbon into sludge biomass. Nitrogen and phosphorus are inorganic nutrients that are undesirable for discharging into receiving waters because they pose environmental threats due to eutrophication and anoxia. For this reason, in biological wastewater treatment, nitrogen and phosphorus are removed by nitrification/denitrification and enhanced biological phosphorus removal techniques, respectively. The removal/retrieval of phosphates and ammonia from wastewater is beneficial from both environmental and economic perspectives, particularly if the unwanted compounds can be extracted to produce a useful and value added product.

Magnesium ammonium phosphate (MAP or struvite) crystallization is an emerging technology that can be used as a means of removing the nitrogen and phosphorus from wastewaters and converting them into a fertilizer. Struvite is an excellent plant fertilizer that is particularly useful because of its slow-release properties and can be directly used in land application [33]. Since fertilizer use in agriculture represents 80–85% of total phosphorus rock consumption [34], the recovery of a useful product such as struvite from wastewaters is important in terms of maintaining a sustainable supply of phosphorus, mainly by decreasing the phosphate rock demand and increasing the amount of recycled phosphorus.

In previous studies of our research group [35, 36, 39], a novel microwave technique was developed to release phosphate and ammonia from sewage sludge. Hydrogen peroxide was used to increase the process efficiency. It was found that the combined microwave/H₂O₂ treatment of sewage sludge followed by acid hydrolysis treatment (a two-stage process) resulted in significantly greater yields of soluble phosphates and ammonia; where up to 61% of the total phosphorus was solubilized and 36% of the total Kjeldahl nitrogen (TKN) was solubilized as ammonia [40]. In this study, the effects of combining both the microwave/H₂O₂ advanced oxidation process and the acid hydrolysis together into a single stage process (MW/H₂O₂/H⁺-AOP) were investigated, with the
objective of increasing the process efficiency for sewage sludge treatment and nutrient recovery.

3.3 Experimental design

Four sets of experiments were carried out, each with six replicates, to explore the effects of microwave heating, peroxide and/or acid addition on the solubilization of secondary sludge. All experimental samples were subjected to microwave heating with temperature settings of 60, 80, 100, and 120°C. Sulfuric acid and hydrogen peroxide additions were varied by concentration and examined at all four experimental temperatures. The conditions of these experiments are summarized in Table 4. Set 1 served as a control in which no sulfuric acid and hydrogen peroxide were added. In Set 2, 1 mL of hydrogen peroxide was added to the sludge sample. A portion of the resulting solution was then subjected to hydrochloric acid treatment (1.0 mL HCl added to form a total of 10 mL solution) to form a sub-set, Set 2-1 (a two-stage process). In Set 3, 0.5 mL concentrated sulfuric acid was added to the sludge. In Set 4, 1 mL hydrogen peroxide and 0.5 mL sulfuric acid were added to the sludge samples simultaneously. In the samples with hydrogen peroxide present, the sludge volume was adjusted to give a total volume of 30 mL. Where sulfuric acid was added, it was added to the 30 mL of sample volume to give a total volume of 30.5 mL. Table 5 summarizes the characteristics of the secondary aerobic sludge used in the experiments.

Table 4 Conditions for all experimental sets

<table>
<thead>
<tr>
<th>Sludge used (mL)</th>
<th>H$_2$O$_2$ added (mL)</th>
<th>Acid added (mL)</th>
<th>Total sample (mL)</th>
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<tr>
<td>Set 2</td>
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*Each set was run at 60, 80, 100 & 120°C, with 6 replicates each.*
Table 5 Characteristics of secondary aerobic sludge

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<td>6.2–6.7</td>
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<td>3700–4100 mg L⁻¹</td>
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<tr>
<td>Total phosphorus</td>
<td>133 mg PL⁻¹</td>
<td>123–171 mg PL⁻¹</td>
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<tr>
<td>Total Kjeldahl nitrogen</td>
<td>322 mg NL⁻¹</td>
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<td>Initial Ortho-phosphates</td>
<td>1.7 mg PL⁻¹</td>
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<tr>
<td>Initial ammonia</td>
<td>1.3 mg NL⁻¹</td>
<td>0–2.3 mg NH₃L⁻¹</td>
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3.4 Results and discussion

3.4.1 Soluble phosphorus

A combined hydrogen peroxide and microwave heating process was used in our previous studies to solubilize phosphate, ammonia and organics from the secondary aerobic sludge obtained from an enhanced biological phosphorus removal process [35, 36, 39]. In this two-stage process, the microwave/hydrogen peroxide treatment was used first, and acid digestion was subsequently used as a second treatment step [35, 36, 39]. It was found that the microwave/hydrogen peroxide treatment resulted in the formation of both low molecular-weight polyphosphates and ortho-phosphate in the solution. After further acid treatment, however, most of the polyphosphates were converted into soluble orthophosphate. Based on the best results from these studies, test conditions were chosen for Sets 1, 2, 2-1 and 3 in this study. In addition, a single-stage treatment was employed in Set 4, in which acid addition was incorporated together into the microwave/hydrogen peroxide advanced oxidation process, hereby designated as MW/H₂O₂/H⁺-AOP. Figure 9 presents the results of phosphorous solubilization for all Sets. Comparing the results of Sets 1 and 2, it can be seen that polyphosphates and ortho-phosphate were formed during the hydrogen peroxide addition stage (Set 2); the effects were obvious at the lower temperatures (60 and 80°C). The concentration of ortho-phosphate in solution was the lowest at 80°C, where most of the phosphorus was present in the form of polyphosphates. Kuroda et al. obtained similar results that more polyphosphates were formed at intermediate temperatures between 70–80°C [37]. In the second step, with acid addition, as is Set 2-1, acid hydrolysis broke down the polyphosphates into ortho-phosphates.
Throughout the temperature range, the two-stage process resulted in much more efficient phosphorous solubilization over that of Set 2. For Set 4, the combined single-stage hydrogen peroxide and acid treatment (MW/H$_2$O$_2$/H$^+$-AOP), a decrease in the concentration of ortho-phosphates was not observed. The soluble phosphate increased with the increase of heating temperature. It is likely that the simultaneous addition of sulfuric acid and hydrogen peroxide formed peroxymonosulfuric acid, which was a stronger oxidant and was more stable in solution than hydrogen peroxide [38]. It is also likely that the formation of polyphosphates was immediately broken down into orthophosphates by the existence of acid in the solution. For these reasons, the overall release of ortho-phosphates was substantially higher in the single stage MW/H$_2$O$_2$/H$^+$ treatment. Set 3, a single-stage microwave/acid treatment without hydrogen peroxide, also gave very high soluble ortho-phosphate in the solution, where the concentration of orthophosphate also increased with respect to temperature increase. These results demonstrated that microwave heating temperature played a very important role in the solubilization of phosphorus. The addition of hydrogen peroxide and acid were also critical factors. In terms of selecting the microwave operating temperature and reaction condition for the solubilization of phosphorus, a single-stage microwave/H$_2$O$_2$/acid (MW/H$_2$O$_2$/H$^+$) or microwave/acid (MW/H$^+$) should be used at higher operating temperatures (100–120$^\circ$C). However, at the lower operating temperature regimes (60–80$^\circ$C), a two-stage process, such as Set 2-1, is recommended.
Figure 9 Soluble phosphorus versus microwave heating temperature

3.4.2 Soluble ammonia

Figure 8 presents the results of ammonia release. It can be seen that all treatments (Sets 2, 2-1, and 4) except Set 3 showed significant ammonia release into the solution over the control, Set 1. Also, soluble ammonia increased with heating temperature for Sets 2, 2-1 and 4, with the highest concentrations of ammonia obtained for each set at heating temperature of 120°C. A significantly higher concentration of ammonia was solubilized during the single stage process (Set 4) when compared to the two-stage addition of hydrogen peroxide and acid (Set 2-1), especially at 120°C. However, the standard deviation of the single stage data was also larger than that of the two-stage process. This might due to the different rates of ammonia evaporation in the microwave reaction cell after the microwave treatment at high temperatures (above 100°C), when hydrogen peroxide was present. Results from Set 3 (0.5 mL of acid) showed only limited increase of soluble ammonia in the solution. This might be because of the acidic condition caused by the H₂SO₄ addition, the ammonia is in ionized form, being prevented from escaping as NH₃. However, as can be seen in Figure 10, the addition of inorganic acid alone is
insufficient to increase the soluble ammonia and that hydrogen peroxide addition is required.

![Figure 10 Soluble ammonia versus microwave heating temperature](image)

**3.4.3 Soluble COD**

The soluble chemical oxygen demand (SCOD) after various treatments was also determined. Due to an interference of chloride ion in the two-stage microwave/H₂O₂/acid treatment, the COD concentration was not determined for Set 2-1. Therefore, sulfuric acid, instead of hydrochloric acid, was used for Sets 3 and 4. Over the range of microwave heating temperatures, it was found that the simultaneous addition of sulfuric acid along with hydrogen peroxide resulted in an increase in SCOD with temperature up to 80°C. All of the total COD in the sewage sludge was obtained in soluble form at 80°C, meaning that all of the organic material is solubilized. At higher temperatures, a decrease in the SCOD concentration was observed for Sets 2 and 4 (Figure 11). This trend can be explained in that the increase in SCOD at lower temperatures was due to the solubilization of the organics, whereas at higher temperatures the solubilized organics
were converted via an oxidation process into CO₂. Even with a decrease of SCOD at 120°C, these results of Sets 2 and 4 were still substantially higher than those from the control (Set 1). By utilizing sulfuric acid and hydrogen peroxide simultaneously, COD is almost completely solubilized at lower temperatures. This is very significant, because the COD in soluble form can be beneficially reused within the wastewater treatment plant. Achieving an optimum SCOD concentration allows one to maximize the available organics for reuse as well as to minimize the production of CO₂, a greenhouse gas. Furthermore, this suggests that the process could be equally efficient at lower temperatures regimes (60–80°C), which would reduce the required energy input. Results from Set 2 showed that hydrogen peroxide addition was beneficial in solubilizing COD in the solution. However, the increase of SCOD concentrations was not as much as those of Set 4, except that at 120°C, where a higher SCOD concentration was obtained. It seemed that at 120°C, acid addition favored the production of CO₂, resulting in less SCOD being retained in the solution.

Figure 11 Soluble COD versus microwave heating temperature
3.5 Conclusions

The MW/H$_2$O$_2$/H$^+$ process can be used to solubilize phosphate, ammonia and organics from sludge solids. This innovative process has the potential to be used not only in a simple sludge treatment process, but also for recovering valuable resources from wastewaters. At lower temperature regimes (60–80°C), the soluble phosphate was substantially higher in a two-stage process than in a single stage MW/H$_2$O$_2$/H$^+$ process. However, a higher soluble phosphate concentration was obtained for the single-stage process at higher operating temperature regimes (100–120°C). With the addition of an inorganic acid, a very high yield of soluble phosphate was obtained in the solution at 120°C. With an acid addition, the soluble ammonia concentration increased as temperature increased. For the single stage microwave/H$_2$O$_2$/H$^+$ process, the maximum soluble ammonia concentrations were obtained at 120°C; significant concentrations of soluble COD were also obtained at 80°C.
3.6 References


4 A hydrogen peroxide/microwave advanced oxidation process for sewage sludge treatment

4.1 Summary
The treatment of secondary sludge by means of applying the MW/H2O2-AOP was effective in not only the solubilization of phosphates and ammonia for struvite crystallization, but also the disintegration of sludge seen by an increase in SCOD. In this study, COD was essentially completely solubilized at temperatures of 80°C and above. For the purpose of struvite crystallization, not only the solubilization of phosphates and ammonia is sufficient, so the solubilization of metals from the WAS was also investigated. It was found that a large amount of magnesium was solubilized, making the ratio of magnesium to phosphates and ammonia high, and making ammonia the limiting nutrient in a molar ratio of 1:1:1 for Mg:NH₃:PO₄ in the testing conditions. Since the handling of sludge is typically a biological hazard, the pasteurization of the WAS was also investigated. The treatment temperatures along with a strong oxidant cause bacteria to lose viability, usually at 70°C for 30 minutes. It is speculated that the MW/H2O2-AOP can decrease treatment time as well as lower treatment temperatures to achieve similar pasteurization of WAS.³

4.2 Introduction
The production of large volumes of sludge as an end-product from the activated sludge biological wastewater treatment process poses one of the biggest challenges to the wastewater treatment industry [50]. The handling and disposal of sludge residuals has significant social, environmental, and economic implications. Treatment and disposal of sewage sludge from wastewater treatment plants can account for up to 50–60% of the total cost of wastewater treatment [43, 51]. Currently, residual sludge is digested, incinerated, deposited in landfills, or used as fertilizer through agricultural land

application of the residual biosolids [51]. In current wastewater treatment processes, toxic heavy metals become concentrated in the residual sludge. There may also be pathogenic organisms present in the residuals [53]. For these reasons there are increasing concerns that land application or landfilling of sludge residuals may be harmful to the environment and to public health. Under such social, environmental and economic pressures, it is necessary to use more viable methods of treating and handling sludge. Anaerobic digestion can be used, but is relatively inefficient due to the low biodegradability of the sludge [58]. The benefit of such a process is that the methanogenesis stage of the anaerobic digestion process results in the production of methane (biogas). To improve the efficiency of the anaerobic digestion process, the biodegradability of the sludge must be increased. There are various methods proposed to accelerate the hydrolysis of the sludge particles in anaerobic digestion. A study done by Park et al. [52] investigated the effects of pre-treating secondary sludge by microwave irradiation on anaerobic digestion. The results from this study indicate that as microwave heating time increased, the soluble chemical oxygen demand (COD) increased up to 22%. The increase in soluble COD was indicative of sludge particle disintegration. Furthermore, the microwave treated samples were used for biogas production, and it was found that the COD removal rates and methane production were higher with the microwave-treated samples. This study did not investigate the use of microwave in combination with chemical addition. Chu et al. [42] used ultrasonic technology to treat waste-activated sludge. Similar degrees of COD solubilization can be obtained by ultrasonic treatment as in the microwave treatment process [52]. However, the amount of sludge that could be processed by ultrasonic treatment was significantly lower. Also, the treatment time was an order of magnitude larger for the ultrasonic treatment than for the microwave treatment. The specific energy required by the ultrasonic process was also found to be much larger than for the microwave process. For these reasons the microwave treatment breaks down sewage sludge more efficiently for subsequent anaerobic digestion.

The application of microwave heating in combination with hydrogen peroxide for phosphorus release in sewage sludge was a novel process recently developed at the University of British Columbia [49, 48]. The research was focused on solubilization of
phosphates from sewage sludge for the purpose of magnesium ammonium phosphate (struvite) crystallization. The microwave heating process could break down particles with or without hydrogen peroxide, resulting in carbon and other nutrients becoming solubilized. As a result, the sludge in the solution was reduced in the process. The microwave heating process was also found to limit microbial activity [49], and with hydrogen peroxide, the pasteurization or sterilization of pathogens in the solution can be achieved. Ultraviolet irradiation is already established as a method of disinfecting waters and wastewaters [50], but at present, there is less of an emphasis on the usage of non-ionizing radiation such as microwaves. Studies have shown that various methods of microwave treatment are effective for destroying microorganisms such as E. coli and fecal coliforms [46, 45]. In this paper, the focus is on the effects of microwave heating and hydrogen peroxide addition (MW/H2O2) on the advanced oxidation process (AOP), with respect to sludge treatment, and hence the abbreviation MW/H2O2–AOP.

4.3 Experimental design

A set of twelve experiments were performed in order to investigate the effects of various hydrogen peroxide concentrations in the MW/H2O2.AOP. Experiments were carried out at temperatures of 60, 80, 100, and 120°C. Various concentrations of hydrogen peroxide were tested with the objective of improving the degree of COD and metal solubilization from sewage sludge. Either 1 mL or 2 mL of hydrogen peroxide (30 wt.%) was added to undiluted sludge to make up a total volume of 30 mL for each microwave sample. Table 6 summarizes the experimental conditions tested in this study. A total of 12 microwave vessels were used for each experimental run. Table 7 defines the characteristics of the secondary aerobic sludge over the course of the study.
Table 6 Summary of experimental conditions.

<table>
<thead>
<tr>
<th>Set</th>
<th>Temperature (°C)</th>
<th>H₂O₂ (mL)</th>
<th>Sludge (mL)</th>
<th>Ramp time (min)</th>
<th>Heating time (min)</th>
<th>Total time (min)</th>
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<td>0</td>
<td>30</td>
<td>2</td>
<td>5</td>
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<td>60</td>
<td>1</td>
<td>28</td>
<td>2</td>
<td>5</td>
<td>7</td>
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<td>80</td>
<td>0</td>
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<td>5</td>
<td>8</td>
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<tr>
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<td>2</td>
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<td>5</td>
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Table 7 Aerobic sludge characteristics

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Concentration</th>
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<tr>
<td>TS</td>
<td>0.35-0.40%</td>
</tr>
<tr>
<td>pH</td>
<td>6.2-6.7</td>
</tr>
<tr>
<td>Initial soluble COD (SCOD)</td>
<td>3.8-28.4 mg/L</td>
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<tr>
<td>Total COD</td>
<td>3700-4100 mg/L</td>
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<tr>
<td>Total Phosphorus</td>
<td>146-162 mg P/L</td>
</tr>
<tr>
<td>Initial O-PO₄</td>
<td>0.1-3.2 mg P/L</td>
</tr>
<tr>
<td>Initial NH₃-N</td>
<td>0.0-2.3 mg N/L</td>
</tr>
<tr>
<td>Initial Fe Concentration</td>
<td>Not detectable</td>
</tr>
<tr>
<td>Initial Mg Concentration</td>
<td>Not detectable</td>
</tr>
<tr>
<td>Initial Ca Concentration</td>
<td>0.5-4.9 mg/L</td>
</tr>
<tr>
<td>Initial K Concentration</td>
<td>10.9-19.0 mg/L</td>
</tr>
</tbody>
</table>

4.4 Results and discussion

4.4.1 Sludge reduction

The COD of the samples was measured for each set of experiments. The results are presented in . Figure 12 shows the percentage of soluble COD after treatments for the 3 tested hydrogen peroxide concentrations (0, 1 and 2 mL) at four temperature settings (60, 80, 100, and 120° C). The results showed that for each temperature, there was a significant increase in soluble COD with increased hydrogen peroxide concentrations. At 60° C and 2 mL of H₂O₂ (i.e., 3 wt.% in sample of 30 mL), approximately 80% of the total COD was
found to be in solution; this is almost 8 times of the amount of soluble COD from the control, where no hydrogen peroxide was added. At temperatures of 80°C and above, and at 2 mL of H₂O₂, approximately all 100% of the COD was in soluble form.

Table 8 Solubilization of phosphorous, nitrogen, metals, and COD

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>H₂O₂ (mL)</th>
<th>Ortho-PO₄ (mg/L % of TP)</th>
<th>NH₃ (mg N/L % of TN)</th>
<th>Metals (mg/L)</th>
<th>Soluble COD (mg/L %)</th>
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<tr>
<td>60</td>
<td>0</td>
<td>75.6 48.1</td>
<td>3.5 1.2</td>
<td>ND 23.2</td>
<td>390 9</td>
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<tr>
<td></td>
<td>1</td>
<td>59.0 40.4</td>
<td>29.3 9.6</td>
<td>0.4 19.5</td>
<td>2027 45</td>
</tr>
<tr>
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<td>2</td>
<td>54.1 37.1</td>
<td>66.0 21.6</td>
<td>0.4 18.3</td>
<td>3632 79</td>
</tr>
<tr>
<td>80</td>
<td>0</td>
<td>39.3 25.0</td>
<td>2.1 0.7</td>
<td>ND 19.0</td>
<td>566 13</td>
</tr>
<tr>
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<td>27.5 18.8</td>
<td>29.5 9.7</td>
<td>1.6 13.1</td>
<td>2897 65</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>37.6 23.4</td>
<td>88.7 28.1</td>
<td>ND 13.8</td>
<td>4668 105</td>
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<tr>
<td>100</td>
<td>0</td>
<td>37.2 23.0</td>
<td>1.5 0.5</td>
<td>ND 29.8</td>
<td>812 18</td>
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<td>38.9 24.4</td>
<td>29.8 9.8</td>
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<td>4660 104</td>
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<tr>
<td>120</td>
<td>0</td>
<td>55.6 34.5</td>
<td>1.2 0.4</td>
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<td>2115 47</td>
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<td>60.3 37.4</td>
<td>52.6 17.3</td>
<td>3.2 40.0</td>
<td>3207 72</td>
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<tr>
<td></td>
<td>2</td>
<td>63.3 39.3</td>
<td>108 35.5</td>
<td>1.6 34.8</td>
<td>4333 97</td>
</tr>
</tbody>
</table>

As shown in Figure 12, for all three hydrogen peroxide concentrations (0, 1, and 2 mL), the temperature effects on the soluble COD revealed different trends. For the control (no H₂O₂ addition), the soluble COD increased with increased temperature. However, the rate of this increase (or slope) was small from 60 to 100°C, but at a much faster rate from 100 to 120°C, meaning that without the help of H₂O₂, the solubilization of COD was accelerated only after microwave heating at 100°C and above. With the addition of H₂O₂, the accelerated release of COD into soluble form occurred at lower temperatures. For the 1 mL H₂O₂ addition runs, the maximum soluble COD was achieved at 100°C, as the heating temperature increased to 120°C, the soluble COD actually decreased a bit. A similar trend was also observed for the 2 mL H₂O₂ addition runs, where maximum soluble COD was achieved at 80°C, and stayed at about the same level at 100°C, than there was a more obvious decrease at 120°C. The increased H₂O₂ addition allowed the maximum COD release to occur at lower microwave heating temperatures. The decrease of soluble COD at elevated temperatures of 100 or 120°C was probably due to the
conversion of soluble COD into CO₂. An optimization study is presently underway to further explore the COD solubilization.

Figure 12 Per cent soluble COD under various microwave temperatures and hydrogen peroxide concentrations

From an initial soluble COD of less than 10 mg/L, it is obvious that with any microwave treatment, a large fraction of the COD is converted into soluble form. Essentially all of the COD was converted into soluble form at 80°C and 2 mL of hydrogen peroxide addition. There is no doubt that microwave heating temperatures affected the solubilization of COD, but the addition of H₂O₂ is a more important factor in solubilizing COD. This finding is very significant in sludge treatment, because the anaerobic digestion process requires the use of soluble COD for conversion into methane by methanogenesis. More COD in solution translates into more efficient biogas production. Furthermore, as the conversion of COD into methane reaches 100%, this brings us closer to “zero sludge production”, [60,47] where all of the sludge can be beneficially used with no organic residue produced. A study done by Yoon et al. [60] demonstrated that zero
sludge production can be achieved by using an ultrasonic cell disintegration process in combination with a membrane bioreactor. They found that zero sludge production is achieved even at high organic loading rates of 0.91 kg BOD5/m³d with an MLSS of 7000-8000 mg/L. An ultrasound generator with 600 W of output was used for sludge sonication. This treatment required a treatment time of 1 hour for 1 litre of sludge [52]. However, the specific energy required by this ultrasonic process was comparatively much larger than that of the microwave process. From our results, the microwave treatment could attain 100% COD solubilization from sludge at 80°C with the addition of the 2 mL H2O2. The complete solubilization of COD theoretically approaches zero sludge production, since all of the organic matter becomes solubilized, and can be converted to methane in an anaerobic digestion process. With the anaerobic digestion of the solubilized organics, only inorganic matter will remain in the sludge.

Tanaka et al. [55] investigated the effects of thermal, thermo-chemical, and chemical pretreatment of waste-activated sludge on anaerobic digestion. Their results indicated that all 3 pretreatment processes could improve the efficiency of methane production. The optimal thermal treatment was reported to be at 180°C for 5 minutes. The thermo-chemical pretreatment allowed the temperature to be reduced to 130°C, but required the addition of sodium hydroxide. The thermo-chemical process produced the best results where methane production increased by over 200% over the control. A similar study done by Valo et al.[57] produced similar results, where COD could reach 83%. Our results with the microwave heating advanced oxidation process was superior in that the temperature could be further reduced to 80°C over a treatment time of 5 minutes and essentially solubilize 100% of the COD.

Since the treatment and disposal of sewage sludge from wastewater treatment plants can account for up to 50-60% of the total cost of wastewater treatment,[59] minimizing the sludge volume will greatly reduce the cost of handling and treating the sludge and hence reduce the cost of the wastewater treatment process.
4.4.2 Nutrient release

Struvite is an excellent plant fertilizer with slow-release properties and can be used for direct application on land. [41] Since fertilizer use in agriculture represents 80% of total phosphorus rock consumption, the recovery of a useful product such as struvite from wastewaters is important in terms of maintaining a sustainable supply of phosphorus.[44]

Magnesium present in the sewage sludge can be beneficially reused for this process. Potassium can also be used in place of magnesium for K-struvite (potassium ammonium phosphate) production. With the addition of hydrogen peroxide, the resulting solutions in each experiment became colorless and clear. This process would be beneficial for a subsequent struvite crystallization process since solid concentrations of less than 1000 mg/L is required in addition to the presence of ammonia, phosphate and magnesium in solution. As indicated in Table 8, nutrients such as phosphorus and nitrogen and metals were successfully dissolved into solution in this process. The metal concentrations of the sewage sludge were found to be independent of microwave temperature and hydrogen peroxide concentration. As shown in Table 8, iron was not detectable at any of the 12 experimental conditions. Magnesium, calcium and potassium concentrations ranged from 18.3-40.0 mg/L, 9.9-31.2 mg/L, and 63.7-83.1 mg/L respectively. At 120°C, slightly higher concentration of metals was found; however, a clear trend could not be determined. These results most likely indicate that the metals in the sewage sludge are completely released into solution with bacterial cell lysis under microwave treatment. Since the metal concentrations increased from before to after treatment, but consistent between the treatments, it appears that microwave heating alone is equally as effective as the combination of microwave heating and hydrogen peroxide. The magnesium and potassium solubilized from sewage sludge with microwave heating are consistent with those previously observed by our research group [49]. Table 8 lists the soluble concentrations of ammonia and ortho-phosphate measured after each experiment. Ammonia concentrations ranged from 1.2-108 mg N/L, while ortho-phosphate concentrations ranged from 27.5-75.6 mg P/L. The measured concentrations of soluble ammonia, ortho-phosphate, and magnesium were used to determine the Mg:NH₃:PO₄ molar ratio. From our results, ammonia was determined to be the limiting nutrient without any hydrogen peroxide addition in the microwave process. With the addition of
hydrogen peroxide, ortho-phosphate became limiting. In all cases, magnesium was nonlimiting, indicating for this treatment process that theoretically, no magnesium addition is required for struvite crystallization. From a practical perspective, however, it is important to note that the struvite crystallization process is a very complex process and typically requires a Mg:NH₃:PO₄ molar ratio of at least 1.2:5:1.

The microwave treatment and/or microwave/hydrogen peroxide AOP not only can solubilize carbon for methane production, but also can solubilize nutrients for crystallization of fertilizer products, such as struvite. It provides a novel sludge management option for the wastewater industry. The emergence of this technology is beneficial in terms of improving resource management and reducing the economic impact of wastewater treatment. From a social standpoint, this novel process is beneficial because it also represents a promising option for pathogen reduction and sludge sterilization.

4.4.3 Sludge sterilization

Pasteurization of sludge is achieved when it is treated at temperatures at 70°C or above for 30 minutes or greater [56]. With the microwave operating temperatures between 60 and 120°C in this study, sludge pasteurization would occur in the microwave process, most likely even at 60°C and at shorter treatment times, because of the addition of a strong oxidizing agent such as hydrogen peroxide, known to be an effective disinfectant. In a conventional heating process, the treatment time required for the complete elimination of pathogenic organisms is dependent on temperature. Pasteurization can be achieved at lower temperatures with a longer treatment time. Conversely, pasteurization can be achieved with much shorter treatment times with higher temperatures. For example, E. coli can be eliminated at a treatment of 60°C for 60 minutes, or at 70°C for 5 minutes [56]. A study by Hong et al. [45] demonstrated that at a temperature of 65°C, colony forming unit (CFU) counts of fecal and total coliforms were zero after only 1.5 minutes of treatment. Bacterial activity completely ceased at temperatures above 68°C. In these experiments it was evident that microorganism inactivation occurred even at shorter treatment times. In another study by Koutchma and Ramaswamy [46] similar results were
obtained, where a combined microwave/hydrogen peroxide process at temperatures of 65°C was enough to reduce the survival ratio of E. coli K-12 to 0.0000001:1 with less than 5 minutes of heating. In addition, it was found that there was a synergistic effect on the effectiveness of E. coli destruction with the microwave heating and hydrogen peroxide addition on microbial destruction.

At higher temperatures of 100°C and above, sterilization of the sludge will occur. Previous studies performed by our research group demonstrated that without hydrogen peroxide addition, microbial activity in the sewage sludge was still present after microwave treatment at 60°C for 5 minutes, but ceased at temperatures of 100°C and above [49]. The addition of hydrogen peroxide will further facilitate the destruction of microorganisms present in the sludge, because it is a powerful oxidizing agent. In combination with the microwave treatment, the oxidizing effect of the hydrogen peroxide becomes magnified. From the experimental results, the complete solubilization of COD is indicative of sludge pasteurization, since all of the biosolids are converted into dissolved organic matters, such as soluble polypeptides, volatile acids and carbohydrates [56]. The breakdown of the biosolids by a microwave heating process or a microwave advanced oxidation process thus results in the cessation of microbial activity in the sewage sludge. Further research in this area is currently underway in our laboratory.

4.5 Conclusions

The aerobic secondary sludge used in this study had an initial soluble COD of less than 1% of the total COD. When it was subjected to the MW/H2O2-AOP, a large fraction of the COD was converted into soluble form. With the microwave heating temperature at 80°C and the hydrogen peroxide at 2 mL (3 wt.%), essentially 100% of the COD was converted into the soluble form. Attaining 100% COD solubilization is equivalent to converting the biosolids into dissolved organics. This significantly enhances the biodegradability of the sludge, and thus will greatly improve the efficiency of a subsequent anaerobic digestion process for methane production.
It appeared that metals did solubilize with any microwave treatment, but the addition of hydrogen peroxide did not seem to have any beneficial effects. Comparable metal concentrations were measured in samples subjected to the microwave heating process, as well as in samples treated by the combined microwave heating/hydrogen peroxide process. The results indicated that the metals were likely released upon bacterial cell lysis under any microwave treatment process. Magnesium, calcium and potassium concentrations ranged from 18.3-40.0 mg/L, 9.9-31.2 mg/L, and 63.7-83.1 mg/L respectively. Ammonia concentrations ranged from 1.2-108 mg N/L, while orthophosphate concentrations ranged from 27.5-75.6 mg P/L. The magnesium ammonium phosphate molar ratio was determined at the tested experimental conditions. Based on the stoichiometric molar ratio of 1:1:1 for Mg:NH3:P04, ammonia was found to be the limiting nutrient for the complex without any hydrogen peroxide addition in the microwave process at all temperatures. With the addition of hydrogen peroxide, orthophosphate became the limiting nutrient. In all cases, magnesium was nonlimiting, indicating that theoretically for this treatment process, no magnesium addition is required for any subsequent struvite crystallization.

In terms of sludge pasteurization, the microwave heating temperatures used in combination with a strong oxidizing agent such as hydrogen peroxide would cause microbial activity to cease, since all of the organic matters in the sludge were broken down and converted to soluble form. Further studies in this area are currently underway in our laboratory.
4.6 References


5 Sludge reduction and volatile fatty acid recovery using microwave advanced oxidation process

5.1 Summary
Soluble COD can contain many different forms of VFAs, including acetic acid, propionic acid, butyric acid, and valeric acid. The occurrence of VFA is usually the product of anaerobic digestion, where the majority of VFAs are in the form of acetic acid. VFAs are very useful to different processes. They can be used as substrates for the bio-P removal process, where VFAs are external carbon sources that are essential to the process. When subsequent processes require VFAs as substrates, such as those for polyalkanoates production or biogas production, their production is ideal. The formation of VFAs from the MW/H₂O₂-AOP is unknown, so an investigation into the process was performed. The factors affecting the solubilization of COD and subsequent oxidation processes to reduce solubilized COD was also investigated. It was found that the addition of hydrogen peroxide will increase the solubilized COD in solution, but subsequent additions of hydrogen peroxide will tend to oxidize the existing solubilized COD from solution. Likewise, the addition of sulfuric acid subsequent to hydrogen peroxide treatment lead to a decreased concentration of solubilized COD from solution. The addition of sulfuric acid, however, led to increases in VFA production, where up to 25% of the solubilized COD was in the forms of VFA. ⁴

5.2 Introduction
The treatment and disposal of excess sludge produced in wastewater treatment plants (WWTP) is very costly; just the sludge disposal alone can account for 40–60% of the total operating cost of a WWTP. For this reason, the destruction of sludge is becoming an integral component of wastewater treatment. Not only would sludge volume reduction result in reduced operating and disposal costs, it would also alleviate the environmental

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impact through disposal by landfill or incineration. Furthermore, the solubilization of nutrients in the sludge, such as carbon, nitrogen, and phosphorus could be very beneficial if a nutrient recovery process could be implemented to extract these nutrients for reuse. The organic components of the sewage sludge are mostly in the solid phase with only a small fraction in the dissolved form. For the sludge used in this study, it was observed that the soluble chemical oxygen demand (SCOD) was less than 1% of the total chemical oxygen demand (TCOD). The solid organic components of sewage sludge generally consist of four major ingredients: protein, carbohydrates, lipids (fats and oils), and fibres. When these ingredients were subjected to a microwave-hydrogen peroxide-enhanced advanced oxidation process (MW/H\textsubscript{2}O\textsubscript{2}-AOP), a significant fraction of the solid matter was dissolved \[64, 65\]. The MW/H\textsubscript{2}O\textsubscript{2}-AOP could facilitate the release of a large amount of the sludge-bound phosphorus; more than 84% of the total phosphorus could be released at a microwave heating time of 5 minutes at 170\degree C. The combined effects of H\textsubscript{2}O\textsubscript{2} concentration and acid hydrolysis on ammonia and phosphorus release were also studied \[71\].

A greater concentration of polyphosphates was detected at a lower microwave temperature regime between 60 and 120\degree C. At microwave-heating temperatures of 100\degree C and 120\degree C, an increase of H\textsubscript{2}O\textsubscript{2} concentration under acidic conditions resulted in a beneficial effect where not only on phosphorus was solubilized, but ammonia was also released. The combination of H\textsubscript{2}O\textsubscript{2} and acid hydrolysis resulted in the release of up to 61% of total phosphorus and 36% of TKN into the solution, as ortho-phosphates and ammonia, respectively. In one of our previous studies where sewage sludge was subjected to the AOP, it was found that at microwave heating temperatures of 80\degree C and above, essentially 100% of the chemical oxygen demand (COD) could be solubilized in the MW/H\textsubscript{2}O\textsubscript{2}-AOP process, meaning that all of the sludge bio-solids were in dissolved organic form \[72\]. The soluble organic components from the treatment process could potentially be used as substrates for other purposes \[68\]. It was also observed that the dissolved COD decreased significantly when acid was present in the solution. Therefore, this study was conducted to investigate the combined effects of microwave heating, hydrogen peroxide and acid (sulfuric) addition on the solubilization of sludge bio-solids,
and the production of volatile fatty acids (VFA). This paper reports the effects of reaction conditions on the productions of soluble COD and VFA in the AOP process.

5.3 Experimental design

In Phase 1 of this study, four sets of experiments, each with six replications, were carried out at a temperature of 120°C (Table 9). Samples without hydrogen peroxide addition were used as the control (Set A). Various concentrations of hydrogen peroxide were tested with the objective of improving the degree of COD and VFA yields from the sewage sludge. For Sets B and C, 1 and 2 mL of hydrogen peroxide (30 wt %) was added to the undiluted sludge, respectively to make up a total sample volume of 30 mL for each microwave treatment. For Set D, 2 mL of hydrogen peroxide and 0.5 mL of concentrated sulfuric acid were added to make up a total volume of 30 mL. For Sets B, C and D, the amount of oxidant (H₂O₂) used was between 14,500 and 29,000 mg/L in the solutions. The total COD concentration of the raw sludge was 5,231 mg/L. Therefore, hydrogen peroxide demand was 2.9 to 5.9 times of the total COD concentration (Table 9). In Phase 2 of this study, the resulting solutions from Sets B, C and D were subjected to further microwave treatments. For Treatment 1 (Sets B1, C1 and D1), 0.5 mL of hydrogen peroxide was added to 15 mL of the resulting solutions of Sets B, C and D, respectively. For Treatment 2 (Sets B2, C2 and D2), 0.5 mL of hydrogen peroxide and 0.25 mL concentrated sulfuric acid were added to 15 mL of the solutions. And for Treatment 3 (Sets B3, C3 and D3), 0.25 mL of concentrated sulfuric acid was added to 15 mL of the solutions. These nine sets of experiment, each in duplicates, were carried out at a microwave temperature of 120°C. The experimental conditions tested in this study are summarized in Table 9.
Table 9 Summary of all experimental conditions

<table>
<thead>
<tr>
<th>Phase</th>
<th>Set</th>
<th>pH</th>
<th>Substrate volume (mL)</th>
<th>$\text{H}_2\text{O}_2$ (mL)</th>
<th>$\text{H}_2\text{SO}_4$ (mL)</th>
<th>Initial total COD (mg L$^{-1}$)</th>
<th>$\text{H}_2\text{O}_2$ demand (mg L$^{-1}$ COD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A</td>
<td>5.93</td>
<td>30.0</td>
<td>0.00</td>
<td>0.00</td>
<td>5231 ± 52.5</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>4.09</td>
<td>29.0</td>
<td>1.00</td>
<td>0.00</td>
<td>5231 ± 52.5</td>
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<tr>
<td></td>
<td>C</td>
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<tr>
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<td>D</td>
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<td>0.50</td>
<td>5231 ± 52.5</td>
<td>5.9</td>
</tr>
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<td>B1</td>
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<td>15.00</td>
<td>0.50</td>
<td>0.00</td>
<td>3083 ± 87.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C1</td>
<td>6.60</td>
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<td>0.50</td>
<td>0.00</td>
<td>4932 ± 70.5</td>
</tr>
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<td></td>
<td></td>
<td>D1</td>
<td>1.95</td>
<td>15.00</td>
<td>0.50</td>
<td>0.00</td>
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<tr>
<td></td>
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<td>C2</td>
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<td>D2</td>
<td>1.69</td>
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<td>0.50</td>
<td>0.25</td>
<td>2784 ± 70.5</td>
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<td>Treatment 3</td>
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<td>3083 ± 87.5</td>
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<td>15.00</td>
<td>0.00</td>
<td>0.25</td>
<td>2784 ± 70.5</td>
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</table>

*30 wt%.

5.4 Results and discussion

The solubilization of the sludge organic matter by the MWH$_2$O$_2$-AOP process can be assumed to occur by two major reaction processes similar to the wet-air oxidation process. The first process involves the breakdown of the large particulate organic matters into smaller and soluble organic components, and the second process involves oxidation or gasification of the resulting organic by-products. According to the model proposed by Shanableh and Shimizu [69], intermediate oxidation products and thermal decomposition products are formed first in the oxidation processes. These products can be further oxidized to form final products, such as VFA and CO$_2$. Overall, the accumulation of dissolved organic matter, in terms of SCOD concentration, in the AOP process, depends on the rates of production and the consumption of intermediate oxidation products. Production is via thermal decomposition, mainly hydrolysis, of the particulate organic matter. Consumption is achieved through mechanism such as oxidation and gasification. Accumulation occurs when the rate of production exceeds the rate of consumption [70].

5.4.1 Solubilization of sludge solids

The results of the solubilization of the sludge, in terms of SCOD, are presented in Table 10 and Figure 13. For the control, Set A (without hydrogen peroxide and acid), only 17%
of the TCOD (both particulate and soluble) was solubilized. It was expected that most of the soluble products were the decomposition products, derived from thermal destruction only. Indeed, a very low concentration of the VFA (less than 1.78 mg/L) and low ORP (−24 mV) were observed in the solution. There was a significant increase in soluble COD with increased hydrogen peroxide concentrations. About 59% of TCOD was solubilized with an addition of 1 mL of H₂O₂ (Set B), while 94% of the TCOD was converted into soluble form with an addition of 2 mL of H₂O₂ (Set C). This was also reflected by hydrogen peroxide demand, as a higher hydrogen peroxide demand yielded more soluble COD. The hydrogen peroxide demands were 2.8, 5.9 and 5.9 for Sets B, C and D, respectively (Table 9). A higher dosage of hydrogen peroxide gave a higher yield of soluble products (Table 10). It was apparent that the amount of hydrogen peroxide used for Set B was not sufficient, and as a result, there was a low yield of soluble organic matter. It should be noted that with additions of H₂O₂, the corrected ORP readings for Sets B, C and D remained relatively high, compared to that of Set A. Higher ORP values indicate that the resulting solutions were in the relative higher oxidation states. It was assumed that with an addition of H₂O₂, more intermediate oxidation products were formed in the resulting solutions. The ORP value is a good indicator for this MW/H₂O₂-AOP process. However, the relationship of oxidation products and the ORP has not been fully established yet. When the samples were subjected to additions of both acid and H₂O₂, the SCOD decreased to 53% (Set D). The yield was even less than that found in Set B (with 1 mL of H₂O₂). The COD results were consistent with our previous works [72]. It appeared that when acid was present in the reaction medium, the reaction promoted further oxidation and gasification; carbon dioxide was produced and escaped into the gas phase, which resulted in the reduction of TCOD in the solution. Therefore, less SCOD concentration was obtained. The stability of hydrogen peroxide may be another factor. Hydrogen peroxide is more stable in an acidic condition, as its rate of decomposition decreases in the presence of an inorganic acid, such as when sulfuric acid is added. This would also help the solubilization process. The VFA produced from the reaction could also affect the overall reaction outcome. Acetic acid acted as an oxygen carrier in the reaction medium; its catalytic activity was not only due to the H⁺ release in
the aqueous phase, but also due to its capacity to react with hydrogen peroxide to form peracids. This would therefore increase its oxidation potential [62].

Table 10 Results of solubilization and acetic acid production

<table>
<thead>
<tr>
<th>Phase</th>
<th>Set</th>
<th>pH</th>
<th>Initial TCOD (mg L⁻¹)</th>
<th>Soluble COD (mg L⁻¹)</th>
<th>Reduction or Solubilization (% COD)</th>
<th>Acetic Acid (mg L⁻¹)</th>
<th>ORP (mV)</th>
<th>Corrected ORP (mV)</th>
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<td></td>
<td></td>
</tr>
<tr>
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<td>A</td>
<td>5.93</td>
<td>5231 ± 52.5</td>
<td>865 ± 17</td>
<td>17</td>
<td>1.78</td>
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<td>-24</td>
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<td>3083 ± 87.5</td>
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<td>48.2</td>
<td>371</td>
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<td>94</td>
<td>99.6</td>
<td>364</td>
<td>240</td>
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<tr>
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<td>D</td>
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<td>5231 ± 52.5</td>
<td>2784 ± 70.5</td>
<td>53</td>
<td>257</td>
<td>486</td>
<td>256</td>
</tr>
<tr>
<td>2</td>
<td>Soluble COD*</td>
<td>Solubilization</td>
<td>Reduction</td>
<td></td>
<td></td>
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<td></td>
</tr>
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<td>Treatment 1</td>
<td>B1</td>
<td>5.63</td>
<td>3083 ± 87.5</td>
<td>3893 ± 581</td>
<td>299 ± 54</td>
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<td>C1</td>
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<td>70 ± 5</td>
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<td>D1</td>
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<td>1024 ± 141</td>
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<td>3770 ± 211</td>
<td>269 ± 4</td>
<td>499</td>
<td>244</td>
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<td>4932 ± 70.5</td>
<td>3875 ± 628</td>
<td>21</td>
<td>260 ± 16</td>
<td>510</td>
<td>256</td>
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<tr>
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<td>2784 ± 70.5</td>
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<td>225 ± 10</td>
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<td>Treatment 3</td>
<td>B3</td>
<td>1.69</td>
<td>3083 ± 87.5</td>
<td>1569 ± 264</td>
<td>49</td>
<td>344 ± 10</td>
<td>435</td>
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<tr>
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<td>1.73</td>
<td>4932 ± 70.5</td>
<td>2291 ± 36</td>
<td>54</td>
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<td>1253 ± 19</td>
<td>55</td>
<td>336 ± 8</td>
<td>418</td>
<td>158</td>
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</tbody>
</table>

*In Phase 2, the initial COD is the soluble COD from Phase 1.

Figure 13 Soluble COD concentrations after various treatments
Acetic acid concentrations obtained from the treatments are shown in Figure 14. More than 98% of the VFA produced from the AOP process was acetic acid for all cases. As expected in the control Set A, no acetic acid or any other acids were produced. The production of acetic acid increased substantially with an addition of H₂O₂. The yield of acetic acid depended on the amounts of hydrogen peroxide and inorganic acid added in the reaction medium. A higher acetic acid concentration was obtained with an increase in H₂O₂ in the solutions (Sets B and C). When an inorganic acid was added (Set D), the acetic acid concentration was found to be 257 mg/L. This represented 10% of the SCOD in the solution. These results suggest that the productions of the SCOD and VFA can be controlled by the amount of hydrogen peroxide and inorganic acid added to the reaction medium. The MW-AOP process without acid addition favors SCOD production, and more soluble carbon was retained in solution. Under acidic conditions, the process would produce more VFA in solution; however, less soluble carbon is retained. It should be noted that due to different amounts of oxidants and acid added, the characteristics of the resulting solutions (Sets A, B, C and D) were completely different from the starting sludge solution, and among themselves. In general, more oxidation products would be expected for resulting solutions from Sets C and D, as they favored complete oxidation reactions due to more (or excess) oxidants present in solution. The MW/H₂O₂/H⁺-AOP is superior to the conventional wet air oxidation (WAO). The WAO process is the oxidation of soluble and suspended particles by using oxygen in the aqueous phase, at high temperatures (150–350°C) and high pressures (5–20 MPa) [67]. However, the MW/H₂O₂/H⁺-AOP is operated at a much lower temperature and pressure regime. As reported previously, it could be operated at relatively low temperatures, as low as 60°C [64]. It could also be completed within a very short period of time, less than 5 minutes. The amounts of SCOD in the liquor can be controlled by the amounts of chemicals added. Over 98% of TCOD could be retained in the liquor without any inorganic acid addition. If an inorganic acid is added in the process, further oxidation can be expected, and therefore, less SCOD is retained in the solution.
5.4.2 Oxidation of soluble organic matter

The resulting solutions from Sets B, C and D were used as new substrates, and were subjected to H₂O₂ (Treatment 1), H₂O₂/acid (Treatment 2), and acid (treatment 3) treatments, respectively. As mentioned previously, the residual solids were separated via centrifugation and filtration processes. No suspended solids were observed in these resulting solutions; the total COD concentrations were the same as the SCOD. The main purpose of the study in Phase 2 was to facilitate further oxidation reactions, not for destruction of sludge solids. It was assumed that when more hydrogen peroxide was used, thermal decomposition products in the resulting solutions would be further hydrolyzed into smaller molecular products, or oxidized into intermediate oxidation products and into final oxidation products. The resulting products after these treatments would produce more oxidation products such as alcohols, aldehydes, ketones, carboxylic acids, VFA in solution, or carbon dioxide [66]. The identification of these intermediate compounds, though not done in this study, is of great interest and will be the focus of our continuing work. During the course of this study, we were aiming mainly at the soluble carbon

![Figure 14 Acetic acid concentrations after various treatments](image)
source, which could be recirculated to the front end of the biological nutrient removal (BNR) process train or as feed to the subsequent anaerobic digestion (AD) process. Therefore, in this paper, changes of the SCOD and VFA in the solutions were recorded and discussed. The ORP readings for the resulting solutions did decrease for most of the treatments. This indicated that all solutions were in the oxidation states, however, no trend was revealed. Further study is needed to explore the relationship between the ORP and VFA or intermediate products. The results are presented in Table 10, Figure 13 and Figure 14. For substrate B, the results did not give a clear trend on SCOD reduction. About 49% of SCOD was reduced for Set 3 with an addition of sulfuric acid (Treatment 3). The SCOD concentrations for Sets B1 and B2 remained the same as Set B when hydrogen peroxide and/or acid were added. For substrates C and D, an addition of H₂O₂ (Treatment 1) or sulfuric acid (Treatment 3) led to reductions of SCOD. With additions of both H₂O₂ and sulfuric acid (Treatment 2), only limited SCOD reductions were observed. It was unexpected that the COD results obtained from Sets B1 and B2 were higher than that of Set B (Figure 13). Since solid organic matter in B had been filtered, the treatments should lead to the transformation of compounds from lower oxidation to higher oxidation products only. The SCOD concentrations for B1 and B2 should be similar or less than that of Set B. The solutions of B1 and B2 might have contained residual hydrogen peroxide; as a result, higher than actual COD readings were recorded [61]. The SCOD remained very high for B1. As reported earlier in Phase 1, the hydrogen peroxide dose for Set B was insufficient. The solution might contain mostly thermal decomposition products and some of intermediate oxidation products. Additional hydrogen peroxide treatment would only transform thermal decomposition products into final oxidation products. Therefore, the SCOD concentration for Set B1 was high. For Sets C1 and D1, the expected products would be mostly intermediate oxidation products, instead of thermal decomposition products. With an addition of H₂O₂, these intermediate oxidation products could be oxidized to form mostly carbon dioxide. Therefore, very low concentrations of the SCOD were obtained in the final solutions. A higher SCOD concentration was obtained for Set D1 than Set C1, even though the starting SCOD for Set D was much less than Set C. Apparently, acid in the reaction medium could make a difference. An inorganic acid (H₂SO₄) was present in Set D1 (from Set D), but not in Set
C1. The same trend was also shown for Treatment 2 (H$_2$O$_2$ and acid), where most of the SCOD for Sets B2, C2 and D2 were retained. Acid became a stability factor to retain the SCOD in solution. Unlike in Set D, the SCOD concentration decreased by additions of H$_2$O$_2$ and acid into sludge. This might be due to different reaction mechanisms for the different substrates; sludge organic matters versus soluble compounds in the reaction medium. We postulate that the results of overall oxidation products of these sets might end in the higher oxidation products, instead of forming carbon dioxide. Indeed, more acetic acid concentrations were observed in the solution with an inorganic acid addition. With acid treatment (Treatment 3), the SCOD decreased significantly for all. This can mostly be attributed to the decarboxylation reaction of carboxylic acids. Other intermediate oxidation products such as aldehydes and ketones, under acidic condition and an elevated temperature would also be transformed into acetic acid. The concentrations of acetic acid did indeed increase for Sets B3, C3 and D3. Acetic acid concentration reached 480 mg/L for Set C3 (Figure 14). This represents 25% of the SCOD in the solution. This result points out that a two-stage reaction, first with hydrogen peroxide and subsequently with acid reaction, favors the VFA productions from sludge mass.

5.5 Conclusions

The results indicate that the MW/H$_2$O$_2$-AOP process could be used to solublize sludge solids. Over 96% of TCOD was dissolved into the solution, while up to 25% of the SCOD was in the form of acetic acid. The amounts of the SCOD and acetic acid produced depended on the volumes of hydrogen peroxide and acid in the reaction medium. For sludge organic matter, a higher volume of hydrogen peroxide addition not only favored the destruction of sludge solids, but also conserved carbon content. A higher volume of VFA could be produced when an inorganic acid was present; however, the SCOD concentration would be decreased. The effects of hydrogen peroxide and acid addition on the reaction of soluble substrates were very different from that of sewage solution. The SCOD concentrations were retained when inorganic acids were present in the reaction media. The highest VFA concentration was obtained for soluble substrates
with acid treatment only. The SCOD and the VFA concentrations of the resulting solution could be controlled by amounts of acid used in the MW/H₂O₂-AOP process.
5.6 References


6 The effects of irradiation rates on sewage sludge using the microwave enhanced advanced oxidation process

6.1 Summary

Thus far, much research has gone into the treatment of WAS. The factors affecting nutrients release including acidic conditions, treatment temperature, oxidant dosage, and total solids content have all been investigated. The athermal effects, meaning the contribution from factors other than heat; however, has not been studied in its effect on nutrients release or solids disintegration for the MW/H₂O₂-AOP. This study concentrates on differentiating the athermal effects from thermal effects as best as possible. In addition to that, a range of pH levels were tested as one of the conditions, as acidic and alkaline conditions are known to aid in the destruction of bacterial cells from sludge. It appeared that for solids disintegration, nutrients solubilization, as well as energy efficiency purposes, the highest level of power treatment at 1000W was most ideal. Confirmation on the effects of temperature being one of the most important in the MW/H₂O₂-AOP for COD solubilization was also achieved as a tertiary objective. COD release in alkaline conditions was very pronounced, more so than in acidic conditions. It was also found that phosphates release into solution was very much so time dependent.  

6.2 Introduction

Municipal wastewater treatment plants produce large amounts of sludge through biological nutrient removal processes, which present a serious disposal problem. Many treatment methods for reduction of the excess sludge, such as heat treatment, thermochemical treatment using ozone, acids or alkali, and mechanical methods, have been reported. Thermal treatment, in the temperature range from 60 to 180°C, destroyed

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5 A version of this chapter will be submitted for publication. Chan, W.I, P.H. Liao, K.V.Lo. The effects of irradiation rates on sewage sludge using the microwave enhanced advanced oxidation process.
the cell membrane, and made the intracellular material accessible [83, 86]. As a result, thermal pretreatment would improve the dewaterability of sludge: there were noticeable improvements at temperatures of 150°C and above, where the effect was even more pronounced above 180°C. However, at such high temperatures, about a third of soluble COD produced were refractory compounds, which was not treatable [77].

Thermochemical treatment using acids or alkali decomposed the less degradable compounds into more easily degradable ones through the combined action of temperature and acids or alkali [89, 86, 87]. It was concluded that either acid or alkali was efficient in reducing the residual sludge amounts, and also improving the sludge dewaterability. Furthermore, an increase a ratio of biochemical oxygen demand to chemical oxygen demand (BOD/COD) indicated the treated effluents could be a valuable carbon source for other biological processes. The optimum conditions were at a temperature of 100°C, pH around 10, and for a 60-min reaction time for alkaline thermal sludge treatment, while for acid treatment, they were at temperatures above 120°C, pH of 3 with a 60 min reaction time [88].

Chemical oxidation techniques, such as ozone, wet air oxidation, and Fenton reagent, are applied to sludge treatment to reduce sludge solids. Ozone pretreatment was able to solubilize two-thirds of organic matter of the sludge, and enhanced the subsequent anaerobic digestion, but had a negative effect on sludge dewaterability [85, 91]. For wet air oxidation process, the reduction of the volatile fraction of waste was also complete, while the total sludge solids reduction was 75-80%, and volume of sludge was reduced by 86% [75]. The process is usually conducted at high temperatures and under pressure.

The microwave enhanced advanced oxidation process (MW/H₂O₂-AOP) has been proven effective for treating sewage sludge. Different factors including pH, treatment temperature, treatment time, oxidant (hydrogen peroxide or ozone) dosage can affect the extent of carbonaceous matters and nutrients release, and they have all been investigated and correlated with different constituents release [81, 93, 95]. However, the effects of irradiation strength and time on the MW/H₂O₂-AOP process have not yet been investigated.
It has been reported that waste activated sludge was treated by conventional heating and microwave heating, and it was found that microwave heating contributed to the increase in the solubility of waste activated sludge (WAS), and biogas production was also increased [76]. Likewise, the heating of WAS by microwave alone increased SCOD by 125% at 72.5°C. Besides DNA destruction by microwaves, bacterial cellular membranes have also been proven to be damaged by microwave irradiation, independent of thermal heating at temperatures below 68°C [80]. Such an effect on the treatment process, besides heating, is referred to as athermal effects.

It is proposed that the MW/H₂O₂-AOP can achieve carbonaceous matters and nutrients release, through floc and bacterial mass destruction. Various chemical conditions ranging from acidic to alkaline-treated WAS were tested in combination with the MW/H₂O₂-AOP at different power level treatments to investigate the degree of nutrients release and trends for solids destruction. In this research, an attempt were made to address the athermal effects and they were examined to correlate their effects to different objectives including degree of solids destruction, ammonia release, phosphates release, nitrates and nitrites release, and chemical oxygen demand (COD) solubilization.

6.3 Experimental design and analysis

Table 11 summarizes the characteristics of the secondary aerobic sludge used for the different sets of experiments. Six individual experiments were performed at five different pH levels: pH 2.2, 4.9, 7.0, 10.0, and 11.0. Hydrogen peroxide (30% concentration) dosage remained at 0.25 mL for the 30 mL of sewage sludge used for Experiments A, B, D, E and F, with the exception of experiment C, where a 0.5 mL dosage was used (Table 11). Each experiment consisted of three different levels of power output to dictate treatment, constituting Sets 1, 2, and 3. Set 1 included a treatment time of 1.5 minutes at 1000 W, Set 2 included a treatment time of 3 minutes at 500 W, while Set 3 included a treatment time of 30 minutes at 50 W. All three sets of Experiments A to F received an equivalent power input of 90 kW. In essence, Sets 1 to 3 have the same treatment conditions with differences in parameters including energy level input and treatment
temperatures. When the power level as well as treatment time has been set, the treatment temperature was allowed to increase for the duration of the treatment time to any temperature the input energy level was capable of raising the samples to, depending on the initial temperature, and the rate of heat loss. In the cases of Experiments A, B, E, F, eight samples were treated. Six replicates were used for analyses for all sets of experiments A to F.

Three samples for each set of Experiments A to F were used for the size distribution analyses. Duplicates of the initial substrate were analyzed for total chemical oxygen demand (TCOD). Ten mL of samples from each replicate was collected without centrifugation for subsequent size distribution analysis.

Table 11 Initial conditions

<table>
<thead>
<tr>
<th>Experiment</th>
<th>TS (%)</th>
<th>Peroxide (mL)</th>
<th>pH</th>
<th>TKN (mgL⁻¹)</th>
<th>TP (mgL⁻¹)</th>
<th>COD (mgL⁻¹)</th>
<th>TOC (mgL⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.43</td>
<td>0.25</td>
<td>2.2</td>
<td>300</td>
<td>170</td>
<td>52 +/- 2</td>
<td>9.1 +/- 0.36</td>
</tr>
<tr>
<td>B</td>
<td>0.44</td>
<td>0.25</td>
<td>4.9</td>
<td>300</td>
<td>170</td>
<td>46 +/- 3.6</td>
<td>30 +/- 1.3</td>
</tr>
<tr>
<td>C</td>
<td>0.29</td>
<td>0.50</td>
<td>7.0</td>
<td>250</td>
<td>130</td>
<td>-</td>
<td>24 +/- 3.5</td>
</tr>
<tr>
<td>D</td>
<td>0.33</td>
<td>0.25</td>
<td>7.0</td>
<td>270</td>
<td>140</td>
<td>16 +/- 4</td>
<td>13.4 +/- 0.85</td>
</tr>
<tr>
<td>E</td>
<td>0.39</td>
<td>0.25</td>
<td>10.0</td>
<td>290</td>
<td>160</td>
<td>87 +/- 37</td>
<td>11.26 +/- 0</td>
</tr>
<tr>
<td>F</td>
<td>0.60</td>
<td>0.25</td>
<td>11.0</td>
<td>360</td>
<td>200</td>
<td>83 +/- 36</td>
<td>36 +/- 8.5</td>
</tr>
</tbody>
</table>

6.4 Results and discussion

The results presented below will concentrate on NH₄, PO₄, NOₓ, SCOD, TOC, and particle size distribution to signify the difference in their release and degree of treatment due to irradiation strength and time. In terms of solid disintegration, SCOD and TOC represent how much of the solid phase becomes dissolved into solution. The measurements of NH₄, PO₄, and NOₓ are for nutrients release. The figures presented for NH₄, PO₄, and NOₓ were in terms of percentage of TKN and TP, which could potentially be correlated between the different experiments. Table 11 outlines the initial conditions, while Table 12 outlines the treatment conditions for experiments A to F. Table 13 lists concentration levels of different constituents for samples after treatment.
6.4.1 Temperature

As shown in Figure 12, temperatures were more than 105°C for Sets 1 and 2 of all experiments, temperature differences between Sets 1 and 2 ranged between 1 to 7°C, which was considered to be close to each other in high treatment temperatures of over 100°C. Temperatures reached for Set 1 were always higher than that of Sets 2 and 3. For Sets 3, temperatures were much lower than those of Sets 1 and 2. Even though an equivalent power input of 90 kW was used for three sets, temperatures for Sets 3 with the lowest irradiation energy used (50W) only reached between 56 and 63°C.

For conventional thermochemical (acid or alkaline) treatment of sewage sludge, it was suggested that operating temperatures should be maintained over 100°C for a heating period of 60 minutes to yield the best results [87]. For the MW/H2O2-AOP process, temperatures could reach over 100°C with a short time frame of 1.5 minutes, at the same time, producing significant amounts of soluble materials. As discussed later in this paper, it showed, in general, sludge solids disintegration and nutrient release for Sets 1 and 2 were even or better than Sets 3 for all experiments. It took 30 minutes of heating time to reach a reaction temperature of more than 56°C for Sets 3; whereas Sets 1 and 2 were operated at near optimal temperatures. In view of these, it would be recommended to use a high power treatment to increase temperature in a short amount of time to have better overall results.

Table 12 Treatment conditions
<table>
<thead>
<tr>
<th>Experiment</th>
<th>Set</th>
<th>Treatment Time (min)</th>
<th>Power Level (W)</th>
<th>Initial Temperature (°C)</th>
<th>Final Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Set 1</td>
<td>1.5</td>
<td>1000</td>
<td>23</td>
<td>107</td>
</tr>
<tr>
<td></td>
<td>Set 2</td>
<td>3</td>
<td>500</td>
<td>21</td>
<td>105</td>
</tr>
<tr>
<td></td>
<td>Set 3</td>
<td>30</td>
<td>50</td>
<td>24</td>
<td>63</td>
</tr>
<tr>
<td>B</td>
<td>Set 1</td>
<td>1.5</td>
<td>1000</td>
<td>19</td>
<td>105</td>
</tr>
<tr>
<td></td>
<td>Set 2</td>
<td>3</td>
<td>500</td>
<td>23</td>
<td>106</td>
</tr>
<tr>
<td></td>
<td>Set 3</td>
<td>30</td>
<td>50</td>
<td>22</td>
<td>56</td>
</tr>
<tr>
<td>C</td>
<td>Set 1</td>
<td>1.5</td>
<td>1000</td>
<td>22</td>
<td>129</td>
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<tr>
<td></td>
<td>Set 2</td>
<td>3</td>
<td>500</td>
<td>23</td>
<td>122</td>
</tr>
<tr>
<td></td>
<td>Set 3</td>
<td>30</td>
<td>50</td>
<td>22</td>
<td>56</td>
</tr>
<tr>
<td>D</td>
<td>Set 1</td>
<td>1.5</td>
<td>1000</td>
<td>20</td>
<td>126</td>
</tr>
<tr>
<td></td>
<td>Set 2</td>
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<td>500</td>
<td>23</td>
<td>124</td>
</tr>
<tr>
<td></td>
<td>Set 3</td>
<td>30</td>
<td>50</td>
<td>23</td>
<td>56</td>
</tr>
<tr>
<td>E</td>
<td>Set F</td>
<td>1.5</td>
<td>1000</td>
<td>23</td>
<td>113</td>
</tr>
<tr>
<td></td>
<td>Set G</td>
<td>3</td>
<td>500</td>
<td>24</td>
<td>109</td>
</tr>
<tr>
<td></td>
<td>Set H</td>
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<td>50</td>
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<td>57</td>
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<tr>
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<td>1000</td>
<td>22</td>
<td>109</td>
</tr>
<tr>
<td></td>
<td>Set 2</td>
<td>3</td>
<td>500</td>
<td>23</td>
<td>107</td>
</tr>
<tr>
<td></td>
<td>Set 3</td>
<td>30</td>
<td>50</td>
<td>26</td>
<td>62</td>
</tr>
</tbody>
</table>

Table 13: Concentrations after treatment

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Set</th>
<th>NH4 (mgL-1)</th>
<th>PO4 (mgL-1)</th>
<th>NOx (mgL-1)</th>
<th>SCOD (mgL-1)</th>
<th>TOC (mgL-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Initial</td>
<td>0.87 +/- 0</td>
<td>3 +/- 0</td>
<td>0.74 +/- 0</td>
<td>52 +/- 2</td>
<td>9.1 +/- 0.36</td>
</tr>
<tr>
<td></td>
<td>Set 1</td>
<td>2.74 +/- 0.22</td>
<td>10.8 +/- 0.43</td>
<td>26.48 +/- 1.07</td>
<td>612 +/- 37</td>
<td>131 +/- 32</td>
</tr>
<tr>
<td></td>
<td>Set 2</td>
<td>2.72 +/- 0.45</td>
<td>10.7 +/- 1.44</td>
<td>45.5 +/- 4.67</td>
<td>558 +/- 20</td>
<td>169 +/- 50</td>
</tr>
<tr>
<td></td>
<td>Set 3</td>
<td>2.12 +/- 0.12</td>
<td>12.4 +/- 1.07</td>
<td>14.4 +/- 0.26</td>
<td>651 +/- 50</td>
<td>110 +/- 48</td>
</tr>
<tr>
<td>B</td>
<td>Initial</td>
<td>0.18 +/- 0.02</td>
<td>0.16 +/- 0.06</td>
<td>0.16 +/- 0.06</td>
<td>46.4 +/- 3.6</td>
<td>30 +/- 1.3</td>
</tr>
<tr>
<td></td>
<td>Set 1</td>
<td>4.25 +/- 0.29</td>
<td>10.9 +/- 0.67</td>
<td>14.8 +/- 0.96</td>
<td>702 +/- 11</td>
<td>157 +/- 12</td>
</tr>
<tr>
<td></td>
<td>Set 2</td>
<td>4.34 +/- 0.23</td>
<td>10.9 +/- 1.1</td>
<td>10.3 +/- 0.48</td>
<td>751 +/- 130</td>
<td>151 +/- 28</td>
</tr>
<tr>
<td></td>
<td>Set 3</td>
<td>3.46 +/- 0.12</td>
<td>11.5 +/- 1.2</td>
<td>5.38 +/- 0.58</td>
<td>609 +/- 18</td>
<td>114 +/- 8.6</td>
</tr>
<tr>
<td>C</td>
<td>Initial</td>
<td>0.23 +/- 0.09</td>
<td>0.23 +/- 0.04</td>
<td>3.48 +/- 1.02</td>
<td>---</td>
<td>24 +/- 3.5</td>
</tr>
<tr>
<td></td>
<td>Set 1</td>
<td>4.61 +/- 0.22</td>
<td>11.2 +/- 1.59</td>
<td>3.69 +/- 0.15</td>
<td>---</td>
<td>515 +/- 100</td>
</tr>
<tr>
<td></td>
<td>Set 2</td>
<td>3.66 +/- 0.36</td>
<td>7.8 +/- 2.3</td>
<td>8.80 +/- 0.13</td>
<td>---</td>
<td>400 +/- 63</td>
</tr>
<tr>
<td></td>
<td>Set 3</td>
<td>3.90 +/- 0.15</td>
<td>34.2 +/- 2.3</td>
<td>9.86 +/- 0.33</td>
<td>---</td>
<td>79 +/- 17</td>
</tr>
<tr>
<td>D</td>
<td>Initial</td>
<td>0.12 +/- 0.01</td>
<td>0.11 +/- 0</td>
<td>2.17 +/- 0</td>
<td>16 +/- 4</td>
<td>13 +/- 0.85</td>
</tr>
<tr>
<td></td>
<td>Set 1</td>
<td>2.25 +/- 0.20</td>
<td>12.4 +/- 1.64</td>
<td>9.60 +/- 0.04</td>
<td>1270 +/- 11</td>
<td>317 +/- 126</td>
</tr>
<tr>
<td></td>
<td>Set 2</td>
<td>2.67 +/- 0.40</td>
<td>10.2 +/- 2.5</td>
<td>8.13 +/- 0.21</td>
<td>1220 +/- 160</td>
<td>230 +/- 17</td>
</tr>
<tr>
<td></td>
<td>Set 3</td>
<td>5.71 +/- 0.55</td>
<td>18.6 +/- 1.14</td>
<td>6.18 +/- 0.31</td>
<td>518 +/- 74</td>
<td>103 +/- 38</td>
</tr>
<tr>
<td>E</td>
<td>Initial</td>
<td>0.38 +/- 0</td>
<td>3.62 +/- 0</td>
<td>1.40 +/- 0</td>
<td>87 +/- 37</td>
<td>11 +/- 0</td>
</tr>
<tr>
<td></td>
<td>Set 1</td>
<td>3.28 +/- 0.12</td>
<td>15.2 +/- 0.58</td>
<td>4.42 +/- 0.12</td>
<td>1800 +/- 140</td>
<td>279 +/- 21</td>
</tr>
<tr>
<td></td>
<td>Set 2</td>
<td>3.29 +/- 0.43</td>
<td>20.6 +/- 3.99</td>
<td>4.11 +/- 0.42</td>
<td>1900 +/- 34</td>
<td>234 +/- 5.8</td>
</tr>
<tr>
<td></td>
<td>Set 3</td>
<td>29.9 +/- 2.53</td>
<td>47.5 +/- 3.22</td>
<td>2.93 +/- 0.53</td>
<td>697 +/- 30</td>
<td>151 +/- 28</td>
</tr>
<tr>
<td>F</td>
<td>Initial</td>
<td>0.32 +/- 0.16</td>
<td>1.11 +/- 0.03</td>
<td>0.16 +/- 0.06</td>
<td>82.7 +/- 36</td>
<td>36 +/- 8.5</td>
</tr>
<tr>
<td></td>
<td>Set 1</td>
<td>2.99 +/- 0.09</td>
<td>27.7 +/- 1.9</td>
<td>4.58 +/- 0.30</td>
<td>1370 +/- 63</td>
<td>991 +/- 80</td>
</tr>
<tr>
<td></td>
<td>Set 2</td>
<td>3.18 +/- 0.15</td>
<td>27.0 +/- 2.22</td>
<td>4.10 +/- 0.75</td>
<td>1340 +/- 40</td>
<td>923 +/- 145</td>
</tr>
<tr>
<td></td>
<td>Set 3</td>
<td>7.43 +/- 0.59</td>
<td>32.6 +/- 1.17</td>
<td>---</td>
<td>1010 +/- 51</td>
<td>588 +/- 83</td>
</tr>
</tbody>
</table>
6.4.2 Ammonia

Ammonia release was observed in all samples after treatment with the MW/H₂O₂-AOP (Table 13 and Figure 15). In the acidic and neutral experiments of Experiments A to D, an increase of ammonia concentration in solution was apparent after treatment, but no significant difference can be seen between the sets of the different experiments. Treatment temperature and irradiation effects were not contributing strongly to its release in acidic and neutral conditions. In experiments E and F, it appeared that with the longer treatment time and lower treatment temperatures in Set 3, the concentration of ammonia released into solution increased. It was noticed that ammonia concentration of Set 3 of Experiment E appeared erroneously high; no reason could be given at this moment.

Figure 15 Per cent TKN as ammonia
6.4.3 Phosphates

Phosphates release was apparent in all treatments in Experiments A to F (Figure 16). In previous experiments testing phosphates release, only hydrogen peroxide dosage and treatment temperature was investigated [73]. In this research, the time factor as well as the power level parameters are also tested. From the results listed in Table 13, a few trends were noticed. No significant difference was noticed between the three sets for Experiments A and B. This phenomenon could be due to the low hydrogen peroxide dosage used. In Experiments C to F, more pronounced increases in phosphates concentration were found in all three sets; however, an even more significant increase was found in Set 3 for these experiments. It appears that phosphates release was enhanced by the addition of base, and increases with treatment time, despite lower treatment temperatures for these longer treatment times of Set 3. Time does not appear to aid phosphates release in the acidic trials of Experiments A and B. In the neutral Experiments C and D, phosphates release was not different from the other Experiments in Sets 1 and 2, but increased more drastically in Set 3. Although it is known that in acidic conditions, phosphates can be released in large amounts even at lower treatment temperatures of 60°C [73], it is likely that the membrane breakdown taking place in alkaline conditions can also help in releasing phosphorous into solution. The higher levels of phosphates release in Experiments E and F was thought to be caused by the breakdown of cellular membranes [80], hence releasing any phosphates from within the cell, which are subsequently broken down into soluble phosphates by oxidation with hydrogen peroxide. Even in alkaline conditions, the longer reaction time aided in the release of phosphates into solution.
6.4.3 Nitrates/Nitrites

Nitrates/nitrites were released into solution upon treatment with the. Its concentration can give light to other constituents of TKN that was released into solution by the MW/H₂O₂-AOP (Table 13 and Figure 17). Sets 1 and 2 consistently released more NO₃ into solution compared to Set 3 with exception to Experiments C and F, where Set 3 of Experiment F could not be analyzed for NO₃ due to complications with instrumentation. In previous studies on NO₃ release from sludge performed by this group, low concentrations were typically released into solution after MW/H₂O₂-AOP treatment, and were excluded from reporting. No correlation can be drawn between the different Sets and Experiments. With the exception of Experiments C and F, concentrations of NO₃ were lowest for Set 3 of all Experiments. This trend signifies that treatment temperatures can play a role in NO₃ release. Experiment C had an increase in NO₃ concentration with treatment time; this experiment was also the one with the highest oxidant dosage compared to TS of the WAS. It is likely that the abundance of hydrogen peroxide can aid the oxidation of nitrogen to form NO₃ over time.
Figure 17 Per cent of TKN as NO$_x$
### 6.4.4 Soluble COD

Soluble COD was tested for all experiments except for Experiment C due to residual hydrogen peroxide interference (Table 13). It was problematic for SCOD to be measured; hence TOC was measured instead. The measurement of SCOD can shed light to the degree of disintegration of cellular material that is abundant in the WAS. COD solubilization by the MW/H₂O₂-AOP is usually temperature-dependent, meaning that the higher the treatment temperature, the higher the solubilization, up to the point where the rate of solubilized COD materials being oxidized into CO₂ exceeds the rate of solubilization of COD from solid materials into solution [92]. The concentration of SCOD is highly dependent not only on the hydrogen peroxide dosage, treatment temperature and pH adjustments, but it is also dependent on the TS level of the initial WAS [92, 87].

In Experiments A and B, little difference in COD solubilization can be seen between the three sets (Figure 18), but all three sets had increases in concentrations. Acidic treatments may cause extracellular polymeric substances (EPS) to break off the activated sludge surface, which makes it easy for agglomeration of sludge, and improves the dewaterability of sludge [86]. It was also reflected in the particle size distribution graphs discussed in a latter part, where larger particles were observed in the treated solutions. It was apparent that some of sludge was aggregated to form larger flocs in acidic conditions.

The SCOD for WAS could be greatly increased, while decreasing volatile solids (VS) when treated with base, and more so when combined with thermal treatment [75, 84]. Experiments D and F showed a significant increase in COD solubilization in Sets 1 and 2, compared to Set 3. Sets 1 and 2 were operated at near-optimum temperatures, resulting in higher SCOD yield. It was reported that the optimum conditions were at a temperature of 100°C, pH around 10, and for a 60-min reaction time for alkaline thermal sludge treatment [86]. Indeed, higher SCOD concentrations were obtained for Sets 1 and 2 in Experiment E (pH of 10). Neyens et al. (2003) stated that at extremely alkaline conditions, the cell loses its viability, at which point it is not able to maintain an appropriate turgor.
pressure and its membrane degrades, allowing intracellular materials to flow out of the cell. It was said that alkali solubilizes the cell membrane by means of saponification, hence degrading the sludge solids. It was also reported that the bacterial surface becomes increasingly negatively charged as an increase of pH, creating high electrostatic repulsion which causes desorption of some parts of extracellular polymers [82]. High SCOD concentrations in alkaline treatment were the overall results of these factors.

6.4.5 TOC

This test can be a good indication on how much readily biodegradable material is available in solution (Figure 19). The trends found in the TOC analysis were correlated with that of COD, but in lower concentrations. As with COD, it appears that the effect of treatment temperature was the most dominant factor for Experiments C to F. This was signified by higher concentrations in Sets 1 and 2, with a drastic decrease in concentration in Set 3, where the treatment temperature was the lowest. Like COD, in acid treatments, Experiments A and B, appeared to show little difference in TOC release.
with respect to treatment temperature, signified by the relatively constant concentrations in all three sets. It may be most of SCOD obtained was mainly due to the digestion of EPS. The highest TOC release was found in Experiment F, where the level of causticity was the highest at pH 11. In alkaline conditions, as mentioned earlier that the cell membrane is more prone to breakdown, releasing most of its intracellular matter into solution, signified by increased SCOD. Up to 10 and 30% of SCOD solubilization could be achieved within 30 minutes of room temperature reaction time at pH 10 and 12 respectively [90].

![Figure 19 Concentration of TOC](image)

6.4.6 Size distribution of particles within a sample

The effects and degree of microwave irradiation on WAS solids destruction was of interest for this study. It has been observed that in acidic conditions, settleability is increased, while in alkaline conditions, especially with NaOH being the base added, sodium deteriorates settleability [87, 88]. It was found that when monovalent to divalent cation ratio exceeded 2:1, decreased settleability and dewaterability was found [78].
this research, only sodium hydroxide was added to sludge, so sodium, being a monovalent cation, was highly in excess of divalent cations, causing low settleability in Experiments E and F. Qualitatively, it was seen that the solution was cloudy over a long period of time, compared to a clear solution in acidic treatments of Experiments A and B. In order to differentiate the effect of treatment temperature from athermal effects on WAS solubilization, a look into the particle size distribution change before, after treatment, and between different treatments with approximately the same treatment temperature can potentially provide insight into the process. The graphs to be presented in this section will be in terms of per cent volume by particle size. It should be noted that because of the existence of significantly smaller molecules present in solution compared to microbial cells, the per cent volume of particles counted for is not representative of the actual number of particles in a given sample; one larger particle would account for a higher per cent volume than many more smaller-particles in solution.

In Experiment A, a high acidity of pH 2.2 was the condition adopted for testing. Aside from nutrient solubilization purposes, increased settleability can also be achieved by acid treatments, which is highly favourable in WAS treatment processes for subsequent sludge disposal [86]. The treated samples appeared to be clear in solution with coagulated sludge, some floating and mostly settled. In Figure 20, one can notice the trend for size distribution of particles in solution before and after the different treatments. In the raw sludge, the majority of particles lie in the range of 17 to 316 μm, which is typical for bacterial cells and flocs in sewage sludge. The floc size found from WAS in one study was 98.9μm [74]. After treatment, in Sets 1 to 3, it was noticed that the majority of particles shifted to the higher diameter size range of 60 to 1660 μm. The difference in treatment temperature between Set 1 and 2 are only apart by 2°C, but it is clear that Set 1 produced more of the bigger particles than Set 2. Since only a treatment time of 1.5 min and the power input of 500 W differ for the two sets, it can be inferred that the higher power input aided in producing the larger particles. It should be noted that the solubilized portion of the sample would not be detectable, and if it was detected, the volume these molecules would have taken up would be minimal compared to the volume that one bigger particle took up. Despite the fact that a large portion of the bacterial cells in
solution would have been solubilized to undetectable particle sizes, signified by the large increase in TOC and COD, the sample that is accounted for in the size distribution test would have only accounted for the remainder of the sample that was still detectable by the instrument, meaning that the actual per cent of volume taken up by that same size particle after treatment would be less than that of before treatment. The remaining undestructed particles would account for 100% of the sample volume. The increased average particle size; however, does indicate that the particles may have coagulated after treatment with the MW/H_{2}O_{2}-AOP, with Set 1 being the most efficient for the purpose of increasing particle size. This is not indicative of particle density, but qualitatively, the particles for Experiments A and B were more easily settled to the bottom of the sample tubes compared to the other Experiments. Experiment B was performed at pH 4.9 and the size distribution graph can be seen in Figure 21. A similar trend can be seen between Experiment A and Experiment B, as they both exhibit properties associated with that of acidic conditions. It should be noted that in Experiment B, the size range of the majority of particles after treatment was between 11 to 1260 μm, smaller diameter sizes than that of Experiment A. This could be due to the fact that Experiment A took place in a more acidic condition than Experiment B, so the effects of acid on the samples were more pronounced. Like Experiment A, the difference in treatment temperature between Set 1 and 2 for Experiment B were was by a minor 1°C, which means that the difference in treatment may likely be due to the power input.
Figure 20 Size distribution for Experiment A

Figure 21 Size distribution for Experiment B
Experiments C and D were performed at a neutral pH of 7, with the difference being the hydrogen peroxide dosage. Experiment C included a higher oxidant dosage compared to D, and the effects of the treatment are quite noticeable. Figure 22 and Figure 23 show the size distribution graphs for Experiments C and D respectively. In Figure 22, one can notice that Sets 1 and 2 included a wider range of particle size, while Set 3 was narrower. The initial raw material included a much narrower range of particle size as well. While Sets 1 and 2 included both larger and smaller particles compared to the raw material, the distribution curve in Set 3 only shifted to the left, signifying that smaller particles compared to the untreated were dominant in solution. It should also be noted that in Set 1, an increase in volume per cent can be seen in the small particles range, indicating that particle breakdown was achieved. Even if a fraction of a per cent increase was found in each smaller size range, it signifies that a large number of particles this size were detected to aid in this increase. The larger particle sizes can possibly due to the coagulation of smaller particles over time, upon detachment of EPS. Of the three sets, Set 1 appeared to have the most spread out particle sizes given what was detectable in the given sample. The change in particle size distribution after treatment compared to before treatment for Experiment D was not as pronounced as Experiment C since the particle size range remained quite constant over the three treatments in Sets 1 to 3. One note to make is that Set 1 appeared to have a more spread out particle size range compared to others, as can be seen by the decreased per cent volume in the 52 μm size, but increased per cent volume in the higher and lower size ranges. An explanation for this difference in treatment between the two experiments taking place at the same pH is the effects of hydrogen peroxide. Experiment C had double the oxidant dosage as Experiment D given the similar TS levels; hence a more pronounced effect of the MW/H₂O₂-AOP can be seen on the size distribution.
Figure 22 Size distribution for Experiment C

Figure 23 Size distribution for Experiment D
Experiments E and F included an alkaline environment of pH 10 and 11 respectively. The size distribution graph of Figure 24 did not appear to show much difference before and after treatment. Set 1 of this Experiment appeared to have an increased lower size range of particles. The size distribution graph for Experiment F shown in Figure 25 was similar to Experiment E, where pronounced effects were not found. Sets 1 and 2 of this experiment showed some change after treatment with the MW/H2O2-AOP. The most common particle size decreased in per cent volume, meaning that in the treated sample, other sizes of particles increased in terms of per cent volume. The treated samples also appeared cloudier, emulsified, and less defined to the eye compared to the acidified and neutral samples in Experiments A to D. Divalent cations such as calcium could be used to improve settleability, or a different base other than sodium hydroxide could potentially yield better settleability and dewaterability results [87]. If settleability is not a concern upon sodium hydroxide treatment, operating the MW/H2O2-AOP at 1000 W would give good results in terms of nutrients release and larger particle sizes.

Figure 24 Size distribution for Experiment E
Besides Experiment A, the size distribution for Set 3 remained quite constant over the different pH levels, that is, the majority of the particles in solution remained around 50 to 70 μm. This may indicate that Set 3, incorporating the lowest treatment temperature, may be less effective in the breakdown of bacterial cells in the solution.

6.5 Conclusion

The results gave some insight on the nutrient release trend from different microwave power levels combined with different pH levels.

Ammonia was released into solution from all the different treatments, but trends of release were not apparent except that in alkaline conditions, longer treatment time and/or lower treatment temperatures contributed to ammonia solubilization. Significant amounts of soluble phosphorous was also found in treated samples from all experiments, where in acidified samples, no difference was found between different treatment temperature, time,
and power levels. In the neutral and alkaline experiments, a longer treatment time despite lower temperatures yielded higher concentrations of phosphates. NO\textsubscript{x} was released by treatment with the highest irradiation power of 1000W in acidic conditions; however, no trends were found. The higher COD solubilization was attained with higher power levels of treatments in the neutral and alkaline. TOC release trends were correlated with that of COD release.

In terms of trends of particle size distribution after treatment, in acidic conditions, detectable particles generally increased in size, with the largest fraction of larger particles in a given sample being the treatment with highest irradiation power. In neutral condition treatments, the higher the irradiation power provided to the samples, the more spread out the particle sizes range. In alkaline condition treatments, an increase in smaller particles were found after treatment; higher power irradiation yielded significantly more volume of smaller particles. For the purpose of nutrient solubilization, it is recommended to operate the MW/H\textsubscript{2}O\textsubscript{2}-AOP at 1000 W in an alkaline condition; however, at this condition, settleability appears to be compromised.
6.6 References


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7 Solubilization of blood meal to be used as a liquid fertilizer

7.1 Summary
Agricultural wastes pose one of the largest environmental concerns when not treated and disposed of properly. Agricultural wastes also have immense amounts of nutrients beneficial for many different processes when treated and reused properly. Blood meal is a by-product created in copious amounts at slaughterhouses. It contains copious amounts of nitrogen, which constitutes it as a valuable organic fertilizer. Blood meal is currently used in greenhouse hydroponics operations in BC. The solubility of blood meal poses as a problem for the distribution system in these greenhouse operations. The solubilization of blood meal by means of the microwave-hydrogen peroxide enhanced advanced-oxidation process (MW/H\textsubscript{2}O\textsubscript{2}-AOP) was studied. It was found that over the treatment temperature range of 60 to 120°C, solids particle reduction, ammonia and orthophosphate production could be achieved by this process. Large protein molecules were broken down into intermediate compounds with low molecule weights, ammonia and nitrate. Intermediate compounds, such as peptides and amino acids, can also be easily converted to nitrogenous nutrients for plant growth by bacteria. Soluble nitrogen content increased with an increase in microwave heating temperature when acid was added; significant amounts of ammonia were obtained at higher temperatures. Nitrate decreased in concentration with an increase of treatment temperature. Orthophosphate concentrations increased after the advanced-oxidation process (AOP) treatments, with and without acid addition; but were more pronounced with acid addition. Maximum solubility of chemical oxygen demand (COD) occurred at 80°C. Without the addition of acid, soluble COD decreased due to protein denaturation and coagulation out of the solution.\footnote{A version of this chapter has been published. Chan, W.I., K.V. Lo and P.H. Liao. 2007. Solubilization of blood meal to be used as a liquid fertilizer. Journal of Environmental Science and Health, Part B-Pesticides Food Contaminants and Agricultural Wastes, 42 (4): 417-422}
7.2 Introduction

Blood meal, the blood of animals processed into a dehydrated powder form, is a major by-product from slaughterhouses. It contains copious amounts of nitrogen (approximately 13%), mainly in the form of proteins, which make up ~80% of blood meal. Hence, blood meal can potentially be a good source of nitrogen, for use as a fertilizer. Indeed, it is presently being used as a major source of available nitrogen at an organic greenhouse operation in Langley, B.C. However, this application is not without problems; solids in the liquid fertilizer can build up and plug nozzles and valves resulting in partially block pipelines and reduced liquid flow. A pre-treatment process is required to convert suspended solids and insoluble particles in the blood meal solution into a soluble liquid form.

Conventional enzymatic methods can be used to break down proteins. The drawbacks, however, include the high prices of enzymes, and the long period required for the process. It was thought that the microwave-enhanced advanced oxidation process (MW/H₂O₂-AOP) developed at the University of British Columbia could help in this case. The MW/H₂O₂-AOP was found to be an efficient means to digest organic slurries to release nutrients, and to reduce suspended solids [97, 98]. Most of the suspended solids were dissolved when sewage sludge was subjected to the MW/H₂O₂-AOP at temperatures over 120°C. More than 45% of the suspended solids were also dissolved at a lower temperature region (60 to 100°C).

In this preliminary study, the MW/H₂O₂-AOP was employed as a pretreatment method to reduce suspended solids (SS) in the blood meal solution, and to release nutrients into the solution; so that they can become available for crops in greenhouse operations. To our knowledge, no literature in this area is available. Therefore, the purpose of this research was to examine the possibility of using the MW/H₂O₂-AOP in a “digestion” mode to make blood meal acceptable as an ingredient of liquid fertilizer for greenhouse hydroponics operations.
7.3 Materials and methods

7.3.1 Experimental design

Four sets of experiments were conducted in this study. Table 14 presents the experimental conditions of the MW/H\textsubscript{2}O\textsubscript{2}-AOP on blood meal solution. All samples used in this study consisted of 30 mL of the blood meal solution. For Sets A and B, four levels of microwave heating temperatures, (60, 80, 100, and 120°C) were selected, based on our previous work on sewage sludge. For each temperature setting, six samples were heated simultaneously inside the microwave Digestion Labstation. In Set A, 0.5 mL of hydrogen peroxide (30%), and 0.5 mL of sulfuric acid (30%) were added to each vessel to make up a total of 31 mL of sample. In Set B, 0.5 mL of hydrogen peroxide (30%) was added to each vessel, and no sulfuric acid was added. For Sets C and D, four samples were heated simultaneously for each temperature setting, at three levels (60, 90, and 120°C). Set C consisted of 30 mL of blood meal solution with 0.5 mL of hydrogen peroxide (30%) and 0.5 mL of sulfuric acid (30%). Set D was run in a similar fashion as Set C, except that there was no acid addition. In our original experimental design, a fifth set with only microwave heating, i.e., without the addition of H\textsubscript{2}SO\textsubscript{4} and H\textsubscript{2}O\textsubscript{2}, was planned to serve as a control. However, it was aborted due to the fact that microwave heating alone caused excessive coagulation and denaturation of the protein in the blood meal, resulting in very little solubilization. Also from the AOP point of view, there would not be radicals produced without the addition of H\textsubscript{2}SO\textsubscript{4} and H\textsubscript{2}O\textsubscript{2}, the potential advantages of the AOP could not be realized by using microwave heating alone.

Table 14 Experimental conditions of microwave advanced oxidation process (MW-AOP) on blood meal

<table>
<thead>
<tr>
<th>Set</th>
<th>Temperature (°C)</th>
<th>Volume of blood meal (mL)</th>
<th>TS of blood meal (%)</th>
<th>H\textsubscript{2}SO\textsubscript{4} (mL)</th>
<th>H\textsubscript{2}O\textsubscript{2} (mL)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Set A</td>
<td>60, 80, 100, 120</td>
<td>30</td>
<td>0.88</td>
<td>0.5</td>
<td>0.5</td>
<td>1.8</td>
</tr>
<tr>
<td>Set B</td>
<td>60, 80, 100, 120</td>
<td>30</td>
<td>0.88</td>
<td>0</td>
<td>0.5</td>
<td>6.5</td>
</tr>
<tr>
<td>Set C</td>
<td>60, 90, 120</td>
<td>30</td>
<td>0.88</td>
<td>0.5</td>
<td>0.5</td>
<td>1.8</td>
</tr>
<tr>
<td>Set D</td>
<td>60, 90, 120</td>
<td>30</td>
<td>0.88</td>
<td>0.5</td>
<td>0.5</td>
<td>6.5</td>
</tr>
</tbody>
</table>

*30% by weight.
7.3.2 Microwave process and sampling

The blood meal solution was prepared in the proportion of dissolving one gram of powdered blood meal into 100 mL of distilled water. A fresh batch was prepared every day to ensure the consistency of the blood meal solution. Acid was added to the sample followed by hydrogen peroxide in sets A and C. In set D, foaming took place when hydrogen peroxide was added to the sample inside the vessel, causing unequal mixing within the solution. In set B, the effect of foaming found in set D was alleviated by using a large beaker to hold the blood meal solution while adding hydrogen peroxide. The resulting solution was allowed to settle for five minutes, and was subjected to microwave treatment. Samples were then placed into two vials. One was centrifuged for 15 minutes at 4000 rpm and filtered while the other remained unfiltered. All chemical analyses of the blood meal solutions, before and after the treatments, were conducted according to the Standard Methods [96]. All analyses were carried out at least in triplicate, except for COD analyses in sets C and D. Only duplicated samples were used in both sets.

7.4 Results and discussion

The MW/H2O2-AOP was employed over a range of experimental treatment temperatures (60, 80, 100 and 120°C), both with sulfuric acid addition (sets A and C) and without acid addition (sets B and D). Some clear trends can be seen for nutrients solubilization. For set B, very little ammonia was detected in the sample solutions after treatment with the addition of hydrogen peroxide (Figure 26). It seemed that at all heating temperatures, ammonia levels actually decreased. Set D, without acid addition, also showed the same trend as set B. However, for set A, when acid was added, ammonia concentration increased with increasing microwave heating temperature, from 16.8 ± 0.5 mg/L at 60°C to 166 ± 27 mg/L at 120°C. With the addition of acid, ammonia could be retained in solution in the form of NH₄⁺ ions. A pronounced effect of ammonia solubilization was obtained at a high treatment temperature of 120°C. A similar trend was also obtained in set C, in which acid was added. This clearly indicated that, in the MW/H2O2/H⁺-AOP, acid addition favored ammonia solubilization and retention. Results of nitrate release in the solution did not show a clear trend with respect to the different temperatures. However, when both hydrogen peroxide and acid were added to the samples (set A),
nitrate concentration appeared to decrease with temperature increase (Figure 27). Nitrate release was consistently higher over the temperature range when acid was added, but at 120°C, nitrate concentrations were similar for treatments with or without acid addition. It should be noted that nitrate, not as volatile as ammonia, is also an important and readily available nitrogen source for plant growth. Total nitrogen (TKN) for the initial solution was 2140 ± 104 mg/L, while total soluble nitrogen was determined to be 850 ± 64 mg/L. As can be seen from Figure 28, total nitrogen content was relatively constant between 1993 ± 47.3 mg/L to 2033 ± 90.7 mg/L over the experimental temperature range. However, a drastic difference in solubilized total nitrogen can be found between set A and set B. In set A, soluble TKN increased from 1410 ± 28 mg L⁻¹ at 60°C to 1590 ± 0 mg/L at 120°C; where in set B, soluble TKN remained between 104 ± 0.7 mg/L and 143 ± 5.0 mg/L, with no noticeable trend. Due to uneven sampling errors from protein-denaturation, total nitrogen data were omitted from set B, but they were expected to be close to those of set A. From the trends of ammonia formation, and total nitrogen found in experimental data, it can be postulated that although there were dissolved nitrogen compounds in the starting material, they were likely not in the easily usable form by plants, but in long-chain proteins. Low initial ammonia and nitrate levels (2% of initial total soluble nitrogen) suggest that this statement was correct. Upon treatment with the microwave enhanced AOP, ammonia coupled with nitrate level was at a maximum of 20% of initial total soluble nitrogen content, suggesting that the long-chain proteins have been broken down into more usable forms, and also possibly as amino acids, which are still usable by bacteria, but not detected as nitrate or ammonia. No significant amounts of orthophosphates can be extracted from the blood meal solution, since total phosphorous content in the initial solution was only 34 mg/L. However, orthophosphates were still released as can be seen in Figure 29. When hydrogen peroxide was added to the set, orthophosphate values increased with increasing temperature. When acid and hydrogen peroxide were added to the samples, orthophosphate content also increased with increasing temperature. It seemed that acid addition did not provide much help in the solubilization of phosphates at lower treatment temperatures (60, 80 and 100°C), but was more helpful at 120°C. The observed maximum amounts of phosphorous release were 47% and 58% of the initial total phosphorous for sets C and A, respectively.
Figure 30 shows both soluble and total COD for set A. Soluble COD was 92, 98, 100, and 104% of total COD for temperatures of 60, 80, 100, and 120°C, respectively. This was very close to that of total COD until over 80°C where soluble COD equals total COD. At temperatures above 80°C, both total and soluble COD decreased, as higher oxidation reactions yielded CO₂ which escaped out of the solution. For sets B and D, significantly lower soluble COD values were obtained over the range of temperatures (Figure 31). Without acid addition, proteins in the blood meal solution denatured and coagulated under heat. This phenomenon caused difficulty in the measurement of total COD, as the unfiltered sample solutions contained pieces of denatured protein that caused uneven sampling. Even after using a micro-blender, variations between samples were high. Compared to the soluble COD value of 11.2 g/L before treatment, solubilization of COD can be noted after the hydrogen peroxide and acid treatment. This initial value was found to be higher than the soluble COD obtained after treatment with only hydrogen peroxide. Soluble peptides and proteins were denatured and precipitated out of the solution without the addition of acid, causing the soluble COD value to decrease. The measurements of untreated soluble COD concentrations might be higher than what they actual are, due to possible color interferences. In general, when acid was added to the blood meal and hydrogen peroxide solution prior to microwave treatment, higher yields of nutrients can be realized through solubilization. However, with the acid addition, the solution pH decreased to 1.8, which would not be ideal for plant growth. As a test, a post-treatment sample solution of set A was neutralized with 0.1 N of NaOH, and it was found that neutralization occurred with no precipitation. With a neutralization step, acid addition in the MW-AOP to obtain nutrient-release would not pose a problem for plants. With the destruction of solid particles in the blood meal solution, it is possible to incorporate blood meal into a liquid organic fertilizer. In view of the results of soluble COD, ammonia and ortho-phosphate, it appeared that blood meal should be subjected to the MW/H₂O₂-AOP treatment at 120°C. When both hydrogen peroxide and acid are used, it would produce the highest ammonia concentration, and the least soluble COD in the resulting solution, since ammonia is a valuable fertilizer for plant growth. An additional study is under preparation and a pilot-scale hydroponics potting trial will be conducted, to determine the
feasibility of using the MW/H₂O₂-AOP treated blood meal to supply the nitrogen component of the liquid fertilizer in the greenhouse.

Figure 26 Ammonia concentrations at respective treatment temperatures

Figure 27 Nitrate concentrations at respective treatment temperatures
Figure 28 Total soluble nitrogen content at respective treatment temperatures

Figure 29 Ortho-phosphate concentrations at respective treatment temperatures
Figure 30 Chemical oxygen demand (COD) concentrations of hydrogen peroxide and acid addition treatments

Figure 31 Chemical oxygen demand (COD) concentrations of hydrogen peroxide addition treatments

7.5 Conclusions
In the MW/H₂O₂/H⁺-AOP, acid addition favored ammonia solubilization and its retention. Up to 166 ± 27 mg N/L of ammonia was found in solution compared to the initial value of 15 ± 1.9 mgN/L. Ammonia release was most prominent with acid addition and heated
at 120°C. No appreciable amounts of ammonia were found in the solution after treatment with only hydrogen peroxide. There is no detectable trend in nitrate release after treatment except with the addition of acid, where nitrates appeared to decrease in concentration with an increase in treatment temperature. Nitrate release was enhanced with the addition of acid. Total nitrogen solubilization also increased with acid addition in the treatment. Ortho-phosphates increased in concentration with an increase in treatment temperature, regardless of acid treatment. A high degree of COD solubilization could be achieved when hydrogen peroxide and sulfuric acid were added. At temperatures of 80°C and up, approximately 100% solubility could be achieved, but at higher temperatures, CO₂ was formed and both total and soluble COD concentrations decreased. Maximum solubilization of COD, without losses due to CO₂ formation, occurred at 80°C. Without the addition of acid, minimal COD could be solubilized due to protein-denaturation and coagulation. With significant amounts of solubilized COD, ammonia, and ortho-phosphates in the treated solution, this MW/H₂O₂-AOP process looks promising in making blood meal an ingredient for greenhouse liquid fertilizer.
7.5 References


8 Nutrient release for fish silage using microwave-enhanced advanced oxidation process

8.1 Summary
Fish silage is currently used in greenhouse hydroponics operations as a fertilizer for its rich nutrient values. Fish silage is a by-product where it must undergo enzymatic breakdown or anaerobic digestion prior to its use as a fertilizer due to its high solids content, but both of which methods are timely and expensive. The microwave enhanced advanced oxidation process (MW/H₂O₂-AOP) was used to reduce its solids and soluble carbonaceous materials. Fifteen sets of experiments with varying hydrogen peroxide dosages and treatment temperatures were conducted to evaluate the effectiveness of the MW/H₂O₂-AOP on the solubilization of fertilizer constituents. It was found that up to 26% of total Kjeldahl nitrogen could be released as ammonia with 6% hydrogen peroxide dosage at 170°C. An increase of nitrate/nitrite concentration was observed with higher hydrogen peroxide dosage and higher microwave temperature. The highest concentration of 10.2 mg/L of nitrates/nitrites was released at the same operating condition. Up to 20±9.5 % of total chemical oxygen demand was reduced at temperatures between 120 and 170°C.

Volatile fatty acids were generated in large quantities at lower temperatures, corresponding to an increase in soluble COD, but not at higher temperatures. The treatment of fish silage using the MW-AOP appears to be promising.  

8.2 Introduction
Fish silage is a valuable by-product, rich in nitrogen and phosphorus, suitable for use as an organic fertilizer for greenhouse hydroponics operations. However, a pretreatment process is required to achieve: 1) reduction of suspended solids/carbonaceous matters

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7 A version of this chapter has been submitted to Journal of Environmental Science and Health, Part B–Pesticides Food Contaminants and Agricultural Wastes. W.I Chan, P.H. Liao, K.V. Lo. Nutrient release for fish silage using microwave-enhanced advanced oxidation process
which may cause plugging of nozzles and valves along the irrigation lines, and 2) solubilization of nitrogen into ammonia for easier crop uptake. A commonly used pretreatment process is anaerobic digestion, which reduces suspended solids (SS) and releases some of the total nitrogen content as soluble ammonia and nitrates/nitrites into solution. However, the digestion process is slow and requires a long hydraulic retention time, hence a high capital cost. It also requires skilled operators.

The microwave enhanced advanced oxidation process with hydrogen peroxide (MW/H$_2$O$_2$-AOP) has been recognized for improving the release of nutrients and reducing suspended solids from wastewater sludge [103, 100]. The MW/H$_2$O$_2$-AOP occurs in two reaction processes, similar to the wet-air oxidation: the breakdown of large particulate organic matters such as proteins into smaller and more soluble organic components of amino acids, and further oxidation or gasification of the resulting organic products [106, 104]. The resulting oxidation products can be in the form of proteins, amino acids, ammonia, volatile fatty acids (VFAs) and/or CO$_2$ depending on the reaction conditions [102]. There is an advantage in operating the MW/ H$_2$O$_2$-AOP process at a higher temperature; it would release CO$_2$ as a final oxidation product and, therefore, producing a solution with less carbonaceous matters. The reduction of carbonaceous matters is beneficial since carbonaceous matters can aid bio-film growth and clog pipes and nozzles of the nutrient distribution system in the greenhouse.

It was thought that the MW/H$_2$O$_2$-AOP process could be used to treat fish silage for nutrient release and solids reduction. This would make fish silage more acceptable as an ingredient of liquid fertilizer for greenhouse hydroponics operations. The effects of heating temperature and hydrogen peroxide dosage of the MW/H$_2$O$_2$-AOP process on solids reduction and nutrient release were examined in this study.

8.3 Materials

Fish silage, which has a nitrogen: phosphorus: potassium (N:P:K) ratio of 3:2:0, was supplied for these experiments by a local organic greenhouse in Surrey, British Columbia,
Canada. The initial total solids concentration (TS) was 24.1%. Approximately 76-95% of total phosphorus (TP) of the initial silage was in the form of orthophosphates (ortho-PO₄), but contains significantly less other soluble nutrients (excluding phosphorus). About 3.8% of the total Kjeldahl nitrogen (TKN) was in the form of soluble ammonia. Fish silage was further diluted using distilled water to 13.1 and 7.2% for this study. The characteristics of the fish silage samples used in this study are therefore presented in Table 15 and Table 16.

Table 15 Summary of initial concentrations I

<table>
<thead>
<tr>
<th>Initial</th>
<th>TS (%)</th>
<th>TP (mg/L)</th>
<th>soluble TP (mg/L)</th>
<th>TKN (mg/L)</th>
<th>soluble TKN (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7%</td>
<td>7.2 +/- 0.02</td>
<td>5275 +/- 71</td>
<td>4030 +/- 141</td>
<td>7838 +/- 88</td>
<td>6720 +/- 537</td>
</tr>
<tr>
<td>13%</td>
<td>13.1 +/- 0.17</td>
<td>9138 +/- 620</td>
<td>9062.5 +/- 830</td>
<td>15430 +/- 106</td>
<td>12600 +/- 35</td>
</tr>
<tr>
<td>24%</td>
<td>24.1 +/- 0.01</td>
<td>18525 +/- 1150</td>
<td>16313 +/- 370</td>
<td>31580 +/- 350</td>
<td>27500 +/- 2120</td>
</tr>
<tr>
<td>24%</td>
<td>24.1 +/- 0.01</td>
<td>18525 +/- 1150</td>
<td>16313 +/- 370</td>
<td>31580 +/- 350</td>
<td>27500 +/- 2120</td>
</tr>
</tbody>
</table>

Table 16 Summary of initial concentrations II

<table>
<thead>
<tr>
<th>Initial</th>
<th>TCOD (mg/L)</th>
<th>SCOD (mg/L)</th>
<th>NH3-N (mg/L)</th>
<th>o-PO₄ (mg/L)</th>
<th>VFA (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7%</td>
<td>66350 +/- 2330</td>
<td>32400 +/- 1570</td>
<td>458 +/- 4</td>
<td>4000 +/- 170</td>
<td>148</td>
</tr>
<tr>
<td>13%</td>
<td>143160 +/- 25000</td>
<td>65400 +/- 1170</td>
<td>960 +/- 64</td>
<td>8600 +/- 200</td>
<td>546</td>
</tr>
<tr>
<td>24%</td>
<td>259800 +/- 5800</td>
<td>149600 +/- 1460</td>
<td>1930 +/- 28</td>
<td>17600 +/- 920</td>
<td>87</td>
</tr>
<tr>
<td>24%</td>
<td>278000 +/- 5801</td>
<td>154500 +/- 1500</td>
<td>2333 +/- 32</td>
<td>15800 +/- 35</td>
<td>--</td>
</tr>
</tbody>
</table>

8.3.1 Experimental Design and Analysis

Fifteen sets of MW/H₂O₂-AOP experiments, each with 6 replicates, were conducted in this study (Table 17). The first twelve sets were conducted with varying conditions generated by a statistical program, in order to obtain optimal conditions with minimum required runs. The Box-Behnken design (JMP-In® 5.1) was then used to produce response surface plots predicting trends of nutrient release [105]. Sets 13 to 15 were performed for verification purposes with conditions outside the testing ranges of the first twelve sets. Sets 13 to 15 used a higher oxidant dosage of 6% at 120, 150, and 170°C (Table 17).
Table 17 Summary of conditions

<table>
<thead>
<tr>
<th>Set</th>
<th>% Solids</th>
<th>Temperature</th>
<th>Dosage (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13.1</td>
<td>60</td>
<td>1.5</td>
</tr>
<tr>
<td>2</td>
<td>24.4</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>24.4</td>
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<td>4</td>
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<tr>
<td>4</td>
<td>7.2</td>
<td>60</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>7.2</td>
<td>120</td>
<td>2</td>
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<tr>
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<td>80</td>
<td>2</td>
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<tr>
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<td>7.2</td>
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<td>0.75</td>
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<td>80</td>
<td>0.25</td>
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<td>80</td>
<td>3</td>
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<td>24.4</td>
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<td>10</td>
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<tr>
<td>15</td>
<td>24.4</td>
<td>120</td>
<td>8</td>
</tr>
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<td>16</td>
<td>24.4</td>
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<td>6</td>
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<tr>
<td>18</td>
<td>24.4</td>
<td>170</td>
<td>6</td>
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Sets 1 to 12 were run with samples consisting of 30 mL of fish silage solution and varying amounts of hydrogen peroxide (30% wt) adding to different total volumes. In these twelve sets, fish silages with three solids concentrations, 24.4% (undiluted), 13.1% and 7.2%, were tested, since different solids concentrations can potentially affect the dielectric properties for heating. Peroxide dosages were also varied, from a maximum of 100% to 0%, where 100% represents 1 mL hydrogen peroxide (30% wt) per 30 mL of 7.2% solids. This is approximately the ratio used for these sets of experiments in which four microwave heating temperatures were tested: 60, 80, 100, and 120 °C.

For sets 13, 14 & 15, 6 mL of hydrogen peroxide were added to samples for a total volume of 30 mL and heated at 120, 150, and 170°C, respectively. Dilution effects of hydrogen peroxide added to the samples were taken into account for calculating constituents concentrations.

For each set, portions of four of the six replicates were used for total chemical oxygen demand (TCOD) analyses. All six samples were filtered with glass-fiber filter papers (pore size of 1.6 μm) for VFA, orthophosphates, ammonia, and nitrates analyses. The
combinations of variables were entered into a custom design option of JMP-In® 5.1 for statistical analysis. The runs and combinations of variables are listed in Table 17.

8.4 Results and Discussions

8.4.1 Ammonia

Ammonia and nitrate are very important nitrogenous components for plant growth. The results of ammonia solubilization are presented in Table 18. The results of soluble ammonia and the ratio of ammonia concentrations to the initial concentrations are shown in Figure 32. The response surface plot predicting ammonia solubilization trend is presented in Figure 33. The Pareto plot shows the significant factors affecting ammonia solubilization (Figure 34).

<table>
<thead>
<tr>
<th>Set</th>
<th>TCOD (mg/L)</th>
<th>SCOD (mg/L)</th>
<th>NH3-N (mg/L)</th>
<th>o-PO4 (mg/L)</th>
<th>VFA (mg/L)</th>
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<tr>
<td>1</td>
<td>143800 ± 25500</td>
<td>73000 ± 3100</td>
<td>980 ± 12</td>
<td>8800 ± 300</td>
<td>390 ± 14</td>
</tr>
<tr>
<td>2</td>
<td>317800 ± 40300</td>
<td>161700 ± 8500</td>
<td>1900 ± 41</td>
<td>17500 ± 400</td>
<td>1130 ± 10</td>
</tr>
<tr>
<td>3</td>
<td>298892 ± 33705</td>
<td>167200 ± 6700</td>
<td>2450 ± 56</td>
<td>22100 +/- 600</td>
<td>1300 ± 23</td>
</tr>
<tr>
<td>4</td>
<td>58700 ± 1800</td>
<td>33800 ± 1500</td>
<td>470 ± 4</td>
<td>4300 ± 47</td>
<td>840 ± 12</td>
</tr>
<tr>
<td>5</td>
<td>63800 ± 4400</td>
<td>37600 ± 1700</td>
<td>620 ± 48</td>
<td>4500 ± 56</td>
<td>450 ± 3</td>
</tr>
<tr>
<td>6</td>
<td>119800 ± 5700</td>
<td>81800 ± 7500</td>
<td>980 ± 12</td>
<td>9000 ± 150</td>
<td>700 ± 12</td>
</tr>
<tr>
<td>7</td>
<td>123500 ± 4850</td>
<td>72917 +/- 1276</td>
<td>1000 ± 24</td>
<td>8900 ± 77</td>
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</tr>
<tr>
<td>8</td>
<td>59000 ± 6150</td>
<td>36300 ± 4900</td>
<td>490 ± 17</td>
<td>4000 ± 220</td>
<td>395 ± 61</td>
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<tr>
<td>9</td>
<td>60100 ± 2900</td>
<td>35000 ± 1100</td>
<td>480 ± 11</td>
<td>4400 ± 100</td>
<td>390 ± 4</td>
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<tr>
<td>10</td>
<td>276900 ± 13600</td>
<td>161000 ± 7600</td>
<td>2100 ± 62</td>
<td>19400 ± 690</td>
<td>1200 ± 3</td>
</tr>
<tr>
<td>11</td>
<td>274500 ± 8300</td>
<td>166900 ± 6700</td>
<td>2700 ± 140</td>
<td>19600 ± 650</td>
<td>600 ± 2</td>
</tr>
<tr>
<td>12</td>
<td>115600 ± 6700</td>
<td>74100 ± 300</td>
<td>1200 ± 62</td>
<td>9000 ± 150</td>
<td>620 ± 4</td>
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<tr>
<td>13</td>
<td>253700 ± 7900</td>
<td>173900 ± 12300</td>
<td>2500 ± 144</td>
<td>16500 ± 390</td>
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<td>175300 ± 9200</td>
<td>4900 ± 1100</td>
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<td>--</td>
</tr>
<tr>
<td>15</td>
<td>237700 ± 21500</td>
<td>171000 ± 11000</td>
<td>8200 ± 520</td>
<td>16300 ± 470</td>
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</tr>
</tbody>
</table>

Ammonia solubilization was noticeable in some runs only. The percentages released compared to the initial concentration were the highest for Sets 5, 11 and 12, and the treatment temperatures at these sets were also the highest (Figure 32). From three figures of response surface, it can be seen that the general trend is identical for all three levels of solids treatment (Figure 33). The most significant factor was microwave heating
temperature, since the slope of the surface with respect to temperature was found to be larger than with respect to hydrogen peroxide dosage. This concurred with the results seen from the Pareto plot in Figure 34. Sets 13-15 also show a clear trend of increasing ammonia release with an increase in temperature, as shown in Figure 32, also concurring with Figure 33 and Figure 34. As the H₂O₂ dosage was constant, the increase in heating temperature doubled the ammonia concentration for every 20 °C from 120 to 170 °C.

![Graph](image)

**Figure 32** Soluble ammonia concentrations and per cent of initial
Due to the slightly acidic nature of fish silage (pH of 3.8), most of the soluble ammonia is in the non-volatile form of ammonium ion, therefore, it was retained in the solution after the breakdown of organic material. Likewise, in the previous study of blood meal solubilization, ammonia was very well kept in solution and increased dramatically with temperature when acid was added [101]. In the first 12 sets of experiment, up to 8.6% of TKN can be solubilized by using temperatures up to 120°C; still a small amount compared to the total TKN available in the silage. A possible reason could be that the majority of nitrogen is degraded into intermediate products, such as amino acids or peptides, while only small amounts of ammonia were formed in the process [102].

In a previous preliminary study of fish silage treatment using MW/H2O2-AOP, significant amounts of ammonia were released at 170°C. However, considering industrial applications, such high temperatures may not be cost effective. Sets 13-15 were
performed to validate the claim for high ammonia release at such high treatment temperatures, and the results support this claim. At 170°C, 26% of TKN was released as ammonia compared to the initial 6-7% soluble ammonia in the untreated samples. It showed that ammonia concentration was significantly higher than the other constituents. The second most significant factor is the combined effect of solids and H$_2$O$_2$ dosage. Hydrogen peroxide dosage indeed affected ammonia release; however, the extent of its effect on ammonia release was not fully analyzed. The lack of a clear trend of hydrogen peroxide influence on ammonia release may be due to relatively low dosages applied in these experiments.

8.4.2 Nitrates/Nitrites

Nitrates/Nitrites (NO$_x$) are fertilizer components necessary for plant growth. The concentration of NO$_x$ in the initial fish silage was in a low amount of 0.68 mg/L. After the MW-H$_2$O$_2$-AOP treatment, the NO$_x$ concentrations in the first twelve sets of experiments improved by up to more than 500%, but still did not exceed 3.5 mg/L. After the high treatment temperature of 170°C with 6% hydrogen peroxide dosage, the NO$_x$ concentration was increased to 10.2 mg/L, constituting a 15 fold increase from the untreated amount. No obvious trend was observed, and the low concentrations could not be presented with confidence. For sets 13, 14, and 15, the NO$_x$ concentrations were 3.0, 6.2, and 10 mg/L, respectively. This was significantly more release compared to the other trials. A concentration of 10.2 mg/L constitutes only 0.03% of the TKN available in the untreated sample, but this was still a significant increase from the initial concentration. It seemed that temperature and oxidant dosage affected the formation of NO$_x$, however, confident conclusions could not be drawn from these trials.

8.4.3 Chemical Oxygen Demand

The COD results for the experiments are presented in Table 18. Soluble and total COD concentrations as well as the percentage release from the initial concentration are shown in Figure 35 and Figure 36, respectively. Figure 37 shows the surface response graphs with respect to COD solubilization effects from different parameters. At various solids
concentrations tested, SCOD increased with an increase of hydrogen peroxide dosage. In treating the diluted samples at 7.2% solids concentration (Figure 37), SCOD increased slightly with temperature, compared to the higher increase in SCOD from the increase of hydrogen peroxide dosage. The trend of SCOD increase with respect to temperature quickly levelled off after 80°C. This could mean that the SCOD was easily converted into CO₂ at this solids concentration, or that the rate of COD solubilization was slower than that of the rate of CO₂ generation. At higher treatment temperatures, however, an increase in hydrogen peroxide dosage did not constitute a large increase in solubilization. This was likely due to CO₂ formation, causing a slightly decreased concentration of SCOD compared to the same hydrogen peroxide dosage at a slightly lower treatment temperature. It seemed that despite solids concentration changes, COD solubilization increased with temperature until CO₂ evolved, at which point TCOD decreased, which usually takes place at temperatures higher than 80°C [107]. It might be that at lower temperatures, formation of VFAs contributed to an increase in SCOD, whereas at higher temperatures VFAs become further oxidized to CO₂. At 24.4% solids concentration, an increase in hydrogen peroxide dosage as well as an increase in temperature yielded higher soluble COD concentration. One should expect that at this solids concentration, the rate of CO₂ generation was significantly slower than that of the other two concentrations. Overall, the solubilization of COD was dictated by the initial total solids concentrations as indicated in Figure 35. A higher solids concentration yielded a higher SCOD concentration, which coincided with the Pareto plot results in Figure 7, indicating that solids concentration followed by treatment temperature affected COD solubilization the most.
Figure 35 Soluble COD concentration and per cent of initial Soluble COD

Figure 36 Total COD concentration and per cent of initial Total COD
Figure 37 Surface plot prediction COD solubilization for 7% solids, 13% solids, and 24% solids respectively

Figure 38 Pareto plot for COD solubilization factors

Ideally, COD should have been removed to inhibit bacterial growth in pipes, however, temperatures and hydrogen peroxide dosages used in the first twelve sets were not high enough to oxidize COD into CO₂. A higher hydrogen peroxide dosage was used in Sets 13-15. The results indicated that at a higher hydrogen peroxide dosage and temperature, TCOD of fish silage decreased (Figure 36). It was clear that the amount of TCOD decreased with an increase in temperature. The increase in temperature did not constitute a higher amount of COD solubilization, suggesting that the rate of COD solubilization and the rate of CO₂ generation might be relatively constant.
8.4.4 Volatile Fatty Acids

Although not directly related to plant growth, some interesting trends were found in the results of VFA production. Figure 39 shows the concentrations of acetic acid equivalents of treated samples in concentration as well as the percentage to the initial values. After the AOP treatment of samples at 24.4% solids, large amounts of VFA in the forms of acetic, propionic, iso-butyric, n-butyric, iso-valeric, and n-valeric were found. From the initial concentration, an increase of 13 times in VFA concentration was found at 60°C treatment temperature from an initial of 100 mg/L. This value decreased to 12 times at 80 and 100°C, and finally decreased to 7 times at 120°C. Trends of VFA formation can be found in Figure 40 with the use of response surface plots. Generally speaking, the lower temperatures yielded the highest VFA results for that specific solids concentration. Sets 13 to 15 were not analyzed for VFA since its generation was not expected in large quantities at high temperatures.

Figure 39 VFA concentrations and per cent of initial VFA concentrations
8.4.5 Orthophosphates

Soluble phosphorus constituted 75-95% of total phosphorus in fish silage. Since the release was already near its maximum from the beginning, the differences in its release throughout the different trials were not significant. Higher hydrogen peroxide dosage combined with higher treatment temperatures applied to treating sewage sludge always yielded the largest amount of release for orthophosphates, but this was not always the case for fish silage [108]. In sewage sludge, phosphates were mostly encased in biological cells and in the form of polyphosphates, where the addition of hydrogen peroxide along with temperature treatment will cause large amounts of release of phosphates as orthophosphates, contrary to fish silage where bacterial cells do not dominate the substrate; hence the reaction dictating the release of phosphates will be different for the two different substrates. Results of initial substrate analyses for soluble total phosphorus and soluble phosphorus (Table 18) also indicated that the available phosphorus was all in the form of orthophosphates.

8.5 Conclusions

The MW/H₂O₂-AOP could be an effective pre-treatment method for fish silage prior to its use as a fertilizer for greenhouses. This process released significant amounts of
ammonia at 170°C with 6% hydrogen peroxide dosage, totalling up to 26% of Total Kjeldahl Nitrogen. Temperature is the most significant controlling parameter for ammonia release. The acidity of the fish silage contributed to the retention of ammonia in solution.

In the higher range of treatment temperatures of 170°C and 6% hydrogen peroxide dosage, nitrates/nitrites solubilization resulted in a concentration of 10.2 mg/L, a 15 fold increase from its initial concentration of 0.68 mg/L.

The SCOD was increased with an increase in temperature until 120°C, where SCOD remained quite constant with increases in temperature. Due to CO₂ generation from oxidation reactions, TCOD decreased at operating temperature over 120°C. TCOD was also found to have decreased to 86% with 6% hydrogen peroxide at 170°C. It was also decreased to 81% at 120 °C without hydrogen peroxide addition. The Pareto plot ranked solids concentration as the most significant factor, followed by treatment temperature, then oxidant dosage.

Corresponding to an increase in SCOD, VFAs were generated in large quantities. It was observed that more VFA was generated at lower temperatures, while the higher temperatures did not.

No trends could be deducted from orthophosphates release, since the majority of phosphorus was already in its soluble form.
8.6 References


10 Conclusions and Recommendations

The investigations conducted give an insight into the effectiveness of the MW/H₂O₂-AOP on its treatment of organic slurries including waste-activated sludge, blood meal, and fish silage [109, 110, 111, 113, 114]. Various parameters have been studied and associated with nutrients release from different substrates. The solubilized nutrients from these substrates can benefit subsequent processes including struvite crystallization, biogas generation, EBNR feed recycle, and pH generation [112]; whereby agricultural applications are also feasible.

These series of studies provided some promising results including the release of orthophosphates, ammonia, NOₓ, COD, metals, and VFA. The addition of an inorganic acid such as sulfuric acid to the MW/H₂O₂-AOP helped in the breakdown of sludge and other substrates; the addition of sludge aided in the release of phosphates, retention of ammonia and COD in solution, metals solubilization and VFA generation. Up to 25% of soluble COD was composed of acetic acid in one of the studies. 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 the solutions. It was found that with a 3 wt% hydrogen peroxide dosage, up to 61% of TP was solubilized as phosphates, while 39% of TKN was solubilized as ammonia. The MW/H₂O₂-AOP along with sulfuric acid in higher temperature treatments of 120°C was more effective in the solubilization of phosphates and ammonia into solution [109].

COD solubilization was achieved at almost 100% with a treatment temperature of 80°C, after which, no further improvement in solubilization was found. The solubilized COD was found to have further oxidized to form carbon dioxide at treatment temperatures above 100°C. The pasteurization of sludge is also achieved at these high operation temperatures. Pasteurization is likely to occur at low temperatures of 60°C since the MW/H₂O₂-AOP utilizes hydrogen peroxide, a strong oxidant.
The athermal effects of the MW/H₂O₂-AOP was apparent, in that differences were found in nutrients release in different power treatments despite similar treatment temperatures and identical total power input. The amounts of carbonaceous matters and nutrient released into solution as well as the particle size distribution after various power level treatments were presented, and it was noted that the highest operating power level was the most ideal in the solubilization of nutrients and as an energy conserving aspect. Detectable particles increased in size in acidic conditions, with the largest fraction of larger particles in a given sample being the treatment with highest irradiation power. Neutral condition treatments along with higher irradiation power yielded a larger range of particle sizes in a given sample. Alkaline condition treatments yielded an increase in smaller particles after treatment whereas the higher power irradiation yielded significantly higher numbers of smaller particles.

Blood meal solubilization was achieved applying the MW/H₂O₂-AOP with sulfuric acid (0.5% overall acid concentration). It was found that over the treatment temperature range of 60 to 120°C (treatment temperatures held for 5 minutes with a ramp time of 20°C/min), solids particle reduction, ammonia and orthophosphate production could be achieved. Ortho-P concentrations increased after treatment with the MW/H₂O₂-AOP regardless of acid addition, but solubilization was more pronounced with sulfuric acid addition. Significant amounts of ammonia were obtained at higher temperatures with acid. Nitrate decreased in concentration with an increase of treatment temperature. COD solubilization for blood meal was achieved at 80°C [110].

The solubilization of fish silage with the MW/H₂O₂-AOP was studied to make it a suitable organic fertilizer in greenhouse hydroponics applications. Up to 26% of total Kjeldahl nitrogen was released as ammonia with 6% hydrogen peroxide dosage at 170°C. Nitrate/nitrite concentration was also increased with a higher hydrogen peroxide dosage and a higher treatment temperature. The reduction of COD was also achieved where up to 20 ± 9.5 % of the total chemical oxygen demand was reduced at treatment temperatures between 120 and 170°C.
Nutrient solubilization was achieved by the lab-scale process in this research group. The lab-scale apparatus; however, cannot fully represent full-scale operations potentially used in industry. A pilot-scale operation is underway, but it is recommended that a larger pilot-scale operation be studied prior to a full-scale operation. Although most parameters controlling the release of different nutrients have been identified, the behaviour of the reactions may vary significantly depending on the conditions of a full-scale operation. Issues such as reaction time, reaction temperature, heat loss and mixing should be addressed as well. Thus far, there is no economic analysis of the MW/H₂O₂-AOP compared with conventional treatment processes. In order for a full-scale operation to be put into place, a thorough study of capital and operating costs should be taken into account.

Further study should take place in the areas of controlling parameters. Since the studies performed on the controlling parameters were not entirely conclusive on each substrate being treated, more optimization models should be performed to investigate the relationships between each parameter and each substrate with regards to nutrient release. More investigation should also be performed in the areas of athermal effects. It would be beneficial if the instrument used for particle sizing was able to detect smaller particles.
10.1 References


