ABSTRACT
Organic wastes like sewage sludge and dairy manure were subjected to microwave enhanced advanced oxidation process (MW/H$_2$O$_2$-AOP). The MW/H$_2$O$_2$-AOP was developed to release nutrients like phosphorus and nitrogen in the soluble form from the organic waste; these nutrients could be further recovered and reused. In the past, this process has been successfully applied to a series of organic waste for the purpose of solubilizing nutrients. The objectives of this research were to: (1) improve the MW/H$_2$O$_2$-AOP in terms of nutrient release by determining the different factors that influence the treatment, (2) define the factors affecting the process in their order of significance and (3) check the efficacy of the process on various waste.

In the MW/H$_2$O$_2$-AOP, the role of mixing was verified, using municipal sewage sludge (aerobic and anaerobic). It was speculated that mixing the samples during the process would facilitate uniform heating and thus promote more nutrient release. At a microwave temperature of 80 °C, heating time of 5 minutes and hydrogen peroxide dosage of 1 mL per 1% of total solids, the results showed that mixed samples gave a higher nutrient solubilization compared to the unmixed. Subsequently, mixing and solids concentration were incorporated in a screening design with the other proven important factors viz., microwave temperature and hydrogen peroxide dosage. The results showed that microwave temperature and hydrogen peroxide dosage were the most significant factors for the release of orthophosphate, ammonia and soluble chemical oxygen demand.

Preliminary experiments treating anaerobic sludge using MW/H$_2$O$_2$-AOP showed a decrease in orthophosphate concentration below the initial untreated value while for ammonia and volatile fatty acids the concentrations remained same as the initial. In this case, the set microwave temperature was 80 °C with 5 minutes heating and hydrogen peroxide dosage of 1 mL per 1% total solids at pH 7. To investigate this behavior, anaerobic sludge was treated at two pH conditions (7.8 and 4) at microwave temperatures ranging from 80 to 160 °C with hydrogen peroxide dosage of 1 mL per 1% total solids for 5 minutes. The results showed that acid addition helped in the destruction of sludge solids and release of nutrients.
The MW/H$_2$O$_2$-AOP was used to treat separated solid dairy manure. Solid dairy manure with total solids 1.6% was subjected to microwave temperature of 120 °C for 10 minutes with a hydrogen peroxide dosage of 2 mL per 1% total solids at three pH conditions (3.5, 7.3 and 12). Only at pH 3.5, substantial quantity of orthophosphate, ammonia, soluble chemical oxygen demands and volatile fatty acids could be released. Further, a screening experiment was designed including microwave temperature, hydrogen peroxide dosage and heating time, to determine the factors most affecting nutrient solubilization from solid dairy manure. Hydrogen peroxide dosage and temperature were important factors in orthophosphate release while microwave temperature and heating time were important in the release of ammonia and volatile fatty acids.

The results clearly define the efficacy of the MW/H$_2$O$_2$-AOP on various organic waste as well as the conditions under which the treatment can be optimized.
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ACKNOWLEDGEMENTS
I would like to express my gratitude to the following people and organization for their advice and support through the entire project:

• Dr. Victor Lo, Research Supervisor, Department of Civil Engineering, UBC

• Dr. Ping Liao, Research Associate, Department of Civil Engineering, UBC

• Natural Sciences and Engineering Research Council of Canada (NSERC), Research Funding

• Paula Parkinson, Lab Technician, Environmental Engineering Lab, Department of Civil Engineering, UBC

• Fred Koch, UBC Pilot Plant Manager, UBC

• Winnie Chan and Yang Yu, Graduate Students, Department of Civil Engineering, UBC.
CO-AUTHORSHIP STATEMENT

This thesis has been written in a manuscript-based format and it covers a total of five papers. A version of these papers has been/will be submitted for publication. Kenge, A. A., Liao, P. H., and Lo, K.V. (2008) “Role of mixing on microwave enhanced advanced oxidation process in treating sewage sludge” will be published in the J. Environmental Science & Health Part A, 43(12): 1431-1440. Kenge, A. A., Liao, P.H., and Lo, K.V. (2008) “Factors affecting microwave enhanced advanced oxidation process for sewage sludge treatment” has been submitted to the J. Environmental Science & Health Part A.

This project was initiated by discussions with Dr. Ping Liao (research associate) and Dr. Victor Lo (supervisor). The experimental designs were generated by reference to the past data and with assistance and guidance from Dr. Liao. Dr. Lo and Dr. Liao have also been integral in interpreting and analyzing the data. Following the analysis, Dr. Liao has also been helpful in searching the literature to explain parameters that appeared un-informative and random at first. With the assistance of Dr. Lo and Dr. Liao it was possible to explore the project further by applying the process on various organic waste. Also, for the first time an attempt to release sugar from dairy manure was made with the close guidance Dr. Liao. The manuscripts have been revised and edited by Dr. Lo and Dr. Liao.
1.0 INTRODUCTION

1.1 Preface

Currently, sewage sludge treatment and disposal represents a rising challenge for wastewater treatment (WWT) facilities because of the environmental, economic and regulatory factors, and it accounts for 50-60% of the total operating cost of the WWT process. Thus, reduction of the sludge volume is becoming an integral component of wastewater treatment. Not only would sludge reduction result in reduced operating and disposal costs, but also help in alleviating the environmental impacts through disposal by landfill or incineration. Furthermore, since sludge is an abundant source of nutrients, there are increasing demands for the recovery of usable energy and materials from sewage sludge.

A wide range of treatment technologies, such as mechanical, thermal, chemical, biological and oxidative methods have been developed for the treatment of sludge solids and reutilization of nutrients (Camacho et. al., 2002; Odegaard et. al., 2002). For thermal-oxidative process, thermal treatment mainly breaks up the microorganisms, while oxidative treatment destroys them and releases minerals (Camacho et. al., 2002). Advanced oxidation process (AOP) is one of the effective methods, which involves the generation of highly reactive hydroxyl radicals to achieve sludge treatment (Sanz et. al., 2003). The AOP’s commonly use a combination of ozone, hydrogen peroxide, ultraviolet (UV), and microwave radiation. The application of the microwave irradiation together with a strong oxidant to the sewage sludge offers a unique approach, which could achieve both nutrients release and sludge volume reduction (Liao et. al., 2007). Besides heating, both bacterial cellular membranes and DNA were damaged or destroyed by microwave irradiation (Hong et. al., 2004; Eskicioglu et. al., 2007). The effect of microwave irradiation on the process is referred to as athermal. The solubilized nutrients and carbonaceous matters from sludge, such as carbon, nitrogen and phosphorus could be reused for other purposes, such as struvite (magnesium ammonium phosphate) crystallization or methane production (Liao et. al., 2005; Liao et. al., 2005).

The microwave enhanced advanced oxidation process (MW/H₂O₂-AOP) developed by the Environmental Engineering Group at the University of British Columbia, has the advantage
of increased efficiency in both sludge treatment and nutrient solubilization. The process has been applied to sewage sludge for nutrient release and suspended solids reduction. The process has been examined at a range of temperature of 40-200°C, various amounts of hydrogen peroxide dosage (0.05 to 1%) and heating times of 1.5 to 20 minutes. Microwave treatment was chosen over the conventional heating because it is a rapid and efficient process for the treatment of organic slurries: the reactions could be completed within five minutes of heating, and high efficiencies of solubilization, in terms of increases in soluble chemical oxygen demand (SCOD), orthophosphate and ammonia, could be obtained.

Following the successful application of MW/H_{2}O_{2}-AOP on sewage sludge, the treatment was further applied on dairy manure. The confined animal operations have caused great environmental concerns because of the large amount of animal manure produced at these facilities. The conventional management practice, land application, is coming under environmental and regulatory scrutiny due to the limited amount of land available for manure disposal. Application of manure on croplands not only helps improve the soil productivity but also has other benefits like increased soil aggregation, soil strength and erosion resistance, increase in the soil water-holding capacity, etc. (Darwish et. al., 1995; Schjonning et. al., 1994). Its application on agricultural lands could provide as an alternative nutrient source to synthetic fertilizers along with providing a suitable method for disposal. However, land application of animal manure as a fertilizer can pose problems including the loss of nutrients from the soil to ground water and streams. Nutrients from the manure can degrade the water quality if they are over-applied to land and enter water resources through runoff or leaching. These nutrients could enter water bodies, causing eutrophication, thus, resulting in water pollution. Eutrophication is a widespread problem in rivers, lakes, estuaries and coastal oceans, caused by over-enrichment with P and N (Carpenter et. al., 1998). In water bodies, contamination through P and N causes problems like toxic algal blooms, loss of oxygen, fish kill and also the water quality impairs enough to make the water unsuitable for agricultural, industrial or recreational use. Some of the nitrogen also volatilizes as ammonia into the atmosphere. Nitrates and bacteria (eg. E. coli) can also enter aquifers, degrading the quality of the water and causing health problems. Efficient use of manure is the second problem faced when using animal manure as a fertilizer on croplands. The two major issues include, cost of hauling and the nutrient value of manure. Over a period, the nitrogen content in
manure is reduced, due to nitrous oxide emission and loss as ammonia to the atmosphere, while; methane and carbon dioxide are emitted during storage causing greenhouse gas emissions (Petersen et. al., 1998; Moller et. al., 2004). Also, the cost of delivering the manure nutrients could be greater than the value of the nutrients, depending upon the storage (Fleming et. al., 1998; Araj et. al., 2001). The development of new waste management strategies is necessary. Converting dairy manure into value-added products provides a potential alternative for treatment and disposal of such materials.

The solid dairy manure exists as fats, proteins, lignin, carbohydrates and inorganic residue, which contains not only a variety of nutrients including nitrogen, phosphorus, and minerals, but a high content of carbon (Rico et. al., 2005). Lignocellulosic components from dairy manure can be transformed into fermentable saccharides via enzyme, acid and hydrolysis conversion, which can further be converted into ethanol and other value-added products (Wen, et al., 2004; Liao, et al., 2006; Liao, et al., 2007). As a waste to energy treatment system, thermo-chemical conversion of dairy manure was used to produce gases, bio-oil and solids, depending on the treatment temperature, pressure, heating rate and resident time. The gases produced are a mixture of H₂, CO, N₂, water vapor, hydrogen gases, and tar (Cantrell, et al., 2007). The above mentioned processes utilize carbonaceous matters in dairy manure for ethanol, energy and bio-oil conversion. Nutrient and metals, such as phosphorus, nitrogen, and potassium were not reported. Therefore, this study was initiated to examine the feasibility of nutrients extraction from dairy manure using the microwave enhanced advanced oxidation process (MW/H₂O₂-AOP) for subsequent processes. The solids disintegration, in terms of volatile fatty acid and soluble chemical oxidation, was also determined.

The composition of dairy manure will depend on the age, feed, and conditions in which the cow is kept in the farm. The liquid fraction of dairy manure, which contains soluble nutrients, is responsible for the part of the pollution problem in the rural areas. Many of the solid dairy manure are either not biodegradable or degrade very slowly, which are needed to be treated before they can further be utilized. It was also reported that most of phosphorus is tied up in the solid portion of the manure, and up to 65% of phosphorus is in an organic form (Barnett, 1994). Recovery of phosphorus from farm manure, in a form suitable for fertilizer use,
presents an integrated strategy to reduce the overall phosphorus use in the agricultural sector (Greaves et. al., 1999).

1.2 Literature Review

1.2.1 Microwave treatment

Microwaves have been used as a heating method since the 1940s (Mermelstein, 1997). A microwave oven employing the microwave radiations is commonly used as a household device to cook or heat food. Industrial/Commercial applications of microwave oven began with its use in restaurants and vending companies to rapidly heat food. Later, a microwave oven was also recognized as a useful device in drying potato chips, roasting coffee beans and peanuts, defrosting, precooking and tempering meat, drying cork, ceramics, paper, leather, textiles, tobacco etc. (Metaxas and Meredith, 1983). Further, microwave ovens are also widely used in laboratories to prepare samples and for cell fixation and in polymer and medicine industries. The basic principal remains the same in all applications, heating the material and removing water and other liquids from the product.

Principle of microwave

Microwaves are electromagnetic waves with wavelengths ranging from 1 mm to 1 m or frequencies between 300 MHz and 300 GHz. The microwave frequency is higher than radio waves and lower than infrared light, in the electromagnetic spectrum. Microwaves are emitted from a magnetron; to heat the water and other polarized molecules within the material to be heated. Microwave energy penetrates the material and produces a volumetrically distributed heat source, due to molecular friction resulting from dipolar rotation of polar solvents and from the conductive migration of dissolved ions. The dipolar rotation is caused by variations of the electrical and magnetic fields in the product (Alton, 1998). Water is the main source for microwave interactions due to its dipolar nature. Since, heating occurs through radiation it is fairly even compared to conventional heating, which occurs through conduction and convection. Microwave oven used for household purposes operates at a frequency of 2.45 GHz while a large industrial/commercial microwave oven commonly uses a frequency of 0.915 GHz. Three other microwave frequencies exist which
are not commonly used for microwave cooking due to cost and high power requirement viz., 5.8 GHz, 24.125 GHz and 433.92 MHz (Microwave processing of materials, 1994).

Benefits of microwave

The prime benefit of microwave heating is that it is fast and efficient. The electromagnetic waves pass through the material to be heated and cause its molecules to oscillate, generating heat, unlike conventional heating where the material’s surface heats up first and then the heat moves inward. Thus, microwave heats the material and not the container. Also, the energy entering the microwave is unable to escape, thereby creating a higher density electromagnetic field. Thus, the temperature of the material to be heated rises very rapidly in a short processing time. Since, heat is generated within the material, the entire amount is heated at about the same rate.

Other advantages of microwave are space saving and energy efficiency, since most of the electromagnetic energy is converted into heat. Automatic control, variable power output and accurate temperature control make the handing even easier.

Application of microwave in wastewater treatment

Microwaves are commonly used in various technological and scientific fields to heat materials. The use of microwave in the field of wastewater treatment is gaining interest with its growing applications. The primary benefit of replacing the conventional methods with microwave is its ability to fasten the process. When sewage sludge was microwave treated, using the microwave-induced pyrolysis process, the sludge volume was reduced by more than 80% (Menéndez et al., 2002). The microwave single extractions was found to be a suitable alternative to the conventional method used to extract heavy metals from sewage sludge as microwave heating considerably reduced the operating time with minor differences in the extraction efficiency (Cid et al., 2001). Microwave energy was also identified as a source to fasten decomposition of volatile organic compounds from the environment; reducing the operational time from 2 ~ 16 hours (conventional method) to 90 seconds using microwave (Jon and Tai, 1998). Another application of microwave heating in the field of
environmental engineering was the chemical oxygen demand (COD) analysis using microwave digestion. The time taken for the analysis could be reduced from 2h to 7 min for a sample with COD values up to 1000 mg/L (Jardim and Rohwedder, 1989). Microwave energy was successfully used in the field of wastewater treatment mainly to reduce the long operational time needed to test the environmental samples, however, the effect of microwave irradiation on the sludge solids was not broadly discussed.

1.2.2 Advanced oxidation process (AOP)

Advanced oxidation processes (AOPs) are primarily based on the generation of powerful oxidizing species, such as the hydroxyl radicals (OH), to make the reactions more rapid and complete. This chemical treatment was developed in the early 1970s to remove organic and inorganic materials in wastewater by oxidation (Parsons, 2004). The samples have to be exposed to an electromagnetic radiation along with addition of a strong oxidant like hydrogen peroxide; the material to be treated must absorb the incident radiation and undergo degradation.

Fundamental

The oxidation process involves the generation of \( ^\cdot \text{OH} \) radical through photolysis of \( \text{H}_2\text{O}_2 \) or/and ozone. The most direct method for generation of hydroxyl radicals is through the cleavage of \( \text{H}_2\text{O}_2 \). Photolysis of \( \text{H}_2\text{O}_2 \) produces two hydroxyl free radicals (\( ^\cdot \text{OH} \)) per photon absorbed (Parsons, 2004). The symbol \( ^\cdot \) indicates the radical centre and represents a single unpaired electron.

\[
\text{H}_2\text{O}_2 + h\nu \rightarrow \cdot\text{OH} + \cdot\text{OH} \quad (1)
\]

\[
\cdot\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2^* + \text{H}_2\text{O} \quad (2)
\]

\[
\text{HO}_2^* + \text{H}_2\text{O}_2 \rightarrow \cdot\text{OH} + \text{H}_2\text{O} + \text{O}_2 \quad (3)
\]

\[
\text{HO}_2^* + \text{HO}_2^* \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad (4)
\]
In the AOP, where irradiation is involved, degradation of the organic compound can take place either by direct or indirect photolysis. An organic molecule can undergo photochemical transformation only if the light energy is absorbed by the molecule to produce an electronically excited state molecule and chemical transformations of the excited state are competitive with deactivation processes (Parsons, 2004). According to the Grotthus-Draper law: only the light, which is absorbed by a molecule, can be effective in producing photochemical changes in the molecule. The molecule absorbs light in several regions of electromagnetic spectrum, corresponding to different kinds of molecular transitions.

1.2.3 Nutrient recovery

In the present research, the objective was to recover nutrients from organic waste like municipal sewage sludge and dairy manure, using the MW/H$_2$O$_2$-AOP. The nutrients of interest were orthophosphate, soluble ammonia, VFA and SCOD.

**Orthophosphate**

Phosphorus is an essential element in the metabolism of all living organisms and it exists in the environment most commonly as phosphates. In nature, phosphorus has to be mined from phosphate rock, majority of which is used in making fertilizers. While in the various forms of life, phosphates are an essential part in the form of the DNA, RNA materials and also take part in energy distribution.

In wastewater, phosphorus exists in surplus in the forms of total phosphorus, soluble phosphorus, particulate phosphorus and total phosphate (Dueñas et. al., 2003). Removal of phosphorus from wastewater is a crucial aspect in limiting water pollution due to eutrophication. Also, recovery of phosphorus is necessary to combat the problem that could be faced in future due to exhaustion of the phosphate rock. It is estimated that at the present rate of utilization, the phosphate rock reserves will suffice for less than the next 100 years (Heinonen-Tanski and van Wijk-Sijbesma, 2005). Due to these limitations, there is an urgent need to find methods to utilize the available resources. Animal manure and wastewater
sludge are such resources (Heinonen-Tanski and van Wijk-Sijbesma, 2005). Phosphorus is recovered from these wastes in soluble form as orthophosphate.

**Soluble ammonia**

Nitrogen is an essential element for all forms of life. In organic waste, nitrogen is found in four different forms, viz., organic nitrogen, ammonia, nitrite and nitrate. These different forms constitute to the total nitrogen content. The main groups of solids in organic wastes are proteins, carbohydrates, fats and oils. Proteins contain about 16% of nitrogen and along with urea form the major source of nitrogen in sewage sludge and animal manure (Werther and Ogada, 1999). Majority of the nitrogen exists as organic nitrogen and ammonia. The organic nitrogen is to be converted to ammonia, to recover the N from organic waste in the form of soluble ammonia. Application of these wastes on land or disposal in ocean can cause pollution due to eutrophication. Removal and recovery of nitrogen from these wastes is thus necessary to prevent water pollution as well as reuse the nutrient.

**Volatile Fatty Acids**

Volatile fatty acids (VFA) are products of fermentation of organic matter and mainly exist as acetic acid. Under anaerobic conditions, the organic carbon involves a plethora of naturally occurring bacteria. The many different species of bacteria breakdown complex organic molecules through a four-phased process: hydrolysis, acidogenesis (fermentation), acetogenesis and methanogenesis. In the hydrolysis step, complex organic matter like carbohydrates, proteins and fats are converted to soluble organic molecules like sugars, amino acids and fatty acids. In the fermentation step, these organic molecules are converted to volatile fatty acids. VFA’s could be recovered from sludge and manure in the form of acetic acid and used as resources for subsequent processes.

**Soluble Chemical Oxygen Demand**

The chemical oxygen demand (COD) test is commonly used to measure the amount of organic compounds in wastewater. COD is a useful measure of water quality, and there are
stringent regulations regarding maximum COD allowed in wastewater effluents before discharge. Using the microwave treatment, the COD could be solubilized and the recovered organics mainly C and H could be utilized.

1.2.4 Using the recovered nutrients

Struvite crystallization

Struvite also known as magnesium ammonium phosphate (Mg(NH₄)PO₄·6H₂O), is a white to yellowish crystal. It is a problem in sewage and wastewater treatment industry, due to its accumulation on pipe walls and equipment surfaces of anaerobic digestion and post-digestion processes (Ohlinger et al., 1998). Struvite is known for plugging pipes and fouling pumps, aerators, screens and other equipments, where struvite precipitation occurs due to release of magnesium, ammonium and phosphate from the waste material as a result of the biosolids degradation. Under certain circumstances, these wastewater constituents combine to form the struvite crystals, which cling to sludge particles in suspension and surfaces of equipment, tanks and pipe walls. The crystal growth could be rapid and could clog pipes within months. Remediation is either not practical or very costly, thus, making struvite an essentially unwanted by-product.

Struvite crystallization is dependent primarily upon the formation of Mg²⁺, NH₄⁺, PO₄³⁻ ions, pH and temperature of the wastewater (Uludag-Demirer, 2008). The simplified equation for struvite precipitation can be written as follows:

\[ \text{Mg}^{2+} + \text{NH}_4^+ + \text{PO}_4^{3-} + 6\text{H}_2\text{O} \rightarrow \text{Mg(NH}_4\text{)PO}_4\cdot6\text{H}_2\text{O} \]

While, struvite is a problem in wastewater treatment plants, in agriculture it is a potential fertilizer because of its slow-release properties. Thus, precipitating struvite under controlled conditions from the sewage sludge will not only capture the fouling problem but also facilitate use of the nutrients in the form of fertilizer. Other benefits of precipitating struvite include reducing the phosphorus and nitrogen load of side-stream and sludge liquors recirculated to the head (Doyle and Parsons, 2002). The primary requirement for struvite
crystallization is the presence of magnesium, ammonium and phosphate in the soluble form. The MW/H2O2-AOP, helps release ammonia and orthophosphate in the solution, these recovered nutrients could be used in struvite crystallization. Also, recovery of phosphorus causes a reduction in the sludge volume by up to 49% (Doyle and Parsons, 2002).

**Calcium phosphate crystallization**

Calcium phosphate is a mineral containing calcium ions (Ca\(^{2+}\)) and orthophosphates (PO\(_4^{3-}\)). It is used in the production of fertilizers and phosphoric acid. It is used as a nutritional supplement and also used in dental products for remineralization. In wastewater treatment, calcium phosphate compounds are found as hard deposits on the heat exchanger surfaces (Amjad, 1988). Similar to struvite, the precipitation of calcium phosphate is also governed by the level of supersaturation, pH, temperature and presence of ions (Amjad, 1988). Due to the vast application of calcium phosphate in industry, it is practical to use phosphate recovered from organic waste in producing calcium phosphate crystals (Alamdari and Rohani, 2007).

**Enhanced biological phosphorus removal process**

The enhanced biological phosphorus removal (EBPR) process requires a sufficient supply of VFA’s in the anaerobic zone (Guisasola et. al., 2007). The EBPR process is based on the enrichment of activated sludge with polyphosphate accumulating organisms (PAO). These PAO’s take up organic matter (preferably VFAs) under anaerobic conditions (Guisasola et. al., 2007) and store them as polyhydroxyalkanoates (PHA). The VFA recovered from organic waste using the MW/H\(_2\)O\(_2\)-AOP can thus be applied as feed in the EBPR process.

**Biogas production**

Biogas typically refers to a gas produced by the biological breakdown of organic matter in the absence of oxygen; it is used as a low-cost fuel. For biogas production, manure and sewage sludge have been used due to the presence of C, H and N in surplus in these wastes, which are the major constituents of biogas. VFA’s are produced in the acidogenesis step in biogas production, which later are converted to methane and carbon dioxide in the
methanogenesis step by microorganisms. Using the MW/H₂O₂-AOP, large quantity of VFA can be recovered very rapidly from sewage sludge and dairy manure, which could be used in biogas production, thus speeding up the process.

1.2.5 JMP-IN®: Statistical Computer Software

JMP has been used in this study to define factors that are statistically important in optimization of the treatment. The two methods used to design the experiments were the custom design and response surface design.

Custom Design

Using the custom design feature, a new design depending upon the requirements could be generated. Custom design allows the freedom to choose the factor type, viz., continuous, categorical, blocking, mixture, covariate or constant (Sall et. al., 2005). A flexibility of choosing the number of experiments is also provided by this design. After specifying all the requirements, the custom design solution generates an appropriate optimal design.

Response Surface Design

The response surface designer in JMP uses a set of pre-formulated RSM designs for two to eight continuous factors; these are commonly used for optimization (Sall et. al., 2005). Response Surface Methodology (RSM) is an experimental technique used to find the optimal response within the specified ranges of the factors (Sall et. al., 2005). The response surface experiments try to focus on the optimal values for a set of continuous factors. The design used is this study was the Box-Behnken design. The Box-Behnken design combines a fractional factorial with incomplete block designs in such a way as to avoid the extreme vertices and to present an approximately rotatable design with only three levels per factor (Sall et. al., 2005). This design has no points at the vertices of the cube defined by the ranges of the factors.
After the analysis, the data was interpreted by using a pareto plot and a surface profile. In studies that needed factor screening a pareto plot was more useful while surface profile was suitable where a trend was desired.

**Pareto Plot**

The Pareto Plot creates a Pareto chart, which is a bar chart; in this chart the factors are displayed in the order of their severity or significance. The defining characteristics of Pareto plots is that the bars are in descending order of values, thus visually emphasizes the most important parameters. The t-ratio values are used to align the factors in their order of significance. The t-ratio is the ratio of the estimate to its standard error. The t-ratio value should be greater than 2 for the corresponding significance to have a probability of minimum 95%.

**Surface Profile**

A surface profile can be created only for experimental designs using the pre-formulated designs in JMP. The surface profile displays a trend thus defining the behavior of the process. Using the surface profile the future trend can also be predicted.
1.3 Materials & Methods

1.3.1 Apparatus

Figure 1.1 - Microwave oven digestion system

The Milestone Ethos TC microwave oven digestion system (Milestone Inc., USA) was used in this study. Fig. 1.1 shows a picture of the apparatus. The system operates at a frequency of 2450 MHz with a maximum power output of 1000 W. It is equipped with dual independent magnetron system each magnetron with a capacity of 800 W and a rotating pyramid diffuser for uniform distribution of the microwave radiations. A maximum operating temperature of 220 °C and pressure up to 435 psig (30 bar) can be attained by the system.
A total of 12 vessels, including one reference vessel (Fig. 1.2), each with an approximate volume of 100 mL can be used in one single run. The vessels are made from PTFE Teflon and use the vent-and-reseal design. The reference vessel is provided with a thermowell, wherein the thermocouple (Fig. 1.2) is plugged in during the run, providing a real-time temperature feedback. A LCD screen control panel (Fig. 1.3) (Model 320, Milestone Inc., USA) is connected to the microwave, it is used to program the run by feeding operating temperature and heating time; along with monitoring the run. A magnetic mixing device is provided which allows mixing the samples during the microwave process.
1.3.2 Sample analysis

After microwave treatment, the samples were allowed to cool down to the room temperature, approximately 28 °C. The samples were then centrifuged between 3000 to 4000 rpm for 10-15 minutes, depending on the substrate treated; the supernatant was later filtered using 4.5 μm fiberglass filter. The filtered samples were analyzed for SCOD, orthophosphate and soluble ammonia. Soluble nitrates/nitrites (NO\textsubscript{x}) and volatile fatty acids (VFA) were also analyzed in some cases. A small portion of each treated sample was left unfiltered and used for the total chemical oxygen demand (TCOD) analysis. The initial untreated (raw) samples were also centrifuged and filtered and analyzed for SCOD, orthophosphate, soluble ammonia, soluble NO\textsubscript{x} and VFA, while the unfiltered samples were analyzed for TCOD, total phosphate (TP), total Kjeldahl nitrogen (TKN) and TS. All the analysis except the TS and COD were performed at the Environmental Engineering Laboratory at the Civil Engineering Department in UBC and used the flow injection analysis method (LachatQuik-Chem 8000 Automatic Ion Analyzer, Lachat Instruments, USA). The analytic procedures were in accordance with those enlisted in Standard Methods (1998).

A Hewlett Packard 5890 Series II gas chromatograph, equipped with a flame ionization detector (FID), was used to measure VFA. Volatile separation was accomplished with an HP FFAP (free fatty acid phase) column (0.25 m x 0.31 mm with 0.52 μ 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 69 kPa.

1.4 Research Objectives

The present research was focused towards enhancing the release of nutrients from sewage sludge and dairy manure using the microwave enhanced advanced oxidation process (MW/H\textsubscript{2}O\textsubscript{2}-AOP). The optimum conditions needed for the treatment were studied and incorporated in the experimental design to increase the efficiency of the process. The following studies were conducted:

- Based on the previous studies, it's been proven that microwave temperature, hydrogen peroxide dosage and acid addition are the most significant factors affecting the
MW/H₂O₂-AOP (Wong et. al., 2007). It was speculated that mixing the samples during the treatment might increase the yield. Thus, in the present study, experiments were performed to check the role of mixing in solubilization of nutrients from municipal anaerobic and aerobic sewage sludge (Chapter 2).

- Factors affecting solubilization of nutrients in MW/H₂O₂-AOP from sewage sludge were studied in Chapter 3. Mixing was incorporated in a screening design along with microwave temperature, hydrogen peroxide dosage and solid concentration.

- In Chapter 4, the MW/H₂O₂-AOP was applied on municipal anaerobic sludge to check the effectiveness of the process. The motive was to identify the optimum operating conditions in terms of microwave temperature and pH, for better solid disintegration and higher nutrient release.

- The treatment was applied to solid dairy manure to check its effectiveness. The objective in this study (Chapter 5) was to check extent of the nutrient release under neutral, acidic and alkaline pH conditions.

- In Chapter 6, a screening design was generated using microwave temperature, hydrogen peroxide dosage and heating time as the factors; the motive was to determine the optimum conditions when treating solid dairy manure.
1.5 References


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Schjonning, P., Christensen, B. T., and Carstensen, B. “Physical and chemical properties of a sandy loam receiving animal manure, mineral fertilizer or no fertilizer for 90 years”. European Journal of Soil Science, 1994, 45: 257-268


2.0 ROLE OF MIXING ON MICROWAVE ENHANCED ADVANCED OXIDATION PROCESS IN TREATING SEWAGE SLUDGE

2.1 Abstract

The microwave enhanced advanced oxidation process (MW/H$_2$O$_2$-AOP) was used for the release of nutrients and the disintegration of suspended solids from both anaerobic sludge and aerobic sludge. The purpose of this study was to determine the effects of mixing on the performance of the process, in terms of soluble ammonia, orthophosphate and soluble chemical oxygen demands. Experiments were conducted on sludge samples with various total solids concentrations (1.1-3.7%) and hydrogen peroxide dosage (1% per 1% of total solids) at 80°C of microwave temperature and five minutes of heating time. The results indicated that mixing affected solids disintegration and nutrient solubilization of sewage sludge, regardless of the sludge used, anaerobic or aerobic. However, the effects of mixing on the MW/H$_2$O$_2$-AOP were dependent on the total solids concentration of the sludge. A paired $t$-test was performed on data for aerobic sludge: at 2.9% of total solids (TS), the difference for solubilization of nutrients and solid disintegration was statistically significant at a 95% confidence level between mixing and non-mixing samples. At a lower TS of 1.7% only soluble chemical oxygen demand showed significant difference between mixing and non-mixing. The results suggest that, for sludge with higher solids content, the MW/H$_2$O$_2$-AOP can be more effective if a mixing device is implemented.

2.2 Introduction

The microwave enhanced advanced oxidation process (MW/H$_2$O$_2$-AOP) has been applied to sewage sludge for nutrient release and suspended solids reduction at the University of British Columbia. The process has been examined at a range of temperature of 40-200°C, various amounts of hydrogen peroxide dosage (0.05 to 1%) and heating times of 1.5 to 20 minutes. Microwave treatment was chosen over the conventional heating because it is a rapid and efficient process for the treatment of organic slurries: the reactions could be completed within

1 A version of this chapter has been published. Kenge, A. A.; Liao, P.H.; and Lo, K.V. (2008) Role of mixing on microwave enhanced advanced oxidation process in treating sewage sludge. J. Environmental Sci. Health Part A, 43(12): 1431-1440
five minutes of heating, and high efficiencies of solubilization, in terms of increases in soluble chemical oxygen demand (SCOD), orthophosphate and ammonia, could be obtained.

These previous studies have proved that heating temperature, heating time, oxidant dosage and sulfuric acid addition are the deciding factors for the release of nutrients and disintegration of solids (Liao et. al., 2005; Wong et. al., 2006; Wong et. al., 2007). Using the MW/H2O2-AOP to treat sewage sludge, a large quantity of SCOD and volatile fatty acids (VFA) was obtained in the solution. The dosage of hydrogen peroxide and heating temperature played very important roles for the disintegration of microorganisms' cells. Orthophosphate released into the solution would largely depend upon the thermal decomposition of microbial cells. Microwave heating temperature was a very significant factor for phosphate release. Nitrogen is usually present in domestic sewage sludge in the form of proteinaceous matter, which can be broken down and oxidized to form ammonia. Soluble ammonia, therefore, was affected by the dosage of hydrogen peroxide and the heating temperature applied in the process.

When these studies were conducted, the microwave digestion system (Milestone Microwave Labstation) had not been equipped with a mixing devise. Therefore, the results reported previously were representative of the MW/H2O2-AOP with unmixed samples. The Milestone Microwave Labstation has since been upgraded in 2007 so that the option of mixing is available if needed.

It was thought that mixing of sludge samples while undergoing the microwave treatment, not only allows for uniform heating, but also facilitates the oxidation process to disintegrate complex compounds. Therefore, a series of parallel studies were conducted to compare the results of the MW/H2O2-AOP process on anaerobic and aerobic sludge samples with and without mixing. This paper reports the findings of the role of mixing on the MW/H2O2-AOP in terms of solids reduction, and solubilization and release of nutrients from sludge samples.
2.3 Materials & Methods

2.3.1 Feed substrate

Anaerobic sludge obtained from the Lulu Island wastewater treatment plant, Richmond, British Columbia, Canada and secondary aerobic sludge from the wastewater treatment pilot plant, University of British Columbia (UBC) were used for this study. The characteristics of the sludge, both anaerobic and aerobic are presented in Table 2.1. Anaerobic sludge, which had initial total solids (TS) of 3.7%, was diluted by addition of distilled water to obtain TS levels of 2.3% and 1.6%. Aerobic sludge, with initial TS of 0.7%, was thickened by centrifuging to obtain 2.9, 1.8, and 1.1% of TS.

2.3.2 Experimental design

Based on the previous studies (Wong et. al., 2006; Yin et. al., 2007; Yin et. al., 2008), a microwave heating time of 5 minutes and a heating temperature of 80°C were selected for this study. Under these experimental conditions, significant amounts of solubilized nutrients and SCOD were expected. No acid was added. The ramp time, the time taken by the microwave unit to reach the set temperature, was fixed at 3 minutes (i.e., a temperature increase of 20 °C per minute). Hydrogen peroxide (30% conc.) was used and the dosage varied depending upon the total solids (TS). Approximately, one mL of hydrogen peroxide was used per 1% of TS. For samples to be tested with mixing, magnetic stirrers were put in the sample vessels; no stirrers were used for the unmixed samples.

Four sets of experiments were conducted in this study, as shown in Table 2.2. Set 1 was conducted to study the effects of mixing on solids disintegration of anaerobic sludge using the MW/H2O2-AOP. A sample volume of 30 mL, each with three replicates, was used for all runs in this Set. Three TS levels of 3.7, 2.3, and 1.6% were used, and hydrogen peroxide dosages of 3.5, 2.0 and 1.5 mL were applied, respectively.

The purpose of Set 2 was to examine the mixing effects on the solids disintegration and nutrient release of the secondary aerobic sludge. Hydrogen peroxide dosages of 2.5, 1.2 and
0.7 mL were added into the aerobic sludge samples with TS at 2.9, 1.8 and 1.1 %, respectively.

The aim of Set 3 was to determine the effects of acid addition on the solubilization of phosphorus, from the anaerobic sludge. A total of 12 samples at 2.3 % of TS, each with 30 mL, were divided equally into three subsets 3a, 3b and 3c. No acid was added in four samples with initial pH of 6.3 (Set 3a). For Set 3b, 2 drops 30% conc. sulfuric acid was added in each sample, to decrease the pH from 6.3 to 5.1. For Set 3c, four samples were subjected to the microwave treatment first, and then 2 drops of acid were added to the supernatants of each sample to reduce pH from 6.8 to 2.9. The supernatants were further conventionally heated (on a block digester) for 10 minutes. This was intended to ascertain if any polyphosphates were formed during treatment due to the absence of acid.

In Set 4, a solution of 100 mg P L\(^{-1}\) of orthophosphate, prepared from KH\(_2\)PO\(_4\), was used to explore if polyphosphates could be formed under the MW/H\(_2\)O\(_2\)-AOP. All tests were conducted with a sample size of 30 mL and a hydrogen peroxide dosage of 0.2 mL. One subset with three replicates was treated without an acid addition, the other subset with five replicates with acid.

A paired T test was done using GraphPad Prism\textsuperscript{®} version 5 software to analyze the data to determine if mixing is significantly different from no-mixing (Motulsky, 1999).
### Table 2.1 - Characteristics of anaerobic and aerobic sludge

<table>
<thead>
<tr>
<th>Substrate</th>
<th>TS (%)</th>
<th>pH</th>
<th>Initial soluble COD (mg L⁻¹)</th>
<th>Total COD (mg L⁻¹)</th>
<th>Total phosphorus (mgP L⁻¹)</th>
<th>Total Kjeldahl nitrogen (mgN L⁻¹)</th>
<th>Initial soluble phosphate (mgP L⁻¹)</th>
<th>Initial soluble ammonia (mgN L⁻¹)</th>
<th>Initial soluble nitrate (mgN L⁻¹)</th>
<th>Initial VFA (mg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anaerobic</td>
<td>3.7</td>
<td>6.5±0.2</td>
<td>8892±198</td>
<td>67×10³±2000</td>
<td>2235±125</td>
<td>12×10³±100</td>
<td>140±2</td>
<td>488±6</td>
<td>0.47±0.13</td>
<td>4050±427</td>
</tr>
<tr>
<td></td>
<td>2.3</td>
<td>6.5±0.2</td>
<td>5600±130</td>
<td>40×10³±1200</td>
<td>870±85</td>
<td>4800±50</td>
<td>102±8</td>
<td>420±23</td>
<td>0.7±0.06</td>
<td>3050±275</td>
</tr>
<tr>
<td></td>
<td>1.6</td>
<td>6.5±0.2</td>
<td>4600±84</td>
<td>37×10³±540</td>
<td>760±30</td>
<td>3600±40</td>
<td>80±1.25</td>
<td>362±4</td>
<td>0.7±0.01</td>
<td>2200±40</td>
</tr>
<tr>
<td>Aerobic</td>
<td>2.9</td>
<td>6.5±0.2</td>
<td>140±30</td>
<td>31×10³±1750</td>
<td>860±40</td>
<td>1400±13</td>
<td>11±0.3</td>
<td>0.89±0.07</td>
<td>-</td>
<td>5±1.8</td>
</tr>
<tr>
<td></td>
<td>1.8</td>
<td>6.5±0.2</td>
<td>110±8</td>
<td>18×10³±2100</td>
<td>620±86</td>
<td>1020±165</td>
<td>4±1</td>
<td>0.28±0.04</td>
<td>-</td>
<td>2.2±1</td>
</tr>
<tr>
<td></td>
<td>1.1</td>
<td>6.5±0.2</td>
<td>97±8.5</td>
<td>9×10³±445</td>
<td>450±37</td>
<td>752±64</td>
<td>3.2±0.2</td>
<td>0.1±0.08</td>
<td>-</td>
<td>negligible</td>
</tr>
</tbody>
</table>

Note: All initial values shifted to account for the dilution made during treatment by addition of hydrogen peroxide.
Table 2.2 - Experimental design

<table>
<thead>
<tr>
<th>Set no.</th>
<th>Substrate</th>
<th>TS (%)</th>
<th>pH</th>
<th>Temperature (°C)</th>
<th>H$_2$O$_2$ dosage (mL)</th>
<th>Sample volume (mL)</th>
<th>Heating time (mins)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Anaerobic</td>
<td>3.7</td>
<td>6.5±0.2</td>
<td>80</td>
<td>3.5</td>
<td>33.5</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.3</td>
<td>6.5±0.2</td>
<td>80</td>
<td>2</td>
<td>32</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.6</td>
<td>6.5±0.2</td>
<td>80</td>
<td>1.5</td>
<td>31.5</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>Aerobic</td>
<td>2.9</td>
<td>6.5±0.2</td>
<td>80</td>
<td>2.5</td>
<td>32.5</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.8</td>
<td>6.5±0.2</td>
<td>80</td>
<td>1.2</td>
<td>31.2</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.1</td>
<td>6.5±0.2</td>
<td>80</td>
<td>0.7</td>
<td>30.7</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>Anaerobic</td>
<td>2.3</td>
<td>a. 6.3±0</td>
<td>80</td>
<td>2</td>
<td>32</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>b. 5.1±0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>c. 6.3±0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>100 mg P/L</td>
<td>-</td>
<td>4.7±0</td>
<td>80</td>
<td>0.2</td>
<td>30.2</td>
<td>5</td>
</tr>
</tbody>
</table>

Note: All runs had a fixed ramp time of 3 minutes.

2.4 Results & Discussion

Anaerobic sludge is characterized by high COD, very high volatile fatty acids and high solid concentrations (Korsak and Moreno, 2006). It also has very high concentrations of soluble nutrients, such as ammonia and orthophosphate, in the solution. On the other hand, aerobic sludge has most of phosphorus and ammonia contained within microorganism cells. Fresh aerobic sludge has very low concentrations of soluble nutrients as indicated in the Table 2.1.

The chemical constituents are also quite different between the anaerobic and aerobic sludge. The ratio of TKN to total COD was in a range of 1:5.8 to 1:10.3 for anaerobic sludge, whereas it was from 1:12.4 to 1:22.4 for aerobic sludge (Table 2.1). The anaerobic sludge contained a higher amount of nitrogen compounds, probably proteins, while the aerobic sludge had more organic carbons, probably carbohydrates. Even the extra cellular polymeric
substances (EPS) of the two were quite different. Gross chemical analysis of these EPS indicated that anaerobic and activated sludge polymers do differ; protein was the dominant fraction in anaerobic samples, while carbohydrate was in activated sludge (Morgan et. al., 1990). All of sludge solids and their EPS extracts carried an overall negative charge, however, the charge carried by both anaerobic granular sludge and their EPS extracts were found to be less negative than that of the activated sludge.

2.4.1 Soluble COD

![Figure 2.1 - Soluble COD in anaerobic sludge after treatment](image)

Anaerobic sludge was used as it provided the high solids concentration without any pretreatment process (Set 1). The SCOD results from the MW/H2O2-AOP on the anaerobic sludge (Set 1) are presented in Figure 2.1 and Table 2.3. It was observed that an adequate mixing was not provided for a thick solution of 3.7% TS. The resulting SCOD concentrations were 13,130 and 15,285 mg L⁻¹ for mixed and unmixed samples, respectively. Even though the SCOD increased by 6.3% and 9.5% based on the initial TCOD, this represented increases
of 48 and 71% of SCOD in the respectively solutions. It could not be explained why the unmixed samples had a higher soluble COD compared to that of the mixed samples. It could be possible that due to poor mixing, the electric-field uniformity within sample was not established (Plaza-Gonzalez et al., 2005). This might have caused different dielectric loss factors in different parts within the microwave cell. Another possible reason could be that of uneven distribution of hydrogen peroxide in the solution, therefore oxidation occurred only locally. As a result, a higher SCOD was obtained from unmixed samples.

At 2.3% TS concentration, percentage increases of SCOD were 18.5% for mixed and 14% for unmixed samples, based on the initial TCOD. For samples with 1.6% TS, an increase of 12 and 9% was observed for the mixed and unmixed sets, respectively. The results indicated that mixing would increase sludge disintegration for the process.

The results proved that the MW/H$_2$O$_2$-AOP is also an effective means to disintegrate anaerobic sludge. It could also be derived that mixing is an important factor for solids disintegration; with adequate mixing, a higher level of solids disintegration (in terms of SCOD could be obtained in the solution. The other factors, heating temperature, heating time, oxidant dosage and sulfuric acid addition, are also very important for disintegration of solids (Wong et al., 2006; Wong et al., 2007; Liao et al., 2005).

Table 2.3 - Overview of results for anaerobic sludge (Set 1)

<table>
<thead>
<tr>
<th>Operation Mode</th>
<th>TS (%)</th>
<th>Soluble COD (mg/L)</th>
<th>Soluble phosphate (mgP/L)</th>
<th>Soluble ammonia (mgN/L)</th>
<th>Soluble nitrates (mgN/L)</th>
<th>Soluble VFA (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixed</td>
<td>3.7</td>
<td>13130±485</td>
<td>84±1.2</td>
<td>518±5</td>
<td>1.3±0.07</td>
<td>3830±180</td>
</tr>
<tr>
<td></td>
<td>2.3</td>
<td>12920±1575</td>
<td>75±7</td>
<td>450±5</td>
<td>1.7±0.2</td>
<td>2470±260</td>
</tr>
<tr>
<td></td>
<td>1.6</td>
<td>9125±655</td>
<td>61±7</td>
<td>368±6</td>
<td>1.3±0.08</td>
<td>1970±69</td>
</tr>
<tr>
<td>Unmixed</td>
<td>3.7</td>
<td>15285±1210</td>
<td>84±1</td>
<td>530±4</td>
<td>1.2±0.08</td>
<td>4130±820</td>
</tr>
<tr>
<td></td>
<td>2.3</td>
<td>11072±1030</td>
<td>76±2</td>
<td>455±7</td>
<td>1±0.03</td>
<td>2360±156</td>
</tr>
<tr>
<td></td>
<td>1.6</td>
<td>7825±804</td>
<td>58±3</td>
<td>368±7.5</td>
<td>0.97±0.05</td>
<td>2150±266</td>
</tr>
</tbody>
</table>
In order to provide an adequate mixing for samples, the highest TS concentration used was 2.9% for aerobic sludge. The SCOD results are shown in Table 2.4 and Figure 2.2. Overall, the results of aerobic sludge were very comparable to those of the previous studies (Yin et. al., 2007; Yin et. al., 2008). It herein only emphasizes on the difference between mixing and non-mixing for the results of aerobic sludge.

It is observed that at 2.9% TS, samples with mixing showed approximately 25% increase in SCOD, while samples without mixing showed an increase of approximately 19%, based on the TCOD of the starting material. The difference between SCOD for mixed and unmixed samples was most evident at 2.9% TS, there was a difference of 6%. At 1.8% TS, approximately 22 and 18% increase was observed in mixed and unmixed samples, respectively. For 1.1% TS, approximately 28% increase in SCOD was obtained when the samples were mixed compared to approximately 25% increase obtained when samples were not mixed. Thus, the difference in SCOD for 1.8 and 1.1% varied in a range of 3-4%, again depending upon the solids concentration. The results showed that indeed mixing had some effects on sludge disintegration. The mixing effect is more pronounced for the aerobic sludge with a higher TS content.

It is also interesting to note that the SCOD/TCOD ratios were higher than those of the anaerobic sludge. This may due to the relatively more organic carbons in the aerobic sludge. Similar results were reported that increases of 9 and 5% of SCOD/TCOD respectively for aerobic sludge and anaerobic sludge were observed for the microwave treatment of sewage sludge (Hong et. al., 2006).

A higher TS content, the MW/H\textsubscript{2}O\textsubscript{2}-AOP would yield a higher SCOD in the solution as reported previously (Yin et. al., 2007). This study also proved that a higher SCOD was obtained for samples with higher TS. It had an advantage to use a higher solid content for the process, as long as an adequate mixing was provided. This was also a reason that 2.9% of TS content was the highest solid content that could be used in this experiment.
Figure 2.2 - Soluble COD in aerobic sludge after treatment

Table 2.4 - Overview of results for aerobic sludge (Set 2)

<table>
<thead>
<tr>
<th>Operation Mode</th>
<th>TS (%)</th>
<th>Soluble COD (mg/L)</th>
<th>Soluble phosphate (mgP/L)</th>
<th>Soluble ammonia (mgN/L)</th>
<th>Soluble VFA (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixed</td>
<td>2.9</td>
<td>7836±0</td>
<td>48±11</td>
<td>141±11</td>
<td>25±2.8</td>
</tr>
<tr>
<td></td>
<td>1.8</td>
<td>3985±846</td>
<td>23±4.6</td>
<td>59±3</td>
<td>8±0.8</td>
</tr>
<tr>
<td></td>
<td>1.1</td>
<td>2654±210</td>
<td>15.5±1.8</td>
<td>50±1.5</td>
<td>7.5±1.25</td>
</tr>
<tr>
<td>Unmixed</td>
<td>2.9</td>
<td>6221±267</td>
<td>43±3</td>
<td>120±16</td>
<td>22±0.5</td>
</tr>
<tr>
<td></td>
<td>1.8</td>
<td>3428±287</td>
<td>20±5.5</td>
<td>53±2</td>
<td>7±0.2</td>
</tr>
<tr>
<td></td>
<td>1.1</td>
<td>2352±287</td>
<td>14±2.6</td>
<td>44±2.5</td>
<td>6±1</td>
</tr>
</tbody>
</table>
2.4.2 Volatile fatty acids (VFA)

Figure 2.3 - Volatile fatty acids in anaerobic sludge after treatment

Very high VFA concentrations were observed in the anaerobic sludge (Table 2.1). The high VFA concentration is attributed to the inherent characteristics of anaerobic sludge. The resulting VFA concentrations after the MW/H$_2$O$_2$-AOP are shown in Table 2.3 and Figure 2.3. They neither varied much from the initial concentrations, nor varied much between the mixed and the unmixed processes. It could not be explained why the VFA concentrations were retained in anaerobic sludge.
The VFA results of the aerobic sludge can be seen in Table 2.4 and Figure 2.4. Unlike that in the anaerobic sludge, the initial VFA concentration was much lower in the aerobic sludge. For TS levels of 2.9, 1.8 and 1.1%, the initial VFA were 5 mg L\(^{-1}\), 2.2 ml L\(^{-1}\) and negligible amount, respectively. The VFA were increased after the MW-H\(_2\)O\(_2\)-AOP treatment. For sludge samples at 2.9% TS a larger difference was observed between the mixed and unmixed samples, and the VFA were 48 and 43 mg L\(^{-1}\) for mixed and unmixed, respectively. The VFA were 23 and 20 mg L\(^{-1}\) for mixed and unmixed samples at 1.8% TS.

### 2.4.3 Soluble phosphorus

The results of phosphorus release of the anaerobic sludge are presented in Table 2.3 and Figure 2.5. The initial soluble phosphate was higher than those of the MW/H\(_2\)O\(_2\)-AOP treated
samples. It also showed that there was not much difference between mixing and non-mixing samples.

To examine the decrease in soluble phosphorus from the initial sludge, an anaerobic sludge with a 2% TS was used (Sets 3a, 3b & 3c). After the MW/H₂O₂-AOP, the resulting soluble phosphorus concentrations were 74, 61 and 56.4 mg P/L for Sets 3a, 3b and 3c, respectively. The final pH values were 6.8, 5.1 and 2.9, respectively. These results also showed that orthophosphates in the treated supernatants were less than those of the initial concentrations. It might be that orthophosphate combined either with cations, or with EPS in the sludge to form complex compounds, which were not soluble any more. It could also be the production of polyphosphates, causing a reduction of orthophosphate.

To examine if polyphosphates could have been formed under the MW/H₂O₂-AOP, an experiment (Set 4) was also conducted. A standard solution of 100 mgP L⁻¹ was subjected to the MW/H₂O₂-AOP process: one subset with an acid addition, the other with no acid addition. If polyphosphates were formed in the process, the sulfuric acid could help in breaking any polyphosphates into orthophosphate. After the MW/H₂O₂-AOP treatment, orthophosphate concentrations of both subsets remained the same as the initial, confirming that no polyphosphates was formed in the MW/H₂O₂-AOP process.

The results from both Set 3b and Set 4 clearly showed that it was unlikely that the decrease in soluble phosphate was due to the formation of polyphosphates. Therefore, most likely it was due to the incorporation of phosphorus with divalent cations and EPS to form flocs (Forster and Lewin, 1972). It is also interesting to note that they were found to contain two predominant elements, more than 85%, phosphorus and calcium in the ash extracts (Morgan et. al., 1990). This behavior of anaerobic sludge was further investigated, as seen in Chapter 4.
The orthophosphate results of aerobic sludge are shown in Table 2.4 and Figure 2.6. Orthophosphates increased for all of the treatments. The results were similar to the previous studies (Yin et. al., 2007; Yin et. al., 2008). Orthophosphate concentration is higher in mixed samples compared to those of unmixed. The difference was higher for samples at 2.9% TS when compared to samples at 1.8% and 1.1% TS. At 2.9% TS, soluble phosphate increases of 16% and 14% (based on the initial TP) were observed for the mixed and unmixed sets, respectively. Similarly, at 1.8% TS, 9 and 8% increases were observed for mixed and unmixed sets, respectively. For sludge samples at 1.1% TS, a 10% increase was seen when samples were mixed and a 9% increase when samples were unmixed. The results varied by 1-2% between mixed and unmixed.
2.4.4 Soluble ammonia & nitrate

The results for soluble ammonia and nitrate using anaerobic sludge are presented in Table 2.3 and Figure 2.7 and 2.8. The results between mixed and unmixed samples were not significantly different. A slightly increase of soluble ammonia in the solutions was observed after the MW/H$_2$O$_2$-AOP treatment. For substrates with TS levels of 3.7 and 2.3%, the ammonia concentration was up to 30 mg N L$^{-1}$, more than the initial concentrations; for substrate with 1.6% of TS it remained the same as in the initial concentration. The disintegration of sludge suspended solids, and subsequent oxidation of nitrogenous compounds in the process would release ammonia into the solution. Ammonia could also be converted to form nitrate. It could be ascertained that un-ionized ammonia was volatilized, and some be converted to nitrates during treatment. As a result, overall ammonia concentration remained about the same as that of the initial substrate.
For samples with mixing, the nitrate concentrations of anaerobic sludge after treatment were increased. There were 1.3, 1.7, and 1.3 mg N L⁻¹ for sludge of 3.7, 2.3 and 1.6% TS, respectively. There were 1.2, 1 and 0.97 mg N L⁻¹ for samples without mixing at 3.7, 2.3 and 1.6% TS (Table 2.3 and Figure 2.8). The results showed a slightly higher nitrate concentration in the mixed than the unmixed samples. Mixing favored nitrate formation in the process. It could be speculated that a small amount of ammonia was converted into nitrate during the treatment, but also a majority of the ammonia might have escaped into air.

Figure 2.7 - Soluble ammonia in anaerobic sludge after treatment
Figure 2.8 - Soluble nitrate in anaerobic sludge after treatment

The soluble ammonia results of aerobic sludge (Table 2.4 and Fig. 2.9) looked similar to soluble phosphate results in that with a higher percentage increase in the case of 2.9% TS. At 2.9% TS, percentage increases of 1.7 and 1.5 were seen in mixed and unmixed samples, respectively. At 1.8% TS, percentage increases were about 0.76% and 0.66% for mixed and unmixed sets, respectively. Similarly, at 1.1% TS, 0.98 and 0.78% increases were seen for mixed and unmixed samples. The difference between mixed and unmixed samples was from 0.1% to 0.2%. As reported previously that there was, in general, not a significant increase of soluble ammonia in the MW/H₂O₂-AOP (Yin et al. 2008).
Table 2.5 - Results for the paired t-test analysis using aerobic sludge

<table>
<thead>
<tr>
<th>Factors</th>
<th>TS (%)</th>
<th>P value (paired t-test)</th>
<th>Mixed vs. unmixed significant?*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soluble COD</td>
<td>2.9</td>
<td>0.0219</td>
<td>yes</td>
</tr>
<tr>
<td></td>
<td>1.8</td>
<td>0.0032</td>
<td>yes</td>
</tr>
<tr>
<td>Soluble Phosphate</td>
<td>2.9</td>
<td>0.0047</td>
<td>yes</td>
</tr>
<tr>
<td></td>
<td>1.8</td>
<td>0.0521</td>
<td>no</td>
</tr>
<tr>
<td>Soluble Ammonia</td>
<td>2.9</td>
<td>0.0082</td>
<td>yes</td>
</tr>
<tr>
<td></td>
<td>1.8</td>
<td>0.3949</td>
<td>no</td>
</tr>
</tbody>
</table>

* At 95% significant level.
It was observed that there was a visible difference between the means of mixed and unmixed samples that were analyzed for soluble COD, ammonia, orthophosphate and VFA, but it wasn’t evident if this difference was significant enough to consider mixing a factor enhancing solubilization of nutrients in sludge. Paired $t$-tests were therefore conducted to find out if there is a significant difference between the means of two different groups.

Comparison was done with respect to soluble COD, orthophosphate and ammonia. It was observed that the difference between mixed and unmixed samples was more pronounced at a high solids concentration; therefore, the test was performed for 2.9% and 1.8% TS only.

When the results were analyzed using the Graphpad Prism® (Motulsky, 1999), it was observed that at a high solid concentration (2.9% TS) the means of mixed and unmixed samples were significantly different for all the parameters analyzed but in case of 1.8% TS, only soluble COD showed means with significant difference. The results are listed in Table 2.5.

On this basis (using a 95% significance level), it was proved that at a high solids concentration mixing plays a significant role in solubilization of nutrients using the MW/H$_2$O$_2$-AOP but this couldn’t be said to be true at a lower solid concentration. In Chapter 3, mixing was ranked among other important factors in the MW/H$_2$O$_2$-AOP.

2.5 Conclusion

The results indicated that the mixing during the MW/H$_2$O$_2$-AOP affected solids disintegration and nutrient solubilization of sewage sludge. Higher yields, in terms of SCOD, orthophosphate and ammonia, were obtained in the cases of samples with mixing than those without mixing. The extent of the difference was dependent upon the solids concentration of the sludge. The effects of mixing were more pronounced on the sludge samples with higher solids content.

At TS of 2.9%, the difference between mixing and non-mixing was significant for all the parameters, but at a lower solids concentration, only soluble COD showed a significant difference between mixing and non-mixing.
2.6 References


3.0 FACTORS AFFECTING MICROWAVE ENHANCED ADVANCED OXIDATION PROCESS FOR SEWAGE SLUDGE TREATMENT

3.1 Abstract

The microwave enhanced advanced oxidation process was applied to sewage sludge for solubilization of nutrients and solids disintegration. Four factors, temperature, hydrogen peroxide dosage, mixing, and solids concentration were chosen for a screening experiment. These factors were ranked according to their significance for affecting the process. In general, microwave heating temperature and hydrogen peroxide dosage are the two key factors affecting the process, while mixing is the least significant factor. Microwave temperature was the most significant factor for the release of orthophosphate, while hydrogen peroxide dosage played the prime role in ammonia release. Solids disintegration, in terms of soluble chemical oxygen demand, was largely dependent on the microwave temperature and hydrogen peroxide dosage. In volatile fatty acids (VFA) release, mixing was the most significant factor. For samples heated at higher temperatures with mixing, more VFA was released into the headspace, resulting in less VFA concentration retained in the solution. In this study, the best results, in terms of yield of soluble carbonaceous matters and nutrient release, were obtained at 120 °C, and the dosages of 0.75 and 1.0 mL of hydrogen peroxide per one percent of total solids in 30 mL of sludge sample.

3.2 Introduction

The primary factors affecting the MW/H₂O₂-AOP are the microwave heating temperature, hydrogen peroxide dosage and sulfuric acid addition (Liao et. al., 2005; Wong et. al., 2006). Orthophosphate release is dependent on the thermal decomposition of microbial cells, thus, microwave temperature is the most important factor in case of orthophosphate release. However, the release of nitrogen in the form of ammonia is dependent on the breaking down and oxidation of proteins in the sewage sludge, and hydrogen peroxide dosage is the most significant factor. Also, acid addition helped to retain ammonia in the solution. The concentration of soluble chemical oxygen demand (SCOD) is greatly affected by both

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2 A version of this chapter has been submitted for publication. Kenge, A. A.; Liao, P. H.; and Lo, K. V. (2008) Factors affecting microwave enhanced advanced oxidation process for sewage sludge treatment.
microwave heating temperature and hydrogen peroxide dosage (Wong et. al., 2007). The effect of mixing on the treatment efficiency was not examined in those studies (Liao et. al., 2005; Liao et. al., 2005; Wong et. al., 2006; Wong et. al., 2007). In a subsequent study, wherein the role of mixing in solubilization and destruction of sewage sludge using the MW/H_{2}O_{2}-AOP was explored; mixing was found to be a factor on the treatment efficient but largely dependent on the solids concentration (Kenje et. al., 2008).

Though it was known that mixing enhanced the treatment in terms of yield, it was not certain if the role played by mixing was as significant as the other factors such as microwave temperature, hydrogen peroxide dosage and sulfuric acid addition. Thus, a factor screening test was designed using the computer statistical software (JMP-IN® 5.1) (Sall et. al., 2005). Using this program, the factors influencing the MW/H_{2}O_{2}-AOP could be ranked in the order of their significance. The factors chosen in this study were microwave temperature, hydrogen peroxide dosage, mixing and solids concentration. The aim of this study was to define the ranking of these factors, and to find near optimal conditions for the treatment of sewage sludge.

### 3.3 Materials & Methods

#### 3.3.1 Feed substrate

Secondary aerobic sludge was obtained during the course of the study from a wastewater treatment pilot-plant located at the University of British Columbia, Vancouver, British Columbia, Canada. The sludge had an initial concentration of 0.7% total solids (TS). For the experiment, it was thickened by centrifuging to obtain a higher concentration of TS.

#### 3.3.2 Experimental design

The factors chosen for optimization of the treatment were microwave temperature, hydrogen peroxide dosage, mixing and solids concentration. The computer statistical software package JMP-IN® 5.1 was used to design the experiments (Sall et. al., 2005). A total of 24 experiments were developed by the program using a custom design (Table 3.1). Three levels of solids concentration (2.8, 2.2 and 1.2%) were used. The characteristics of the sludge are presented in Table 3.2. Sets 1, 2 and 3, were designated for solids concentrations at 2.8, 2.2
and 1.2%, respectively. Each set consists of eight experiments, defined as subsets "a" to "h". Each experiment had three replicates. The heating temperature ranged from 60-120 °C. Hydrogen peroxide dosages were varied from 0 to 100%, where 100% represents approximately 1 mL hydrogen peroxide (30% conc. by wt.) per one percent of TS in 30 mL of sludge solution. The volume and percentage used in each set are listed in Table 3.1. Magnetic stirrers were used to provide mixing to the samples, which need to be mixed during the process. A microwave heating time of 5 minutes, and the ramp time with an increment of 20 °C per minute were chosen based on previous studies (Liao et. al., 2005; Wong et. al., 2006). The sludge was treated at a neutral pH and a sample volume of 30 mL was used.
<table>
<thead>
<tr>
<th>Subset</th>
<th>TS (%)</th>
<th>Operating condition</th>
<th>Temp (°C)</th>
<th>Hydrogen peroxide dosage (mL) (%)</th>
<th>Sample volume (mL) (%)</th>
</tr>
</thead>
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<tr>
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<td>Mixed</td>
<td>60</td>
<td>2.25</td>
<td>75</td>
</tr>
<tr>
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<td>3</td>
<td>100</td>
</tr>
<tr>
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<td>Mixed</td>
<td>80</td>
<td>1.5</td>
<td>50</td>
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<tr>
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<td>Unmixed</td>
<td>80</td>
<td>2.25</td>
<td>75</td>
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<tr>
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<td>100</td>
<td>3</td>
<td>100</td>
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<td>1.5</td>
<td>50</td>
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<td>75</td>
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<tr>
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<td>120</td>
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<td>50</td>
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<tr>
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<td>50</td>
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<tr>
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<td>60</td>
<td>0</td>
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<td>1.2</td>
<td>Unmixed</td>
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<tr>
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<td>100</td>
</tr>
<tr>
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<td>1.13</td>
<td>75</td>
</tr>
<tr>
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<td>Mixed</td>
<td>120</td>
<td>1.13</td>
<td>75</td>
</tr>
<tr>
<td>3h</td>
<td>1.2</td>
<td>Unmixed</td>
<td>120</td>
<td>1.5</td>
<td>100</td>
</tr>
</tbody>
</table>
Table 3.2 - Characteristics of aerobic sludge used in this study

<table>
<thead>
<tr>
<th>Set No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total solids (%)</td>
<td>2.8</td>
<td>2.2</td>
<td>1.2</td>
</tr>
<tr>
<td>pH</td>
<td>6.3</td>
<td>6.3</td>
<td>6.3</td>
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<tr>
<td>TCOD (gL⁻¹)</td>
<td>31.3 ± 0.6</td>
<td>24.8 ± 1.5</td>
<td>13.5 ± 0.2</td>
</tr>
<tr>
<td>SCOD (mgL⁻¹)</td>
<td>113 ± 25.8</td>
<td>84.1 ± 15.7</td>
<td>51 ± 10.6</td>
</tr>
<tr>
<td>TP (mgL⁻¹)</td>
<td>933 ± 43.8</td>
<td>644 ± 89.5</td>
<td>461 ± 38</td>
</tr>
<tr>
<td>PO₄-P (mgL⁻¹)</td>
<td>22.6 ± 1.8</td>
<td>16.6 ± 0.35</td>
<td>2.76 ± 0.26</td>
</tr>
<tr>
<td>TKN (mgL⁻¹)</td>
<td>1512 ± 14.2</td>
<td>1060 ± 176.3</td>
<td>755 ± 65.6</td>
</tr>
<tr>
<td>NH₃-N (mgL⁻¹)</td>
<td>2.2 ± 0.25</td>
<td>0.83 ± 0.1</td>
<td>0.31 ± 0.09</td>
</tr>
<tr>
<td>VFA (mgL⁻¹)</td>
<td>6.3 ± 0.5</td>
<td>5.1 ± 0.3</td>
<td>3.9 ± 0.74</td>
</tr>
</tbody>
</table>

Note: ± represents standard deviation

3.3.3 Data Analysis

The initial sludge characteristics have been adjusted taking into account that addition of hydrogen peroxide would alter the original value and the dilution factor would differ depending up on the amount of peroxide added. The results have been calculated using the adjusted values. The percentage increases for orthophosphate, ammonia and SCOD were calculated as the ratio of increase in orthophosphate, ammonia and SCOD from the initial samples on the basis of TP and TKN and TCOD respectively.

A Pareto plot, i.e., an ordered histogram, which arranges data values from the most important to least important, was used to evaluate the data and explain the importance of mixing along with the other factors. The plot shows a bar chart displaying the magnitude of the categories with a line graph representing a cumulative magnitude of those categories (Figures 3.1 to 3.4). The importance of a factor might vary according to the type of nutrient.
3.4 Results & Discussion

The results of nutrient release from sewage sludge, in terms of orthophosphate and ammonia, are presented in Table 3.3. In a previous study, it was found that the most important factor affecting orthophosphate release was temperature, and both temperature and hydrogen peroxide dosage were important for ammonia release (Wong et al., 2007). The overall effect of mixing on the MW/H$_2$O$_2$-AOP process was of interest in this study.

3.4.1 Orthophosphate

From the tabulated results (Table 3.3), it is evident that the highest percentage increase in orthophosphate concentration occurred at 120 °C, irrespective of the hydrogen peroxide dosage or solids concentration. The lowest percentage increase was obtained at low temperatures (60 and 80 °C) with no hydrogen peroxide added. For sets 1g and 1h (120 °C and also no H$_2$O$_2$), there was a 25.6 and 19.9% increase for mixed and unmixed conditions, respectively. This indicated that the treatment here was a thermal decomposition and not an oxidation process. The orthophosphate release was due to microorganism cell break-up. Operating the MW/H$_2$O$_2$-AOP at a higher temperature had an advantage of achieving more orthophosphate release. It also showed that mixing had a positive effect on the release of orthophosphate as shown in sets 1g and 1h. The results also confirmed that higher orthophosphate concentrations were obtained in samples with mixing than those without mixing in the previous study (Kenge et al., 2008).

Hydrogen peroxide dosage was also an important factor in the solubilization of orthophosphate, particularly at a low temperature. The percentage increase in orthophosphate concentration was quite low at either 0 or 50% of H$_2$O$_2$ dosage, while no significant difference was seen between results obtained from 75 and 100% H$_2$O$_2$ dosage per 1%TS in sludge sample. In sets 2g and 2h, under identical conditions, a higher orthophosphate solubilization was achieved with mixing than without mixing. The results showed that temperature, hydrogen peroxide dosage and mixing all play some roles to release orthophosphate. A Pareto plot, as seen in Figure 3.1, could further explain the significance of factors in solubilization of orthophosphate, starting from the most significant to the least. Temperature is the most dominating factor influencing orthophosphate release, followed by H$_2$O$_2$ dosage and finally mixing.
Solids concentration, within the range tested, displayed little influence on the release of orthophosphate in the solution. To better represent the effects of temperature and peroxide dosage on the treatment, bar charts were plotted (Figures 3.5 to 3.10) by separating each set on the basis of the operating condition (mixed or unmixed) and solids concentration. Clearly, temperature was the most deciding factor in the case of orthophosphate release.
<table>
<thead>
<tr>
<th>Subset</th>
<th>SCOD (mgL⁻¹)</th>
<th>SCOD increase (%)</th>
<th>TCOD (gL⁻¹)</th>
<th>PO₄-P (mgL⁻¹)</th>
<th>PO₄-P increase (%)</th>
<th>NH₃-N (mgL⁻¹)</th>
<th>NH₃-N increase (%)</th>
<th>VFA (mgL⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>2403 ± 635</td>
<td>7.9</td>
<td>28.5 ± 3.1</td>
<td>188 ± 30.4</td>
<td>19.2</td>
<td>11.1 ± 2.2</td>
<td>0.65</td>
<td>62 ± 19.5</td>
</tr>
<tr>
<td>1b</td>
<td>3041 ± 495</td>
<td>10.3</td>
<td>28 ± 4</td>
<td>187 ± 13</td>
<td>19.6</td>
<td>14.2 ± 3.7</td>
<td>0.9</td>
<td>52.3 ± 11.9</td>
</tr>
<tr>
<td>1c</td>
<td>3023 ± 384</td>
<td>9.8</td>
<td>27.8 ± 2.5</td>
<td>75 ± 3.9</td>
<td>6</td>
<td>15.2 ± 1.1</td>
<td>0.91</td>
<td>64.4 ± 9.7</td>
</tr>
<tr>
<td>1d</td>
<td>4425 ± 533</td>
<td>14.8</td>
<td>27 ± 3.2</td>
<td>112.3 ± 8.7</td>
<td>10.5</td>
<td>25 ± 2.7</td>
<td>1.6</td>
<td>113 ± 8.6</td>
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<td>6412 ± 1411</td>
<td>22.1</td>
<td>26.3 ± 5.1</td>
<td>126 ± 12</td>
<td>12.4</td>
<td>34.8 ± 5</td>
<td>2.4</td>
<td>135 ± 30.9</td>
</tr>
<tr>
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<td>4940 ± 384</td>
<td>16</td>
<td>26.7 ± 4</td>
<td>117.7 ± 9.3</td>
<td>10.9</td>
<td>26.5 ± 3.6</td>
<td>1.7</td>
<td>120.3 ± 11.5</td>
</tr>
<tr>
<td>1g</td>
<td>3158 ± 573</td>
<td>9.7</td>
<td>26.4 ± 3.8</td>
<td>208.7 ± 14.5</td>
<td>19.9</td>
<td>11.8 ± 1.7</td>
<td>0.63</td>
<td>64.9 ± 12.7</td>
</tr>
<tr>
<td>1h</td>
<td>3421 ± 353</td>
<td>10.6</td>
<td>26.6 ± 1.5</td>
<td>261.7 ± 24.2</td>
<td>25.6</td>
<td>13.4 ± 0.7</td>
<td>0.74</td>
<td>75 ± 14.9</td>
</tr>
<tr>
<td>2a</td>
<td>2961 ± 589</td>
<td>12.6</td>
<td>21.7 ± 4.7</td>
<td>95.2 ± 19.9</td>
<td>13.5</td>
<td>10.2 ± 5.1</td>
<td>1</td>
<td>23.8 ± 12.9</td>
</tr>
<tr>
<td>2b</td>
<td>801 ± 187.6</td>
<td>2.9</td>
<td>20.1 ± 5.8</td>
<td>60.6 ± 11.4</td>
<td>6.8</td>
<td>5.3 ± 1.5</td>
<td>0.4</td>
<td>5.8 ± 2.4</td>
</tr>
<tr>
<td>2c</td>
<td>3184 ± 359</td>
<td>13.3</td>
<td>19.8 ± 2.9</td>
<td>73.8 ± 10.3</td>
<td>9.6</td>
<td>13.3 ± 3</td>
<td>1.3</td>
<td>30.4 ± 13.4</td>
</tr>
<tr>
<td>2d</td>
<td>3468 ± 450</td>
<td>14.8</td>
<td>20.3 ± 1.1</td>
<td>72.4 ± 4.7</td>
<td>9.6</td>
<td>16.9 ± 2</td>
<td>1.7</td>
<td>37.7 ± 8</td>
</tr>
<tr>
<td>2e</td>
<td>2011 ± 451</td>
<td>7.8</td>
<td>19.4 ± 2</td>
<td>103.1 ± 10.9</td>
<td>13.4</td>
<td>4.9 ± 0.3</td>
<td>0.4</td>
<td>12.5 ± 0.23</td>
</tr>
<tr>
<td>2f</td>
<td>4826 ± 753</td>
<td>20.4</td>
<td>20 ± 2</td>
<td>206.8 ± 7.8</td>
<td>31.6</td>
<td>35.9 ± 12.4</td>
<td>3.5</td>
<td>12.4 ± 1.4</td>
</tr>
<tr>
<td>2g</td>
<td>4118 ± 90</td>
<td>17</td>
<td>19.8 ± 0.8</td>
<td>213.3 ± 12.3</td>
<td>32</td>
<td>19.4 ± 3.4</td>
<td>1.8</td>
<td>82.2 ± 26.9</td>
</tr>
<tr>
<td>2h</td>
<td>3168 ± 541</td>
<td>13</td>
<td>19.7 ± 1.1</td>
<td>197 ± 22.6</td>
<td>29.3</td>
<td>10 ± 2.1</td>
<td>0.9</td>
<td>44.7 ± 7.5</td>
</tr>
<tr>
<td>3a</td>
<td>1467 ± 470</td>
<td>10.7</td>
<td>11.9 ± 1.6</td>
<td>48.5 ± 5.7</td>
<td>10.2</td>
<td>3.2 ± 0.3</td>
<td>0.4</td>
<td>46.3 ± 8.6</td>
</tr>
<tr>
<td>3b</td>
<td>1097 ± 390</td>
<td>7.7</td>
<td>12.3 ± 0.2</td>
<td>40.9 ± 2.9</td>
<td>8.3</td>
<td>2 ± 0.3</td>
<td>0.2</td>
<td>25.3 ± 5</td>
</tr>
<tr>
<td>3c</td>
<td>1673 ± 117</td>
<td>12</td>
<td>12.4 ± 0.4</td>
<td>45.2 ± 4.2</td>
<td>9.2</td>
<td>2.2 ± 0.1</td>
<td>0.25</td>
<td>8.4 ± 3.2</td>
</tr>
<tr>
<td>3d</td>
<td>1986 ± 336</td>
<td>14.7</td>
<td>10.5 ± 3</td>
<td>60.5 ± 12.1</td>
<td>12.8</td>
<td>7.7 ± 3.1</td>
<td>1</td>
<td>8.3 ± 3</td>
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<tr>
<td>3e</td>
<td>2653 ± 264</td>
<td>20.3</td>
<td>10.8 ± 2.6</td>
<td>72 ± 11.8</td>
<td>15.8</td>
<td>10.4 ± 2.5</td>
<td>1.4</td>
<td>25.7 ± 5.4</td>
</tr>
<tr>
<td>3f</td>
<td>2653 ± 359</td>
<td>20</td>
<td>10.6 ± 1.2</td>
<td>56.7 ± 2.5</td>
<td>12.2</td>
<td>8.5 ± 1.8</td>
<td>1.1</td>
<td>25.7 ± 5.4</td>
</tr>
<tr>
<td>3g</td>
<td>4172 ± 511</td>
<td>31.7</td>
<td>10.4 ± 1.3</td>
<td>118.3 ± 1.7</td>
<td>26</td>
<td>23.2 ± 7.1</td>
<td>3.2</td>
<td>56.8 ± 6</td>
</tr>
<tr>
<td>3h</td>
<td>4345 ± 178</td>
<td>33.6</td>
<td>11.5 ± 1.9</td>
<td>127.8 ± 2.2</td>
<td>28.6</td>
<td>30.5 ± 1.7</td>
<td>4.2</td>
<td>79.4 ± 4.7</td>
</tr>
</tbody>
</table>

Note: ± represents standard deviation; Initial values adjusted for each subset using respective dilution factor.
Figure 3.1 - Pareto plot showing the important operating parameters in orthophosphate solubilization

### 3.4.2 Soluble ammonia

From the results, hydrogen peroxide played an important role in solubilization of ammonia (Table 3.3). The least percentage increase was observed when no peroxide was added. A higher H$_2$O$_2$ dosage gave a higher percentage increase of ammonia. As shown in sets 1e and 1f, 2.4 and 1.7 % increase was obtained at H$_2$O$_2$ dosage of 3 and 1.5 mL (100 and 50%), respectively. Mixing was not a significant factor in solubilization of ammonia. In set 1, at 120 °C, even in the absence of H$_2$O$_2$ (sets 1g and 1h), the percentage increase was comparable to the one obtained at 60 °C in the presence of hydrogen peroxide (sets 1a and 1b). Thus, it is noted that temperature was also an important factor in releasing ammonia in the MW/H$_2$O$_2$-AOP process.

In sets 2g and 2h at 120 °C, where 1.25 mL of H$_2$O$_2$ (50%) was added under unmixed and mixed conditions gave a 1.8 and 0.9 % increase, respectively. Mixing actually decreased the percentage increase in this case. It could have been possible that at a high temperature, mixing facilitated the vaporization of ammonia.

In Figure 3.2, a Pareto plot was used to rank the significance of the factors affecting the solubilization of ammonia by the MW/H$_2$O$_2$-AOP, starting from the most significant to the least. Hydrogen peroxide is the most significant factor in solubilization of ammonia from sewage sludge, followed by heating temperature. Optimum results were obtained at 120 °C with a 75% H$_2$O$_2$ dosage per 1% of TS in 30ml sample. Mixing did not enhance the treatment in this. Also, total solids concentration did not affect the solubilization of ammonia.
Figures 3.5 - 3.10, represent the effects of temperature and peroxide dosage on the treatment, bar charts were plotted by separating each set on the basis of the operating condition (mixed or unmixed) and solids concentration. The results reiterate the importance of hydrogen peroxide dosage and microwave heating temperature in the solubilization of ammonia from sewage sludge.

The results clearly re-confirm that temperature and hydrogen peroxide dosage are most important factors affecting nutrient release from sludge (Wong et. al., 2007). The results also indicated that while mixing did affect nutrient release, but was not a dominant factor.

![Figure 3.2 - Pareto plot showing the important operating parameters in ammonia solubilization](image)

### 3.4.3 Volatile Fatty Acids and Soluble COD

The disintegration of sludge solids can be expressed, in terms of SCOD and VFA. The MW/H₂O₂-AOP occurs in two reaction processes: 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 (Liao et. al., 2007). The resulting oxidation products can be in the form of proteins, amino acids, ammonia, VFA and/or CO₂ depending on the reaction conditions. The resulting concentrations of VFA and SCOD are the key parameters measuring the efficacy of the process.

The Pareto plot in Figure 3.3 shows the factors that affected the VFA solubilization, starting from the most significant to the least. Mixing was the most significant factor affecting the
VFAsolubilization. The effect was more pronounced at a higher microwave operating temperature. As shown in Table 3.3, sets 2g and 2h, there were 82.2 and 44.7 mg L\(^{-1}\) of VFA for unmixed and mixed conditions, respectively. Mixing caused a decrease in the yield at 120 °C. This might be due to the vaporization of VFA produced under the mixed condition at a higher operating temperature. Hydrogen peroxide also played very important role for the release of VFA. Figures 3.5 - 3.10, represent the effects of temperature and peroxide dosage on the treatment; bar charts were plotted by separating each set on the basis of the operating conditions (mixed or unmixed) and solids concentration. However, it was difficult to ascertain the trend of VFA release. The results imply that higher VFA concentrations will be obtained at high hydrogen peroxide dosages, and high TS concentrations without mixing in the MW/H\(_2\)O\(_2\)-AOP process.

The results for soluble COD are also tabulated in Table 3.3. Mixing was the least significant factor for SCOD. It was demonstrated in sets 1g and 1h, 10.6% and 9.7% increase in SCOD were observed under mixed and unmixed conditions, respectively. In sets 2g and 2h, 17 and 13 % increase were observed for respective unmixed and mixed conditions.

Temperature and hydrogen peroxides are important factors influencing sludge disintegration. In sets 1e and 1f, at 100 °C under unmixed conditions, a 22.1% increase in SCOD was observed at a H\(_2\)O\(_2\) dosage of 3 mL, while a 16% increase was observed at a H\(_2\)O\(_2\) dosage of 1.5 mL. Also in sets 1 c and 1d, at 80 °C, a 9.8% increase was obtained under mixed conditions and 1.5 ml of H\(_2\)O\(_2\), while a 14.8% increase was obtained under unmixed conditions and 2.25 mL of H\(_2\)O\(_2\). Similar results were obtained in a pair set of 3c and 3d. The least percentage increase was observed at 60 °C and no peroxide (set 2b). The best SCOD yields were obtained at 120 °C. This was also validated in a Pareto plot (Figure 3.4).

Microwave heating temperature was the most significant factor: low temperature (60 °C) gave the lowest percentage while a highest increase in soluble COD was obtained at 120 °C. Secondly, hydrogen peroxide dosage was also a significant factor influencing the process. The best SCOD yield was at 0.75 mL per 1% of TS in 30mL of sample. The results point out that the MW/H\(_2\)O\(_2\)-AOP process should be operated at a high temperature and a high hydrogen peroxide dosage for the best yield of SCOD.
### Figure 3.3 - Pareto plot showing the important operating parameters in VFA solubilization

<table>
<thead>
<tr>
<th>Term</th>
<th>t Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp(60,120) &amp; RS</td>
<td>2.69</td>
</tr>
<tr>
<td>Solid(1.2,2.8) &amp; RS</td>
<td>2.62</td>
</tr>
<tr>
<td>Peroxide(0.3) &amp; RS</td>
<td>2.04</td>
</tr>
<tr>
<td>Temp*Peroxide</td>
<td>1.31</td>
</tr>
<tr>
<td>Mixing(0.1) &amp; RS</td>
<td>1.18</td>
</tr>
<tr>
<td>Mixing*Peroxide</td>
<td>-0.67</td>
</tr>
<tr>
<td>Mixing*Temp</td>
<td>-0.44</td>
</tr>
</tbody>
</table>

### Figure 3.4 - Pareto plot showing the important operating parameters in COD solubilization

<table>
<thead>
<tr>
<th>Term</th>
<th>t Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp(60,120) &amp; RS</td>
<td>8.50</td>
</tr>
<tr>
<td>Peroxide(0.3) &amp; RS</td>
<td>8.45</td>
</tr>
<tr>
<td>Mixing(0.1) &amp; RS</td>
<td>3.28</td>
</tr>
<tr>
<td>Solid(1.2,2.8) &amp; RS</td>
<td>2.64</td>
</tr>
<tr>
<td>Temp*Peroxide</td>
<td>1.76</td>
</tr>
<tr>
<td>Mixing*Peroxide</td>
<td>0.99</td>
</tr>
<tr>
<td>Mixing*Temp</td>
<td>-0.30</td>
</tr>
</tbody>
</table>
Figure 3.5 - Concentrations of nutrients at 2.8% TS for non-mixed samples

Figure 3.6 - Concentrations of nutrients at 2.8% TS for mixed samples
Figure 3.7 - Concentrations of nutrients at 2.2% TS for non-mixed samples

Figure 3.8 - Concentrations of nutrients at 2.2% TS for mixed samples
Figure 3.9 - Concentrations of nutrients at 1.2% TS for non-mixed samples

Figure 3.10 - Concentrations of nutrients at 1.2% TS for mixed samples
3.5 Conclusion

Using the statistical software JMP-INE® 5.1, it was possible to screen the factors microwave temperature, hydrogen peroxide dosage, mixing and solid concentration and rank them according to their order of significance in the MW/H₂O₂-AOP. Microwave operating temperature and hydrogen peroxide dosage are, in general, two key factors affecting the process, while mixing is the least significant factor.

For orthophosphate, temperature was found to be the most significant factor. The highest percentage increase was observed at 120 °C. Secondly, hydrogen peroxide dosage was an important factor too, Mixing helped in enhancing the release of orthophosphate. However, it was less prominent in comparison to temperature and peroxide dosage.

In the case of ammonia, hydrogen peroxide dosage was the most dominating factor in controlling the solubilization. The second prominent factor was microwave heating temperature. At a high temperature, mixing actually would have an adverse effect on the release of ammonia into the solution.

As for VFA solubilization, starting from the most to the least significant, mixing, hydrogen peroxide dosage, solids concentration and microwave operating temperature were the important factors. Better results were obtained at a high hydrogen peroxide dosage and a high concentration of TS without mixing. Mixing prominently decreased the efficiency of the treatment at a high temperature.

SCOD release seemed to be largely dependent on the microwave temperature and hydrogen peroxide dosage. The optimum results were obtained at 120 °C and H₂O₂ dosage of 0.75 mL per 1% of TS in 30 mL. For the purpose of the sludge disintegration, a higher microwave heating temperature is recommended for the MW/H₂O₂-AOP.
3.6 References


4.0 SOLUBILIZATION OF MUNICIPAL ANAEROBIC SLUDGE USING MICROWAVE ENHANCED ADVANCED OXIDATION PROCESS

4.1 Abstract
The microwave enhanced advanced oxidation process on the release of nutrients and solids disintegration from municipal anaerobic sludge was investigated. Three levels of temperature (160, 120, and 80 °C) and two sets of pH, (7.8 and 4) were selected and tested at a microwave heating time of 5 minutes and hydrogen peroxide dosage of approximately 1 mL per 1% total solids. pH was the most dominating factor facilitating the release of nutrients. At pH 4, an increase in heating temperature resulted in increased solubilization and nutrients release. At 160 °C and pH 4, the increase over the initial sludge for increase SCOD, orthophosphate and soluble ammonia, was observed to be 190, 527 and 56 %, respectively. However, at pH 7.8, it decreased by almost 50% from the initial sludge sample. The microwave enhanced advanced oxidation process was an effective means for release of nutrient and solids disintegration from anaerobic sludge. Acid addition helped in the destruction of sludge solids. Low pH and high temperature gave the highest nutrient release and solids destruction.

4.2 Introduction
Using the MW/H₂O₂-AOP, a significant portion of total phosphorus could be released from the aerobic sludge into the solution with a microwave heating time of only 5 minutes. However, when anaerobic sludge was subjected to the process at 80 °C for 5 minutes at pH 6.5, it showed either a decrease or no significant change in orthophosphate and ammonia from the initial substrate (Kenge et. al., 2008). This suggested that the effective treatment conditions for anaerobic sludge might be very different to those for aerobic sludge.

Anaerobic sludge is a rich source of nutrients including phosphorus and nitrogen, and carbonaceous matters (Korsak and Moreno, 2006). Although it contains a high percentage of soluble nutrients in comparison with aerobic sludge, most of the nutrients are bound to solids, in non-soluble forms. The aim of this study was to investigate the potential of applying the

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³ A version of this chapter will be submitted for publication. Kenge, A. A.; Liao, P. H.; and Lo, K. V. Solubilization of municipal anaerobic sludge using microwave enhanced advanced oxidation process.
MW/H₂O₂-AOP on anaerobic sludge in order to release more nutrients into the solution. High levels of long chain fatty acids, proteins and solids in the anaerobic sludge make the degradation more difficult (Korsak and Moreno, 2006). In a previous study, a decrease or no significant change of nutrients in the MW/H₂O₂-AOP treated solutions was observed at 80 °C (Kenge et al., 2008). In this study, therefore, the process was operated at a range of higher temperatures. It was thought that operating the process at higher microwave heating temperatures would facilitate the breakdown of anaerobic sludge. Previous work has proved that acid addition enhances nutrient release from aerobic sludge, thus, acidified sludge was also studied (Liao et al., 2005).

The objective of this study therefore, was to examine the effects of heating temperature and acid addition on the disintegration of municipal anaerobic sludge and the release of nutrients using the MW/H₂O₂-AOP.

4.3 Materials & Methods

4.3.1 Experimental design

The anaerobic sludge used in this experiment was obtained from the Lulu Island Wastewater Treatment Plant, Richmond, British Columbia, Canada. The initial concentration of the sludge used in this experiments, a dilution factor of 0.923 is applied due to an addition of 2.5 mL of hydrogen peroxide into 30ml of the sample (Table 4.1).

Two levels of pH (7.8 and 4), three levels of temperature (80, 120, and 160 °C) were selected. The samples were mixed using magnetic stirrers in the vessels during the process. In a previous experiment, adequate mixing was not achieved for anaerobic sludge samples with 3.7% TS, therefore, in this study, anaerobic sludge was diluted using distilled water from 3.7 to 2.2% TS, and a hydrogen peroxide dosage of 2.5 mL was used for each sample (Kenge et al., 2008). The pH 4 condition was obtained by adding drops of sulfuric acid (30% conc.) to the sludge sample. Each sample with three replicates, consisted of a sludge volume of 30 mL with 2.5 mL of H₂O₂ (30% conc. by wt.), was treated at designated temperature (80, 120 and 160 °C). The ramp time for the microwave treatment was constant at 20 °C per minute up to the desired temperature, and the samples were heated at the set temperatures for a constant 5 minutes for all experiments.
Table 4.1 - Initial sludge parameters

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Anaerobic sludge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total solids (%)</td>
<td>2 ± 0.03</td>
</tr>
<tr>
<td>pH</td>
<td>7.8</td>
</tr>
<tr>
<td>TCOD (gL⁻¹)</td>
<td>27.5 ± 1.4</td>
</tr>
<tr>
<td>SCOD (mgL⁻¹)</td>
<td>3700 ± 140</td>
</tr>
<tr>
<td>TP (mgL⁻¹)</td>
<td>578 ± 58</td>
</tr>
<tr>
<td>PO₄-P (mgL⁻¹)</td>
<td>44 ± 0.8</td>
</tr>
<tr>
<td>TKN (mgL⁻¹)</td>
<td>1490 ± 53</td>
</tr>
<tr>
<td>NH₃-N (mgL⁻¹)</td>
<td>327 ± 4</td>
</tr>
<tr>
<td>NO₃ (mgL⁻¹)</td>
<td>0.16 ± 0.1</td>
</tr>
</tbody>
</table>

Note: ± represents standard deviation; All the values have been adjusted using a dilution factor of 0.923

4.4 Results & Discussion

Due to poor yields of soluble nitrogen and phosphorus at the MW/H₂O₂-AOP in alkaline conditions in our previous trials, this study was focused only for sludge and acidified sludge. Takashima and Tanaka also reported that using thermal-oxidative treatment of anaerobic sewage sludge, the overall performance was superior at an acid condition among various conditions examined (Takashima and Tanaka, 2008). Therefore, the process was conducted under relative high temperatures (160, 120, and 80°C), and low pH (4 and 7.8) in this study.

4.4.1 Disintegration of sludge solids

The effectiveness of solids disintegration of anaerobic sludge was represented as SCOD. Data on TCOD and SCOD provide insight on solids solubilization. At pH 7.8, all TCOD concentrations remained more or less the same at 26 g L⁻¹, regardless of heating temperatures. At pH 4, all TCOD values decreased after the MW/H₂O₂-AOP treatments; it was more pronounced at a higher operating temperature. A significant loss of TCOD (10-17% of initial TCOD) was observed at acid condition. The TCOD decreased from approximately 27.5 g L⁻¹ to 22.8 g L⁻¹ (16.4%) at pH 4 and 160 °C. The results were also
similar to the thermal-oxidative treatment of anaerobic sludge at 170°C (Takashima and Tanaka, 2008). A considerable amount of TCOD was lost in various oxidants and different dosages in acidic conditions. The highest TCOD loss of 28% was obtained for using an oxidant H₂O₂ at dosage of 2 grams per gram of VS and pH at 4.7. With a lower dosage of hydrogen peroxide (0.5 g per g of VS) and at a higher pH of 6.2, a slightly decrease of TCOD was observed. There were no reports on the use of either hydrogen peroxide or ozone in the alkaline conditions. In the presence of acid in the reacting samples, further oxidation and gasification is promoted in the reaction, thus more carbon dioxide is produced, which will escape in the gas phase, resulting in a decrease of TCOD in the solution. Also, in the absence of any acid, the TCOD will be more likely retained in the solution (Takashima and Tanaka, 2008; Liao et al., 2007).

For using sludge without acid treatment, the TCOD concentrations remained the same as the initial anaerobic sludge over a range of relative high temperatures (120-160 °C), whereas for aerobic sludge, the TCOD would have been drastically reduced, with or without acid adjustment (Liao et al., 2007; Chan et al., 2007). The results obtained from this study and others also suggested that it is, overall, more difficult to disintegrate anaerobic sludge than aerobic sludge (Takashima and Tanaka, 2008).

The SCOD concentrations increased in all sets, regardless of treatment conditions. At 160 °C, and a pH of 4, the SCOD after the MW/H₂O₂-AOP increased by 190% with respect to the initial SCOD. While at a pH of 7.8 and same temperature, the SCOD increase was 80% with respect to the initial SCOD (Figure 4.1). Thus, 1.6 times more SCOD was obtained at pH 4 compared to that at pH 7.8. At 120 °C and a pH value of 4, the SCOD increased by 71% with respect to the initial SCOD; however, at a pH of 7.8 and same temperature, the increase in SCOD was 56%. At 80 °C, the increase of SCOD over the initial at pH of 4 and 7.4 was observed to be 89% and 69%, respectively. The highest increase, in terms of a ratio of SCOD to TCOD, was 39% for operating at 160 °C, and a pH of 4. The results were also very comparable to the acidic thermo-oxidative treatment of anaerobic sludge (Takashima and Tanaka, 2008). A significant increase of SCOD was observed, regardless of oxidants used in their experiments, both ozone and hydrogen peroxide would destroy solids to yield SCOD. The effects of pH on SCOD were not very significant for the thermal-oxidative treatment of
anaerobic sludge. It only affected the TCOD concentration, which was decreased significantly at low pH. It can therefore be concluded that at 160 °C, the low pH condition was most favorable for solubilization of organic materials. The results proved that the MW/H₂O₂-AOP could effectively disintegrate anaerobic sludge under acidic condition.

![Figure 4.1 - Soluble COD concentration before and after the microwave treatment](image)

**Figure 4.1 - Soluble COD concentration before and after the microwave treatment**

### 4.4.2 Nutrient release

As mentioned before, various thermal, chemical and thermo-chemical treatment of waste activated sludge have been used as a stabilization process. This is to reduce the amount of organic solids, and also to enhance the subsequent anaerobic digestion process for biogas production. The characteristics of treated sludge, in terms of dewaterability, settlingability and SCOD, have been well documented (Camacho et. al., 2004; Valo et. al., 2004; Takashima and Tanaka, 2008; Eskicioglu et. al., 2006). There were few reports on the aspect of nutrient release and metals in these processes. This study was to attempt to evaluate
nutrient release from anaerobic sludge using the MW/H₂O₂-AOP process, and to differentiate nutrient release pattern between aerobic and anaerobic sludge.

The results of orthophosphate are showed in Figure 4.2. There was an increase in orthophosphate concentration with an increase in temperature at pH 4, while there was a decrease at pH 7.8. At 160 °C and pH 4, the orthophosphate concentration increased from 44 to 276 mg P L⁻¹, an increase of 527% from the untreated soluble phosphate concentration. At 120 and 80 °C, a 336% and 189% increase in soluble phosphate, respectively, was obtained in samples treated at pH 4.

At pH 7.8 and 80 °C, the soluble phosphate remained the same as the initial untreated samples, while at 160 °C it decreased by almost 50% from the initial. The results confirmed the previous findings that a decrease or no significant change in orthophosphate was observed at 80 °C (Kenge et al., 2008). The decrease in soluble phosphate was not due to the formation of polyphosphates during the process. It was likely that orthophosphate combined with divalent cations and extra cellular polymeric substances (EPS) to form flocs (Forster and Lewin, 1972). It was also thought that it would have destroyed these polymers to release orthophosphate again, when anaerobic sludge was operated at higher temperatures. It was un-expected that orthophosphate decreased with an increase of temperature; higher the temperature, lesser the orthophosphate in the solution. TCOD concentration was more or less the same as the initial. A slightly increase of SCOD was obtained for the process, regardless of microwave operating temperatures. This pointed out that phosphorus was firmly combined with organic matters, which could not be easily broken down by raising an operating temperature. Further study is needed to examine the mechanism and products of the process.

Based on results from our previous studies, orthophosphate release increased with an increase of temperature for aerobic sludge (Liao et al., 2005). An addition of acid was not required. The factors affect the release were temperature and hydrogen dosage. Unlike aerobic sludge, in solubilization of phosphorus from anaerobic sludge using the MW/H₂O₂-AOP, pH seems as the major dominating factor.

At pH 4, soluble ammonia increased by 56, 40.4 and 31.5 %, from the initial, at 160, 120 and 80 °C, respectively (Figure 4.3). While at a pH 7.8, the ammonia concentration of treated
samples was not much different from the initial untreated samples. Similar results were obtained from our previous study (Kenge et al., 2008). It could be anticipated that acid helped retain the ammonia in the solution. While in its absence, high temperatures promoted escape of ammonia as a gas. Thus, the application of high microwave heating temperature on anaerobic sludge for solubilization of nutrients in terms of ammonia was successful only when the sludge was acidified.

The samples were analyzed for nitrates/nitrites (NO$_x$) to examine their relationship with ammonia. The results are presented in Figure 4.4. It was seen that at a pH 4, less NO$_x$ were released into the solution compared to those at pH 7.8. At pH 4, 0.4 mgN L$^{-1}$ NO$_x$ were released at 80 °C, while none was observed at 120 °C. At pH 7.8, the NO$_x$ concentration varied from 0.58 mgN L$^{-1}$ at 80 °C to 0.73 mgN L$^{-1}$ at 120 °C. No data was collected at 160 °C. The results indicated that NO$_x$ formation was more favorable at a higher pH.

Overall, the results displayed that for recovery of nutrients from anaerobic sludge using the MW/H$_2$O$_2$-AOP process, acid addition was a very important factor affecting solids destruction and nutrient solubilization. Particularly for orthophosphate and ammonia, better performance was achieved at a low pH. Also, high temperatures proved to be greatly enhancing the nutrient release incase of orthophosphate, ammonia and SCOD, but only when the substrate was acidified.
Figure 4.2 - Orthophosphate concentration before and after treatment

Figure 4.3 - Soluble ammonia concentration before and after treatment
Figure 4.4 - Soluble NOx concentration before and after treatment

4.5 Conclusion

The results prove that the MW/ H2O2-AOP could be successfully applied for releasing soluble matters like carbon, phosphate and ammonia from anaerobic sludge. The pH adjustment was observed as the most dominating factor facilitating the release. Microwave heating temperature also helps increase the yield, but in the absence of acid, it was not a significant factor, especially for phosphate and ammonia. Thus, it could be said that acid addition helped in the destruction of sludge solids. Low pH and high temperature gave the highest nutrient release. At 160 °C and pH 4, 40% of the total phosphorus was released into the supernatant while ammonia concentration increased by 56% from the initial. However, at 160 °C and pH 7.8, ammonia concentration remained similar to the initial concentration. It could be anticipated that a small amount of ammonia is converted to nitrates/nitrites in the absence of acid while phosphates are getting trapped into the solid portion, as a result, less orthophosphate in the solution.
4.6 References


Takashima, M., and Tanaka, Y. “Comparison of thermo-oxidative treatments for the anaerobic digestion of sewage sludge”. Jounal of Chemical Technology and Biotechnology, 2008, 83: 637-642
5.0 TREATING SOLID DAIRY MANURE BY USING THE MICROWAVE ENHANCED ADVANCED OXIDATION PROCESS

5.1 Abstract

The microwave enhanced advanced oxidation process was used to treat separated solid dairy manure for nutrient release and solids reduction. It was conducted at a microwave temperature of 120 °C for 10 minutes, and a hydrogen peroxide dosage approximately 2mL per 1% TS for a 30 mL sample. Three pH conditions of 3.5, 7.3 and 12 were examined to find the favorable conditions for the nutrient release. The results indicated that substantial quantities of nutrients could be released into the solution at pH of 3.5. However, at neutral and basic conditions only volatile fatty acids and soluble chemical oxygen demand could be released. The analyses on orthophosphate, soluble chemical oxygen demands and volatile fatty acids were verified by repeating similar sets of experiments. It was found that the orthophosphate concentration for untreated samples at a higher %TS was suppressed and lesser than actual. To overcome this difficulty, the initial orthophosphate concentration has been measured at 0.5% TS.

5.2 Introduction

Using MW/H₂O₂-AOP to treat solid dairy manure would be of benefit, if rich sources of nutrients and carbonaceous matters from the dairy manure could be solubilized and recovered for further uses.

The measurement of water extractable phosphorus (WEP) in manure has not been well established. To assess the WEP content in dairy manure, various extraction methods were used (Keleinman et. al., 2002; Chapuis-Lardy et. al., 2003; Gungor and Karthikeyan, 2005; Wolf et. al., 2005). Varying dry matter/distilled water ratio (1 to 20:200) revealed that the greater dilution of manure dry matter increased WEP (Chapuis-Lardy et. al., 2003; Gungor and Karthikeyan, 2005). Using repeated water extraction method, it was reported that there was a sharp initial increase in phosphorus extractability, and up to 70% of total phosphorus was extracted after third extraction out of seven (Gungor and Karthikeyan, 2005). The

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4 A version of this chapter will be submitted for publication. Kenge, A. A.; Liao, P. H.; and Lo, K. V. Treating solid dairy manure by using the microwave enhanced advanced oxidation process.
experiments conducted in this laboratory showed that the same sample under different dilutions gave uncertain orthophosphate results (Pan, MS thesis, 2005). Four sets of manure and distilled water (1:0, 1:1, 1:4 and 1:9) were used to extract orthophosphate from diluted dairy manure. It revealed that a greater dilution of liquid dairy manure increased orthophosphate concentration. It was, however, found that it was due to a positive interference, a higher ratio of liquid/manure gave a higher interference. It was also reported that significant errors in phosphorus analysis by the colorimetric method were observed in soil and plant materials, the resulting values were not accurate (Kowalenko and Babuin, 2007). The manure WEP method was proposed that it should be measured at the solution of 0.5%TS using either inductively coupled plasma (ICP) or colorimetric method (Wolf et. al., 2005). The two methods were highly correlated; the colorimetric procedure was approximately 7% higher than phosphorus measured by ICP. Pan also reported that it had less interference for orthophosphate determination at near 0.5%TS of liquid dairy manure using the colorimetric method (Pan, MS thesis, 2005).

This study was to attempt to find a means of utilization of dairy manure as a source of useful products. The microwave-enhanced advanced oxidation process (MW/H2O2-AOP) has proved that it is an effective means to release nutrient and to disintegrate solid organic matter (Chan et. al., 2007). This study was to use the MW/H2O2-AOP to extract valuable products from dairy manure. The first objective of this preliminary study was to examine the effectiveness of the MW/H2O2-AOP on separated solid dairy manure. The second objective was to verify the results obtained from chemical measurements for dairy manure, particularly for orthophosphate analysis.

5.3 Materials & Methods

5.3.1 Substrate

The solid dairy manure used in this study was obtained from the UBC Dairy Education & Research Centre in Agassiz, British Columbia, Canada. The solid portion of dairy manure obtained after solid-liquid separation was used in this study. Once collected from the farm the manure was stored at 4 °C. The initial total solids (TS) were found to be 33%, which consisted of a lot of fiber and sand. The dairy manure was homogenized first using a blender,
and sand was then removed from the slurry via settling. The final TS of approximately 2% were achieved by adding distilled water.

The concentrations of the dairy manure used in samples were altered by hydrogen peroxide addition. The initial values have been adjusted using a dilution factor, which is calculated as the ratio of dairy manure volume by total sample volume in the vessel during the run. The initial concentrations of the dairy manure used in this part of the study are listed in Table 5.1.

Table 5.1 - Initial characteristics of dairy manure used in part 1

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Solid dairy manure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total solids (%)</td>
<td>1.6 ± 0.09</td>
</tr>
<tr>
<td>pH</td>
<td>7.3 ± 0.6</td>
</tr>
<tr>
<td>TCOD (gL⁻¹)</td>
<td>32.2 ± 3.8</td>
</tr>
<tr>
<td>SCOD (mgL⁻¹)</td>
<td>2272 ± 416</td>
</tr>
<tr>
<td>TP (mgL⁻¹)</td>
<td>84.3 ± 1.8</td>
</tr>
<tr>
<td>PO₄-P (mgL⁻¹)</td>
<td>38.3 ± 4.75</td>
</tr>
<tr>
<td>TKN (mgL⁻¹)</td>
<td>570.2 ± 19.8</td>
</tr>
<tr>
<td>NH₃-N (mgL⁻¹)</td>
<td>92.4 ± 7.6</td>
</tr>
<tr>
<td>NOₓ (mgL⁻¹)</td>
<td>0.15 ± 0.05</td>
</tr>
<tr>
<td>VFA (mgL⁻¹)</td>
<td>4.97 ± 1.8</td>
</tr>
</tbody>
</table>

Note: ± represents standard deviation; Above values have been adjusted using a dilution factor of 0.88

5.3.2 Experimental design

The experiment was divided into two parts. The first part was to examine the effectiveness of the MW/H₂O₂-AOP on separated solid dairy manure. The second part was to evaluate the reliability of orthophosphate analysis, as well as others for dairy manure.

Part 1

The experimental design for this part is shown in Table 5.2. To examine the effect of pH on release of nutrients from dairy manure using the MW/H₂O₂-AOP, three sets of pH of 3.5, 7.3
and 12 were used in this study. The pH was adjusted to 3.5 by adding a few drops of 30% conc. sulfuric acid, while pH 12 was obtained by using 0.25 mL of 1M NaOH. In order to break down the fibers in solid dairy manure, a high microwave temperature and long heating time was required. A microwave temperature of 120 °C and heating time of 10 minutes was chosen based on a pervious study where highest orthophosphate release (85%) was obtained when dairy manure samples were treated at 120 °C for 10 minutes (Pan et. al., 2006). The ramp time, time taken by the microwave system to reach the set temperature, was 5 minutes i.e., 20 °C/ min. Due to the complex nature of the manure, a high hydrogen peroxide dosage of 4 mL for a 30 mL sample volume was used, which was approximately 2 mL per 1% TS for a 30 mL sample. Three replicates were used for each set.

Table 5.2 - Experimental design for part 1

<table>
<thead>
<tr>
<th>Set No.</th>
<th>TS (%)</th>
<th>pH</th>
<th>Temp (°C)</th>
<th>H₂O₂ dosage (mL)</th>
<th>Sample volume (mL)</th>
<th>Heating time (mins)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.6</td>
<td>3.5 ± 0.28</td>
<td>120</td>
<td>4</td>
<td>34</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>1.6</td>
<td>7.3 ± 0.6</td>
<td>120</td>
<td>4</td>
<td>34</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>1.6</td>
<td>12 ± 0.5</td>
<td>120</td>
<td>4</td>
<td>34</td>
<td>10</td>
</tr>
</tbody>
</table>

Note: All experiments run with a ramp time of 20 °C/min.

Part 2

This section is divided in two sub-sections. The first sub-section was dealt with the untreated samples (used to obtain the initial concentrations), while the second sub-section was with microwave treated samples. Though the primary reason to do this investigation was orthophosphate, SCOD and VFA analysis were also verified in some cases.

Several dairy manure samples were generated with different percentage TS to be used in this part of the study. The same samples were also diluted by adding distilled water to obtain 0.5% TS. Since, previous research has proved that the most accurate results could be achieved at 0.5% TS, it was used as a basis for comparison (Chapuis-Lardy et. al., 2003; Pan,
Four sets of TS were used viz., 0.5, 1.6, 3.4 and 6.1% and the analysis were repeated. The samples had an approximate pH of 8. Three replicates were used.

Table 5.3 shows the experimental design for the second section of the part 2. Two sets of TS of 0.5 and 3.4% were used in this part of the study. The samples were treated at 120 °C, which can be able to compare with results from part 1. The samples were also treated at a low temperature (70 °C) to examine if the pattern varied with temperature. This temperature was chosen to avoid any polyphosphates formation in the solution. Polyphosphates are formed at temperatures between 80-100 °C (Pan et. al., 2006; Wong et. al; 2006). All the samples were acidified to an approximate pH of 4 by adding few drops 30% conc. sulfuric acid. The heating time was maintained at 10 minutes, and the ramp time was set as 20 °C/min. The hydrogen peroxide dosage was kept as approximately 2 mL per 1% TS for a 30 mL sample. Set 1 (120 °C) was analyzed for orthophosphate, soluble chemical oxygen demand (SCOD), and volatile fatty acids (VFA), while Set 2 (70 °C) was analyzed only for orthophosphate and SCOD. Three replicates were used for each set.

Table 5.3 - Experimental design for part 2 (microwave treated samples)

<table>
<thead>
<tr>
<th>Set No.</th>
<th>TS (%)</th>
<th>pH</th>
<th>Temp (°C)</th>
<th>H₂O₂ dosage (mL)</th>
<th>Sample volume (mL)</th>
<th>Heating time (mins)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>0.5</td>
<td>4</td>
<td>120</td>
<td>1</td>
<td>31</td>
<td>10</td>
</tr>
<tr>
<td>1b</td>
<td>1.6</td>
<td>3.5</td>
<td>120</td>
<td>4</td>
<td>34</td>
<td>10</td>
</tr>
<tr>
<td>1c</td>
<td>3.4</td>
<td>4</td>
<td>120</td>
<td>6</td>
<td>36</td>
<td>10</td>
</tr>
<tr>
<td>2a</td>
<td>0.5</td>
<td>4</td>
<td>70</td>
<td>1</td>
<td>31</td>
<td>10</td>
</tr>
<tr>
<td>2b</td>
<td>3.4</td>
<td>3.7</td>
<td>70</td>
<td>6</td>
<td>36</td>
<td>10</td>
</tr>
</tbody>
</table>

Note: All experiments run with a ramp time of 20 °C/min

5.4 Results & Discussion

The MW/H₂O₂-AOP has proved very effective for solubilization of a variety of organic slurries, such as sewage sludge, blood meal and fish silage (Chan et. al., 2007; Chan et. al., 2008; Wong et. al., 2007). This study was an attempt to examine how effectiveness of this process to digest separated dairy manure for the release of useful soluble materials. The
results of the nutrient release and solids disintegration from the MW/H₂O₂-AOP are expressed as SCOD, VFA, orthophosphate, soluble ammonia, and NOₓ.

5.4.1 Part 1

Soluble phosphate

The results for orthophosphate are summarized in Table 5.4 and Figure 5.1. The dairy manure samples had a %TS of 1.6 with an initial orthophosphate concentration of 38.3 mgP/L and a total phosphate concentration of 84.3 mgP/L.

At pH 3.5, the soluble phosphate concentration increased to 65.8 mgP/L, an increase of 71.7%. A decrease of 74.7 and 72.9% was observed at pH 7.3 and pH 12, respectively. Thus, it could be clearly seen that acid addition was essential for releasing phosphorus from solid dairy manure. The results were similar to a previous study applying MW/H₂O₂-AOP on liquid dairy manure, wherein, the samples had to be acidified to obtain phosphorus release (Chan et al., 2008). It is interesting to note that treating the sewage sludge, orthophosphate was released irrespective of the pH in the MW/H₂O₂-AOP (Chan et al., 2007). The reason could be that sludge particles are mostly microbial cells and microwave radiation causes cell lysis resulting in release of orthophosphate from the cells into the solution. Whereas solid dairy manure contains a lot of undigested animal feed like straws along with organic matters and lipids. Phosphorus in dairy manure could not be solubilized without H₂SO₄. In fact, the reaction was reversed; it was converted to an insoluble form in the absence of acid as showed in Table 5.4. It might be due to the formation of struvite, or k-struvite (potassium magnesium phosphate) under neutral or basic condition, as a result, orthophosphate was precipitated out of the solution. This was similar to the previous study that less orthophosphate was obtained in the basic solution for dilute dairy manure (Pan, MS thesis, 2005).
Table 5.4 - Summary of results for part 1

<table>
<thead>
<tr>
<th>Set No.</th>
<th>pH</th>
<th>SCOD (gL⁻¹)</th>
<th>SCOD increase (%)</th>
<th>TCOD (gL⁻¹)</th>
<th>PO₄-P (mgL⁻¹)</th>
<th>% increase PO₄-P</th>
<th>NH₃-N (mgL⁻¹)</th>
<th>% increase NH₃-N</th>
<th>NOₓ (mgL⁻¹)</th>
<th>VFA (mgL⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.5</td>
<td>2.8 ± 0.6</td>
<td>22.3</td>
<td>9.8 ± 2.7</td>
<td>65.8 ± 0.98</td>
<td>71.7</td>
<td>208 ± 3.6</td>
<td>125</td>
<td>negligible</td>
<td>391 ± 31.3</td>
</tr>
<tr>
<td>2</td>
<td>7.3</td>
<td>2.75 ± 0.1</td>
<td>21</td>
<td>7.85 ± 1</td>
<td>9.7 ± 0.35</td>
<td>-74.7</td>
<td>89.2 ± 4.4</td>
<td>-3.5</td>
<td>0.6 ± 0.3</td>
<td>48.6 ± 0.91</td>
</tr>
<tr>
<td>3</td>
<td>12</td>
<td>2.5 ± 0.3</td>
<td>7.7</td>
<td>13.3 ± 5.5</td>
<td>10.4 ± 0.29</td>
<td>-72.9</td>
<td>97.1 ± 3.2</td>
<td>5</td>
<td>0.17 ± 0.07</td>
<td>54.1 ± 13.4</td>
</tr>
</tbody>
</table>

Note: - ve indicates a decrease

![Figure 5.1 - Orthophosphate and ammonia release at different pH conditions](image)

**Ammonia and NOₓ**

The results for soluble ammonia are presented in Table 5.4 and Figure 5.1. At TS of 1.6%, the solid dairy manure had an initial soluble ammonia concentration of 92.4mgN/L and a TKN value of 570 mg/L.
Acid addition helps retain ammonia in the solution (Wong et al., 2007). After microwave treatment at pH 3.5, the ammonia concentration had an increased of 125%. The treatment was found ineffective for samples with pH 7.3 and 12. At pH 7.3, it was of a 3.5% decrease of ammonia in the solution, and a mere 5% increase was observed at pH 12. It could be anticipated that in the absence of acid, high microwave temperature promoted volatilization of ammonia. The results indicate the benefit of using acid as a catalyst for the treatment of dairy manure. It released not only more orthophosphate, but also more ammonia in the solution.

The results for soluble NO\textsubscript{x} are presented in Table 5.4. Initially the samples had a NO\textsubscript{x} concentration of 0.15mgN/L. After treatment the acidified samples showed no presence of nitrates and nitrites, while, at pH 7.3, the NO\textsubscript{x} concentration increased to 0.6mgN/L. At pH 12, the NO\textsubscript{x} concentration after treatment remained almost the same as the initial at 0.17mgN/L. Ammonia could have got converted to NO\textsubscript{x} when no acid or base was added to the solid dairy manure samples, thus, showing a high NO\textsubscript{x} level at pH 7.3.

**Volatile fatty acids**

The results for VFA are summarized in Table 5.4 and Figure 5.2. The initial soluble VFA concentration was observed to be very low at 4.97 mg/L. The biodegradable organic matter in dairy manure will be transformed to VFA at high temperatures in the thermal process (Rico et al., 2007). The VFA was present mainly in the form of acetic acid, however, the other volatile fatty acids such as propionic, butyric, valeric, hexanoic and heptanoic were also found along with acetic acid after the treatment.

For pH 3.5, after treatment the VFA concentration increased to 391 mg/L, which was a remarkable increase from the initial value. At pH 7.3 and pH 12, the VFA concentration, in terms of acetic acid, increased to 48.6 and 54.1 mg/L, respectively. The results proved that VFA could be released into the solution irrespective of the pH. Acid treated samples released extensive quantities of VFA than those of neutral or base samples. Previous study using MW/H\textsubscript{2}O\textsubscript{2}- AOP on sewage sludge, also found that under acidic conditions the process produces more VFA (Liao et al., 2007).
Soluble COD

The results for soluble COD are summarized in Table 5.4 and Figure 5.2. The solid dairy manure samples had an initial soluble COD concentration of 2272 mg/L and initial TCOD concentration of 32.2 g/L.

At pH 3.5, a 22.3 % increase was obtained in SCOD concentration after treatment. Increases of 21% and 7.7% were observed at pH 7.3 and 12, respectively. Samples treated at pH 12 showed the least increase. It can be concluded that the soluble COD concentration was increased irrespectively of the pH. After treatment, the TCOD concentrations dropped incredibly for all the three sets. Acid addition promoted more oxidation and gasification causing carbon dioxide to be released as a gas and thus reducing the TCOD value (Chan et. al., 2007). In this case, at pH 3.5 and pH 7.3, the decrease in TCOD was the most; while at pH 12 the TCOD concentration was higher than the other two sets. It was suggested that at
high pH, it might produce crude soap, therefore, SCOD increase was least among the treatments, and also retained the most TCOD.

The results indicated that the MW/H₂O₂-AOP was very effective to treat separated solid dairy manure under acid condition. More studies are underway in this laboratory. In order to obtain valuable-added products from dairy manure, other technologies commonly used in the sewage treatment, such as thermal, chemical, and thermal-oxidative, will also be studied (Camacho et. al., 2004; Valo et. al., 2004; Takashima and Tanaka, 2008; Wen et. al., 2004).

5.4.2 Part 2

Due to interference problems with colorimetric measurement of phosphorus in soil, plant materials and manures, the resulting values might not be accurate (Wolf et. al., 2005; Kowalenko and Babuin, 2007). It was suggested that for dairy manure the orthophosphate analysis be performed at 0.5%TS, since least interference occurs at this point.

The results for part 2 are summarized in Tables 5.5a & 5.5b. Table 5a presents the results for untreated samples i.e. the initial concentrations of SCOD, PO₄ and VFA at TS 0.5, 1.6, 3.4 and 6.1%.

Considering that the results obtained at 0.5% TS were accurate for orthophosphate analysis. The values obtained at 1.6% TS were compared to the values obtained from 0.5% TS by multiplying with 3.2, which is the ratio of 1.6 by 0.5. If the values obtained at 1.6% TS were close or within the standard deviation, then the analysis result was considered to be correct. For example: at 1.6% TS the initial orthophosphate concentration was 8.8 mg/L which was much below the data obtained for 0.5% TS (12.1 mg/L). Thus, the actual initial orthophosphate concentration for 1.6% TS should have been around 38 mg/L (12.1 mg/L multiplied by 3.2). Similar results were obtained at other TS (3.4 and 6.1%), which proves that the orthophosphate values obtained at higher TS were suppressed. The SCOD results seemed to be quite reliable, with the values obtained for both 3.4 and 6.1% TS being within the standard deviation. Figure 5.3 showed that the R² value was quite low for orthophosphate. Thus, it was clear that the orthophosphate concentration did not show a linear increase with TS. It was seen in Figure 5.3 that SCOD and VFA showed a linear increase with TS. The results indicate that only orthophosphate analysis seems to give incorrect measurements. To
overcome this problem, the initial orthophosphate value for Part 1 (1.6% TS) was calculated using the data for 0.5% TS; the orthophosphate value for 0.5% TS was multiplied by 3.2.

Table 5.5b presents the data obtained from microwave treated samples. Here, set 1 represents the samples heated at 120 °C while set 2 represents samples heated at 70 °C. The comparison was done on similar basis as above. For 1.6% TS, the data obtained at 0.5% TS was multiplied by 3.2, and if the values were within the standard deviation, the analysis are correct. At 120 °C, when the data from 0.5% TS was compared with that obtained from 1.6 and 3.4% TS, both the SCOD and PO₄ values were within the standard deviation. While the VFA concentration obtained at both 1.6% and 3.4 % TS were much higher than the one obtained at 0.5% TS. At 70 °C, the orthophosphate results were found to be quite close when compared between 0.5 and 3.4% TS. However, the SCOD values at 3.4% TS for 70 °C (Table 5.5b) were less when compared as above to 0.5% TS. It could be speculated that at 70 °C, the sample was not properly heated (cold spots were formed since sample was thick). The VFA analysis was not done in this case.

Table 5.5a - Summary of results for part 2 (untreated samples)

<table>
<thead>
<tr>
<th>TS (%)</th>
<th>Initial SCOD (mgL⁻¹)</th>
<th>Initial PO₄-P (mgL⁻¹)</th>
<th>Initial VFA (mgL⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>381 ± 4.4</td>
<td>12.1 ± 1.5</td>
<td>1.37 ± 1.2</td>
</tr>
<tr>
<td>1.6</td>
<td>2272 ± 416</td>
<td>8.8 ± 1</td>
<td>4.97 ± 1.8</td>
</tr>
<tr>
<td>3.4</td>
<td>2755 ± 504</td>
<td>31.6 ± 0.5</td>
<td>6.24 ± 1</td>
</tr>
<tr>
<td>0.5</td>
<td>489 ± 6.8</td>
<td>6.52 ± 0.05</td>
<td>1.2 ± 0.5</td>
</tr>
<tr>
<td>6.1</td>
<td>5520 ± 261</td>
<td>28.1 ± 1</td>
<td>10.5 ± 6.3</td>
</tr>
</tbody>
</table>

Note: The above values represent the untreated samples with pH 8 (approx.)
Figure 5.3 - Relationship of orthophosphate, SCOD and TS

Table 5.5b - Summary of results for part 2 (microwave treated samples)

<table>
<thead>
<tr>
<th>Set No.</th>
<th>Treated SCOD (mgL⁻¹)</th>
<th>Treated PO₄-P (mgL⁻¹)</th>
<th>Treated VFA (mgL⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>686 ± 52.4</td>
<td>19.2 ± 0.5</td>
<td>15.1 ± 2.6</td>
</tr>
<tr>
<td>1b</td>
<td>3173 ± 600</td>
<td>74.6 ± 0.98</td>
<td>443 ± 31.3</td>
</tr>
<tr>
<td>1c</td>
<td>5694 ± 211</td>
<td>137 ± 7.8</td>
<td>424 ± 20.2</td>
</tr>
<tr>
<td>2a</td>
<td>695 ± 157</td>
<td>15.1 ± 0.4</td>
<td>-</td>
</tr>
<tr>
<td>2b</td>
<td>2878 ± 280</td>
<td>91.6 ± 6.4</td>
<td>-</td>
</tr>
</tbody>
</table>
5.5 Conclusion

The MW/H$_2$O$_2$-AOP proved to be very effective to treat separated solid dairy manure. Acidic conditions were most favorable for releasing nutrients from solid dairy manure. At pH 3.5, a 71.7, 125 and 22.3% increase for orthophosphate, ammonia and SCOD was obtained respectively. The VFA concentration in the solution increased from 4.97 mg/L to 391 mg/L under acidic conditions. The treatment was found to be effective only for VFA and SCOD at pH 7.3 and 12, however, for orthophosphate and ammonia were highly unfavorable.

The verification of the results proved that at a higher % TS the orthophosphate analysis for the initial untreated samples were not accurate. The actual orthophosphate concentrations were much higher than the ones obtained during analysis. However, no such difficulty was encountered for microwave treated samples and all the analyses including orthophosphate were accurate. It was therefore concluded that the initial orthophosphate concentration of dairy manure had to be measured at 0.5% TS.
5.6 References

Barnett, G.M. “Phosphorus forms in animal manure”. Bioresource technology, 1994, 4:139-147


6.0 NUTRIENT RELEASE FROM SOLID DAIRY MANURE USING THE MICROWAVE ADVANCED OXIDATION PROCESS

6.1 Abstract

The microwave enhanced advanced oxidation process was used to treat solid dairy manure for nutrient release and solids reduction. A set of 16 experiments were conducted using microwave temperatures ranging from 80 to 180 °C, hydrogen peroxide doses from 1 mL to 2 mL per one percent of total solids and heating time between 5 to 10 minutes. The pH was adjusted to approximately 4 for every set. A surface profile was constructed to show the trend of release for each nutrient. Temperature and hydrogen peroxide dosage were key factors for orthophosphate release. Orthophosphate concentration increased with an increase of temperature, and with the addition of hydrogen peroxide dosage. Treatment time also contributed to the release of orthophosphate when hydrogen peroxide was added. The highest orthophosphate release was reached at a treatment temperature of 160°C, 10 min of treatment time and 12 mL of hydrogen peroxide. A higher ammonia concentration was obtained at a higher operating temperature with a longer heating time. Hydrogen peroxide dosage affected the solubilization of ammonia; however, it did not play as important a role, as did microwave temperature on the process. Heating time and temperature were also found to be prime factors affecting VFA release. Total chemical oxygen demand concentrations decreased for all of treatments at 160°C, while soluble chemical oxygen demand concentrations were increased. Sugar production was affected by microwave operating temperature and hydrogen peroxide dosage. An increase of microwave temperature increased sugar production. Its yield also increased with an increase of hydrogen peroxide dosage. Sugar production decreased with a longer heating period at low microwave temperatures. The microwave enhanced advanced oxidation process should be operated at a high microwave temperature and a high hydrogen peroxide dosage to have the best results for the release of orthophosphate, ammonia, sugar and the destruction of solid dairy manure.

\[\text{A version of this chapter will be submitted for publication. Kenge, A. A.; Liao, P. H.; and Lo, K. V. Nutrient release from solid dairy manure using the microwave advanced oxidation process.}\]
6.2 Introduction

A previous study applying the MW/H₂O₂-AOP on dairy manure proved that pH needed to be maintained at low pH for obtaining a substantial amount of soluble nutrient (Pan, et al., 2005; Kenge, et al., 2008). The aim of this study was to determine the best operating condition to maximize the recovery of nutrients and solubilization of organic matters from solid dairy manure. Microwave temperature, hydrogen peroxide dosage, microwave heating time, and acid addition are the determining factors affecting the MW/H₂O₂-AOP (Pan, et al., 2005; Wong et. al., 2007). Apart from pH, the proposed factors that could enhance the treatment were microwave temperature, hydrogen peroxide dosage and microwave heating time. Therefore, these three factors were chosen for this study.

6.3 Materials & Methods

6.3.1 Substrate

Solid dairy manure was obtained from the UBC Dairy Education & Research Centre in Agassiz, British Columbia, Canada. The dairy manure used in this study was the solid portion obtained after the solid-liquid separation. Once collected from the farm the dairy manure was stored in a closed container at 4 °C. The dairy manure samples contained lot of fibers and undigested food along with the bedding material (sand in this case). This constituted to the very high total solids (TS) of 33%. The manure samples had to be blended in a blender by adding distilled water, to obtain a homogenous sample. The blended sample was further diluted using distilled water and sand was allowed to settle, the slurry was decanted and sand was removed. It should be noted that all the sand could not be removed, thus, the samples contained some traces of sand. The dairy manure samples used in this study had TS of 6.1%. The primary characteristics of the manure samples are listed in Table 6.1.
Table 6.1 - Characteristics of the substrate used in this study

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Solid dairy manure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total solids (%)</td>
<td>6.1 ± 0.3</td>
</tr>
<tr>
<td>pH</td>
<td>8.2 ± 0.1</td>
</tr>
<tr>
<td>TCOD (gL⁻¹)</td>
<td>40 ± 7.1</td>
</tr>
<tr>
<td>SCOD (mgL⁻¹)</td>
<td>5520 ± 261</td>
</tr>
<tr>
<td>TP (mgL⁻¹)</td>
<td>316 ± 6.75</td>
</tr>
<tr>
<td>PO₄-P (mgL⁻¹)</td>
<td>78 ± 1</td>
</tr>
<tr>
<td>TKN (mgL⁻¹)</td>
<td>457 ± 12.3</td>
</tr>
<tr>
<td>NH₃-N (mgL⁻¹)</td>
<td>20.6 ± 0.3</td>
</tr>
<tr>
<td>VFA (mgL⁻¹)</td>
<td>10.5 ± 6.3</td>
</tr>
</tbody>
</table>

Note: ± represents standard deviation

6.3.2 Experimental design

The factors chosen for optimization of the treatment were microwave temperature, hydrogen peroxide dosage and heating time. It was known that acid addition was of prime importance. Another study applying the MW/H₂O₂-AOP on solid dairy manure proved that it was necessary to treat the manure under acidic pH conditions to release nutrients. Thus, in this study, acid addition was not used as a factor for optimization; instead the samples were acidified to an average pH of 4 using a few drops of 30% sulfuric acid. However, as solid dairy manure had a relatively high solid concentration and complex composition, it was expected that heating time might play a major role in nutrient release. Though, previous studies have proved that considerably high nutrient release for sewage sludge can be achieved with a heating time of 5 minutes (Wong et. al., 2006), it was questionable in the case of dairy manure simply because of its complex composition. Also, compared to sewage sludge, it was expected that dairy manure would require a higher microwave treatment temperature and higher hydrogen peroxide dosage.

A total of 13 experiments were designed using JMP-IN® 5.1 (Sall et. al., 2005) software program with a response surface design (Box-Behnken). This program enables the
determination of important factors in the process and also gives a representation of the trend of nutrient release. The microwave temperatures chosen were 80, 120 and 160 °C while heating times of 5, 7.5 and 10 minutes were used. The hydrogen peroxide dosage was varied from 1 mL per 1 % TS to 2 mL per 1 % TS for a 30 mL sample. The experimental design and operating conditions are seen in Table 6.2. The samples used in this study had a TS concentration of 6.1%. The mixing could not be provided at such a high TS concentration; therefore, the samples were not mixed during the process (Kenge et. al., 2008). A sample volume of 30 mL was used for each set. Each set had three replicate except Set 9, which had 9 replicates. The ramp time, time taken by the microwave to reach the set temperature was fixed at 20 °C per minute.

Sets 14 to 16 were performed for verification purposes. For set 14, microwave temperature was at 180°C, outside the testing range for the first thirteen sets. The experimental conditions are also presented in Table 6.2.

6.3.3 Data analysis

The values in Table 6.1 represent the original sample concentrations, when no peroxide was added. After hydrogen peroxide addition the sample total solids will alter due to the dilution, also affecting the initial concentration values. Taking this into consideration, the calculations use the altered initial values; these values are obtained by multiplying the original values with a dilution factor. The dilution factor is calculated as the ratio of the manure sample volume by total sample volume in the vessel during the run. The adjusted values are reported in Table 6.3.

A surface profile provided by JMP-IN® 5.1 was used to display the magnitude of the categories, in terms of orthophosphate, ammonia, VFA and sugar.
Table 6.2 - Summary of the experimental design and operating conditions

<table>
<thead>
<tr>
<th>Set No.</th>
<th>pH</th>
<th>Temp (°C)</th>
<th>H$_2$O$_2$ dosage (mL)</th>
<th>Sample volume (mL)</th>
<th>Heating time (mins)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.9</td>
<td>80</td>
<td>6</td>
<td>36</td>
<td>7.5</td>
</tr>
<tr>
<td>2</td>
<td>3.9</td>
<td>80</td>
<td>12</td>
<td>42</td>
<td>7.5</td>
</tr>
<tr>
<td>3</td>
<td>3.9</td>
<td>80</td>
<td>9</td>
<td>39</td>
<td>5</td>
</tr>
<tr>
<td>4</td>
<td>3.5</td>
<td>80</td>
<td>9</td>
<td>39</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>4.1</td>
<td>120</td>
<td>6</td>
<td>36</td>
<td>5</td>
</tr>
<tr>
<td>6</td>
<td>4.1</td>
<td>120</td>
<td>12</td>
<td>42</td>
<td>5</td>
</tr>
<tr>
<td>7</td>
<td>4.1</td>
<td>120</td>
<td>6</td>
<td>36</td>
<td>10</td>
</tr>
<tr>
<td>8</td>
<td>4.1</td>
<td>120</td>
<td>12</td>
<td>42</td>
<td>10</td>
</tr>
<tr>
<td>9</td>
<td>4.6</td>
<td>120</td>
<td>9</td>
<td>39</td>
<td>7.5</td>
</tr>
<tr>
<td>10</td>
<td>4.2</td>
<td>160</td>
<td>6</td>
<td>36</td>
<td>7.5</td>
</tr>
<tr>
<td>11</td>
<td>4.2</td>
<td>160</td>
<td>12</td>
<td>42</td>
<td>7.5</td>
</tr>
<tr>
<td>12</td>
<td>4</td>
<td>160</td>
<td>9</td>
<td>39</td>
<td>5</td>
</tr>
<tr>
<td>13</td>
<td>4.1</td>
<td>160</td>
<td>9</td>
<td>39</td>
<td>10</td>
</tr>
<tr>
<td>14</td>
<td>4.1</td>
<td>180</td>
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<td>7.5</td>
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<tr>
<td>15</td>
<td>4.2</td>
<td>160</td>
<td>12</td>
<td>42</td>
<td>10</td>
</tr>
<tr>
<td>16</td>
<td>4.1</td>
<td>160</td>
<td>9</td>
<td>39</td>
<td>7.5</td>
</tr>
</tbody>
</table>
Table 6.3 - Initial concentrations of manure after peroxide addition

<table>
<thead>
<tr>
<th></th>
<th>Set 1-13</th>
<th>Set 14-15</th>
<th>Set 16</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen peroxide dosage</td>
<td>6 mL</td>
<td>9 mL</td>
<td>12 mL</td>
</tr>
<tr>
<td>Dilution Factor</td>
<td>0.83</td>
<td>0.77</td>
<td>0.71</td>
</tr>
<tr>
<td>Total solids (%)</td>
<td>5.1 ± 0.25</td>
<td>4.7 ± 0.23</td>
<td>4.3 ± 0.21</td>
</tr>
<tr>
<td>TCOD (gL⁻¹)</td>
<td>33.2 ± 5.9</td>
<td>30.8 ± 5.5</td>
<td>28.4 ± 5</td>
</tr>
<tr>
<td>SCOD (mgL⁻¹)</td>
<td>4582 ± 217</td>
<td>4250 ± 201</td>
<td>3919 ± 185</td>
</tr>
<tr>
<td>TP (mgL⁻¹)</td>
<td>262.3 ± 5.6</td>
<td>243.3 ± 5.2</td>
<td>224 ± 4.8</td>
</tr>
<tr>
<td>PO₄-P (mgL⁻¹)</td>
<td>64.7 ± 0.83</td>
<td>60.1 ± 0.77</td>
<td>55.4 ± 0.71</td>
</tr>
<tr>
<td>TKN (mgL⁻¹)</td>
<td>379 ± 10.2</td>
<td>352 ± 9.5</td>
<td>325 ± 8.7</td>
</tr>
<tr>
<td>NH₃-N (mgL⁻¹)</td>
<td>17.1 ± 0.25</td>
<td>15.9 ± 0.23</td>
<td>14.6 ± 0.2</td>
</tr>
<tr>
<td>VFA (mgL⁻¹)</td>
<td>8.7 ± 5.2</td>
<td>8.1 ± 4.9</td>
<td>7.5 ± 4.5</td>
</tr>
</tbody>
</table>

6.4 Results & Discussion

Many of the solid dairy manure are either not biodegradable or degrade very slowly, which are needed to be treated before they can further be utilized. Most of phosphorus is contained in the solid portion of the manure, and up to 65% of phosphorus is in an organic form. The MW/H₂O₂-AOP is an efficient means to treat solid dairy manure as demonstrated in the previous study (Kenge, et al., 2008). The solid dairy manure are disintegrated and oxidized to convert to carbon dioxide and water, as well as many stable oxidized organic components. The mechanism of the MW/H₂O₂-AOP for dairy manure is assumed to be similar to the wet-air oxidation process: the breakdown of large particulate organic matters, such as carbohydrate and proteins into smaller and more soluble organic components, and further oxidation or gasification of some of the resulting organic products (Shanableh and Shimizu, 2000; Liao, et al., 2007). As a result, TCOD may decrease in the MW/H₂O₂-AOP process. The effects of the process on nutrient release and solids disintegration were evaluated, in terms of soluble ammonia, orthophosphate, COD, VFA and sugar.
6.4.1 Nutrient release

Nutrient release was reported as soluble ammonia and orthophosphate. The results for orthophosphate are summarized in Table 6.4.

Table 6.4 - Summary of the results

<table>
<thead>
<tr>
<th>Set No.</th>
<th>SCOD (mgL⁻¹)</th>
<th>TCOD (gL⁻¹)</th>
<th>SCOD increase (%)</th>
<th>PO₄-P (mgL⁻¹)</th>
<th>PO₄-P increase (%)</th>
<th>NH₃-N (mgL⁻¹)</th>
<th>NH₃-N increase (%)</th>
<th>VFA (mgL⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>148 ± 6</td>
<td>129</td>
<td>22 ± 1</td>
<td>29</td>
<td>135 ± 11</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>112 ± 13</td>
<td>102</td>
<td>17 ± 2</td>
<td>16</td>
<td>119 ± 8</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>145 ± 24</td>
<td>141</td>
<td>21 ± 3</td>
<td>32</td>
<td>161 ± 2</td>
</tr>
<tr>
<td>4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>144 ± 8</td>
<td>140</td>
<td>35 ± 7</td>
<td>120</td>
<td>184 ± 14</td>
</tr>
<tr>
<td>5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>142 ± 21</td>
<td>120</td>
<td>34 ± 3</td>
<td>99</td>
<td>230 ± 9</td>
</tr>
<tr>
<td>6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>115 ± 7</td>
<td>108</td>
<td>29 ± 4</td>
<td>99</td>
<td>195 ± 13</td>
</tr>
<tr>
<td>7</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>145 ± 8</td>
<td>124</td>
<td>36 ± 3</td>
<td>111</td>
<td>232 ± 16</td>
</tr>
<tr>
<td>8</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>132 ± 7</td>
<td>138</td>
<td>38 ± 2</td>
<td>160</td>
<td>235 ± 8</td>
</tr>
<tr>
<td>9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>129 ± 7</td>
<td>115</td>
<td>32 ± 2</td>
<td>101</td>
<td>204 ± 12</td>
</tr>
<tr>
<td>10</td>
<td>5270 ± 934</td>
<td>27.3 ± 5.5</td>
<td>15</td>
<td>152 ± 8</td>
<td>135</td>
<td>52 ± 10</td>
<td>204</td>
<td>295 ± 24</td>
</tr>
<tr>
<td>11</td>
<td>6063 ± 661</td>
<td>22.2 ± 7.8</td>
<td>54.7</td>
<td>153 ± 6</td>
<td>176</td>
<td>58 ± 5</td>
<td>297</td>
<td>302 ± 20</td>
</tr>
<tr>
<td>12</td>
<td>6244 ± 924</td>
<td>31.7 ± 7.8</td>
<td>46.9</td>
<td>132 ± 32</td>
<td>120</td>
<td>50 ± 17</td>
<td>215</td>
<td>293 ± 64</td>
</tr>
<tr>
<td>13</td>
<td>6011 ± 779</td>
<td>27.9 ± 9.5</td>
<td>41.4</td>
<td>148 ± 12</td>
<td>146</td>
<td>59 ± 7</td>
<td>271</td>
<td>303 ± 42</td>
</tr>
<tr>
<td>14</td>
<td>7800 ± 170</td>
<td>30.3 ± 6.2</td>
<td>92.5</td>
<td>169 ± 35</td>
<td>200</td>
<td>106 ± 72</td>
<td>575</td>
<td>235 ± 35</td>
</tr>
<tr>
<td>15</td>
<td>8246 ± 211</td>
<td>29.8 ± 10.5</td>
<td>104</td>
<td>195 ± 2</td>
<td>250</td>
<td>112 ± 24</td>
<td>513</td>
<td>318 ± 100</td>
</tr>
<tr>
<td>16</td>
<td>8301 ± 371</td>
<td>25.3 ± 3.9</td>
<td>90</td>
<td>205 ± 8</td>
<td>242</td>
<td>118 ± 25</td>
<td>598</td>
<td>273 ± 93</td>
</tr>
</tbody>
</table>

A significant increase in orthophosphate concentration was observed for all the experiments. Figures 6.1a, 6.1b and 6.1c show the effects of temperature, hydrogen peroxide dosage and heating time on the release of orthophosphate. Temperature and hydrogen peroxide dosage were key factors for orthophosphate release. As shown in Figure 6.1a, orthophosphate release was relatively constant with an increase of temperature. At a treatment temperature of 160°C
and highest hydrogen peroxide dosage, the highest orthophosphate release was reached. In general, the combination of both hydrogen peroxide addition and temperature appeared to aid in orthophosphate release. At a low treatment temperature of 80°C, orthophosphate release was decreased with an increase of hydrogen peroxide dosage. The low orthophosphate concentration may be due to the formation of polyphosphates at this temperature.

Figure 6.1a - Surface profile for orthophosphate release with respect to H₂O₂ dosage and temperature

The combined effects of hydrogen peroxide and heating time are shown in Figure 6.1b. More orthophosphate was released at a low hydrogen peroxide dosage and shorter heating time while significant amounts can be released at a higher hydrogen peroxide dosage with a longer heating time. The combined effects of heating time and temperature on orthophosphate release were shown in Figure 6.1c. It is advantageous for the MW/H₂O₂-AOP process to be operated at a higher temperature and a longer heating time to achieve a higher orthophosphate release. The results indicated that temperature might be the most important parameter to release orthophosphates from dairy manure. For example, the highest concentration was obtained at 160°C and the least was at 80°C, when operated with the same
dosage and heating time (12 ml of H₂O₂, and 7.5 min) in this study. The results for set 14, 15 and 16 are also seen in Table 6.4. The orthophosphate concentrations for those sets were in general higher than the previous sets at the same operating conditions. The reason might be due to a new batch of hydrogen peroxide solution used in these sets, which had less decomposition of hydrogen peroxide occurring in the solution. Thus, it was assumed that hydrogen peroxide content in the solution was slightly higher than the old batch. It was observed that more orthophosphate was released at 160°C than 180°C at the same hydrogen peroxide dosage, and at different heating periods (sets 14 and 15). This result also pointed out that orthophosphate release was affected by the length of heating period. However, a significant amount of orthophosphate was released from solid dairy manure at high heating temperature of 180°C. This confirmed that orthophosphate release was mostly dictated by microwave operating temperature and hydrogen peroxide dosage.

Figure 6.1b - Surface profile for orthophosphate release with respect to H₂O₂ dosage and heating time
The results for soluble ammonia are listed in Table 6.4. A drastic increase in the soluble ammonia concentration was observed with an increase in temperature and the highest percent increase of 297% was observed at 160 °C with 12 mL peroxide dose and 7.5 minute heating time in Set 11. The ammonia concentration increased considerably from 120 to 160 °C. At 80 °C, very little ammonia was released into the solution. The temperature effect on the solubilization of ammonia was clearly reflected in Figures 6.2a, and 6.2b. The slopes of ammonia release with respect to treatment temperature in each figure are distinctly steeper than the slopes of ammonia release against other parameters; therefore, treatment temperature was an important factor affecting ammonia release. The combined effects of temperature and heating time were reflected in Figure 6.2a. A higher ammonia concentration was obtained at a higher operating temperature with a longer heating time. Heating time along with microwave temperature would affect the soluble ammonia concentration. The effects of microwave temperature and hydrogen peroxide on the solubilization were shown in Figure 6.2b. Hydrogen peroxide dosage affected the solubilization of ammonia; however, it did not play as important a role, as did microwave temperature on the process.
Figure 6.2a - Surface profile for ammonia release with respect to heating time and temperature

Figure 6.2b - Surface profile for ammonia release with respect to H$_2$O$_2$ dosage and temperature
The ammonia release with respect to heating time and hydrogen peroxide is shown in Figure 6.2c. More ammonia could be solubilized from dairy manure with a longer heating time and a higher hydrogen peroxide dosage. A considerable amount of ammonia was released for sets 14-16. These sets were operated at very high microwave temperature and hydrogen peroxide. The ammonia yields were much higher than those of previous sets at the same operating conditions. It can then be concluded that ammonia release was affected by temperature, a combination of temperature and hydrogen peroxide, and a combination of temperature and heating time. A higher hydrogen peroxide dosage at lower temperatures did not appear to have aided in ammonia solubilization, and even decreased its concentration in the solution.

Figure 6.2c - Surface profile for ammonia release with respect to H$_2$O$_2$ dosage and heating time

6.4.2 Solids disintegration

The MW/H$_2$O$_2$-AOP was an oxidative process for the destruction of total organic solids and biopolymers. The resulting products are destruction compounds, such as sugar, or oxidation products (VFA and others) in the solution, or gases of CO$_2$ and others.
The results for volatile fatty acids are summarized in Table 6.4. The initial VFA concentration in the untreated samples was very low i.e., 10.5 mg/L and mainly comprised of acetic acid. The treated samples had a very high VFA value and comprised of propionic, i-butyric, butyric, i-valeric, valeric, hexanoic, and heptanoic acids. The displayed values are all converted to equivalent concentrations of acetic acid. The highest VFA release was obtained at 160°C. The results indicated that more VFA productions were obtained at high microwave temperatures. It’s an advantage to operate the MW/H₂O₂-AOP process at a high temperature, as it maximizes the VFA yield.

Figures 6.3a, 6.3b, and 6.3c show the effects of temperature, hydrogen peroxide dosage and heating time on the VFA concentrations. Heating time and temperature were found to be prime factors affecting VFA release (Figures 6.3a and 6.3b). The combined effects of temperature and hydrogen peroxide dosage were very important too (Figure 6.3c). The effect of hydrogen peroxide was more pronounced when combined with longer treatment times.

![Surface profile for VFA release with respect to H₂O₂ dosage and heating time](image-url)
Due to an excess of residual hydrogen peroxide in the treated solutions, erroneous values of TCOD and SCOD were obtained at microwave temperature of 120°C or below. TCOD
values were much higher than those of the initial. It has been documented that there is a positive interference in COD determination in the presence of traces of H\textsubscript{2}O\textsubscript{2} (Awan, 2004). It was found that no trace of hydrogen peroxide was found at 160°C. Thus, the COD results only for operating at 160°C or higher are presented in Table 6.4. Heating will increase decomposition of H\textsubscript{2}O\textsubscript{2} into OH\textsuperscript{-} Radicals and therefore enhance the oxidation process, when hydrogen peroxide is applied simultaneously with microwave heating (Eskicioglu, et al., 2008). As a result, there was no hydrogen peroxide in the solution heating at 160°C or higher.

TCOD concentrations decreased for all the treatments at 160°C. It pointed out that a large amount of CO\textsubscript{2} was formed in the process, besides VFA. Hydrogen peroxide dosage and heating time would affect TCOD concentration. The overall TCOD concentration was dictated by a combined effect of temperature and heating time, assuming with a similar hydrogen peroxide dosage. SCOD concentrations increased for all of treatments at 160°C. Due to limited data obtained in this study, it was not clear which was the most significant factor affecting the solids disintegration. It seems that it was a combination of temperature and heating time. This was also clearly observed from the results obtained at sets 14-16.

Figures 6.4a, 6.4b, and 6.4c show the effects of temperature, hydrogen peroxide dosage and heating time on the sugar concentrations. An increase of microwave temperature increased sugar production (Figures 6.4a and 6.4b). An increase of hydrogen peroxide dosage also increased its yield at lower temperatures, while sugar yield was remained relatively constant at higher temperature (Figure 6.4b). It might be due to sugar reacting with an excess of hydrogen peroxide to form oxidation products, such as carbonyl compounds and VFA. It should be noted that residue hydrogen peroxide was found in the resulting solution at low microwave temperatures. At low microwave operating temperature, it would yield less sugar at a longer heating period. It was also indicated that sugar was further oxidized at a longer reaction period. However, the sugar yield was not affected by microwave heating period at high microwave temperatures; the sugar production remained relatively constant (Figures 6.4a and 6.4c). The oxidative reaction using the MW/H\textsubscript{2}O\textsubscript{2}-AOP was completed within five minutes at high temperatures. There was no excess hydrogen peroxide found in the solution at such high operating temperatures, therefore, there was no further oxidation occurred. It should also be noted that VFA yields were increased with a longer heating period at low
microwave temperatures, while VFA concentrations were remained relatively constant at high microwave temperature. The reduced amounts of sugar obtained were that soluble sugar could have been further oxidized to form intermediate oxidized compounds and VFA. It can then be concluded that it is an advantage to operate at high microwave temperature with a high hydrogen peroxide dosage to yield the most of sugar (or lower dosage at shorter heating times).

Figure 6.4a - Surface profile for sugar release with respect to heating time and temperature
The MW/H₂O₂-AOP is an effective means to produce sugar from dairy manure, besides soluble nutrients and oxidation products. It is the first attempt to obtain sugar from dairy manure using the oxidative process, thus the optimal condition has not yet been established. However, the preliminary results indicated that this process can be operated at much lower
operating temperatures, and a short reaction period than the conventional thermo-chemical methods. For conventional acid hydrolysis of lignocellulosic materials in dairy manure for the production of mono-sugars, it required that samples was pre-treated with 75% acid concentration, and 30 min of reaction time for fiber decrystallization, and then they were further hydrolyzed in a 12.5% of acid at 135°C for 10 minutes (Liao, et al., 2006).

6.5 Conclusion

The MW/H₂O₂-AOP could be an effective pre-treatment method for solid dairy manure to release soluble ammonia, orthophosphate and soluble organic matters, such as sugar, VFA and others. The overall results pointed out that the MW/H₂O₂-AOP should be operated at a high microwave temperature and a high hydrogen peroxide dosage to facilitate the destruction of solid dairy manure.

Temperature and hydrogen peroxide dosage were key factors for orthophosphate release. The high orthophosphate release could be obtained either at a low hydrogen peroxide dosage with a longer heating time, or at a higher hydrogen peroxide dosage with a shorter heating time.

A higher ammonia concentration was obtained at a higher operating temperature with a longer heating time. Heating time along with microwave temperature would affect the overall ammonia concentration.

Heating time and temperature were found to be prime factors affecting VFA release. The highest VFA concentrations were obtained at 160°C in this study.

TCOD concentrations decreased for all of treatments at 160°C, while SCOD concentrations were increased. A large amount of CO₂ was formed in the process, besides VFA production at this temperature.

Sugar production was affected by microwave operating temperature and hydrogen peroxide dosage. An increase of microwave temperature increased sugar production, and an increase of hydrogen peroxide dosage also increased its yield.
6.6 References


7.0 RECOMMENDATIONS & FUTURE PROSPECTS

Application of the MW/H2O2-AOP to recover nutrients like P, N and C from organic waste is an innovative technique and a positive step towards sustainable environment. The technology not only allows renewing the resources but also helps in reducing the volume of organic waste, disposal of which is a major issue in waste treatment facilities (Liao et. al., 2007). In the past, this technology has been successfully applied to municipal sewage sludge to release orthophosphate, ammonia, COD and volatile fatty acids (Liao et. al., 2005; Liao et. al., 2005; Liao et al., 2007; Wong et. al., 2006). The objective of the present research was to improve the treatment by enhancing the nutrient recovery as well as the treatment was extended to other organic waste like municipal anaerobic sludge and solid dairy manure.

The results from chapter 2, displayed that mixing helped increasing the yield in terms of all the nutrients but mixing was statistically significant only at high solids concentration. Also, in chapter 3, where experiments were performed to obtain optimum operating condition, proved that although mixing was important, microwave temperature and hydrogen peroxide dosage were the most dominating factors. A study performed by Wong et. al., also showed similar results (Wong et. al., 2007). More nutrients were solubilized at high temperatures and a H2O2 dosage of 1 mL per 1% TS for a 30 mL sample was found as the optimum dose. However, on a large scale, this dose of H2O2 might be very high and large volume of oxidant will be required.

The microwave technology was successfully applied on anaerobic sludge, results seen in chapter 4. pH was the determining factor in this case, and for the experiment pH had to be reduced to approximately 4. Thus, the samples were strongly acidic, this, could add to the costs when the nutrients are utilized for struvite or calcium phosphate crystallization, since both processes need alkaline conditions (Uludag-Demirer, 2008; Amjad, 1988). Similar behavior was also exhibited by solid dairy manure, where pH was the most important factor (chapter 5).

Municipal anaerobic sludge subjected to the microwave treatment under neutral pH conditions observed a decrease in the orthophosphate concentration from the initial. Similar
behavior was also seen when dairy manure was treated at neutral and alkaline pH conditions. It was speculated that orthophosphate is combining with divalent cations and extra cellular polymeric substances (EPS) to form flocs that are insoluble (Forster and Lewin, 1972). Further investigation is needed to ascertain the products in this case. Another problem encountered when dealing with solid dairy manure was the analysis of orthophosphate (initial), where due to interference, incorrect values were obtained. To overcome this difficulty, the data was obtained at 0.5%TS where the interference is least.

The microwave system used in this study is a batch closed-vessel unit operating at a frequency of 2450 MHz. Typically, an industrial microwave operates at a frequency of 915 MHz, thus, for applying this technology on a large-scale, the treatment should be tested first on an industrial microwave. The economic feasibility of the microwave process also needs to be studied. A study to ascertain if the value of the recovered nutrients is greater than the amount spent on energy and chemicals is necessary.

A continuous microwave process would be more practical when applying on a large-scale, but the optimum operating conditions and results will differ considerably between a batch and a continuous process. Thus, a separate study is needed to determine the important factors in a continuous process. When applying this process industrially, the organic waste should be dewatered or high TS must be used, this will help to save some energy. Once the samples are treated, the usual wait time for the samples to cool down is approximately 30 minutes, depending upon the temperature. This would be a drawback if the process were applied industrially. It would be beneficial if the pressure could be reduced inside the vessels and samples could be cooled down to room temperature, immediately.
7.1 References


