SLUDGE AND MANURE TREATMENT USING THE MICROWAVE ENHANCED ADVANCED OXIDATION PROCESS

by

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ABSTRACT

Waste activated sludge (WAS) and dairy manure (DM) present serious environmental concerns since they contain high levels of nutrients, organic matter and pathogens contained. The microwave enhanced advanced oxidation process (MW/H₂O₂-AOP) was used to treat these waste materials for solids disintegration, nutrients solubilization and pathogen destruction.

For pathogen reduction, fecal coliform concentrations were found below detection limits (1000 CFU/L) immediately after treatment when sludge was treated at 70°C with more than 0.04% of H₂O₂. Significant regrowth of fecal coliforms was observed after the treated samples were stored at ambient temperature for 72 hours. However, no regrowth was observed for samples treated at 70°C with 0.08% H₂O₂ or higher, suggesting a complete elimination of fecal coliforms.

With extracted cells that are EPS-free, orthophosphate could be released at lower microwave temperatures and lower H₂O₂ dosages, compared to our previous studies. The amount of DNA in solution was a good indicator of the extent of cell damage; the high concentration of DNA released into solution after treatment indicated significant cell damage.

The effects of pre-microwave heating, microwave irradiation and post-microwave setting on nutrients and organic matters solubilization in continuous MW/H₂O₂-AOP were studied. Pre-microwave heating did not improve the overall orthophosphate solubilization,
but helped in organic matter solubilization. It was beneficial to operate a continuous mode of the MW/H\textsubscript{2}O\textsubscript{2}-AOP at a longer retention time for organic matter solubilization, and at a shorter retention time for orthophosphate solubilization. Sludge settleability was greatly improved with the microwave treatment, with or without the addition of H\textsubscript{2}O\textsubscript{2}. It was found that 69 to 92\% of the TP and up to 90\% of TCOD in DM were in the soluble form, after continuous MW/H\textsubscript{2}O\textsubscript{2}-AOP with an exit temperature of 90\textdegree C and acid dosage of 1.0\% (vol/vol). Acid addition was important in phosphate solubilization but the dosage of acid affect the solubilization to a lesser extent. For organic matter solubilization, acid played an important role – SCOD release increased with the increase of acid dosage. Higher microwave exit temperature resulted in higher SCOD and ortho-P solubilization.
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LIST OF ABBREVIATIONS

BC – British Columbia
BNR – Biological nutrient removal
BOD – Biochemical oxygen demand
CO₂ – Carbon dioxide
COD – Chemical oxygen demand
DM – Dairy manure
EBPR – Enhanced biological phosphorus removal
EPS – Extracellular polymeric substances
MW – Microwave
MW/H₂O₂-AOP – Microwave-enhanced advanced oxidation process
N – Nitrogen
NOₓ – Nitrates and nitrites
NH₄-N – Ammonia nitrogen
Ortho-P – Ortho-phosphates
PHA – Polyhydroxyalkanoates
P – Phosphorus
PO₄ – Phosphates
Poly-P – Polyphosphorus
TS – Total solids
TP – Total phosphorus
VFA – Volatile fatty acid
WAS – Waste activated sludge
WWTP – Wastewater treatment plant
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CO-AUTHORSHIP STATEMENT

This thesis has been written in a manuscript-based format and it covers a total of four papers. A version of these papers has been/will be submitted for publication.

Chapter 2: Disinfection and solubilization of sewage sludge using microwave enhanced advanced oxidation process.
Experiment was designed Yang Yu, Dr. Kwang Victor Lo and Dr. Ping Huang Liao. Experiments were performed by Yang Yu. Data analysis and manuscript was prepared by Yang Yu and modified by Dr. Ping Huang Liao and Dr. Kwang Victor Lo.

Chapter 3: Nutrient release from extracted activated sludge cells using the microwave enhanced advanced oxidation process.
Experiment was designed and modified by Yang Yu, Dr. Ing Wei Lo and Dr. Ping Huang Liao. Experiments were performed by Yang Yu and Dr. Ing Wei Lo. Data analysis and manuscript was prepared by Yang Yu and Dr. Ping Huang Liao with modifications from Dr. Kwang Victor Lo. A version of this paper has been submitted to the Journal of Environmental Science & Health Part A, Toxic/hazardous Substances & Environmental Engineering. (Accepted)

Chapter 4: Sewage sludge treatment using continuous microwave enhanced advanced oxidation process.
Experiment was designed by Yang Yu, Dr. Kwang Victor Lo and Dr. Ping Huang Liao with input from Dr. Ing Wei Lo. Experiment was performed by Yang Yu and Winnie Chan. Data analysis and manuscript was prepared by Yang Yu and modified by Dr. Ping Huang Liao, Dr. Kwang Victor Lo and Winnie Chan.

Chapter 5: Application of continuous microwave enhanced advanced oxidation process to dairy manure solubilization.
Experiment was designed by Yang Yu, Dr. Kwang Victor Lo and Dr. Ing Wei Lo. Experiment was performed by Yang Yu and Dr. Ing Wei Lo. Data analysis and manuscript was prepared by Yang Yu and modified by Dr. Ping Huang Liao and Dr. Kwang Victor Lo.
1.0 INTRODUCTION

1.1 Background

Wastewater has been long known as a hazardous waste product from human daily life. As early as 4,000 B.C.E, the Babylonian Empire had recognized the necessity to convey wastewater away from the city center in order to reduce odour, insects and diseases caused by wastewater (Schladweiler, 2009). Wastewater was discharged into rivers and ditches without treatments from approximately 500 C.E. to 1,500 C.E, during which period the epidemics raged across many cities in Europe. In the 15th century, the connection between wastewater and disease outbreak was finally established and people started to realize the necessity to treat wastewater (Brown, 2005). Centralized wastewater treatment facilities had been constructed and commissioned since then.

In the past, the primary objectives for wastewater treatment were to stabilize the organic matters in wastewater and disinfect the wastewater. However, apart from the rich organic matter content and high levels of pathogens, wastewater also contains nutrients such as nitrogen and phosphorus, solids, pharmaceuticals residues and hazardous chemicals from industrial applications. As the governments and environmental agencies tighten up the regulations for the qualities of wastewater discharge, the focus of wastewater treatment has shifted to nutrients removal since excess nutrients in the wastewater cause eutrophication in water bodies. The most recognizable manifestation of eutrophication is the algae bloom in rivers or lakes during summer time. The decomposition of algae consumes dissolved oxygen in water and therefore threatens the aquatic life. Figure 1.1
depicted a serious blue algae bloom caused by eutrophication in Lake Tai, China during the summer of 2007.

In order to protect the environment from the detrimental effects of eutrophication, many processes were developed to remove excess nutrients from. Biological nutrients removal (BNR) is by far the most popular process in removing nutrients from wastewater. This process utilizes microorganisms to convert nutrients in the wastewater to biomass for microorganism self growth and metabolism. The effluent from this process is able to reduce concentrations of ammonia nitrogen, nitrate nitrogen and soluble phosphorus to as low as 0.5 mgL$^{-1}$, 1-2 mgL$^{-1}$ and 0.1 mgL$^{-1}$ respectively (Jeyanayagam, 2005). The enhanced nutrients removal efficiency has improved the wastewater effluent qualities and protected the water bodies from eutrophication. However, on the other side, this process produces an excess amount of biomass, also referred as wastewater sludge, which also needs proper treatment and disposal. The WAS is enriched with phosphorus, nitrogen and organic matter, hence, its treatment and disposal created new challenges for environmental engineers.

Similar to wastewater sludge, DM is also a type of waste material that is enriched with nutrients, organic matters, cellulose and hemicelluloses. DM is often applied directly as soil amendments. However, there are many problems associated with the direct application of manure to soils including pathogen contamination of surface and groundwater supplies, over-enrichment of soils with nitrogen and phosphorus, and odour generation (Champagne, 2007).
Both WAS and DM are commonly considered as hazardous waste material. However, from the nutrient recovery point of view, sludge and DM are both valuable bioresources. The main hurdles of recovering nutrients from waste materials are: 1) the nutrients concentrations in the waste materials are low, 2) nutrients are not in the soluble form. WAS and DM are perfect sources for nutrient recovery as they all contain high levels of nutrients and organic matters which enable the recovery processes. Most of the nutrients and organic matters in sludge and manure are not readily available for recovery; hence, a microwave enhanced advanced oxidation process (MW/H2O2-AOP) was developed in order to pretreat these waste materials for subsequent processes.

1.2 Literature Review

1.2.1 Microwave Heating

*Introduction to Microwave*

After James Clerk Maxwell first predicted the electromagnetic waves from his famous Maxwell Equations, Sir Jagadish Chandra Bose successfully proved the existence of microwaves by demonstrating radio control of a bell using millimeter wavelengths publicly in 1894. In the Second World War, intensive research into high-definition radar led to the development of microwaves (Meredith, 1998). Since then, numerous studies have been carried out to study this versatile electromagnetic wave with respect to other applications. In the modern society, microwave has been applied to a variety of industries, including communication, remote sensing (radar), navigation, material processing, and
industrial heating. In the post-war era, extraordinary effort had been put in the development of microwave heating for domestic purposes.

Microwave covers a wide range (300MHz to 30GHz) on the electromagnetic spectrum (Figure 1.2), and therefore, the frequencies of microwaves used for various applications had been strictly classified in order to reduce interferences. Special frequency bands are reserved for industrial, scientific and medical (ISM) applications. For microwave heating, the frequencies used for domestic and industrial applications are 2450MHz and 915MHz respectively (Schubert and Regier, 2005).

**Mechanisms of Microwave Heating**

Microwave heating is fundamentally different from conventional heating in that microwave heating is a dielectric heating process which generates heat within the materials by using electromagnetic waves (Metaxas, 1996; Metaxas and Meredith, 1988; Roussy and Pearce, 1995). A dielectric material is commonly known as an insulator, but in the case of microwave heating, a more precise definition for dielectric would be non-metals which could interact with electric, magnetic or electromagnetic fields on a molecular level (Von Hippel, 1954). The basic mechanisms involved in microwave heating are dielectric and ionic (Datta & Davidson, 2000). In dielectric materials, the dipolar components of the molecules couple electromagnetically to the microwave electric fields and tend to realign themselves with it mechanically. Since the microwave field oscillates constantly, the dipoles of the dielectric material tend to realign with the frequency of the microwave as the field reverses. The constant realigning of the dipoles
produces friction between molecules and therefore causes the heating of dielectric materials (Meredith, 1998). Another mechanism of microwave heating is the oscillatory migration of ions which generated heat under the influence of the oscillating electric field (Datta & Davidson, 2000).

**Dielectric Properties**

Two of the most important material properties for microwave heating are the dielectric constant (\( \varepsilon' \)) and the dielectric loss factor (\( \varepsilon'' \)). The dielectric constant is a measure of the amount of energy that can be stored when the material is subjected to an alternating electric field while the dielectric loss factor is a measure of the energy dissipated within the materials (Lewis & Heppell, 2000). The power dissipated (\( P_0 \)) within the samples is given by the following equation (Lewis & Heppell, 2000),

\[
P_0 = 55.61 \times 10^{-14} f E^2 \varepsilon''
\]

where \( P_0 \) = power dissipated (Wcm\(^{-3} \)), \( f \) = frequency (Hz), and \( E \) = electric field strength (Vcm\(^{-1} \)). As shown in the equation, the power dissipated within the material is directly proportional to the frequency, electric field strength and dielectric loss factor of the material. Hence, materials with a high dielectric loss factor are able to absorb microwave energy well.

**Penetration Depth**

The penetration depth (\( d_p \)), which is also known as the skin depth in microwave heating, is defined as the distance an electromagnetic wave can penetrate beneath the surface of the material as the intensity of the wave decreases to \( 1/e \), which is approximately 37%, of
the intensity at the material surface (Buffler, 1993). The penetration depth can be calculated by the following equation (Wang et al., 2003)

$$d_p = \frac{c}{2\sqrt{2\pi f} \left\{ \varepsilon_r \left[ \sqrt{1 + \left( \frac{\varepsilon_r - 1}{\varepsilon_r + 1} \right)^2} \right] \right\}^{1/2}}$$

where \(f\) = frequency of the wave, \(c\) = light of the speed. There are several variations of this equation. However, the key point is that the penetration depth is inversely proportional to the frequency of wave and the dielectric properties of the materials. Hence, for microwave heating, using 915MHz frequency is more advantageous than using 2450MHz frequency as lower frequency would result in a deeper penetration depth. The penetration depth of water is about 0.5cm to 4.7cm in the low GHz range (Schmitt, 2002).

**Applications of Microwave to Sludge and Manure Treatment**

The use of microwave heating in the field of waste treatment has gain tremendous popularity recently. WAS and DM are particular suitable for microwave heating due to the fact that more than 90% of the content of WAS and DM is water. Water has a high dielectric loss factor due to its dipolar nature, making microwave effective in WAS and DM treatment. By using microwave-induced pyrolysis process, the sludge volume can be reduced by as much as 80% (Menéndez et al., 2002). Microwave treated WAS increased the soluble chemical oxygen demand (SCOD) concentrations by 22%, indicating significant solids disintegration. In the subsequent anaerobic digestion, the solid retention time of the microwave treated sludge reduced from 15 days to 8 days without causing any system instabilities (Park et al, 2004). Compared to conventional heating, microwave
heating demonstrated its superiority in SCOD solubilization, biogas production, and dewaterability in terms of capillary suction time of waste activated sludge (Pino–Jelcic et al., 2006). Microwave was also found to be effective in reducing or eliminating pathogens in WAS (Hong et al., 2004; Martin et al., 2005, Pino–Jelcic et al., 2006).

Microwave was also used in the treatment of DM. Pan et al. reported phosphorus release up to 80% from DM after acid-aided microwave pretreatment (2006). In a similar study, phosphorus releases from DM up to 85% after microwave treatment was reported (Qureshi et al., 2008). Microwave heating also resulted in a better treatment performance in terms of COD solubilization, glucan/xylan reduction, phosphorus solubilization and anaerobic digestion when used to treat DM (Jin et al., 2009). The potential of recovering struvite, a value slow-releasing fertilizer, from DM after microwave treatment was found promising (Qureshi et al., 2008; Jin et al., 2009). Increased amount of reducing sugar, which can be recovered as bioethanol in the subsequent process, was reported in a study where microwave was used to pretreat swine manure (Li et al., 2009). In terms of disinfection, microwave was found effective in the inactivation of viruses in liquid manure, although the virucidal effect was reported solely thermal (Bohm et al., 1984).

1.2.2 Microwave Enhanced Oxidation Process (MW/H₂O₂-AOP)

Principles of MW/H₂O₂-AOP

Although microwave alone has already been proved effective in treating various types of waste materials, a new process were developed to enhance the treatment efficiencies. In microwave enhanced oxidation process (MW/H₂O₂-AOP), the substrate is exposed to the
simultaneous treatment of H$_2$O$_2$ and microwave irradiation. H$_2$O$_2$ is a powerful but unstable oxidant which could generate hydroxyl radicals by the cleavage of H$_2$O$_2$ under excitement (Parsons, 2004). The synergistic effect between microwave irradiation and H$_2$O$_2$ produces hydroxyl radicals. Hydroxyl radicals are extremely powerful oxidants which are able to achieve cell destructions as well as solid disintegration in sludge treatment. Table 1.1 lists the oxidation potentials for various oxidants and ranks hydroxyl radicals 2$^{nd}$ with an oxidation potential of 2.8V. Two common processes of producing hydroxyl radicals are by UV irradiation and Fenton’s reagent. No direct measurements of the formation of hydroxyl radicals by microwave irradiation of H$_2$O$_2$, however, many studies have proved the synergistic effects between microwave irradiation and H$_2$O$_2$. The synergistic effects had been clearly demonstrated in the study of E. coli destruction using combined treatment of microwave heating and H$_2$O$_2$ (Koutchma & Ramaswamy, 2000). Liao et al. reported improved phosphorus release from sludge using microwave and H$_2$O$_2$ treatment (2005). These are all indirect evidence for the formation hydroxyl radicals, when H$_2$O$_2$ is combined with microwave irradiation.

**Purposes of MW/H$_2$O$_2$-AOP**

The most important purpose of treating waste materials using MW/H$_2$O$_2$-AOP is to achieve nutrients solubilization and solids disintegration. In WAS and DM, majority of the nutrients are not in the soluble form, and therefore recovering these nutrients is difficult. MW/H$_2$O$_2$-AOP has the superior capability to destroy cells and solids in WAS and DM, making the nutrients contained within the cells or solids available. The solubilized nutrients could be then recovered in the subsequent processes. Excessive
sludge production has always been problematic for wastewater treatment facilities. MW/H₂O₂-AOP also provides a solution for sludge solids disintegration in terms of total chemical oxygen demand (TCOD) reduction and soluble chemical oxygen demand (SCOD) solubilization.

**Advantages of MW/H₂O₂-AOP**

The primary advantage of MW/H₂O₂-AOP is its fast and effective heating. The process is able to raise the temperatures of the waste materials in the order of minutes and requires no warm up time. The addition of H₂O₂ provides the benefits of hydroxyl radical formation which further improves the process efficiency. More importantly, MW/H₂O₂-AOP is versatile in treating different types of wastes, including sludge, manure, blood meal and fish silage. The treated substrates can be used for a variety of applications in the subsequent processes. Other benefits of MW/H₂O₂-AOP include sludge volume reduction, pathogen destruction, sludge dewaterability and settleability improvement and odour reduction.

**Subsequent Processes for MW/H₂O₂-AOP Treated Sludge or Manure**

After sludge or manure being treated by MW/H₂O₂-AOP, the solubilized ammonia-nitrogen and phosphorus can be recovered through the struvite crystallization process. Struvite, formally known as magnesium ammonium phosphate (Mg(NH₄)PO₄·6H₂O), is a valuable slow-releasing fertilizer which can be applied directly to soil. Struvite crystals are being formed as the constituent concentrations exceed their solubility limit by the following reaction (Durrant, et al., 1999),
\[
\text{Mg}^{2+} + \text{NH}_4^+ + \text{PO}_4^{3-} + 6\text{H}_2\text{O} \rightarrow \text{Mg(NH}_4\text{PO}_4.6\text{H}_2\text{O}
\]

Tremendous effort has been dedicated to study the recovery of phosphorus from WAS and manure through controlled struvite formation (Momberg & Oellermann, 1992; Battistoni et al., 1997; Schuiling & Andrade, 1999; Ohlinger et al., 2000; Munch & Barr, 2001). The sludge or manure supernatant, which is enriched with soluble phosphate after MW/H$_2$O$_2$-AOP, is a perfect substrate for struvite crystallization. Recovering phosphorus through struvite also solves the problem of unwanted struvite formation in the pipelines which causes clogging of pipes and fouling of pumps in wastewater treatment plants.

Volatile fatty acids (VFA) are produced from complex organic matters in WAS and DM after MW/H$_2$O$_2$-AOP. Hence, the treated sludge or manure often contains high concentrations of VFA, which could also be recovered as a valuable resource. The recovered VFA can be used as carbon feed for the enhanced biological phosphorus removal process.

The treated sludge or manure can also be used for biogas production through anaerobic digestion. Since MW/H$_2$O$_2$-AOP is able to solubilize SCOD and produce VFA, the complex organic matters in sludge or manure become readily available. Hence, using MW/H$_2$O$_2$-AOP treated sludge or manure for anaerobic digestion could potentially speed up the digestion process and increase the biogas production.
MW/H₂O₂-AOP treatment of DM at elevated temperature with acid and H₂O₂ additions could potentially degrade the DM cellulose and hemicellulose into sugar which could later be converted to bio-ethanol.

1.2.3 Previous Studies of MW/H₂O₂-AOP

**MW/H₂O₂-AOP Treatment of Sludge**

The first study of MW/H₂O₂-AOP compared the difference in phosphate solubilization from sewage sludge between microwave treatment and MW/H₂O₂-AOP treatment. MW/H₂O₂-AOP treatment was found more effective than microwave treatment alone. With 5 minutes of microwave heating at 170°C and 1% (vol/vol) H₂O₂ addition, more than 84% of TP was released as ortho-P (Liao et al., 2005). In a following study, the sludge solubilization of more parameters, including SCOD, metals and ammonia was investigated. High H₂O₂ dosage (3% vol/vol) enabled complete COD solubilization at microwave temperature of 80°C whereas metal release was found independent of H₂O₂ dosage (Wong et al., 2006a). MW/H₂O₂-AOP was also reported effective in sludge reduction in terms of solubilization of TCOD and production of VFA from SCOD. Over 96% of TCOD was dissolved into the solution, while up to 25% of the SCOD was in the form of acetic acid (Liao et al., 2007).

**Optimization of MW/H₂O₂-AOP Treatment of Sludge**

Attempts had been made in the subsequent studies to optimize the treatment efficiency of MW/H₂O₂-AOP. Firstly, Wong et al. varied microwave temperatures from 60 to 120°C and H₂O₂ dosages from 0 to 1%, respectively, in order to study the role of H₂O₂ in
MW/H₂O₂-AOP (2006b). Later, a statistical computer program JMP-IN® was used to identify the most important factors in MW/H₂O₂-AOP treatment of sewage sludge. For maximizing ortho-P solubilization, the order of the most significant factors were: (1) microwave heating temperature, (2) the combined effect of microwave heating temperature and H₂O₂ addition, and (3) sulphuric acid addition while for maximizing ammonia solubilization, the order became: (1) H₂O₂ addition, (2) microwave heating temperature, and (3) sulphuric acid addition (Wong et al., 2007).

**Improvements of MW/H₂O₂-AOP**

More studies of MW/H₂O₂-AOP were carried out in the attempt to further improve the process efficiency. Yin et al. compared the sludge solubilization efficiencies of several oxidation processes and reported that the treatment efficiency of MW/H₂O₂-AOP can be further improved by the addition of ozone (2007). This study was followed up by a more detailed study in the significance of ozone addition in MW/H₂O₂-AOP. It was reported that although ozone addition would improve the treatment efficiency of MW/H₂O₂-AOP, its role was not as significant as microwave heating temperature and H₂O₂ addition (Yin et al., 2008). Ferrous sulfate addition in MW/H₂O₂-AOP was also investigated; however, MW/H₂O₂-AOP alone was reported to have better ortho-P, NH₄-N and COD solubilization than MW/H₂O₂-AOP with ferrous sulphate addition (Lo et al., 2008). Magnetic mixers were implemented in MW/H₂O₂-AOP to investigate the role of mixing in this process for different sludge TS concentrations. It was found that mixing during microwave irradiation resulted in higher yields of ortho-P, NH₄-N and SCOD while the
effect of mixing was more pronounced in sludge with higher TS concentrations (Kenge et al., 2008).

**MW/H₂O₂-AOP Treatment of Other Waste Materials**

Following the successful application of MW/H₂O₂-AOP to WAS treatment, this process was further applied to treat different types of wastes. Pan et al. applied MW/H₂O₂-AOP to DM and reported an ortho-P release of 85% at microwave temperature of 120°C (2006). Qureshi et al. reported similar ortho-P release and concluded that the potential of recovering phosphorus through struvite formation was promising (2007). Significant COD, ortho-P and ammonia solubilization was reported when MW/H₂O₂-AOP was applied to blood meal and fish silage and the treated blood meal and fish silage were reported suitable to be used as greenhouse liquid fertilizer (Chan et al., 2007; Chan et al., 2008).

**1.3 Research Objectives**

This research project attempts to expand the scope of previous work of MW/H₂O₂-AOP. The primary objectives are 1) to further explore the mechanisms and benefits of MW/H₂O₂-AOP; 2) apply continuous flow MW/H₂O₂-AOP to waste material treatment. A set of research questions are formulated as follows,

1. Microwave heating been known for its disinfection power, but the effectiveness of MW/H₂O₂-AOP on disinfection of WAS has not yet been reported. Many of the studies in disinfection of sludge only tested the pathogen concentrations immediately after treatment, without considering the regrowth or reactivation of
pathogens. Can MW/H₂O₂-AOP effectively destruct pathogens and inhibit their regrowth?

2. EPS formed a protective layer around activated sludge cells, and it is responsible for the structural integrity of sludge flocs. With the EPS being extracted from sludge, can the solubilization efficiency of MW/H₂O₂-AOP be improved? To what extent the cells can be damaged by MW/H₂O₂-AOP after the removal of EPS?

3. All previous studies used a batch microwave unit, which only holds a maximum volume of 100mL per vessel. In order to apply MW/H₂O₂-AOP in real-life industrial applications, the process must be operated in a continuous flow manner to handle the large volume of waste material. Is continuous flow MW/H₂O₂-AOP as effective as batch MW/H₂O₂-AOP? Heat can be recovered and used to preheat the influent sludge via heat exchange. Will preheating of sludge improve the overall solubilization efficiency?

4. Continuous flow MW/H₂O₂-AOP has never been applied to DM treatment. Acid addition was found important in previous studies of DM treatment using MW/H₂O₂-AOP. Does the increase in acid dosage improve the solubilization efficiency of continuous flow MW/H₂O₂-AOP in DM treatment?

In order to answer the research questions, the following research objectives were designed,

1. To investigate the disinfection power of MW/H₂O₂-AOP treatment of sewage sludge, with the consideration of regrowth. To compare nutrients solubilization of
MW/H₂O₂-AOP at low H₂O₂ dosages and low microwave heating temperatures with previous studies.

2. To improve the effectiveness of MW/H₂O₂-AOP by removing the EPS from sludge cells and use DNA as indicators for the extent of cell destruction.

3. To apply continuous MW/H₂O₂-AOP to sewage sludge treatment and investigate the effects of pre-microwave heating and post-microwave setting in sludge solubilization.

4. To apply continuous MW/H₂O₂-AOP to DM treatment and investigate the effectiveness of sludge solubilization at various microwave heating temperatures and acid dosages.

In the following chapters, experiments were designed and performed to achieve the individual research objectives listed above.
Table 1.1 Oxidation potentials of the most powerful oxidants.

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Oxidation Potential, V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorine</td>
<td>3</td>
</tr>
<tr>
<td>Hydroxyl radical</td>
<td>2.8</td>
</tr>
<tr>
<td>Ozone</td>
<td>2.1</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>1.8</td>
</tr>
<tr>
<td>Potassium permanganate</td>
<td>1.7</td>
</tr>
<tr>
<td>Chlorine dioxide</td>
<td>1.5</td>
</tr>
<tr>
<td>Chlorine 3.0</td>
<td>1.4</td>
</tr>
</tbody>
</table>

*Adapted from Parsons, 2004*
Figure 1.1 Fish killed by algae bloom in Lake Tai.

*Adapted from the Internet [http://www.51766.com/img/wxth/1181099284275.jpg]

Figure 1.2 Electromagnetic spectrum.

*Adapted from Datta & Anantheswaran, 2001.*
**References**


2.0 DISINFECTION AND SOLUBILIZATION OF SEWAGE SLUDGE USING A MICROWAVE ENHANCED ADVANCED OXIDATION PROCESS

In this chapter, the disinfection capabilities of MW/H$_2$O$_2$-AOP to sewage sludge were investigated. Fecal coliforms destruction was used as indicator of the effectiveness of disinfection. The H$_2$O$_2$ dosages and microwave heating temperatures used in this study were lower than in previous studies and the nutrient and organic matter solubilization results were compared.

2.1 Introduction

The treatment and disposal of waste activated sludge is a major concern for municipal wastewater treatment facilities due to its health and environmental impact, as well as handling and disposal costs. Sludge usually contains high levels of organic matter, nutrients, and metals (Metcalf & Eddy 2003); hence they can be used as fertilizers for agricultural land application. According to USEPA (2002), 54% of the produced sludge was applied to agricultural, horticultural, forest, and reclamation land; however, it poses a health threat because of the possible increase in soil-borne diseases associated with the land application of sludge. Pathogens entering the soil may also lead to both surface and ground water contamination, since any member of the allochthonous or indigenous microbiota in soil will eventually end up in an aquatic environment or be dispersed in aerosols (Santamaria & Toranzos 2003; Boyer & Pasquarell 1999). When sludge is used as fertilizers or soil conditioners, they may come into contact with fruits or vegetables, and possibly induce food-borne diseases. Sludge now must meet stringent pathogen

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1 A version of this chapter will be submitted for publication. Yu, Y.; Liao, P.H. and Lo, K.V. Disinfection and solubilization of sewage sludge using a microwave enhanced advanced oxidation process.
reduction regulations, which is specified in the Standards for the Use or Disposal of Sewage Sludge before it can be applied to land (USEPA 1999). The pathogen reduction requirements are divided into two levels, Class A and Class B, depending on the extent of disinfection. In Class B, disinfection is incomplete; fecal coliform levels are reduced below 2 million colony forming units (CFU) per gram of total solids dry weight (USEPA 1999). Disinfection is more complete in Class A, whereas fecal coliform levels are less than 1,000 most probable numbers (MPN) per gram of total solids dry weight (USEPA 1999).

Over the years, many treatment technologies involving physical, biological and chemical methods have been developed to destroy the pathogens in sludge. Conventional methods mostly involve treating the sludge at an elevated temperature for an extended period of time. Pathogens concentrations were found to be significantly reduced under biological thermophilic conditions (Berg & Berman 1980; Watanabe et al. 1997; Cabirol et al. 2002). However, most of these studies only focused on the reduction of pathogens in the digester effluent samples, without considering reactivation or regrowth of pathogens in the subsequent treatment or storage period (Iranpour et al. 2005). In fact, regrowth or reactivation of pathogens has always been problematic for plant operators. For instance, fecal coliforms in digested sludge increased from $10^3$ MPN/g dry solids (DS) to $10^6$ MPN/g DS after dewatering and storage (Iranpour et al. 2003). In this case, sludge that was in compliance to Class A standard after treatment would no longer satisfy its criteria after storage or dewatering.
Microwave irradiation, a physical treatment method, has recently been used for sludge disinfection processes (Martin, et al. 2005). It was found that 45Kw-s (90s at 500W) of microwave irradiation produced approximately a 4.8 log reduction of E. coli. Complete inactivation of fecal coliform (to below detection limits) could be achieved with 60kW-s and 90kW-s (1kW for 60 and 90s) for primary and waste activated sludge, respectively (Hong et al. 2006; Pino-Jelcic et al. 2006). It should also be noted that the microwave at frequencies of 2450MHz and less are also capable of denaturing DNA molecules and disassociating organic chemical bonds (Reimers et al. 2000).

Hydrogen peroxide is well known for its antiseptic properties. It had been tested as means of disinfection when applied alone or in combination with other chemicals. In a study where hydrogen peroxide was used in combination with iron(II) sulfate (Fenton’s reagent) to treat pig and cattle slurry, the total coliform level was reduced by 99.9% (Tofant et al. 2006). Wagner et al. (2002) also found hydrogen peroxide can effectively reduce fecal coliform in wastewater effluent to the target level of 10000 CFU/100mL, but the high dosage and long contact time required clearly made the option uneconomical.

The microwave enhanced advanced oxidation process (MW/H₂O₂-AOP) utilizes both microwave irradiation and hydrogen peroxide simultaneously, generating hydroxyl radicals which could significantly improved nutrients solubilization and pathogen destruction for treating sludge (Liao et al. 2005). As a result, the treated sludge could meet Class A biosolids requirement. Many previous studies have demonstrated the synergistic effects of MW/H₂O₂-AOP in nutrients solubilization and pathogens
destruction. It has been reported that with 1- 2% hydrogen peroxide addition, the MW/H$_2$O$_2$-AOP is capable of releasing nutrients and other organic matters from different types of waste. Nutrients from wastes such as sewage sludge, DM and blood meal were solubilized into solution for subsequent nutrients recovery purposes (Liao et al., 2005; Qureshi et al. 2006; Chan et al. 2007, Eskicioglu, et al. 2008). In terms of pathogens destruction, microwaves alone can cause significant inactivation of fecal coliforms and *Salmonella* spp. in WAS (Pino-Jelcic et al. 2006). A strong synergistic effect of microwave heating and hydrogen peroxide was observed in the destruction of *Escherichia Coli* pure culture (Koutchma & Ramaswamy 2000). However, the combined treatments of hydrogen peroxide and microwave irradiation have not been tested for the destruction of pathogens in sewage sludge. Consequently, the purpose of this study was to investigate sludge disinfection with the consideration of pathogen regrowth and nutrient solubilization using the MW/H$_2$O$_2$-AOP at low hydrogen peroxide dosages (0.02% - 0.1%) and a low temperature regime (55 - 70°C).

### 2.2 Materials and Methods

#### 2.2.1 Batch Microwave Unit

The batch microwave unit used was Milestone Ethos TC closed vessel Microwave Labstation (Milestone Inc., USA), as illustrated in Figure 2.1. It operates at a frequency of 2450 MHz with a maximum power of 1000 W. The Labstation has the capacity of handling up to 12 vessels for the microwave treatment in a single run: one reference vessel and eleven sample vessels, each with a volume of 100 mL. A thermocouple is inserted into the reference vessel and is connected to the control panel (Figure 2.2), thus
providing real time temperature monitoring during the runs. A magnetic mixing device allows for the stirring of the samples in the vessels during the microwave process. The microwave system can attain a maximum temperature of 220°C and a pressure up to 30 bars.

### 2.2.2 Experimental Design

Fresh secondary aerobic activated sludge was obtained from the UBC Pilot Plant, a pilot-scale activated sludge wastewater treatment plant located at the south campus of the University of British Columbia. Characteristics of the secondary aerobic sludge are listed in Table 2.1.

The experiments were divided into two parts, i.e., with and without the microwave treatments. For the microwave treatments, two levels of temperature (55°C and 70°C), and six levels of hydrogen peroxide dosage (0 to 0.1% as w/w in 0.02% increments) were selected. Vessels containing 30 mL of sludge and hydrogen peroxide were heated in the microwave Labstation at a temperature increment of approximately 20°C/minute, up to the desired temperature, and the samples were held for 5.5 minutes at the set temperature within the Labstation. For experiments without the microwave irradiation, sludge samples were treated by the same varying dosages of hydrogen peroxide for 4 hours at ambient temperature.

Fecal coliforms were used as indicator organisms in this study to investigate the effectiveness of the MW/H\textsubscript{2}O\textsubscript{2}-AOP on disinfection of sewage sludge. Samples were
prepared immediately after the treatment for microbial examinations. For the fecal coliform regrowth study, sludge samples treated with microwave irradiation at 70°C were retained in closed sterile bottles and stored at ambient temperature for 72 hours. Microbial examination was carried out again after the 72-hour period. The fecal coliform concentrations after 72 hours were compared to the concentrations immediately after the treatment.

2.2.3 Chemical Analysis and Microbial Examination

Samples were first centrifuged at 4000 rpm for 10 minutes and the supernatant was collected after passing through a 1.6μm fibreglass filter paper. The supernatant was analyzed for ammonia (ammonia-N), orthophosphate (ortho-P), and soluble chemical oxygen demand (SCOD). Unfiltered raw sludge samples were analyzed for total chemical oxygen demand (TCOD), total phosphate (TP), total Kjeldahl nitrogen (TKN) and total solids (TS) according to the Standard Methods (APHA 1998). Ortho-P, ammonia-N concentrations were determined using flow injection analysis (Lachat Quick-Chem 8000 Automated Ion Analyzer, Lachat Instruments, U.S.A.). Fecal coliform concentrations were determined by using the membrane filtration technique, which is described in Standard Methods Part 9222D (APHA 1998). Sludge samples were appropriately diluted with distilled water, so that the fecal coliform count in each sample was between 10 and 200. The diluted samples were passed through 0.45μm sterilized, gridded membranes where microorganisms were retained. Petri dishes containing agar and Difco™ mFC broth base were prepared according to the
manufacturer’s instruction. The filters were then placed on the prepared Petri dishes and incubated at 45°C for 24±2 hours. Fecal coliform colonies were counted after incubation. The results of fecal coliforms concentrations were reported in the units of colony forming units per liter (CFU/L) in Table 2.3. The detection limit for the analyses was 1000 CFU/L.

2.3 Results and Discussion

2.3.1 Nutrients and COD Release

The results of nutrient release and COD release are summarized in Table 2.2. At 70°C, the ortho-P release decreased from 27.4mg/L to 15.7 mg/L as hydrogen peroxide dosage increased from 0 to 0.1%. This result is consistent with previous studies (Kenge et al. 2008; Lo et al. 2008). The decrease in ortho-P concentration further confirms the previous report that polyphosphate was formed when sludge was treated by microwave irradiation and H2O2 at intermediate temperatures between 60°C and 80°C (Wong et. al 2006). At 55°C, the addition of hydrogen peroxide did not have much influence on ortho-P release, indicating limited interaction between microwave irradiation and hydrogen peroxide. Table 2.4 compares the results from previous studies with similar operating conditions to results of this study. The hydrogen peroxide dosage, in terms of H2O2/g dry sludge weight, was substantially lower in this study than in previous studies, however, the ortho-P release were similar in all these studies. It was, therefore, concluded that high releases of ortho-P could not be achieved in low temperatures regimes (60 – 80°C), regardless of the dosages of hydrogen peroxide.
When the sludge was treated by H$_2$O$_2$ alone at ambient temperature, the ortho-P release remained relatively constant until H$_2$O$_2$ dosages exceeded 0.04%, at which point ortho-P concentration increased with an increase in H$_2$O$_2$ dosage. The highest concentration of ortho-P of 25mg/L was obtained at 0.1% of H$_2$O$_2$ (Table 2.2). For H$_2$O$_2$ dosage exceeding 0.04%, the ortho-P yield was the highest for the H$_2$O$_2$ treatment alone (without microwave irradiation) at ambient temperature compared to the MW/H$_2$O$_2$-AOP. However, it should be noted that the samples were treated for 4 hours, thus, the higher ortho-P release could be solely due to hydrogen peroxide treatment over a longer treatment time.

The results indicated that hydrogen peroxide was not a factor in the ortho-P release, in the low temperatures regimes (60 – 80°C) adopted in this study. Heat energy will increase the generation of free hydroxyl radicals from H$_2$O$_2$, and therefore enhance the oxidation process when H$_2$O$_2$ is applied simultaneously with conventional or microwave heating (Eskicioglu et al. 2008). The results from this study confirm this team’s previous findings that the most significant factor affecting ortho-P release was temperature. More than 84% of total phosphate in the ortho-P form could be released at temperatures exceeding 160°C (Liao et al. 2005).

In general, the release of ammonia is low at low temperatures. The highest soluble ammonia was less than 4.8 mg/L, obtained at 70°C with a dosage of 0.08% H$_2$O$_2$ for the MW/H$_2$O$_2$-AOP, while the highest yield was 8.79 mg/L at a dosage of 0.1% H$_2$O$_2$, with a
longer reaction time of 4 hr without irradiation (Table 2.2). No clear trend was observed for ammonia yield in this narrow range of H₂O₂ dosages and low treatment temperatures.

The soluble COD remained relatively constant for H₂O₂ treatments at ambient temperature without microwave irradiation, regardless of H₂O₂ dosage. When sludge was treated at a microwave temperature of 55°C, the COD release was in the range of 300mg/L to 400mg/L. The increase of hydrogen peroxide dosages did not affect the COD release significantly (Table 2.2). This indicated that at lower treatment temperatures, there was little interaction between hydrogen peroxide and microwave irradiation, and the release of COD was most likely due to the microwave heating. At 70°C, it was obvious that the addition of hydrogen peroxide increased the COD release (Table 2.2). The maximum soluble COD concentration was approximately 1000mg/L (~25% of TCOD of the sludge) at 0.1% H₂O₂. It can also be concluded that at low temperatures (60 – 80°C), compare to previous studies, high dosages of hydrogen peroxide is not necessary for the disintegration of solids and nutrient release in MW/H₂O₂-AOP (Table 2.4).

2.3.2 Destruction of Fecal Coliforms

The results of fecal coliform destruction were summarized in Table 2.3. The efficiency of fecal coliform destruction was dictated by temperature, hydrogen peroxide dosage and microwave irradiation.

Hydrogen peroxide is a powerful oxidant with disinfection powers. However, the fecal coliform reduction was not significant at a low dosage of hydrogen peroxide without
microwave irradiation (Figure 2.3). Although hydrogen peroxide is an excellent antiseptic, it rapidly decomposes into oxygen and water when it comes into contact with organic matters. When hydrogen peroxide was added to sewage sludge, it could quickly react with the rich organic matters instead of destructing fecal coliforms. Hydrogen peroxide will not induce protein, lipid or nucleic acid alteration without the catalysts for radical formation (Juven & Peirson 1996). The inhibition of microbial growth and damage to microorganisms by hydrogen peroxide is rather a result of the toxic radicals than its own oxidative properties in its molecular state (Labas et al. 2008). The formation of free radicals usually requires the presence of catalysts such as metal ions (e.g., Fenton’s reagent), UV or ozone. In this case, the sole addition of hydrogen peroxide limits the chances of free radicals formation and therefore the destruction of fecal coliform were ineffective. In addition, Labas et al. (2008) discovered that the inactivation of pure Escherichia coli culture was ineffective when the H₂O₂ dosage was less than the limiting hydrogen peroxide concentration of 25 mg/L. Similarly, such limiting hydrogen peroxide dosage in disinfection could also exist when sewage sludge is used as substrate instead of pure Escherichia coli culture. Hence, another explanation for the poor fecal coliform inactivation in the treatment of sludge with H₂O₂ alone is that the amount of H₂O₂ used here was below the limiting dosage.

Limited fecal coliforms reduction was achieved by microwave heating at 55°C, but as the addition of hydrogen peroxide increased, the reduction of fecal coliforms increased; however, the reduction levelled off when the hydrogen peroxide dosage reached 0.06%. This result was similar to the SCOD solubilization results in that they both suggested
limited interaction between hydrogen peroxide and microwave irradiation at lower temperatures. The limited reduction of fecal coliforms at 55°C shows a contrast to the results obtained for 70°C, where the fecal coliform counts decreased from 5.1 log to 3 log (detection limit) as hydrogen peroxide dosage increased from 0 to 0.04%. No fecal coliform colonies were detected in all samples treated with more than 0.04% hydrogen peroxide dosage at 70°C. This indicated a strong synergistic effect between hydrogen peroxide and microwave heating in the destruction of fecal coliforms even though the hydrogen peroxide dosages were low. Koutchma & Ramaswamy (2002) have reported similar synergistic effects when microwave irradiation and hydrogen peroxide were used to destruct K-12 *Escherichia coli* culture. The strongest synergistic effect was observed at 0.075 g/100 g (H₂O₂/*E. coli* culture) with microwave heating temperature of 60°C. Although sewage sludge instead of pure *Escherichia coli* culture was used in this study, similar synergistic effects of hydrogen peroxide and microwave irradiation combined treatment can still be seen in this study.

The results of the MW/H₂O₂-AOP for disinfection were similar to the microwave irradiation process reported by Hong et al. (2006). When comparing their microwave disinfection results to those with conventional heating methods, the microwave process was more efficient for the treatment of primary sludge, and equally efficient for the waste activated sludge. The microwave treatment could achieve disinfection in the order of minutes, instead of hours in the case of conventional heating. The destruction of fecal coliform was completed in a very short period for the MW/H₂O₂-AOP. It should also be noted that either the MW/H₂O₂-AOP or microwave irradiation is a thermal treatment
process, where the efficiency of pathogen destruction is dictated by a combination of time and temperature. Hydrogen peroxide dosage also affects the overall efficiency of the disinfection for the MW/H2O2-AOP.

The results proved that the MW/H2O2-AOP not only could be used as means of disinfection and stabilization of sludge, but also recover useful resources via sludge solids disintegration and nutrient release. The treated sludge could also meet the Class A biosolids criteria.

2.3.3 Regrowth of Fecal Coliforms

Reduced concentrations of fecal coliforms immediately after treatment could be deceiving because the regrowth of microorganisms and pathogens could take place rapidly when the conditions become favorable again. The samples treated with 70°C microwave irradiation were stored at ambient temperature for 72 hours before the microbial examination was repeated in order to study the effects of the MW/H2O2-AOP on the regrowth of fecal coliforms. The results are shown in Figure 2.4. For samples treated with lower than 0.08% hydrogen peroxide dosage, significant regrowth of fecal coliforms was observed. After 72 hrs, the fecal coliform counts surpassed the initial counts by approximately 3 orders of magnitude, although the fecal coliform count for some samples were below detection limit immediately after the MW/H2O2-AOP treatment. The regrowth of fecal coliforms could be attributed to: 1) multiplication of survived bacteria; 2) elimination of competitive species. As we discussed earlier, nutrients contained in the biomass were released into the solution, which became readily
available to fecal coliforms and other viable microorganisms and therefore causing the regrowth. Some of the bacteriophages which are capable of infecting *E.Coli* bacteria are also susceptible to microwave heating. For example, Sanborn et al. (1982) reported that complete inactivation of bacteriophage T4 was achieved when the phage was exposed to a household microwave for 3 minutes. Therefore, the lack of competition could be another explanation to the significant regrowth of fecal coliforms after microwave treatment. However, no regrowth was observed for samples treated with microwave heating with over 0.08% hydrogen peroxide dosage. The results suggest that the complete elimination of fecal coliforms was achieved at these conditions. The problem of pathogenic microorganisms regrowth can be avoided with the combined treatment of microwave irradiation and sufficient hydrogen peroxide addition (>0.08% in this case). Based on the results obtained in this study, it can be postulated that for different substrates, complete elimination of pathogenic organisms can also be achieved with adequate microwave irradiation and hydrogen peroxide addition. This could be considered a novel process of pasteurization and stabilization of sewage sludge for generating Class A biosolids.

### 2.4 Conclusions

The following conclusions can be drawn from this study:

(1). The MW/H₂O₂-AOP was an effective way to disintegrate sludge solids, and solubilize nutrients from sewage sludge. Contrary to previous studies, high hydrogen peroxide dosage was not necessary for the solubilization of phosphorus and organic matter in the lower temperature regime. Strong synergistic effects between microwave
heating and hydrogen peroxide could be observed in terms of COD release at 70°C. The interaction between microwave heating and hydrogen peroxide, however, was very limited at 55°C, hence resulting in poor COD solubilization.

(2). The MW/H₂O₂-AOP could also be an efficient means to disinfect or stabilize sewage sludge. A significant log reduction of fecal coliforms was observed at 70°C, regardless of hydrogen peroxide dosages.

(3). Complete destruction of fecal coliforms could be achieved with hydrogen peroxide dosage higher than 0.08% at 70 °C microwave temperature. It would eliminate the problem of coliform regrowth. The MW/H₂O₂-AOP is a promising technology in producing sludge that meets and maintains Class A biosolids requirements.
Table 2.1 Characteristics and FC counts of sludge used in this study.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCOD (mg/L)</td>
<td>59 - 70</td>
</tr>
<tr>
<td>SCOD (mg/L)</td>
<td>3967 - 4076</td>
</tr>
<tr>
<td>TS (%)</td>
<td>0.32</td>
</tr>
<tr>
<td>TP (mg/L)</td>
<td>155 - 176</td>
</tr>
<tr>
<td>TKN (mg/L)</td>
<td>405 - 459</td>
</tr>
<tr>
<td>FC Counts (CFU/L)</td>
<td>$5.8 \times 10^6$ - $10.0 \times 10^6$</td>
</tr>
</tbody>
</table>
Table 2.2 Nutrient solubilization results.

<table>
<thead>
<tr>
<th>H₂O₂ Dosage (%)</th>
<th>COD (mg/L)</th>
<th>Ortho-P (mg/L)</th>
<th>NH₄-N (mg/L)</th>
<th>COD (mg/L)</th>
<th>Ortho-P (mg/L)</th>
<th>NH₄-N (mg/L)</th>
<th>COD (mg/L)</th>
<th>Ortho-P (mg/L)</th>
<th>NH₄-N (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>353.2(10.9)</td>
<td>14.00(0.87)</td>
<td>2.66(0.10)</td>
<td>450.3(52.8)</td>
<td>27.43(0.06)</td>
<td>3.46(0.03)</td>
</tr>
<tr>
<td>0.02</td>
<td>59.1(7.2)</td>
<td>10.13(0.38)</td>
<td>5.59(0.21)</td>
<td>369.5(20.6)</td>
<td>16.20(0.72)</td>
<td>2.65(0.26)</td>
<td>712.5(84.9)</td>
<td>17.73(0.81)</td>
<td>3.21(0.05)</td>
</tr>
<tr>
<td>0.04</td>
<td>52.8(15.0)</td>
<td>10.33(0.31)</td>
<td>7.08(0.21)</td>
<td>406.7(23.5)</td>
<td>18.63(1.44)</td>
<td>3.30(0.37)</td>
<td>812.4(11.0)</td>
<td>17.00(0.70)</td>
<td>3.53(0.23)</td>
</tr>
<tr>
<td>0.06</td>
<td>63.7(12.6)</td>
<td>15.57(0.78)</td>
<td>4.07(2.69)</td>
<td>302.3(20.4)</td>
<td>12.93(0.60)</td>
<td>2.54(0.16)</td>
<td>846.8(11.0)</td>
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<td>3.15(0.93)</td>
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<td>0.08</td>
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<td>308.7(15.5)</td>
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<td>2.57(0.08)</td>
<td>924.0(22.0)</td>
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<tr>
<td>0.1</td>
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<td>25.00(0.87)</td>
<td>8.79(0.41)</td>
<td>330.5(12.3)</td>
<td>12.87(1.33)</td>
<td>2.37(0.13)</td>
<td>995.7(12.5)</td>
<td>15.73(0.90)</td>
<td>2.63(1.06)</td>
</tr>
</tbody>
</table>

*a mean(standard deviation) of 3 replicate*
Table 2.3 Experiment design and fecal coliform destruction results.

<table>
<thead>
<tr>
<th>MW Temp (°C)</th>
<th>Dosage (%)</th>
<th>Immediate after treatment (CFU/L)</th>
<th>72hrs after treatment (CFU/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>55</td>
<td>0</td>
<td>$6.1 \times 10^6$(^b)</td>
<td>NA</td>
</tr>
<tr>
<td>55</td>
<td>0.02</td>
<td>$3.5 \times 10^6$</td>
<td>NA</td>
</tr>
<tr>
<td>55</td>
<td>0.04</td>
<td>$1.4 \times 10^6$</td>
<td>NA</td>
</tr>
<tr>
<td>55</td>
<td>0.06</td>
<td>$4.2 \times 10^5$</td>
<td>NA</td>
</tr>
<tr>
<td>55</td>
<td>0.08</td>
<td>$2.8 \times 10^5$</td>
<td>NA</td>
</tr>
<tr>
<td>55</td>
<td>0.10</td>
<td>$2.1 \times 10^5$</td>
<td>NA</td>
</tr>
<tr>
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\(^b\) mean value of 2 replicates
Table 2.4 Comparison with previous studies.

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<th>COD Release (%)</th>
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Figure 2.1 Milestone Ethos TC closed vessel Microwave Labstation.
Figure 2.2 Control panel of the Microwave Labstation.
Figure 2.3 FC reduction
Figure 2.4 FC regrowth.

[Graph showing FC counts (log CFU/L) vs. H2O2 dosage (%). Lines indicate different time points: Immediately after Treatment, 72hrs after Treatment, Initial, and Detection Limit.]
References


3.0 NUTRIENT RELEASE FROM EXTRACTED ACTIVATED SLUDGE CELLS USING THE MICROWAVE ENHANCED ADVANCED OXIDATION PROCESS

In this chapter, the role of extracellular polymeric substances (EPS) of WAS in MW/H2O2-AOP was investigated. DNA was used as indicator for cell destruction after MW/H2O2-AOP. We attempted to improve the efficiency of MW/H2O2-AOP by removing EPS, which formed a protective layer around the cells, from wastewater sludge. The results of nutrients and organic matters solubilization of sludge with EPS being extracted were compared with previous studies.

3.1 Introduction

Activated sludge floc is a mixture of complex aggregates, consisting of various microorganisms agglomerated and entwined in a polymeric network (Morgan et al., 1990). The extracellular polymeric substances (EPS) are present in large quantities in activated sludge, providing a protective layer against environmental stresses as well as maintaining the structural integrity of the aggregates. The composition of the aggregate depends on the type of wastewater as well as the operating conditions of the treatment plant and the extraction methods (Wilén et al., 2003). EPS are of considerable importance in bioflocculation, settling, and dewatering of sludge from wastewater (Schmidt & Ahring, 1996).

Many advanced sludge treatment (AST) processes have been investigated for improving sludge dewaterability and for facilitating sludge handling and disposal.

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2 A version of this paper has been accepted for publication. Yu, Y; Lo, I.W; Liao, P.H. and Lo, K.V. (2009). Nutrient release from extracted activated sludge cells using the microwave enhanced advanced oxidation process. *Journal of Environmental Science & Health Part A, Toxic/hazardous Substances & Environmental Engineering.*
In general, the fundamental principle of AST is to alter the stable physical structures of the activated sludge flocs, including EPS, cell wall and membrane in order to facilitate treatment. Among various AST processes, the microwave treatment of sludge has been recognized for its ability to cause cell wall structure damage, which leads to the permeabilization of cell membranes, and/or the degradation of the cell membrane to release the intracellular materials (Alvarez et al., 1987; Eskicioglu et al., 2007; Kim et al., 2008). It remained inconclusive whether microwaves could cause DNA alteration and damage. Fundamentally, microwave photon has an energy level of $10^5$ eV which is a million times lower than the theoretical required energy to break the covalent bonds of DNA, however, it has been reported that microwave can induce DNA covalent bond breakage, as well as the destruction of bacterial cell membranes (Jeng et al., 1987; Kakita et al., 1995; Hong, et al., 2004).

The microwave enhanced advanced oxidation process (MW/H$_2$O$_2$-AOP), which utilizes microwave radiation in combination with hydrogen peroxide to generate hydroxyl radicals, has been proven to cause solids destruction and nutrients release from sewage sludge. Hydroxyl radicals are strong oxidants capable of causing base pair damage in DNA (Slupphuag et al., 2003; Eskicioglu et al., 2008).

It was thought that sludge cells after the removal of EPS would be more vulnerable to stresses and could be broken down more easily. Hence, the aim of this exploratory study was to examine the effects of the MW/H$_2$O$_2$-AOP on the extracted cells for nutrients release and solids disintegration, and to correlate the extent of cell damage
by quantifying the amount of DNA released into the solution. The preliminary findings are presented in this paper.

### 3.2 Materials and Methods

#### 3.2.1 Microwave Apparatus and Operating Conditions

The microwave used in this study was the batch microwave unit which was described in Section 2.2.1.

The cells were obtained from sludge taken from the enhanced biological phosphorus removal (EBPR) process via the cation exchange procedure (Frolund et al., 1996). Three replicates of each cells sample were used at four testing temperatures of 60, 80, 100, and 120 °C for the MW/H₂O₂-AOP treatment. The rate of temperature increase was set at 20 °C minute⁻¹ to attain the target temperature, and then the samples were held for additional five minutes. The dosages of H₂O₂ were 0, 0.1, 0.3 and 0.5% (w/w) in 30 mL of samples. The pH of the samples was adjusted to 4 using sulfuric acid.

#### 3.2.2 Chemical Analysis

All of the chemical analyses, except for that of carbohydrate, followed the procedures outlined in Standard Methods (APHA, 1998). The filtered samples (treated and untreated) were analyzed for soluble chemical oxygen demand (SCOD), orthophosphate (ortho-P), ammonia, volatile fatty acids (VFA) and carbohydrate. The initial samples were also analyzed for TS, total chemical oxygen demand (TCOD), total phosphate (TP) and total Kjeldahl nitrogen (TKN).
Total carbohydrate content as glucose was determined spectrophotometrically using the anthrone method (Froloud et al., 1996). The modified Lowry method was used to quantify proteins and humic-like compounds, in which bovine serum albumin (BSA) and humic acids were used as the standards, respectively (Froloud et al., 1996). DNA was determined by the DNA-DAPI (4', 6-diamidino-2-phenylindole·2HCl) fluorimetric method (Kapuscinski & Skoczylas 1977; Brunk et al., 1978).

### 3.3 Results and Discussion

#### 3.3.1 Extraction of EPS

Various EPS extraction methods gave very different results, in terms of quantity and quality of the extracted EPS. The cation exchange procedure selected in this study has been widely accepted and used for EPS extraction from activated sludge, since it gives high extraction efficiencies with little or no cell lysis and polymer disruption (Froloud et al., 1996). The characteristics of activated sludge, extracted cells, loosened EPS (LEPS) and bound EPS (BEPS) are presented in Table 3.1.

In an EBPR process, phosphorus is removed by utilizing polyphosphate accumulating organisms (PAOs) to uptake ortho-P, therefore, the majority of phosphorus is held within cell biomass (Mino et al., 1998). The fact that approximately 80% of the total phosphorus remained in the cells portion after the EPS removal indicated that the extraction method used caused little cell lysis, and the integrity of cells were preserved (Table 3.1). The extracted EPS was about 13.5% of the activated sludge biomass, which was close to the typical value of 15%. It contained the higher nitrogen content than that of the sludge; protein, humic acids and carbohydrate were the major polymeric constituents. The humic acids fraction was the largest in the extracted EPS,
while carbohydrate was the least. The results were in accordance with the cation exchange method (Wilén et al., 2003).

### 3.3.2 Solubilization of Extracted Cells

The solubilization of the cells, rather than EPS, was considered much more important because: 1) majority of the nutrients (phosphorus and nitrogen) and organic matters (COD) was in the cell portion; 2) nutrients and organic matters in the EPS portion were mostly in soluble form. Hence, only the solubilization of extracted cells was examined in this study. The results of the solubilization of cells are presented in Table 3.2. Even though the extracted cells contained a relatively high content of nitrogen, very little soluble ammonia was obtained after the treatment. Ammonia concentration was around 4.6 mg L$^{-1}$ for microwave treatments without H$_2$O$_2$, regardless of microwave heating temperatures. For the MW/H$_2$O$_2$-AOP treatment, ammonia concentration increased with an increase of H$_2$O$_2$ dosage, as well as an increase in treatment temperature. The results were similar to that of a previous study of the MW/H$_2$O$_2$-AOP on secondary sludge (Kenge et al., 2008).

The initial concentration of ortho-P in the cell solution was approximately zero. After the MW/H$_2$O$_2$-AOP treatment, the ortho-P concentration increased to about 90 mg L$^{-1}$, regardless of microwave temperature and H$_2$O$_2$ dosage; this result was not in agreement with those of previous studies. The amounts of ortho-P released from activated sludge were dictated by microwave temperature and H$_2$O$_2$ dosage (Wong et al., 2007; Chan et al., 2007). In this study, extracted cells were exposed directly to chemical and physical stress; acid or alkali would react with the cell wall and membrane in several ways, including the saponification of lipids in cell membranes,
which leads to the damage of cell membrane causing the leakage of intracellular materials (Erdinclar & Vesilind, 2000). The MW/H\textsubscript{2}O\textsubscript{2}-AOP treatment can also destroy or compromise the cell membrane, and therefore make the intracellular material accessible (Wong et al., 2007; Chan et al., 2007; Eskicioglu et al., 2008). Furthermore, the peroxide treatment can also cause permeabilization of cell membrane, changes in membrane fluidity and the induction of apoptosis (Alvarez et al.; 1987). The treatment of extracted cells was not as dependent on operating temperature and H\textsubscript{2}O\textsubscript{2} dosage.

The results for ortho-P solubilization from this study were compared to those of previous studies in Table 3.3. Under similar treatment conditions, ortho-P solubilization from extracted cells was much higher than from the activated sludge. About 80% of the ortho-P could be released from the extracted cell at 60°C, while an operating temperature of 160°C is required for activated sludge to achieve similar ortho-P solubilization efficiency (Liao et al., 2005). In addition, less acid and hydrogen peroxide were required for the extracted cell. The results indicated that the MW/H\textsubscript{2}O\textsubscript{2}-AOP could be operated at a low microwave temperature and a low H\textsubscript{2}O\textsubscript{2} dosage for ortho-P release from the extracted cell, potentially reducing operational costs. It could be advantageous to separate EPS from the activated sludge before treatment with MW/H\textsubscript{2}O\textsubscript{2}-AOP, making it easier to release and recover nutrients from the extracted cells.

The SCOD increased with the increase of both H\textsubscript{2}O\textsubscript{2} dosage and microwave temperature (Table 3.2). Similar to the MW/H\textsubscript{2}O\textsubscript{2}-AOP treatment of activated sludge, heating temperature and H\textsubscript{2}O\textsubscript{2} dosage are important factors influencing SCOD
solubilization of the cell. The smallest percentage increase for SCOD was observed at a heating temperature of 60°C without H₂O₂, while the best SCOD yield was obtained at 120°C, with a H₂O₂ dosage of 0.5%.

VFA in solution increased with the increase of both H₂O₂ dosage and microwave heating temperature. The trend was similar to that of SCOD solubilization.

Carbohydrates, protein and humic acids are also common intracellular materials found within cells. The soluble fractions of carbohydrates, protein and humic acids were all found to be close to zero in the activated sludge and the extracted cells. After the microwave radiation without an addition of H₂O₂, the soluble concentrations for all of the above-mentioned compounds increased, demonstrating cell destruction achieved by microwave radiation. As microwave temperature increased, carbohydrate concentrations in solution were also increased (Table 3.2). For the MW/H₂O₂-AOP treatment, both microwave temperature, and hydrogen peroxide dosage affected the carbohydrate concentrations in solution. Carbohydrate concentrations of the sludge treated at various temperatures all follow similar patterns as H₂O₂ dosage increases. Carbohydrate concentrations first increased as hydrogen peroxide dosage was raised from 0 to 0.1%, then its concentration decreased with a further increase in H₂O₂ dosage (0.3 to 0.5%). The decreased concentrations of carbohydrate could be explained by further oxidation of carbohydrate into simpler compounds such as carbonyl compounds, VFA or CO₂ due to higher H₂O₂ dosages with the aid of microwave radiation. Carbohydrate concentration decrease could also be due to Maillard reactions, which occurred between amino acids and reducing sugars at elevated temperatures; this resulted in polymerization, thereby reducing the solubility.
of protein and sugars (Baisier & Labuza, 1992). Due to interferences caused by the residual H₂O₂ in the solution from the MW/H₂O₂-AOP, values for humic acids and protein were not determined.

3.3.3 DNA as an Indicator of Cell Destruction

As noted earlier, sludge cells were well preserved after the extraction of EPS, hence, the amounts of DNA detected in the solution could indicate the extent of cell disintegration after MW/H₂O₂-AOP treatments. It was reported that *E. coli* cell wall structures were damaged, allowing for an increased amount of DNA released into solution as microwave heating temperatures increased (Woo et al., 2000). Similar DNA leakage patterns were observed when *Bacillus subtilis* was treated by microwave radiation (Kim et al., 2008). In our study, considerable amounts of DNA were released into the solution after all treatments. DNA leakage remained fairly constant for tests with H₂O₂ dosages ranging from 0 to 0.3%, regardless of the microwave heating temperatures applied. An increase of the DNA concentration, however, was observed when the H₂O₂ dosage was increased to 0.5% for microwave temperatures of 80, 100 and 120°C (Figure 3.1). Eskicioglu, et al. (2008) reported that heating would increase the decomposition of H₂O₂ into hydroxyl radicals and therefore enhance the oxidation process when H₂O₂ was applied simultaneously with either conventional or microwave heating. The hydroxyl free radicals might have an impact on different cell components by producing an oxidative stress (Labas et al., 2008). It could therefore be postulated that, at higher temperatures and higher H₂O₂ dosages, the MW/H₂O₂-AOP would generate more hydroxyl radicals, resulting in more DNA leakage out of the cell.
The results showed that higher DNA concentrations were obtained at higher H$_2$O$_2$ dosages, indicating a greater magnitude of cell damage and stronger synergistic effects between H$_2$O$_2$ and microwave radiation.

### 3.4 Summary and Conclusions

The MW/H$_2$O$_2$-AOP was an efficient means for cell degradation to release soluble ammonia, ortho-P, carbohydrate and VFA. High concentrations of ortho-P could be released from the extracted cell at low microwave temperature (60°C) and low H$_2$O$_2$ dosage (0.1%) compared with previous studies where activated sludge was used as substrate. High microwave temperatures and high H$_2$O$_2$ dosages favor the release of SCOD. Carbohydrate could also be released from cells; its concentration first increased as H$_2$O$_2$ dosage increased from 0 to 0.1%, then decreased with a further increase of H$_2$O$_2$ dosage.

The extent of the cell damage is indicated by the amounts of DNA released. The DNA leakage increased significantly as the H$_2$O$_2$ dosage increased to 0.5% at microwave temperatures of 80 to 120°C.
Table 3.1 Characteristics of the sludge, BEPS, LEPS and cells.

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<th>TCOD (mgL⁻¹)</th>
<th>VFA* (mgL⁻¹)</th>
<th>Carbohydrate* (mgL⁻¹)</th>
<th>Proteins* (mgL⁻¹)</th>
<th>Humic acid* (mgL⁻¹)</th>
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* soluble type.
Table 3.2 Nutrient release from the cells after microwave treatment.

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<th>SCOD (mgL⁻¹)</th>
<th>VFA (mgL⁻¹)</th>
<th>Carbohydrate (mgL⁻¹)</th>
<th>Proteins (mgL⁻¹)</th>
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Table 3.3 Comparison of ortho-P solubilization with previous studies.

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Figure 3.1 DNA release from cells after the MW/H$_2$O$_2$-AOP.
References


4.0 SEWAGE SLUDGE TREATMENT USING CONTINUOUS MICROWAVE ENHANCED ADVANCED OXIDATION PROCESS

In Chapter 4, to suit the need of treating WAS in a continuous manner, a continuous flow microwave unit was used in the study of sludge solubilization using MW/H$_2$O$_2$-AOP. Heat exchange could be used to pre-heat the sludge before MW/H$_2$O$_2$-AOP treatment in real-life industrial application to improve the solubilization efficiency. Storing the sludge in isothermal conditions after treatment was also thought to improve the solubilization efficiency. Hence, this study also investigated the effects of pre-microwave heating and post-microwave setting of sludge for nutrients and organic matter solubilization.

4.1 Introduction

As health and environmental regulations become more stringent on effluent qualities, nutrient removal from the wastewater via biological nutrient removal (BNR) processes have increased its popularity among wastewater treatment plants (WWTPs). While BNR processes are capable of removing more nutrients from wastewater, the drawback of this process is a higher volume of sludge produced. Excess sludge volume presents serious treatment and disposal problems; therefore, sludge disintegration technologies, such as mechanical, thermal, chemical and biological methods have been investigated (Camacho et al. 2004; Valo et al. 2004; Eskicioglu et al. 2006; Takasima & Tanaka 2008).

The microwave enhanced advanced oxidation process (MW/H$_2$O$_2$–AOP) has been proven effective in the disintegration and solubilization of sludge. As a result, the

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3 A version of this paper has been submitted for publication. Yu, Y.; Chan, W.I; Lo, I.W; Liao, P.H and Lo, K.V. Sewage sludge treatment using continuous microwave enhanced advanced oxidation process.
sludge biodegradability is enhanced and solubilized nutrient can be recovered in subsequent processes (Liao et al. 2005; Wong et al. 2007; Chan et al. 2007; Danesh et al. 2008; Bhuiyan et al. 2008). In terms of biodegradability, Pino-Jelcic et al. (2006) reported better biogas production from microwave (MW) treated sludge, while Eskicioglu et al. (2008) reported slower biodegradation and lower ultimate methane production for MW irradiation and MW/H₂O₂–AOP treated sludge. Despite the discrepancies between these two studies, both studies acknowledged significant increase in soluble chemical oxygen demand (SCOD), which is an indirect measurement of the degree of solids disintegration. In addition to its sludge solubilization capabilities, the MW/H₂O₂-AOP could potentially improve sludge settling and dewatering properties. It had been observed in our previous studies that the MW and MW/H₂O₂–AOP treated sludge settled well after treatment; however, no quantifications were made to confirm this observation.

In most of the studies of sludge treatment using MW irradiation, the experiments were performed using a batch operation mode and only a small volume of sludge can be treated (Pino-Jelcic et al. 2006; Liao et al. 2005; Wong et al. 2007; Chan et al. 2007; Danesh et al. 2008; Eskicioglu et al. 2008). Another disadvantage of using a batch process is that H₂O₂ must be added to the substrate before the substrate is subjected to MW irradiation. Hydrogen peroxide is a powerful oxidizing agent which reacts quickly with organic matters and decomposes into water and oxygen; hence in a batch process the synergistic interaction between MW irradiation and H₂O₂ is limited. If the MW technology is to be implemented in a WWTP, the process must suit the need of treating sludge in large quantities and in a continuous operation mode. This study was initiated to study the treatment efficiency of the MW/H₂O₂–AOP operating in a
continuous mode. The synergistic effects between MW irradiation and H$_2$O$_2$ can therefore be enhanced by injecting hydrogen peroxide and the feed stream into the MW unit simultaneously.

Heat could be recovered from the microwave treatment process by means of heat exchange to preheat the feed sludge prior to the MW treatment, and hopefully to improve the treatment efficiency and to reduce the hydrogen peroxide dosage in the MW/H$_2$O$_2$-AOP.

In order to optimize the H$_2$O$_2$ dosage, one must take into consideration the activities of catalase, since H$_2$O$_2$ can be broken down into water and molecular oxygen by catalase in most of the activated sludge. Catalase, a terminal respiratory enzyme, is present in all living aerobic cells; its function is to protect cells from damage caused by reactive oxygen species (Guwy et al. 1998; Guwy et al. 1999). It should also be noted that according to the enzyme activity definition, one unit of catalase activity corresponding to the breakdown of 1 µmol of H$_2$O$_2$ per minute under specific conditions (Gabbita & Hzuang, 1984). Catalase is most active at low temperatures between 15 and 45°C, and gradually loses its potency beyond 45°C (Wang et al. 2009). Hence, by pre-heating the sludge to higher temperatures before mixing with H$_2$O$_2$, unnecessary loss of the H$_2$O$_2$ to the catalase could be lowered and the efficiency of MW/H$_2$O$_2$-AOP can be improved.

Some advantages can be realized if the exit temperature from the MW/H$_2$O$_2$-AOP is maintained for a certain period of time. Phosphate was released as a function of time
after the MW treatment, when the samples were retained in an isothermal container (Danesh et al. 2008).

This study was designed with the consideration of the possible benefits of heat recovery and a low H₂O₂ dosage in the MW/H₂O₂-AOP. The main objectives were: 1) Investigate the influence of pre-heating and post-setting in the MW/H₂O₂-AOP on the nutrients release and solid disintegration; and 2) Compare the dewaterability and settleability of the sludges treated by various treatments.

4.2 Materials and Methods

4.2.1 Wastewater Sludge

Thickened waste activated sludge (WAS) used in this study was taken from the wastewater treatment pilot plant located at the south campus of the University of British Columbia. The plant was operated in the enhanced biological phosphorus removal (EBPR) mode. The total phosphorus (TP) concentration from EBPR sludge was relatively high, compared to conventional wastewater sludge. The characteristics of WAS are presented in Table 4.1.

4.2.2 Continuous MW Unit

The continuous MW unit was modified from a household MW oven (Panasonic Genius Prestige Countertop Microwave Oven). A silicon tube with 6.35 mm diameter was wound into a continuous horizontal coil and held by a custom made perforated polypropylene shelf. The total length of the silicon tube inside the MW unit is 40 m and the volume is approximately 1.3 L. Raw sludge and H₂O₂ solution were pumped
simultaneously into the MW unit, and the treated sludge was collected from the outlet in a bucket. Figure 4.1 shows a picture of the modified continuous microwave unit.

The desired H₂O₂ dosage in the process was controlled by the flow rate and the concentration of the prepared H₂O₂. Different exit temperatures after the MW treatment can be achieved by controlling the flow rate of both the sludge and H₂O₂; a higher flow rate yields a lower exit temperature. The MW power output was set at its maximum level (1000 W) throughout this study.

**4.2.3 Experiment Design**

The experiment consisted of two parts: the first part was to examine the effects of pre-microwave heating (pre-heating), post-microwave setting (post-setting) and retention time (RT) of sludge retained in the MW unit, on the MW/H₂O₂-AOP; the second part was to measure settleability and dewaterability of sludge treated by various treatment.

Pre-heating of sludge was achieved by heating the sludge to desired temperatures (40°C, 50°C and 60°C) using a hot plate. The heated sludge was then introduced into the MW unit. Post-setting was achieved by retaining the treated sludge in a hot water bath at 80°C for the duration of 30, 60, 90 and 120 minutes. Sludge samples were collected in the following sequence: after pre-heating, immediately after MW irradiation, post-setting times of 30, 60, 90 and 120 minutes. All samples were maintained at 4°C immediately upon collection. Each experiment was repeated using three different RTs of 5, 7 and 9 minutes. A set of experiments without pre-heating and post-setting served as a control. The H₂O₂ dosage used was 0.2% w/w in all the experiments (Table 4.2).
Four sets of experiments were conducted in the second part including an acid treatment at ambient temperature, MW standalone treatment, MW/H₂O₂-AOP and MW/H₂O₂/H⁺-AOP. The detailed operating conditions and H₂O₂ dosage are listed in Table 4.3.

4.2.4 Chemical Analysis

The supernatants obtained from treated samples were analyzed for orthophosphate (ortho-P), carbohydrates and soluble chemical oxygen demand (SCOD) without passing through fibreglass filter paper, as the unfiltered supernatant was a better representation for a full-scale operation (Danesh et al., 2008). The initial samples were also analyzed for total chemical oxygen demand (TCOD), total phosphate (TP), total Kjeldahl nitrogen (TKN) and total solids (TS). All of the chemical analyses performed followed the procedures outlined in the Standard Methods (APHA 1998).

Carbohydrates concentrations were determined using the anthrone carbohydrate method as described by Raunkjaer et al. (1993) with modifications. A brown or red color developed when H₂O₂ was present, which caused interference. In order to remove the H₂O₂ residue, 1 mL samples were placed in 1.5 mL mini centrifuge tubes and spun at 10,000 rpm (11,050 x g, Thermo IEC Multi rotor) for 10 minutes and subsequently dried at 103°C overnight. The dried samples were then cooled to room temperature and 1 mL of cold ethanol was added to each sample to precipitate carbohydrates. The samples were again spun at 10,000 rpm for 10 minutes and dried at 60°C over night. The dried samples were re-solubilized by 1 mL of distilled water and mixed with 2 mL of anthrone reagents. The mixture was incubated at 100°C for...
15 minutes then cooled at 4°C for 5 minutes. The concentration was measured spectrophotometrically at 625 nm.

Settleability was determined by settling the sludge in a one-litre measuring cylinder over 60 minutes. The sludge was first mixed by a glass rod, and then the sludge level was recorded at 5, 10, 15, 20, 30, 45, and 60 minutes after mixing, in mL. Dewaterability was determined in terms of capillary suction time (CST), by using the Komline-Sanderson capillary suction timer with a paper support block, stainless steel reservoir with 18 mm inner diameter and 25 mm height, and a digital timer.

4.3 Results and Discussion

4.3.1 The Effects of Pre-Heating and Post-Setting on the Solid Disintegration and Nutrient Solubilization

The results for ortho-P concentrations are presented in Figure 4.2. The highest concentration of ortho-P was obtained in the pre-heating stage without any addition of H₂O₂; they were 17 - 24%, 57 - 62% and 55 - 59% of TP at 40°C, 50°C and 60°C, respectively. They were attributed to cell lysis alone causing the release of ortho-P from biomass in the lower temperature regime (~60°C). The phenomenon of phosphorus release under heating was in accordance with a previous study (Kuroda et al. 2001). Ortho-P concentrations were found to increase when activated sludge was incubated at temperatures ranging from 50°C - 90°C for 20 to 120 minutes.

After treatment with the MW/H₂O₂-AOP, ortho-P concentrations decreased sharply from sets with pre-heating; however, the ortho-P concentrations were still significant higher than those of the initial (less than 0.1% of TP). The decrease in ortho-P was
likely caused by its combination with divalent cations and/or extracellular polymeric substances (EPS) to foam flocs. These flocs can be destroyed to release ortho-P again at much higher operating temperatures. The MW unit, however, was not designed to operate under pressure, and therefore, no MW temperature over 100 °C could be reached. The exit temperatures were in the range of 63 °C - 98 °C in this study, as shown in Table 4.2.

When the sludge was treated without pre-heating and post-setting, the ortho-P release was found to be 45%, 39% and 11% for 5, 7 and 9 minutes of RTs, respectively. It was found that ortho-P release corresponded to RT in the MW/H2O2-AOP. It appeared that a better ortho-P release was obtained at a shorter RT, corresponding to a lower exit temperature; the best yield was obtained at 5 minutes of RT in this study. It also released the highest concentration of ortho-P among all MW/H2O2-AOP treatments (Figure 4.2).

Ortho-P concentrations were found to increase as a function of time when the MW treated sludge was kept in a hot water bath (Figure 4.2). It is likely that the increase of ortho-P concentrations was due to the breakdown of poly-P (poly-phosphorus). Kuroda et al. (2001) reported that the poly-P concentrations in the sludge supernatant decreased with an increase of heating time. This clearly indicated that the increase of ortho-P concentrations was due to the degradation of poly-P. Similar results were also reported by Danesh et al. (2008). It is clear from the results that pre-heating and post-setting does not improve overall efficiency of ortho-P release using the MW/H2O2-AOP. It is also noticeable that with conventional heating at 50°C or 60°C,
approximately 60% of TP could be released from sludge, which is similar to the MW/H₂O₂-AOP.

A limited amount of ammonia-N and VFAs were released into the treated solution. Ammonia-N release was between 4 – 18 mgL⁻¹ (0.8 – 2.8% as TKN) and VFA release was between 0 – 35 mgL⁻¹. The results indicated that ammonia-N and VFA release from sludge was extremely low at this low treatment temperature regime of the MW/H₂O₂-AOP.

The significance of SCOD release from sludge was reflected in two aspects. It can indicate the disintegration of sludge solids, leading to reduced sludge volume after treatment. Additionally, more readily available organic matters in the solution increases subsequent anaerobic digestion efficiency. MW treated sludge has been reported to have higher volatile solids reduction and cumulative biogas production, when compared to conventional treated sludge and untreated sludge (Pino-Jelcic et al. 2006).

The results of SCOD release in this study are shown in Figure 4.3. At the pre-heating stage, SCOD release was in the range of 2.6% to 22% as temperatures raised from 40°C to 60°C. A significant increase in SCOD release after treatment with the MW/H₂O₂-AOP was observed in all three RTs. The highest SCOD concentration was also obtained with the highest pre-preheating temperature in all cases. It also showed that post-setting treatment affected SCOD release to a limited extent. Increase of SCOD concentrations with time was observed during the post-setting period. The broken straight lines in Figure 4.3 denoted the SCOD releases for the control set.
without pre-heating or post-setting. SCOD release from sludge treated with a low RT (5 minutes) was lower than those treated with longer RTs (7 and 9 minutes), both with or without pre-heating. In the post-setting period, SCOD release from sludge treated with low RT (5 minutes) increased at a faster rate than those treated with longer RTs (7 and 9 minutes), indicating that pre-heating and post-setting of sludge could offset the disadvantage of using shorter RT.

Intra- and extra-cellular biopolymers within sludge such as sugars, proteins, lipids could be released into the supernatant under microwave irradiation (Eskicioglu et al. 2007). The resulting sugar concentrations at the end of each treatment are presented in Figure 4.4. Sugar concentrations were found to be higher in samples with pre-heating and post-setting. At a pre-heating temperature of 60°C, the sugar concentrations were highest regardless of the retention time. The sugar concentrations decreased as the RT increased. The decrease in sugar concentrations could be due to either the production of further oxidized compounds or the polymerization of amino acids and reducing sugars at elevated temperatures via Maillard reactions (Baisier & Labuza 1992). Similar results were reported previously (Eskicioglu et al. 2007). With the aid of pre-heating and post-setting, the amount of sugars released into the solution can be doubled, or even tripled, as shown in Figure 4.4.

The overall results indicated that exit temperature, which in this study was directly related to the RT of the sludge, had a greater impact than the rate of temperature increase. The smaller impact on the treatment effectiveness may be because the temperature increase rate was in a narrow range in this study: the rates were in a range of 4.2-7.4°Cmin⁻¹ for the sets of pre-heating, while they were between 6.7 and
8.9°C/min for the sets without pre-heating. The results were similar to those of microwave treatment without H₂O₂ operating at a batch mode (Eskicioglu et al. 2007; Toreci et al. 2009). In a temperature range of 56-96°C, there was a linear relation between MW temperature and degree of hydrolysis. At similar MW treatment temperatures, a lower temperature increase rate had a higher degree of SCOD solubilization. However, a higher level of SCOD solubilization was obtained at a higher rate of temperature increase for the MW/H₂O₂-AOP. The optimal rate was at a range of 20-30°C (Lo et al. 2010).

Based on the post-setting results, it is also recommended that insulation be applied to the samples after treatment to increase treatment efficiency in a continuous MW/H₂O₂-AOP. Extra energy does not need to be added to the samples as long as insulation is sufficient.

### 4.3.2 Dewaterability and Settleability of Treated Sludge

Dewaterability is determined by capillary suction time (CST), which measures how fast water can be released from the sludge. Settleability is determined by settling tests. The results of dewaterability and settleability are shown in Figures 4.4 and 4.5, respectively. CSTs of sludge treated by MW and MW/H₂O₂-AOP increased significantly, while CSTs of sludge treated by acid and MW/H₂O₂/H⁺-AOP was approximately the same. In terms of settleability, sludge treated by all four types of treatments settled faster than the untreated sludge, with the MW/H₂O₂/H⁺-AOP treated sludge settling the fastest.
The sludge dewaterability is relative to the amount of EPS attached to sludge cells; CST will decrease with an increase in EPS until an optimal amount, beyond which point, a further increase in EPS will deteriorate CST. (Houghton et al. 2001). It can be postulated that the release of EPS from sludge is responsible for the deterioration of CST in all of the MW treated sludge. The amount of attached EPS is reduced after MW treatment, shifting away from the optimal amount, thereby increasing CST. The MW radiation could cause EPS to detach from the cell surface, resulting in high concentrations of detached EPS in sludge solution. Pores within the filter paper could be blocked by detached EPS, preventing water from escaping from the treated solution (Chen et al. 2001). As a result, a longer CST was obtained for the treated solution than for the sludge. When the sludge is treated with MW/H₂O₂-AOP and MW/H₂O₂/H⁺-AOP, the amounts of the total EPS could also be further reduced in the treated samples; EPS could be broken down into simpler forms. Hence, it will not block pores of the filter paper. This could explain why better CST results were found from MW/H₂O₂-AOP and MW/H₂O₂/H⁺-AOP treatments than the MW treatment. Weak acid could cause EPS to leave the surface of bacterial cells, making the cell particles easier to flocculate, hence reducing the water content in sludge; as a result, the dewaterability was slightly improved for the set of acid treatment (Chen et al. 2001).

As mentioned above, EPS taken out from the cell surface could be beneficial for the agglomeration of sludge, which improves the sludge settleablity. As shown in Figure 4.6, all treatments showed improvements in sludge settleability. Sludge treated by MW/H₂O₂/H⁺-AOP showed the best results. This is likely due to the highest degree of sludge oxidation, which causes both EPS release and solids destruction. These tests
confirmed that MW or MW/H$_2$O$_2$-AOP treatment can improve the settleability of sludges.

**4.4 Conclusions**

A continuous MW unit was used for the MW/H$_2$O$_2$-AOP treatment of sludge with the consideration of pre-heating and post-setting of sludge. The conclusions can be drawn from this study as follows:

1. Pre-heating and post-setting improved organic matter (SCOD and sugar) solubilization but did not help the ortho-P solubilization.

2. In general, longer RT is beneficial for organic matter solubilization while shorter RT favors the ortho-P solubilization. Pre-heating and post-setting could offset the disadvantage of using a shorter RT in MW/H$_2$O$_2$-AOP in terms of organic matter solubilization.

3. Dewaterability of sludge in terms of CST was not improved after MW irradiation, MW/H$_2$O$_2$-AOP and MW/H$_2$O$_2$/H$^-$-AOP treatment. However, significant settleability improvements were observed for all treatment.
Table 4.1 Characteristics of WAS used in this study

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Table 4.2 Experimental design for the MW/H$_2$O$_2$-AOP treatment - part 1

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<th>RT in MW (min)</th>
<th>Pre-heating Temperature ($^\circ$C)</th>
<th>Ave. MW Exit Temperature ($^\circ$C)</th>
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Table 4.3  Experiment designs for dewaterability and settleability - part 2

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<td>MW/H₂O₂/H⁺-AOP</td>
<td>9</td>
<td>0.2%</td>
<td>4</td>
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</table>
Figure 4.1 Continuous microwave unit.
Figure 4.2 Ortho-P release from the treated sludge.

( — Pre-heat temperature = 40°C; — Pre-heat temperature = 50°C; — Pre-heat temperature = 60°C; — MW treatment only, without pre-heating or post-setting)
Figure 4.3 SCOD release from the treated sludge.

(●) Pre-heat temperature = 40°C; (●) Pre-heat temperature = 50°C; (●) Pre-heat temperature = 60°C; (●) MW treatment only, without pre-heating or post-setting).
Figure 4.4 Sugar release from the treated sludge.

(Control, MW/H₂O₂-AOP alone, without pre-heating or post-setting; Pre-heat temperature = 40°C; Pre-heat temperature = 60°C; Pre-heat temperature = 60°C)
Figure 4.5 Capillary suction time (CST) of sludge after various treatments.
Figure 4.6 Sludge level vs. settling time of sludge after various treatments.

( — Raw sludge; — Acid treatment; — Microwave treatment alone; — MW/H₂O₂-AOP; — MW/H₂O₂/H⁺-AOP).
References


5.0 APPLICATION OF CONTINUOUS MICROWAVE ENHANCED ADVANCED OXIDATION PROCESS TO DAIRY MANURE SOLUBILIZATION

In Chapter 5, to follow up the successful application of continuous MW/H₂O₂-AOP to wastewater sludge, this process was applied to dairy manure (DM). The significance of acid dosages and microwave heating temperatures were investigated for nutrients and organic matter solubilization.

5.1 Introduction

Dairy industry is one the most important industries in Canada. According to Canadian Diary Information Center, there were 978,400 dairy cows across Canada, generating total revenue of 5.3 billion Canadian dollars in 2008 (CDIC, 2009). The booming dairy industry however poses serious environmental threats as excessive amount of DM had been produced annually. In 2001, Canadian livestock produce an estimated 177.5 million tonnes of manure and manure produced by dairy cows was accounted for 13.5% of the total manure production (Hoffman & Beaulieu, 2001). DM contains high level of organic matter and nutrients such as phosphate and ammonia, and could cause environmental problems including eutrophication of water bodies, bacterial contamination of water and soil, and over-enrichment of soil with nitrogen and/or phosphorous (Champagne, 2007). Therefore, proper treatment of DM is the key for the future success of Canadian dairy industry. From the nutrient recovery perspective, DM should be deemed as a valuable bioresource, rather than waste, since it contains high concentrations of organic matter and nutrients; phosphate in particular is a scarce non-renewable resource. However, nutrient recovery from DM is difficult due to its

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4 A version of this paper will be submitted for publication. Yu, Y; Lo, I.W; Liao, P.H and Lo, K.V. Application of continuous microwave enhanced advanced oxidation process to dairy manure solubilization.
complex nature. DM has high suspended solids content and low soluble phosphorus content. Most of its phosphorus (up to 65%) is contained within the solid portion of the DM (Barnett, 1994). Hence a pre-treatment step is required for nutrient recovery from DM to break the solids and “free” the nutrients.

Microwave treatment is a potential pre-treatment method for nutrient recovery from DM. The main purpose of microwave treatment is to disintegrate solids and release nutrients and organic matter into the solution in soluble forms for the ease of subsequent recovery. Recently microwave treatment of waste materials such as biosolids, blood meal, and fish silage, has all been recognized for its rapidity and effectiveness in solids disintegration and nutrient release (Liao et al., 2005; Chan et al., 2007; Chan et al., 2009).

In previous studies, acidified DM samples using sulfuric acid (1:50 vol/vol) were treated by MW/H$_2$O$_2$-AOP. Approximately 80% of the total phosphorus (TP) was released into the solution when the samples were heated in the microwave for 5 minutes at a microwave temperature of 170°C (Pan et al., 2006). The orthophosphate (ortho-P) release was further improved to 85% of TP when the microwave heating time was extended to 10 minutes. With the addition of H$_2$O$_2$ (1:20 vol/vol), the same ortho-P release can be achieved at a lower microwave temperature of 120°C, indicating the importance of H$_2$O$_2$ in microwave treatment of DM. Qureshi et al. (2008) further investigated the release of ortho-P and metal ions such as magnesium, calcium and potassium for the potential struvite recovery from microwave treated DM. It was reported that the ortho-P:TP ratio was increased from 0.21 to 0.86 after 5 minutes of microwave treatment at 170°C and upto 90% of the ortho-P can be
removed via struvite formation experiments. Kenge et al. also reported significant ortho-P release (71.7%) when MW/H\textsubscript{2}O\textsubscript{2}-AOP was used to treat acidified DM (2009a). High dosage of H\textsubscript{2}O\textsubscript{2} (4mL of H\textsubscript{2}O\textsubscript{2} in 30mL of samples) was used in her study since the substrate used was the solid portion of the manure after liquid-solid separation. It has to be noted that relatively high dosages of H\textsubscript{2}O\textsubscript{2} and microwave temperatures were used in all these studies. In addition, all these studies were performed using a batch microwave reactor which could only treat twelve 30mL-samples. Applying MW/H\textsubscript{2}O\textsubscript{2}-AOP in continuous mode has several potential benefits over the batch process: 1) large quantities of substrates can be processed continuously; 2) H\textsubscript{2}O\textsubscript{2} can be injected into the influent stream to ensure the simultaneous microwave irradiation of substrates and H\textsubscript{2}O\textsubscript{2}, enhancing the potential synergistic effects between microwave and H\textsubscript{2}O\textsubscript{2}.

Thus, the focus of this study was to investigate the effectiveness in terms of nutrients solubilization and organic matter disintegration of treating DM using a continuous MW/H\textsubscript{2}O\textsubscript{2}-AOP which operates at a low microwave temperature (60 to 90\degree C) and low H\textsubscript{2}O\textsubscript{2} dosage (0.1% vol/vol). Since acid played a significant role in DM treatment using MW/H\textsubscript{2}O\textsubscript{2}-AOP, the acid concentrations were varied and investigated for nutrient and organic matter release. A preliminary comparison study between batch microwave unit and continuous microwave unit was also conducted, to investigate the possible improvements in synergistic effects in continuous microwave treatment.
5.2 Materials and Methods

5.2.1 Microwave Units

Both batch and continuous microwave units were used in this study. These two units had been described in Section 2.2.1 and Section 4.2.2, respectively.

5.2.2 Preparation of Substrate

The substrate used in this study was liquid dairy manure, which was the liquid fraction of the manure after liquid-solid separation, and was collected from UBC Dairy Education & Research Centre in Agassiz, BC. Liquid manure was stored at 4°C cold room through the course of this study. To avoid solids deposition in the silicon tube in the MW unit, liquid DM was first passed through a U.S. Standard No. 18 sieve (1mm openings) to remove fibres and large particles. It was then further diluted four times by water since the TS content of the sieved liquid manure was still relatively high (3.5-4%). The final diluted DM was used in this study and its characteristics are presented in Table 5.1.

5.2.3 Experiment Design

Since previous studies had confirmed the importance of acid addition in MW/H₂O₂-AOP treatment of DM, acid dosages were varied in this study in the attempted to optimize the performance MW/H₂O₂-AOP. The acid dosages used in this study were 0.2, 0.5 and 1.0% (vol/vol). The microwave temperatures were also varied in the low temperature range between 60 to 90°C since this continuous MW unit was not pressurized and unable to achieve exit temperatures higher than the boiling point of water. The exit temperatures of microwave were controlled by the retention time of the sludge in the microwave. Figure 5.1 shows the relationship between microwave
exit temperature and sludge retention time in the microwave. Appropriate volume of concentrated sulfuric acid (98%) was added to the DM to make up to the desired acid dosage. The detailed operating conditions are presented in Table 5.2.

A preliminary study of batch MW/H₂O₂-AOP treatment of DM was conducted to investigate the treatment effectiveness in SCOD and ortho-P release from DM. The results were used to compare with continuous MW/H₂O₂-AOP under the similar treatment conditions, i.e. microwave temperature, temperature increase rate, H₂O₂ and acid dosages. The microwave temperatures selected were 60°C and 90°C, which covered the lowest and highest microwave exit temperatures in the continuous DM treatment. The operating conditions for both batch and continuous MW/H₂O₂-AOP treatment are listed in Table 5.3.

5.2.4 Chemical Analysis

The raw substrate and treated samples were tested for total chemical oxygen demand (TCOD), soluble chemical oxygen demand (SCOD), total phosphorus (TP), orthophosphate (ortho-P), total Kjeldahl nitrogen (TKN), ammonia nitrogen (NH₄-N), volatile fatty acid (VFA), according to the Standard Methods for the Examination of Water and Wastewater (1998). TP, ortho-P, TKN and NH₄-N were determined by flow injection (Lachat Quick-Chem 8000 Automated Ion Analyzer, Lachat Instruments, U.S.A.). VFA was determined using a Hewlett Pacard 5890 Series II gas chromatograph equipped with a flame ionization detector. Carbohydrates concentrations were determined using the anthrone carbohydrate method as described by Raunkjaer et al. (1993) with modifications. A brown or red color developed when H₂O₂ was present, which caused interference. In order to remove the H₂O₂ residue, 1
mL samples were placed in 1.5 mL mini centrifuge tubes and spun at 10,000 rpm (11,050 x g, Thermo IEC Multi rotor) for 10 minutes and subsequently dried at 103°C overnight. The dried samples were then cooled to room temperature and 1 mL of cold ethanol was added to each sample to precipitate carbohydrates. The samples were again spun at 10,000 rpm for 10 minutes and dried at 60°C over night. The dried samples were re-solubilized by 1 mL of distilled water and mixed with 2 mL of anthrone reagents. The mixture was incubated at 100°C for 15 minutes then cooled at 4°C for 5 minutes. The concentration was measured spectrophotometrically at 625 nm. Flow rate was measured using a measuring cylinder and a stop watch, while temperature was measured by a digital thermometer.

5.3 Results and Discussion

5.3.1 Continuous MW/H2O2-AOP

The most pronounced effect of increase in MW temperatures is on the increase of SCOD, as illustrated in Figure 5.2. Initially 35% to 47% of the TCOD in the untreated DM was in the soluble form. At 60 to 70°C, MW/H2O2-AOP does not have much effect on SCOD solubilization regardless of the acid dosages since low MW temperature did not induce the synergistic effects between chemicals and MW irradiation. As MW temperature increased from to 80 and 90°C, the percentage of SCOD as TCOD increased from approximately 40% to 76 ~ 90%, indicating that the majority of the organic materials had been converted to soluble form after intense MW/H2O2-AOP treatment. The results showed that MW temperature is the dominant factor in SCOD solubilization in continuous MW/H2O2-AOP treatment of DM. The results were in accordance with previous results (Kenge et al., 2009b). The influence of the acid dosage to the substrate does not affect the SCOD solubilisation greatly. At
low temperatures (60 and 70°C), further addition of acid did not improve the solubilization. At higher temperatures (80 and 90°C), the increase in acid had resulted in better SCOD solubilisation to a limited extent as shown in Figure 5.2.

Figure 5.3 illustrated the relationships between ortho-P solubilization, microwave temperature and acid dosages. It was evident that having an acidic pH condition is critical in solubilizing ortho-P from DM. Without acid addition, as microwave temperature increased from 60 to 90°C, the percentage of soluble ortho-P as TP decreased from 34% to 11%, which was all lower than the ortho-P:TP ratio of the untreated substrate. The decrease in soluble ortho-P as temperature increased was similar as MW/H2O2-AOP was used to treat sewage sludge (Wong et al., 2006). When acid was added to the process, the ortho-P solubilization was greatly improved indicated by the increase of ortho-P percentages as TP – up to 92% of the TP was in the form of ortho-P after continuous MW/H2O2-AOP. However, different acid dosages did not display significant effects on the ortho-P solubilization. The results demonstrated that MW/H2O2-AOP was extremely effective in converting insoluble P to soluble ortho-P in DM. Acid addition was the key for ortho-P solubilization from DM; however, high acid dosage was not necessary.

NH4-N presents approximately 42 to 55% of the TKN in raw DM. Continuous MW/H2O2-AOP did not demonstrate significant NH4-N solubilization from DM at MW temperature of 60 to 80°C, regardless of the acid dosages (Figure 5.4). At 90°C, the percentage of NH4-N increased to approximately 70% of the TKN in the DM for MW/H2O2-AOP treatment. The effect of acid dosage on NH4-N solubilization was similar to that on ortho-P solubilization – addition of acid was important, however
high acid dosage was not necessary. A considerable amount of VFA was released from the DM after MW/H$_2$O$_2$-AOP. Overall, MW/H$_2$O$_2$-AOP with medium acid dosage (0.5%) yielded the best VFA production of approximately 330 to 420mgL$^{-1}$. More acid addition would result in a decrease in VFA in DM (Figure 5.5).

DM is also a potential source for bio-ethanol production. A research group at Washington State University had reported a process for hydrolyzing lignocellulosic materials from manure into fermentable sugars (Wen et al., 2004; Chen et al., 2003). MW/H$_2$O$_2$-AOP also involved in treating DM at elevated temperature with acid and H$_2$O$_2$ additions, and therefore this process potentially could degrade the DM cellulose and hemicellulose into sugar which could later be converted to bio-ethanol. Hence, sugar as glucose was also reported in this study. As shown in Figure 5.6, after MW/H$_2$O$_2$-AOP, soluble sugar in DM decrease in most cases. The decrease in sugar could be explained by the further degradation of soluble sugar into simply forms after MW/H$_2$O$_2$-AOP. It can be postulated that the MW temperatures used in this study were not sufficient to degrade the fiber contents into sugar; hence no significant increase in sugar concentrations was observed. Higher MW temperatures and acid dosages could be used in future studies to investigate the effectiveness of MW/H$_2$O$_2$-AOP degradation of manure fibers into sugar.

5.3.2 Batch vs. Continuous MW/H$_2$O$_2$-AOP

There were many fundamental differences between the batch and the continuous MW unit which could potentially affect the nutrients and organic matter solubilization of manure, but the most important operational conditions such as MW temperature, temperature increase rate, H$_2$O$_2$ and H$_2$SO$_4$ dosages were kept similar for both
systems in this experiments. The results of SCOD and ortho-P solubilization from manure using both systems are presented in Table 5.4. When manure was treated with MW alone, without the addition of H$_2$O$_2$ and H$_2$SO$_4$, the SCOD and ortho-P solubilization results of the two MW systems were comparable, except that, at 90°C, the continuous system showed superiority in SCOD solubilization over the batch system. With the addition of H$_2$O$_2$ and H$_2$SO$_4$, the continuous system was able to release more ortho-P than the batch system, increasing the ortho-P concentrations by 57.0% and 70.8% at MW temperatures of 60 and 90°C. For the SCOD solubilization, the continuous system also achieved better results at 90°C. The superiority of ortho-P and SCOD solubilization of the continuous MW/H$_2$O$_2$-AOP could be attributed to the better synergistic effects between MW irradiation and H$_2$O$_2$. Since H$_2$O$_2$ was injected into the influent stream right before the mixture was pumped into the continuous MW unit, the reaction between the DM and H$_2$O$_2$ was limited prior to MW irradiation. Once the mixture was in the MW unit, simultaneous reaction between H$_2$O$_2$ and MW irradiation took place immediately. The synergistic effect was maximized, enhancing the nutrients and organic matter solubilization.

5.4 Summary and Conclusions

In this experiment, continuous MW/H$_2$O$_2$-AOP was used to treat liquid DM in order to solubilize organic matters as well as nutrients – phosphorus in particular. 0.2% of H$_2$O$_2$ and various acid dosages were used along with microwave temperatures ranged from 60 to 90°C in this experiment. It was found that continuous MW/H$_2$O$_2$-AOP was very effective in treating liquid DM in terms of organic matter solubilization and ortho-P release. Temperature was the dominate factor for organic matter solubilization. Up to 90% of the TCOD of liquid DM became SCOD with microwave temperature of
90°C and 1.0% acid addition. Acid addition was however not the dominant factor in organic matter solubilization – without acid addition, 76% of the TCOD was still in the soluble form after MW/H₂O₂-AOP. For ortho-P solubilization, it was found that MW/H₂O₂-AOP is only effective when the pH is acidic. However, more acid dosage would not improve the ortho-P solubilization. Up to 90% of the TP was in the form of soluble ortho-P after MW/H₂O₂-AOP treatment at 90°C with acidic pH conditions. It has to be noted that, the continuous MW unit used in this study has a limited maximum power of 1200W, hence the rate of temperature increase can be achieved is only 5°C/min approximately. With previous lab results indicating that the rate of temperature increase plays a significant role in MW/H₂O₂-AOP process, it can be postulated that with a higher power microwave unit, better results could be obtained.
Table 5.1 Characteristics of the diluted liquid dairy manure.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Concentration</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>TS (%)</td>
<td>0.83 ± 0.03</td>
<td>0.79 - 0.89</td>
</tr>
<tr>
<td>SCOD (mg/L)</td>
<td>3993 ± 279</td>
<td>3511 - 4247</td>
</tr>
<tr>
<td>TCOD (mg/L)</td>
<td>10652 ± 861</td>
<td>9172 - 11892</td>
</tr>
<tr>
<td>Ortho-P (mg/L)</td>
<td>23 ± 3</td>
<td>20 - 27</td>
</tr>
<tr>
<td>TP (mg/L)</td>
<td>85 ± 3</td>
<td>80 - 87</td>
</tr>
<tr>
<td>Ammonia-N (mg/L)</td>
<td>314 ± 53</td>
<td>245 - 380</td>
</tr>
<tr>
<td>TKN (mg/L)</td>
<td>578 ± 20</td>
<td>541 - 611</td>
</tr>
<tr>
<td>VFA (mg/L)</td>
<td>41 ± 27</td>
<td>2.8 - 79</td>
</tr>
<tr>
<td>Sugar (mg/L)</td>
<td>79 ± 15</td>
<td>57 - 103</td>
</tr>
</tbody>
</table>
Table 5.2 Operating conditions for the continuous MW/H$_2$O$_2$-AOP treatment of dairy manure.

<table>
<thead>
<tr>
<th>Exit Temp. (°C)</th>
<th>H$_2$O$_2$ (%)</th>
<th>H$_2$SO$_4$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>1</td>
</tr>
<tr>
<td>70</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>1</td>
</tr>
<tr>
<td>80</td>
<td>0</td>
<td>0</td>
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<tr>
<td></td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>1</td>
</tr>
<tr>
<td>90</td>
<td>0</td>
<td>0</td>
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<tr>
<td></td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>1</td>
</tr>
</tbody>
</table>
Table 5.3 Operating conditions for the comparative study between batch and continuous MW/H$_2$O$_2$-AOP.

<table>
<thead>
<tr>
<th>MW Systems</th>
<th>MW Exit Temp. ($^\circ$C)</th>
<th>Treatment Time (min)</th>
<th>H$_2$O$_2$ (% vol/vol)</th>
<th>H$_2$SO$_4$ (% vol/vol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batch</td>
<td>60</td>
<td>8</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>8</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>14</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>14</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Continuous</td>
<td>60</td>
<td>8</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>8</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>14</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>14</td>
<td>0.1</td>
<td>0.2</td>
</tr>
</tbody>
</table>
Table 5.4 Ortho-P and SCOD release comparison between batch and continuous MW unit.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>H$_2$O$_2$ and H$_2$SO$_4$</th>
<th>Ortho-P Increase (% of TP)</th>
<th>SCOD Increase (% as TCOD)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Batch</td>
<td>Continuous</td>
</tr>
<tr>
<td>60</td>
<td>No</td>
<td>-3.2</td>
<td>5.3</td>
</tr>
<tr>
<td></td>
<td>Yes</td>
<td>26.0</td>
<td>57.0</td>
</tr>
<tr>
<td>90</td>
<td>No</td>
<td>-7.1</td>
<td>-14.4</td>
</tr>
<tr>
<td></td>
<td>Yes</td>
<td>28.2</td>
<td>70.8</td>
</tr>
</tbody>
</table>
Figure 5.1 Exit temperature vs. retention time in microwave unit.

\[ y = 2.6138x + 48.184 \]

\[ R^2 = 0.8605 \]
Figure 5.2 SCOD release from dairy manure at various MW heating temperatures and acid dosages.
Figure 5.3 Ortho-P release from dairy manure at various MW heating temperatures and acid dosages
Figure 5.4 NH₄-N release from dairy manure at various MW heating temperatures and acid dosages.
Figure 5.5 VFA release from dairy manure at various MW heating temperatures and acid dosages
Figure 5.6 Sugar release from dairy manure at various MW heating temperatures and acid dosages.
References


6.0 OVERALL CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The results from Chapter 2 proved the disinfection power of MW/H₂O₂-AOP in WAS treatment. It was also found that high dosage of H₂O₂ alongside microwave irradiation would inhibit the regrowth of fecal coliforms. In the same study, nutrients and organic matter solubilization at low microwave heating temperatures and low H₂O₂ dosages were compared to previous studies. The results indicated that low microwave heating temperatures and low H₂O₂ dosages were also effective for nutrients and organic matter solubilization.

In Chapter 3, EPS was removed from wastewater activated sludge, and the cells without EPS were subjected to MW/H₂O₂-AOP. Compared to previous studies (Chan et al., 2007; Wong et al., 2007), MW/H₂O₂-AOP was more effective in nutrients release from cells than from intact sludge. DNA was used in this study as indicator for the cell destruction. A higher DNA concentration was related to higher microwave temperatures and higher H₂O₂ dosages.

Chapter 4 investigated the application of MW/H₂O₂-AOP to sludge treatment in a continuous flow manner. Pre-MW heating and post-MW setting were found effective in organic matter release but not ortho-P release. Seattleability of sludge was found greatly improved after microwave treatment.

In Chapter 5, the continuous MW/H₂O₂-AOP was applied to dairy manure (DM). It was found that up to 92% of the TP and 90% of TCOD in manure were in the soluble
form after treatment. The results also confirmed phosphate release from DM using a batch MW reactor (Pan et al., 2006; Qureshi et al., 2008). Acid dosage played an important role in SCOD release. Acid addition was the key in ortho-P release from manure; however, higher dosage of acid was not required in this process.

6.2 Contributions

This study explored aspects of waste treatment using MW/H2O2-AOP that have not been investigated previously. Destruction of fecal coliforms in WAS using MW/H2O2-AOP was first reported in this study. Nutrients and organic matter solubilization of cells that were EPS-free was compared to previous studies where intact sludge was used as substrate. By removing EPS, MW/H2O2-AOP could be more effective in nutrient and organic matter release from wastewater sludge.

All previous studies were performed using a batch microwave unit. However, if this technology were to be applied in industrial scale, the waste stream must be treated in a continuous flow manner. This study first applied continuous flow MW/H2O2-AOP to both WAS and DM treatments. The results could be used in the future for pilot-scale microwave unit development. The effects of pre-MW heating and post-MW setting in sludge solubilization were investigated. The results provided evidence for the future design of a large-scale microwave unit where the substrates could be pre-heated using a heat exchanger, to lower the microwave temperature or improved the treatment efficiencies.
6.3 Recommendations

As discussed in Section 1.2.1, material dielectric properties are extremely important in heating involved with microwave. Thus, a detailed study of dielectric properties of different types of waste material would help in designing and predicting the performance of MW/H2O2-AOP. The microwave frequency used in this study, and all previous studies of MW/H2O2-AOP, was 2450MHz. The penetration depth of microwave would improve approximately 3 times if 915MHz microwave were used. The efficiency of MW/H2O2-AOP can be improved greatly with 915MHz frequency microwave. Study of MW/H2O2-AOP using a pilot-scale microwave unit with 915MHz frequency would be the corner stone in upgrading the current MW/H2O2-AOP to industrial scale.

In future studies, an entire waste stream treatment could be completed by adding a subsequent struvite recovery process after MW/H2O2-AOP to produce fertilizer in the form of magnesium-ammonia-phosphate, MAP. The treated sludge from MW/H2O2-AOP could be used in the next step to test the feasibility of implementing MW/H2O2-AOP in a real waste treatment process. In addition, economic feasibility of using MW/H2O2-AOP regarding the capital and operational costs could be studied.
References


