

APPLICATIONS OF MICROWAVE TECHNOLOGY TO WASTEWATER
TREATMENT

by

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Abstract

A microwave enhanced advanced oxidation process using hydrogen peroxide (MW/H₂O₂-AOP) was used for the release of nutrients and the destruction of solids from secondary municipal sewage sludge. The significant factors affecting the MW/H₂O₂-AOP that would yield maximum soluble substrates were studied. Using a computer statistical software package for experimental design and data analysis, four factors including microwave heating temperature, heating time, hydrogen peroxide dosage, and sludge solids content, were selected and examined. The initial sludge TS content and hydrogen peroxide dosage were the most significant factors for the solubilization of COD and nutrients release under the experimental conditions selected in this study. Overall, the maximum solubilization of nutrients was obtained at 2.5 % of total solids content, 2% of hydrogen peroxide by weight, 5 min. of microwave heating and 120 °C. The effects of combination of microwave treatment and oxidative reagents on solids destruction and nutrients release were also investigated. Microwave enhanced advanced oxidation processes (MW-AOP), such as MW/O₃, MW/H₂O₂ and MW/H₂O₂/O₃, were conducted at 100 °C. In terms of nutrients release and solids reduction, the MW/H₂O₂/O₃-AOP yielded the best result. Subsequently, three factors including microwave heating temperature, hydrogen peroxide dosage, and ozone dosage, were investigated. The best result, in terms of the release of phosphate and ammonia, and solids reduction, was obtained with additions of 2 % hydrogen peroxide by weight and ozone dosage of 5.09 mg/ml, and operating at 120°C. About 95%, 32% and 78% of TP, TKN and COD were released into the solution, respectively. The microwave enhanced advanced oxidation processes, with and without an addition of ferrous sulfate (MW/H₂O₂-AOP and MW/H₂O₂/Fe⁺²-AOP),

were also studied for reducing solids, and solubilizing nutrients from the secondary sewage sludge. For the MW/H₂O₂/Fe⁺²-AOP, the best results of solubilization, in terms of orthophosphate, ammonia and soluble chemical oxygen demand, were obtained at treatment temperatures of 40 °C, the yields decreased as the temperature was increased. The highest yields of solubilization were obtained at 60 °C for orthophosphate, and at 80 °C for both ammonia and soluble chemical oxygen demand.

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Chapter 1 Introduction

1.1 Background

Phosphorus, in the form of phosphate, is derived from a wide variety of sources. These sources include atmospheric water, agricultural and urban drainage waters, domestic and industrial wastewaters, and to a very limited extent, groundwater (G Fred Lee et al. 1978). Human actions: mining phosphorus (P) and transporting it in fertilizers, animal feeds, agricultural crops, and other products—are altering the global P cycle, causing P to accumulate in soil. In terms of human consumption, over 38 million tonnes of phosphate (as P_2O_5 in mined rock) are extracted per annum (Driver, et al., 1999). The scarcity of phosphate-abundant rocks available for mining on earth represents a significant challenge to the phosphate industry as world demand increases while reserves are being depleted at an alarming rate. Conservative estimates indicate that world phosphate rock reserves will run out within 100 years, while other scenarios suggest that the lifetime of raw phosphate rock reserves could run out by 2050 (Driver, et al., 1999).

Biologically available N originates from either endogenous or exogenous sources. Primary production supported by endogenous N is referred to as “regenerated production,” while exogenous production is termed “new” production. (Hans W. Paerl, 1997). Human activities have profoundly altered the global biogeochemical cycle of N. Humans have approximately doubled the rate of N input into the terrestrial N cycle, and these rates are still increasing (Smith VH et al. 1999). Instances of human impact on the P and N cycle leading to accumulation of P and N in upland systems have been discovered both locally and regionally.

Sewage sludge contains considerable amounts of carbon and nutrients that can be recycled. The challenge is to develop a sustainable management strategy that can effectively recover these nutrients and carbon source, and produce a useful product at the same time (Lampert, 2003). The microwave enhanced advanced oxidation process (MW/H₂O₂-AOP) for nutrients release and solids disintegration from sewage sludge has been developed and studied at the University of British Columbia (Liao, et al., 2005a; Wong, et al., 2006). The microwave heating process could break down particles with or without hydrogen peroxide, resulting in carbon and other nutrients becoming solubilized. At temperatures of 80°C and above, most of the sludge suspended solids was solubilized by MW/H₂O₂-AOP (Wong, et al., 2006). The microwave process was also found to limit microbial activity, and with hydrogen peroxide, the pasteurization or sterilization of pathogens in the solution can be achieved (Liao, et al., 2005b).

Ozone is a very reactive oxidant, and it does not produce harmful byproducts, but only H₂O and O₂. Hydroxyl radicals can be formed when ozone enters into water. Since hydroxyl radical has a very high oxidation potential, it is a much more effective oxidant than ozone itself. Ozone would also help dissociate H₂O₂ to form hydroxyl radical too. It was thought that by using a combination of ozone and hydrogen peroxide in the process (designated as MW/H₂O₂/O₃-AOP), the efficacy of the treatment could be improved.

Fenton reagent is one of the most common advanced oxidation processes (AOPs) used for nutrient release and sludge disintegration. Fenton reagent is a mixture of H₂O₂ and ferrous iron, which generates hydroxyl radical according to the following equation:



Most of the works involving Fenton's reaction were operated at temperatures between 20 to 40 °C. The rate of reaction increased with an increase of temperature. However, the efficiency of H₂O₂ utilization declined as temperatures increased above 40–50 °C (Kitis, 1999). The time needed to complete Fenton reactions depends on the catalyst dosage and the wastewater strength. In general, the reactions could take from 30 minutes to several hours to complete. In a study on the treatment of synthetic phenol solutions and of surfactant wastewaters, the effects of the Fenton reaction to that of a microwave enhanced AOP (MW-AOP) were compared (Kolthoff and Medalia, 1949). However, microwave irradiation was not applied to the Fenton reaction. It was expected that a combination of both microwave irradiation and Fenton reagent would increase the efficiency of the overall MW-AOP.

1.2 Objectives

The overall objective of this thesis is to determine the optimum conditions under which the microwave pre-treatment of municipal wastewaters will facilitate the maximum nutrients release and solids disintegration. It is also necessary to identify the major factors associated with microwave enhanced AOP that will affect nutrients release and solids reduction and further determine the optimum conditions in order to optimize the MW-AOP. The screening design and response surface methodology will be employed to reduce the number of experiments required to obtain the optimum conditions for maximum nutrients release and solids disintegration.

In particular, the following are the main objectives in this research:

1. Demonstrate that microwave heating treatment of sewage sludge will result in nutrients release and solids reduction

2. Identify the major factors associated with MW-AOP that affect nutrients release and solids reduction by using a screening design to eliminate insignificant factors.
3. Explore the role of these significant factors, specifically, advanced oxidation, ozone and chemical addition, on enhancing nutrients release and solids reduction from sewage sludge
4. Evaluate the efficacy of the microwave treatment by using a combination of ozone or Fenton reagent in the MW-AOP
5. Determine the optimum MW-AOP operating conditions, under which maximum nutrients release and solids disintegration is obtained

1.3 Literature review

1.3.1 Phosphorus, Ammonia and Struvite

1.3.1.1 Phosphorus

Phosphorus (P) is a naturally occurring element that can be found in the earth's crust, water, and most living organisms. Phosphorus (P) is one of 16 elements that are essential for plant growth. The element phosphorus does not occur by itself in nature. It is always combined with other elements to form phosphates. Phosphates can be very complex and more than one form of phosphate will be found in soils, water, plants, animals and humans. In aqueous solutions, phosphorus is typically in the form of orthophosphate, polyphosphate and organic phosphate (Metcalf and Eddy, 2003). Orthophosphate can be found in the following forms: PO_4^{3-} , HPO_4^{2-} , H_2PO_4^- and H_3PO_4 . Polyphosphates are phosphate chains that are often made up of orthophosphate monomeric units. Organic phosphates can be found in many forms, of which DNA and proteinaceous material in

biological organisms are most common. In humans, there is typically 0.3 - 0.4 kg per capita per year of P found in urine, and a further 0.2 kg per capita per year from faeces (Balmer, 2004).

Since phosphorus is essential for all living processes, there is concern that the exploitation of this non-renewable resource to meet current demand is not sustainable. Estimates of current reserves that can be exploited vary from 250 years to as little as 50 to 100 years. At present there are three main uses of phosphorus. About 79% is used to make fertilizer for use in agriculture for food production, around 11% is used to make feed grade additives for animal feeding stuffs, and approximately 7% is used to make detergents (A. E. Johnston and I. Steén, 2003). The remainder is used in speciality products as diverse as additives for human food and metal surface treatments to delay corrosion. Over 38 million tonnes of phosphate rock are mined per annum in order to meet the heavy demand for a high quality source of phosphorus (Driver, et al., 1999). Two major opportunities for increasing the life expectancy of the world's phosphorus resources lie in recycling by recovery from municipal and other waste products such as wastewater and in the efficient use in agriculture of both phosphatic mineral fertilizer and animal manure. In particular, there is clearly a need to develop a more sustainable method of recovering and recycling the phosphorus that can be found readily in sources such as domestic wastewater.

Domestic wastewater contains significant amounts of nutrients including phosphorus, nitrogen, and organic carbon in non-soluble forms. Phosphorus is an inorganic nutrient that is undesirable for discharging into receiving waters because it poses environmental threats due to eutrophication and anoxia. Untreated domestic wastewater typically

contains phosphorus in the range of 4-12 mg/l (Metcalf and Eddy, 2003). To treat this phosphorus, there are many processes available that can generally be classified under chemical or biological phosphorus removal processes. Chemical processes typically involve the addition of metal salts, such as aluminum and ferrous salts, which precipitate out the phosphorus (Rittman and McCarty, 2001). More commonly, however, biological processes are used in wastewater treatment and are known as enhanced biological phosphorus removal (EBPR) processes. In such processes, polyphosphate accumulating organisms (PAO) removes the phosphorus in the sludge by microbial uptake and storage (Rittman and McCarty, 2001; Seviour, et al., 2003; Ubukata, 1994).

1.3.1.2 Ammonia

Nitrogen exists in eight different oxidation states, i.e. +5, +4, +3, +2, +1, -1, -2, -3, of which ammonia has the lowest oxidation state. Ammonia combines with water to form inorganic ammonium ions. The form of nitrogen can change by both chemical and biological means, and depends to a large extent on the physico-chemical conditions in which the nitrogen exists. The ammonia levels discharged into receiving waters is of particular concern particularly in cases where aquatic species exist. A small but significant fraction of the total agricultural N applied to land is in excess of plant requirements for growth, and this surplus N may: (1) accumulate in soils; (2) move from the land into surface waters; (3) migrate into ground waters; or (4) enter the atmosphere via ammonia volatilization and nitrous oxide production. Discharge of excessive levels of ammonia not only are directly toxic to aquatic organisms, but also encourage the growth of algae (in combination with phosphorus) to cause algal blooms and eutrophication problems where depletion of dissolved oxygen can cause severe problems to aquatic

organisms. Free ammonia at concentrations as little as 0.2 mg/l can cause fatalities to aquatic species (Sawyer, et al., 2003).

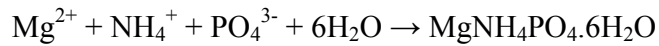
In untreated domestic wastewater, ammonia concentrations generally range between 12 – 45 mg/l (Metcalf and Eddy, 2003). Nitrogen is removed by nitrification/denitrification techniques in biological wastewater treatment. In the wastewater treatment process, the sludge itself will have a large quantity of organic nitrogen, especially in the form of proteinaceous material. The breakdown of this sludge biomass and the subsequent conversion to ammonia could potentially be used in combination with the phosphorus released from the biomass for the production of fertilizer products such as magnesium ammonium phosphate, more commonly known as struvite.

The removal/retrieval of phosphates and ammonia from wastewater is beneficial from both an environmental and economic perspective, particularly if the unwanted compounds can be extracted to produce a useful product in a value-added process.

1.3.1.3 Struvite

Magnesium ammonium phosphate (struvite) crystallization is an emerging technology that can be used as a means of removing the nitrogen and phosphorus from wastewaters and converting it into a fertilizer. Struvite is an excellent plant fertilizer that is particularly useful because of its slow-release properties and can be directly used in land application (Bridger, et al., 1962). Since fertilizer use in agriculture represents 80-85% of total phosphorus rock consumption (Driver, et al., 1999), the recovery of a useful product such as struvite from wastewaters is important in terms of maintaining a sustainable supply of phosphorus, mainly by decreasing the phosphate rock demand and increasing the amount of recycled phosphorus.

The chemical formula for struvite is $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$. Struvite is a white, crystalline substance that forms in the reaction:



Struvite crystallization can be a purely chemical process when the constituent concentrations exceed the solubility limit (Durrant, et al., 1999), but studies have shown that while struvite crystallization chemistry is extremely complex and highly dependent on the local conditions, pH, temperature, ionic strength and the degree of supersaturation play an important role in determining whether struvite crystallization occurs (Adnan, et al., 2004; Bouropoulis and Koutsoukos, 2000; Doyle and Parsons, 2002). A major advantage in recovering nutrients via struvite crystallization is: (1) it reduces the amount of unwanted struvite that causes fouling in process equipment, (2) it recovers nutrients (orthophosphate and ammonia) from a waste product, and (3) it produces a valuable fertilizer product that can be directly used in agricultural applications (Adnan, et al., 2004). There are many technologies available for struvite crystallization (Stratful, et al., 1999), but the fundamental requirement of magnesium, phosphorus and ammonia as the raw material is common to all crystallization processes.

1.3.2 Microwave technology

Microwaves lie in the region of the electromagnetic spectrum between millimetre waves and radio waves. Specifically, they are defined as those waves with wavelengths of between 0.01 and 1 metre, corresponding to frequencies of between 30 and 0.3GHz. In order to avoid interference with these uses, the wavelengths at which industrial and domestic microwave apparatus may operate are regulated at both national and international levels. In the majority of countries, 2.450 (+/- 0.050) GHz is the major

operating frequency for this purpose, although other frequency allocations, namely 915 MHz, 5.8 GHz, and 24.124 GHz exist (Williams, 1967). Where apparatus is built to operate outside these bands, efficient shielding must be used to prevent radiation leakage. All domestic ovens operate at 2.45GHz, and their popularity in recent years has resulted in progressively cheaper microwave sources at this frequency. It has long been known that materials may be heated with the use of high frequency electromagnetic waves. The heating effect arises from the interaction of the electric field component of the wave with charged particles in the material. Two major effects, namely, conduction and dipolar polarisation, are responsible for the heating which results from this interaction. If the charged particles are free to travel through the material (electrons in a sample of carbon, for example), a current will be induced which will travel in phase with the field. If, on the other hand, the charged particles are bound within regions of the material, the electric field component will cause them to move until opposing forces balance the electric force. The result is a dipolar polarisation in the material (Williams, 1967)

Homogeneous distribution of the polar material thus allows for the volumetric heating of a substance, in which the heat energy supplied to the material is transferred through the surface electromagnetically rather than as a heat flux (Meredith, 1998). The entire volume of the material is heated simultaneously, unlike in conventional thermal processes where heat transfer only occurs at the surface of the material and thermal diffusion is required for heat to reach the core of the material. Because of this phenomenon, volumetric heating times can often be reduced to less than 1% of the time required to heat the same material through a conventional conduction/induction heating process. The microwave processing of materials is advantageous in that it possesses several defining

characteristics where it has the ability to provide penetrating radiation, with controllable electric field distributions. The net result is that rapid, selective heating of materials is provided when microwave irradiation is used.

Typically, the generation of microwaves relies on the use of the magnetron, which can provide microwaves with output up to 1 MW in power. The magnetron generates the microwaves by applying both electric and magnetic fields to electrons perpendicular to one another in order to produce microwaves at the desired frequency. The interaction of the electrons travelling through the electric and magnetic fields results in the generation of microwaves (National Academy Press, 1994). Manipulation of the strength of the electric and magnetic fields controls the power and frequency of the generated microwave field. Typically microwave ovens consist of magnetrons in conjunction with a waveguide, which is a physical structure that directs the microwave field from the outlet of the magnetron to the microwave cavity. The waveguide allows for the homogeneous distribution of the microwave field in the microwave unit.

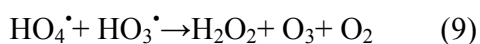
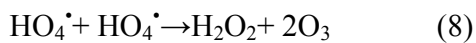
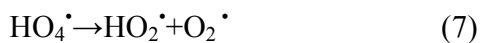
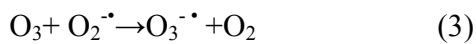
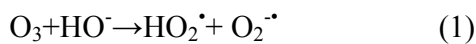
In previous studies of our research group (Liao, et al., 2005a; Liao, et al., 2005b; Wong , et al., 2006), novel microwave technique was developed to release nutrients and reduce solids from sewage sludge. The microwave heating process could break down particles, resulting in carbon and other nutrients becoming solubilized. As a result, the sludge in the solution was reduced in the process. The microwave heating process was also found to limit microbial activity (Liao, et al., 2005a), and with hydrogen peroxide, the pasteurization or sterilization of pathogens in the solution can be achieved. Studies have shown that various methods of microwave treatment are effective for destroying

microorganisms such as *E.coli* and fecal coliforms (Hong, et al., 2004; Koutchma and Ramaswamy, 2000).

1.3.3 Ozone technology

Ozone and its chemistry in aqueous media

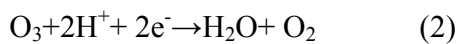
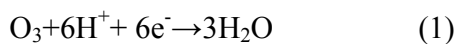
Ozone is an irritating and corrosive gas that is usually colorless but becomes blue at high concentrations. Ozone is sparingly soluble in water (12mg/dm³ at 25°C) and its behaviour in aqueous media can be evaluated by examining O₃⁻ decomposition kinetics. Once ozone enters into water, it becomes highly unstable and rapidly decomposes through a complex series of reactions (Leonardo and Wilson, 2006; Rice and Netzer, 1982). According to the literature (Leonardo and Wilson, 2006; Zoubov and Pourbaix, 1974), ozone decomposition in water can be described as:



According to this mechanism hydroxide ions (HO⁻) initiate a chain of reactions when ozone enters into water. The chain reaction is sustained by HO₂[•] formation via step II, which can then initiate further reactions. The hydroxyl radical (HO[•]) is the most

important species formed during ozone decomposition. Thus, ozone can react in an aqueous medium directly with substrates, such as molecular-ozone, or indirectly, via radical-intermediates formed during ozone decomposition in aqueous media. Thus, depending on the ozone behaviour in the aqueous medium, the selectivity of ozonation can be high (direct reaction) or low (indirect reaction) (Leonardo and Wilson, 2006).

Since the HO[•] radical is not selective and possesses a very high oxidative potential, this species is therefore a much more effective oxidant than ozone itself. Depending on the influence of the partial pressure of the dissolved oxygen, the following semi-reactions are representative of the standard redox potentials (Leonardo and Wilson, 2006; Zoubov and Pourbaix, 1974):



According to these semi-reactions, even in cases where the reaction represented by Equation 2 is considered, the hydroxyl radical is by far a stronger oxidant than ozone.

1.3.3.2 Ozone generation

Because ozone is highly reactive and cannot be stored over an extended period of time, it has to be generated on site. According to the literature (Leonardo and Wilson, 2006; Tatapudi and Fenton, 1994), ozone can be generated "in situ" using the following technologies: (i) Photochemistry (UV-radiation); (ii) Corona (silent electric discharge) and the (iii) Electrochemistry (electrolysis of aqueous solutions). The most common technology for the ozone production is the Corona process, where a dry gas, either air or pure oxygen, is subjected to a silent electrical discharge (Leonardo and Wilson, 2006). In this case a reaction between the oxygenated species ($\text{O}^{\bullet} + \text{O}_2$), assisted by the free

energetic electrons that are created from an electric spark, occurs in the gas phase, generating the O₃-molecule. Although this technology requires a lower specific power consumption ($\sim 10 \text{ W h g}^{-1}$) the concentration of the O₃ in the gaseous phase (O₂ + O₃) is low (~ 2.5 to $7.5 \text{ wt}\%$), thus restricting its use in environmental applications involving recalcitrant pollutants.

1.3.3.3 Applications to environmental engineering

Costs associated with ozone production have dropped by 50% in the last decade and, therefore, a great number of new industrial applications has appeared in recent years (Leonardo and Wilson, 2006). Potential markets for ozone technology exist especially in water treatment, surface sterilisation, wood pulp bleaching, materials processing, treatment of textile wastewater, and treatment of cooling water (Leonardo and Wilson, 2006). An important aspect of ozone application in water treatment is its use as disinfectant in purified water loops for the pharmaceutical and electronic industries (Leonardo and Wilson, 2006). Besides, it is worthwhile to mention that ozone application, unlike that of chlorine, does not leave harmful residues such as haloforms after reaction. So, the environmental advantages of ozone over chlorine justify its higher cost of generation for an increasing number of applications. Several applications for ozonation and related AOP in wastewater treatment are available (Leonardo and Wilson, 2006; Sequeira, 1994). Examples of the use of ozone to degrade organic contaminants in wastewaters are pulp and paper production, shale oil processing, production of pesticides, dye manufacture, textile dyeing and pharmaceutical production. Ozone application in wastewater treatment is a promising technology and its efficiency depends on optimisation of several operating conditions: (i) ozone distribution in the liquid phase

using specially designed diffuser systems; (ii) ozone concentration in the gaseous phase (O_2/O_3); (iii) nominal ozone dosage, and (iv) contact time. However, no studies was reported in terms of the efficacy of using the combination of microwave heating technology and ozone technology.

1.3.4 Fenton reagent

The Fenton reagent process has been widely studied and has been used routinely for industrial wastewater treatment. Fenton reagent is a mixture of H_2O_2 and ferrous iron, which generates hydroxyl radical according to the following equation:



There are also other reactions involved in the Fenton's process:



The ferrous iron initiates the decomposition of H_2O_2 , resulting in the generation of hydroxyl radical (Kitis, 1999). If a hydroxyl radical is not trapped by species that can react with it, another Fe^{+2} will react with it to form another Fe^{+3} and another OH^- as indicated in Equation (ii). On the other hand (Kolthoff and Medalia, 1949), the hydroxyl radicals formed can also react with hydrogen peroxide, as in equation (iii), thus generating perhydroxyl radicals, OOH^0 , which can react with ferric ions present in the reaction media to give off oxygen gas as the byproduct, Equation (iv). The Haber-Weiss cycle, which consists of equations (ii), (iii) and (iv), is inclusive of the Fenton reactions. Whether or not a Fenton reaction becomes a Haber-Weiss cycle depends on the stoichiometries of the reactants. If there is a lot of hydrogen peroxide and little Fe^{+2} , then

the Haber-Weiss cycle is more likely to take place, whereas, if there is very little hydrogen peroxide and lots of Fe^{+2} , then Fenton reaction alone takes place.

Most of the works involving Fenton's reaction were operated at temperatures between 20 to 40 °C. The rate of reaction increased with an increase of temperature. However, the efficiency of H_2O_2 utilization declined as temperatures increased above 40–50 °C (Walling, 1975). The time needed to complete Fenton reactions depends on the catalyst dosage and the wastewater strength. In general, the reactions could take from 30 minutes to several hours to complete. There have been no literatures reported on the use of a combination of microwave irradiation and Fenton reagent in the AOP, hereby, abbreviated as MW/ H_2O_2 / Fe^{+2} -AOP.

Chapter 2 Sewage Sludge Treatment Using Microwave Enhanced Advanced Oxidation Process

2.1 Introduction

Sewage sludge contains considerable amounts of carbon and nutrients that can be recycled. The challenge is to develop a sustainable management strategy that can effectively recover these nutrients and carbon source, and produce a useful product at the same time (Lampert, 2003). The application of microwave enhanced advanced oxidation process (MW/H₂O₂-AOP) for nutrients release and solids disintegration from sewage sludge has been developed at the University of British Columbia (Liao, et al., 2005; Wong, et al., 2006a). The results indicated that major factors, such as microwave heating temperature, heating time, and hydrogen peroxide dosage, affected nutrients solubilization (Wong, et al, 2006b). It was observed that significant amounts of nutrients, up to 96% of total phosphorus and 78% of the TKN, were released into the solution at 200 °C. The most significant factor affecting phosphorus release was the microwave temperature, while for ammonia release it was the hydrogen peroxide dosage. The significant factors affecting sewage solids disintegration were, however, not reported.

This study was initiated to determine the significant factors affecting the MW/H₂O₂-AOP that would yield maximum soluble substrates. A higher sludge solids concentration was considered an important parameter, and therefore, incorporated into this study. A computer statistical software package (JMP-IN[®] 5.1) was therefore used to design the experiments and for the data analysis (Sall, et al., 2005). The objectives were to: 1) determine the most significant factors affecting nutrients release, and solids disintegration;

and 2) report the yields of the nutrient release and solid disintegration under various operating conditions.

2. 2 Materials and methods

2.2.1 Apparatus

A closed-vessel microwave digestion system (Ethos TC Digestion Labstation 5000, Milestone Inc., U.S.A. Figure 2.1) with a maximum output of 1000W was used in this study. The system operates at 2450 MHz and consists of dual independent magnetrons with a rotating microwave diffuser for homogeneous microwave distribution. The system has the capacity of accommodating up to 12 vessels (each with a volume of approximately 100 ml) in a single run, at operating temperatures and pressures of up to 220 °C and 30 bar (435 psig), respectively. The microwave digestion system, using an independent system controller, provides real-time temperature control.

2.2.2 Experimental methodology

2.2.2.1 Screening design

Screening designs are generally used to narrow a set of suspected factors affecting a response to a restricted number of variables in order to perform a feasible analysis of the factors. This tool is particularly powerful when attempting to obtain optimum conditions for the particular response, since the number of experimental runs increases dramatically with the number of factors (especially with a conservative experimental approach such as a full factorial design).

2.2.2.2 Response surface methodology

The response surface methodology involves the use of experimental designs (factorial analysis) that focus on a small segment of the sample space (Sall, et al., 2005). By investigating the local curvature of the response over the experimental range of factors, the general direction in which maxima or minima values exist can be determined. By performing experiments successively (over multiple iterations) using the results of previous runs as a guide, optimum conditions can be obtained. There are two general experimental designs that can be used with response surface methodology. These are the central composite design (CCD) and the Box-Behnken design. The Box-Behnken design is of interest because it is useful for the optimization of three continuous factors, and is useful in the sense that fewer experiments are required compared to a full factorial design to generate a prediction model for the purposes of determining the optimum conditions within the sample space. The Box-Behnken design typically requires only 15 experiments based on a three-factor optimization study.

Sophisticated statistical analysis software such as JMP-IN® 5.1 can be used to design a set of experiments involving the use of methods of screening design and response surface design.

2.2.3 Experimental design

Using a computer software package, JMP IN® 5.1, (Sall, et al., 2005), sludge solids content, heating temperature, heating time, and hydrogen peroxide dosage were selected as major factors for the MW/H₂O₂-AOP. Based on the software design, using response surface methodology, it would not only minimize the numbers of tests required, but also indicate the near optimal condition for the experiments using the selected parameters.

Statistical analysis, using the “analyze-fit model” in JMP-IN ® 5.1, was also carried out in this study.

A set of nine experiments, each with six replicates, were carried out in this study. Experiments were performed at three levels of solids content of 0.5, 1.5 and 2.5%, heating temperatures of 80, 100 and 120°C, heating time of 1.5, 3 and 5 minutes, and hydrogen peroxide dosage of 0, 1 and 2 ml (30 wt %), respectively (Table 2.1). The results from previous studies by our research group indicated that the release of nutrients was not affected by heating period over five minutes (Liao et al., 2005a). To examine the nutrients release within 5 minutes, the heating time of 1.5, 3 and 5 minutes were selected. Ideally, the heating time of 1, 3 and 5 minutes should be selected to keep a constant gradient. Considering 1 minute might be short for heating, we used 1.5 minutes instead of 1 minute.

2.2.4 Experimental procedures and sampling

Secondary aerobic sludge was taken daily from the wastewater treatment pilot-plant located at the University of British Columbia (UBC) campus. The characteristics of sludge used in this study are listed in Table 1. The concentrated sludges (I and II) were obtained via the centrifugation process.

Test samples, each with a total volume of 30 ml, were subjected to microwave treatment at the selected temperatures. The heating time was set at 1.5, 3 and 5 minutes. However, with a temperature increment setting of 20 °C per minute, the ramp times varied until the desired heating temperature was reached. Immediately after the MW-AOP treatment, samples were taken from the microwave digestion labstation, and centrifuged for 15

minutes. The mixed liquors from all samples were spun in a centrifuge at 4000 rpm. The resulting supernatants were filtered through Whatman No.4 filters and analyzed.

Chemical oxygen demand (COD), nitrogen (ammonia, $\text{NH}_3\text{-N}$), phosphorous (ortho- PO_4), Total solids (TS), total phosphate (TP) and Kjeldahl nitrogen (TKN) were determined according to the Standard Methods (APHA, 1995). All analyses, except COD and TS, were analyzed using the flow injection analysis (Lachat Quik-Chem 8000 Automated Ion Analyzer, Lachat Instruments, U.S.A.).

A Hewlett Packard 5890 Series II gas chromatograph equipped with a flame ionization detector (FID) was used to measure volatile fatty acids (VFA). Volatile separation was accomplished with an HP FFAP column (0.25 m \times 0.31 mm with 0.52 μ film thickness). The injection temperature was set at 175 $^\circ\text{C}$ and the FID detector was at 250 $^\circ\text{C}$. Helium gas was used as the carrier at a head pressure of 10 psi.

2. 3 Results and discussion

The initial sludge contains a negligible amount of soluble substrates (soluble orthophosphate and ammonia) as indicated in Table 2.2. The soluble substrates obtained from the MW/ H_2O_2 -AOP would represent the degree of nutrient release and sludge solid disintegration.

2.3.1. Sludge disintegration and soluble COD

The scale estimate for the solubilization of COD is shown in Figure 2.2. The bar chart is for comparing the relative significance of the effects with respect to one another. The scaled estimate increases from -2811.18 to +2962.89 with an increase of hydrogen peroxide dosage from 0 to 2 ml. The difference is the largest among the factors studied.

Therefore, the most significant factor is the amount of hydrogen peroxide used in the process. The sludge TS content also plays a very important role; and as expected higher TS content in samples tended to yield more soluble COD in the solution. The four most significant factors for the solubilization of COD are in the following order, from the most to the least: hydrogen peroxide dosage, sludge TS content, microwave heating time and microwave temperatures.

The results of the SCOD are presented in Table 2.3. Figure 2.3 shows the effects of TS, peroxide dosage, and heating time on the yield of the SCOD. The most obvious effects can be seen from data of Set 7, 8 and 9 at 120 °C, where the SCOD increased with increases of the initial sludge TS (from 0.5 % to 2.5%), peroxide dosage (from 0 to 2 ml), and heating time (from 1.5 to 5 min). As shown in Figures 2.2a and 2.2b, there was a clear trend that the SCOD increased with an increase of the initial sludge TS at 120 °C (Sets 7, 8, and 9). This was not only due to the initial sludge concentration, but also the dosage of hydrogen peroxide. The amounts of hydrogen peroxide used in the process increased with a higher sludge TS. However, No clear trend can be seen for the treatments at 80 or 100 °C, wherein the amounts of hydrogen peroxide added were not increased with an increase of the initial sludge TS concentration. At 80 °C, 1 ml, 2 ml and 0 ml of H₂O₂ was added to the sludge samples with TS concentrations of 2.5%, 0.5% and 1.5%, respectively (Sets 1, 2 and 3). At this temperature of 80 °C, the highest SCOD in the solution was observed in Set 1 with the highest sludge loading at 2.5% TS, while the lowest SCOD was obtained from Set 3, with an initial sludge TS of 1.5% and no H₂O₂. Similarly, low SCOD results were observed for Set 5 (2.5% TS at at 100 °C) and Set 7 (0.5% TS at 120 °C), where there was no hydrogen peroxide added in both sets (Fig.

2b). The interaction between sludge TS concentration and hydrogen peroxide can also be demonstrated in Figure 2a and 2b. The lowest SCOD in the whole study was obtained for Set 7 at 0 ml of H₂O₂ and 120 °C. Without the addition of H₂O₂, the process became a usual thermal destruction process with microwave heating, which would yield about 16-24 % of SCOD in the solution (Sets 3, 5 and 7).

The highest SCOD concentration occurred in Set 9, in which the highest sludge loading (2.5% TS) and H₂O₂ dosage (2 ml) were used. The higher dosage of hydrogen peroxide would favor the destruction of sludge solid, as a result, yielded more SCOD. At a dosage of 2 ml of H₂O₂, the yields of SCOD were 5991, 4527 and 13772 mg/l at initial TS of 0.5, 1.5 and 2.5%, respectively (Sets 2, 4 and 9). The SCOD reached as high as 87% of total COD for Set 2. This was due to a low initial sludge TS and a high H₂O₂ used in the process.

The results clearly indicated that two most significant factors for soluble COD are hydrogen peroxide and sludge TS content. From Figure 2.2 we can see, COD solubilization changed significantly when these two factors changed. Less significant factors are microwave heating time and temperature, as indicated in Figure 2.2. This demonstrates that the computer statistical software package (JMP-IN[®] 5.1) is very useful in experimental design and for data analysis.

2.3.2. Sludge disintegration and VFA

Sludge disintegration using the MW/H₂O₂-AOP was proposed to occur by two major reaction processes similar to the wet-air oxidation (Liao, et al., 2007). The first process involved the breakdown of the large particulate organic matters into smaller and soluble organic components, and the second process involved oxidation or gasification of the

resulting organic by-products. The resulting oxidation products are VFA and/or CO₂ (Shanableh and Shimizu, 2000).

The amounts of the SCOD and acidic acid produced in the MW/H₂O₂-AOP depended on the hydrogen peroxide dosage and inorganic acid in the reaction medium. A higher volume of acetic acid was obtained when an inorganic acid was used. Up to 25% of the SCOD was in the form of acetic acid in the MW/H₂O₂-AOP (Liao, et. al., 2007).

Acetic acid was found to be more than 90% of the total VFA in the samples. Therefore, only acetic acid was analyzed and reported in this paper. The scale estimate for acetic acid is presented in Figure 2.4, which shows that the most significant factor for acetic acid production is the dosage of hydrogen peroxide. Other factors, including microwave temperature, heating time, sludge TS, played a very minor role in the VFA production.

Figure 2.5 indicates that regardless of the TS content of the initial sludge, if no hydrogen peroxide was used in the microwave process, very low concentrations of acetic acid would be produced (Sets 3, 5 and 7). A higher amount of H₂O₂ in the solution resulted in a higher acetic acid production. The highest acetic acid production of 273 mg/l occurred at 120 °C, 2% of H₂O₂, 2.5% of TS and 5 minute heating time.

It is postulated that the function of hydrogen peroxide in the MW/H₂O₂-AOP for the sludge treatment is similar to that of the ozonation of sludge, as reported by Ahn et al. (2002). It could have involved two steps: 1) the disintegration of suspended solids, and 2) the oxidization of soluble organic matters into minerals. If there is no hydrogen peroxide in the process, the oxidation step will not take place. It should also be noted that this is to propose the role of hydrogen peroxide in the MW/H₂O₂-AOP. The mechanism of the MW/H₂O₂-AOP should be similar to the wet air oxidation process mentioned earlier.

2.3.3. Nutrient release

The biological nutrient removal (BNR) sewage sludge was used for this study. It contains a fair amount of organic phosphorus in the sludge solids and they are not very soluble. Using sewage sludge (containing 0.64% of TS), Wong et al. (2006a; 2006b) reported that the MW/H₂O₂-AOP process could release up to 84% of the sludge-bounded phosphorus into a soluble form of orthophosphate at 170 °C. In this study, higher initial sludge concentrations, 1- 2.5% TS, were used.

The scale estimates of significant factors examined for phosphate solubilization are presented in Figure 2.6. It shows that the most important single factor for phosphate solubilization is the initial TS content (Figure 5); other three factors (heating time, microwave temperature and hydrogen peroxide) were not as effective as the TS content. The relationship between the soluble phosphate and the initial sludge TS content is clearly demonstrated in Figure 2.7a. The yield of soluble phosphate is dictated by TS of the initial sludge. A higher initial sludge TS used would give more soluble phosphate (Sets 1, 5 and 9). It can also be seen that the best three percentage yields, in terms of orthophosphate/TP, were 62, 64 and 76% for Sets 3, 8 and 9, respectively. Set 3 was operated at 80°C, 1.5% TS, 5 minutes, no H₂O₂, while Set 8 was at 120°C, 1.5% TS, 3 min and 1ml of H₂O₂. With the same TS of 1.5% for both Sets, the solubilization results were similar, regardless of other operating factors. The best solubilization of phosphate occurred in Set 9, at 120 °C, 2.5% TS, 5 min heating and 2 ml of H₂O₂ (Table 2). This demonstrated that the initial sludge TS was a key factor for phosphate solubilization in the MW/ H₂O₂-AOP. This is also reflected in Figure 5; there is a much higher value of scaled estimate for TS.

The results of ammonia solubilization and the statistic analysis are presented in Table 2.3 and Figures 2.7. Ammonia release was dependent on the following factors, from most to least significant: TS, microwave temperature, heating time, and hydrogen peroxide dosage (Figure 2.8). The relationship between ammonia and the initial sludge TS content is also clearly demonstrated in Figure 2.9a. The initial sludge TS would affect the total soluble ammonia in the resulting solution. Regardless of other operating factors, the higher sludge TS used in the process gave more soluble ammonia, as indicated in Sets 1, 5 and 9 (Table 2.3).

2.3.4 Nutrient release

In a study, using the MW/H₂O₂-AOP for nutrient solubilization from sewage sludge, various heating times (a range of 5 to 20 minutes) were used for screening purposes (Wong, 2006). Pan et al, 2006, also used this process for phosphorus solubilization from liquid dairy manure. It achieved up to 85% of total phosphate release at 120 °C and 5 minutes of microwave heating. The results from these studies indicated that the release of nutrients was not affected by a heating period over five minutes. Three levels of microwave heating time, 1.5, 3 and 5 minutes, were thus used in this study.

The relationship between soluble substrates and heating time can also be extracted from the least square means as showed in Figures 1, 3, 5 and 7. It is estimated that about 70% of soluble COD, 62% of ortho-phosphate, and 52 % of soluble ammonia are reached at 1.5 minutes, assuming that 100% at 5 minutes. It is also projected that at heating time of 3 minutes, there is a slightly increase of soluble phosphate and ammonia. There are about 70% of soluble COD, 76% of ortho-phosphate, 77% of ammonia.

This demonstrates that while heating time is also a factor for the MW/H₂O₂-AOP, it is not as significant as TS concentration, microwave temperature and hydrogen peroxide dosage.

2.3.5. Prediction model

The prediction models were generated using the JMP-IN 5.1 statistical modeling computer program (Sall, et al., 2005). A series of response surface curves were produced to predict the near optimal condition for the nutrient release and solid disintegration. To get the response surface curves, we input all the factors into the software. The software would generate a series of 3-D response surface curves. Each 3-D curve would use two factors as X and Y coordinates and use the response as Z coordinate. The response surface curves for the COD, VFA, phosphate and ammonia are showed in Figures 2.10, 2.11, 2.12 and 2.13.

The prediction model indicates that the sludge solids content is the most significant factor for nutrient release and solid disintegration. The maximum productions of soluble phosphate and ammonia were observed from tests using the sludge solids content at near 2%. However, the maximum yields for the SCOD and VFA are at near 2.5% of sludge TS. This suggests that there is an advantage to operate the MW/H₂O₂-AOP at a higher temperature or a larger hydrogen peroxide dosage.

The best results for nutrient release and solids disintegration, was obtained with operating conditions at 2.5 % of total solids content, 2 wt % of hydrogen peroxide, 5 min. of microwave heating and 120 °C.

2.4 Conclusions

The results demonstrated that the factors, such as TS of sludge, hydrogen peroxide, microwave temperature, and heating time, would affect the sludge solid disintegration and nutrient release.

The initial sludge TS content and hydrogen peroxide dosage were the most significant factors for the solubilization of COD under the experimental conditions selected in this study. A higher initial sludge TS would also produced more total soluble COD. Therefore, a thickened sludge will be more suitable for the MW/H₂O₂-AOP.

The yield of acetic acid was solely decided by an amount of hydrogen peroxide dosage. A higher hydrogen peroxide used gave a better yield.

The most significant factor for the nutrient release was the initial sludge TS concentration. More ortho-phosphate and ammonia were solubilized in the process with a higher initial TS concentration.

The microwave heating time was a factor for the MW/H₂O₂-AOP, however, it was not as significant as the TS concentration, microwave temperature and hydrogen peroxide dosage. It could achieve the release of most soluble substrates within a heating time of five minutes.

The maximum yield for nutrient release and sludge disintegration was obtained at 2.5 % of total solids content, 2 wt % of hydrogen peroxide, 5 min. of microwave heating and 120 °C.



Figure 2.1 Microwave digestion system—Ethos TC Digestion Labstation 5000

| Term | Scaled Estimate* | Plot Estimate** | Least Sq Mean (mg/l) |
|----------------------|------------------|-----------------|----------------------|
| Intercept | 5671.11 | | |
| Hydrogen Peroxide[0] | -2811.78 | | 2859 |
| Hydrogen Peroxide[1] | -151.11 | | 5520 |
| Hydrogen Peroxide[2] | 2962.89 | | 8634 |
| TS[0.5] | -2099.44 | | 3572 |
| TS[1.5] | -958.11 | | 4713 |
| TS[2.5] | 3057.56 | | 8729 |
| Time[1.5] | -423.78 | | 5247 |
| Time[3] | -871.78 | | 4799 |
| Time[5] | 1295.56 | | 6967 |
| Temp[80] | 328.22 | | 5999 |
| Temp[100] | -1113.11 | | 4558 |
| Temp[120] | 784.89 | | 6456 |

*: The scaled estimate is coefficient estimate multiplied by the standard deviation of the input parameter such that the estimates can be reasonably compared with each other. The scaled estimate is not restricted to any particular range.

** : The plot estimate is the bar chart to show the scaled estimate. The middle, right side and left side of the bar chart represent zero, positive number and negative number, respectively.

Figure 2.2 Scaled estimates of significant factors examined for COD solubilization

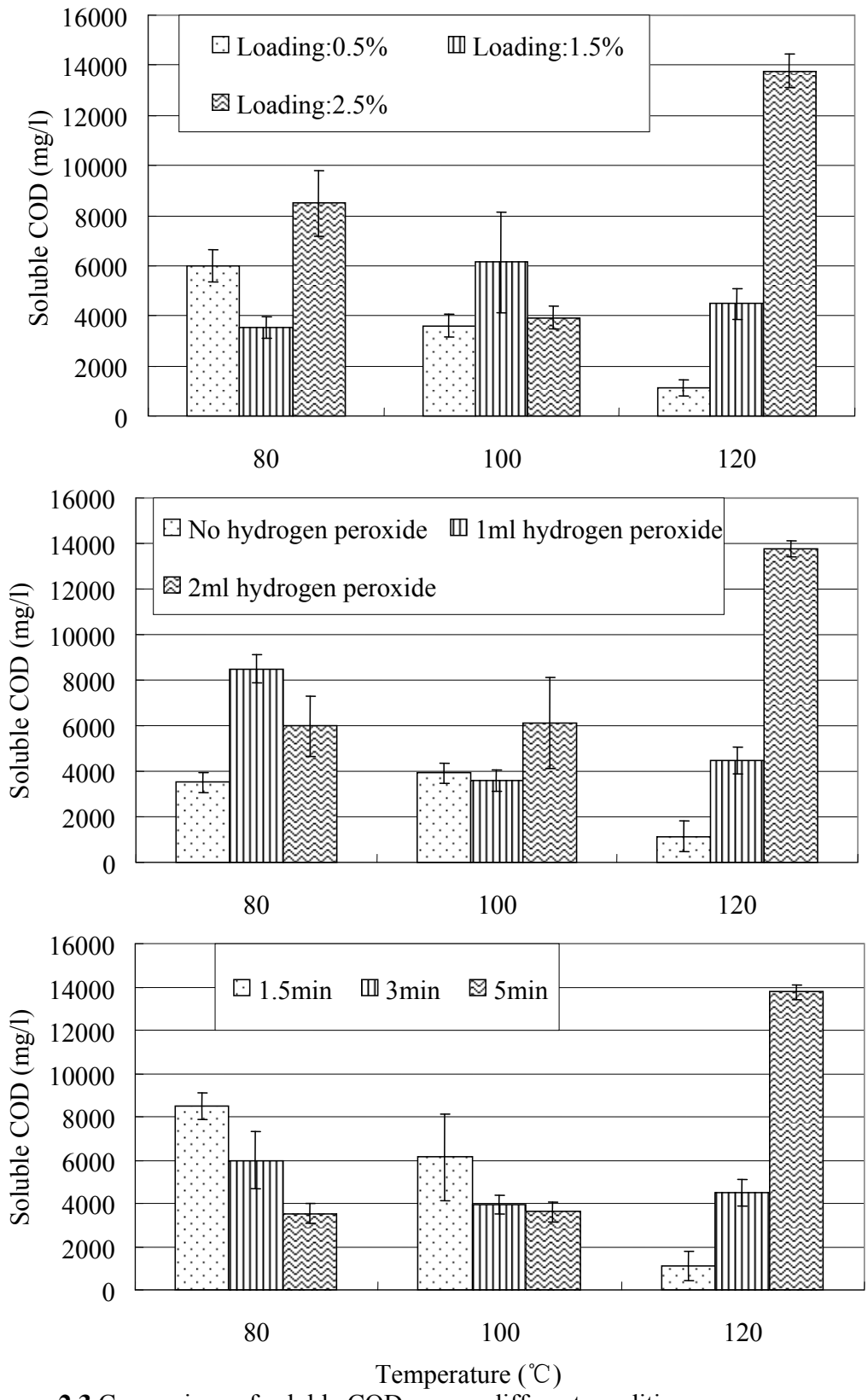


Figure 2.3 Comparison of soluble COD among different conditions

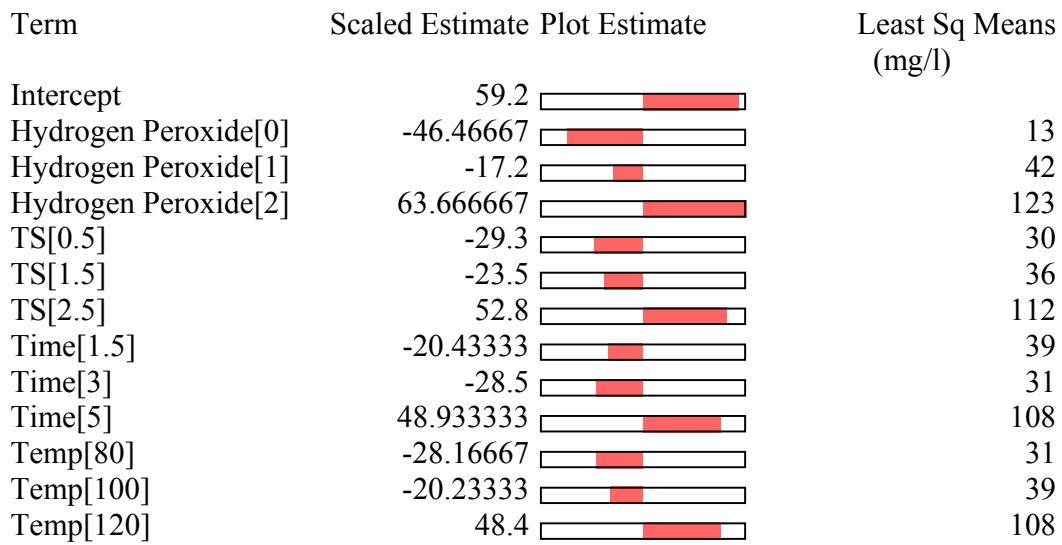


Figure 2.4 Scale estimates of significant factors examined for VFA

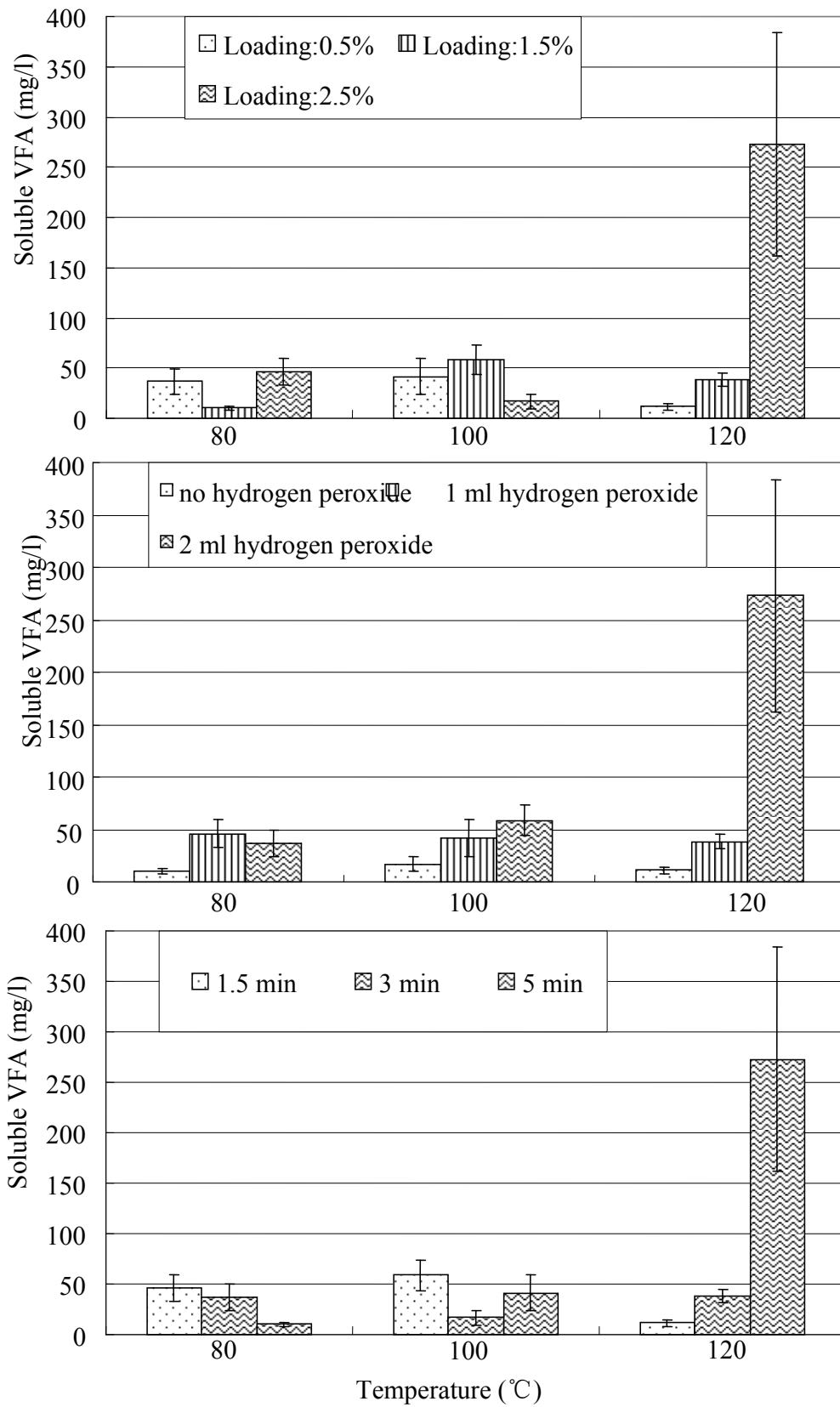


Figure 2.5 Comparison of VFA among different conditions

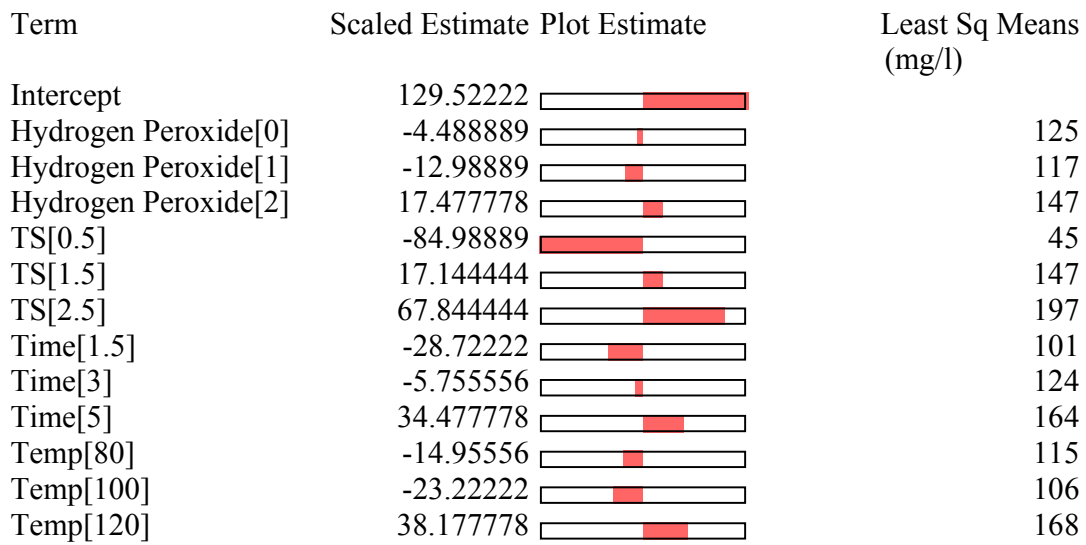


Figure 2.6 Scale estimates of significant factors examined for Ortho-P solubilization

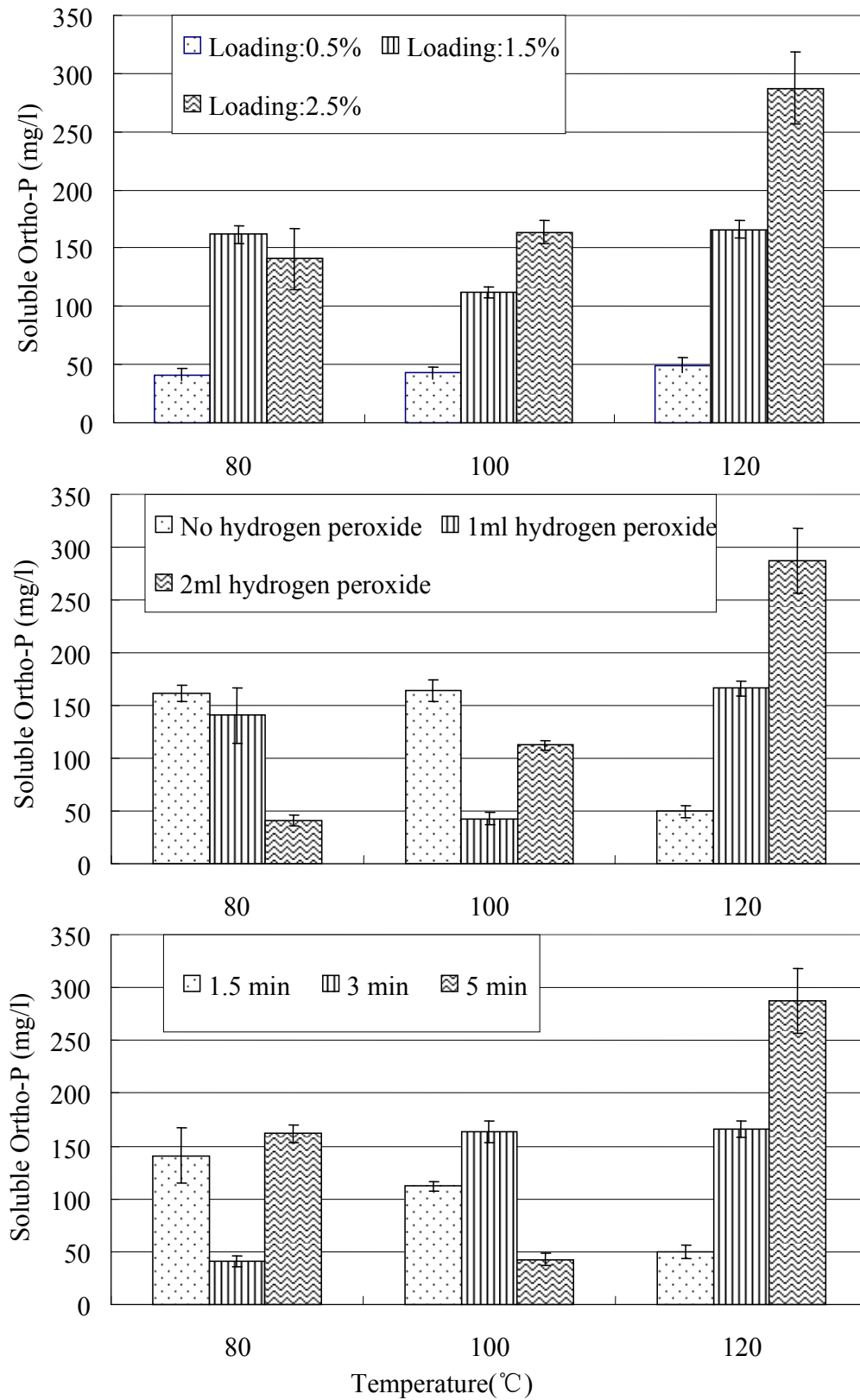


Figure 2.7 Comparison of soluble ortho-P among different conditions














| Term | Scaled Estimate | Plot Estimate | Least sq mean (mg/l) |
|----------------------|-----------------|---|----------------------|
| Intercept | 57.111111 |  | |
| Hydrogen Peroxide[0] | -13.311111 |  | 44 |
| Hydrogen Peroxide[1] | -4.811111 |  | 52 |
| Hydrogen Peroxide[2] | 18.122222 |  | 75 |
| TS[0.5] | -29.144444 |  | 28 |
| TS[1.5] | -8.044444 |  | 49 |
| TS[2.5] | 37.188889 |  | 94 |
| Time[1.5] | -18.244444 |  | 39 |
| Time[3] | 0.755556 |  | 58 |
| Time[5] | 17.488889 |  | 75 |
| Temp[80] | -17.244444 |  | 40 |
| Temp[100] | -19.344444 |  | 38 |
| Temp[120] | 36.588889 |  | 94 |

Figure 2.8 Scale estimates of significant factors examined for ammonia solubilization

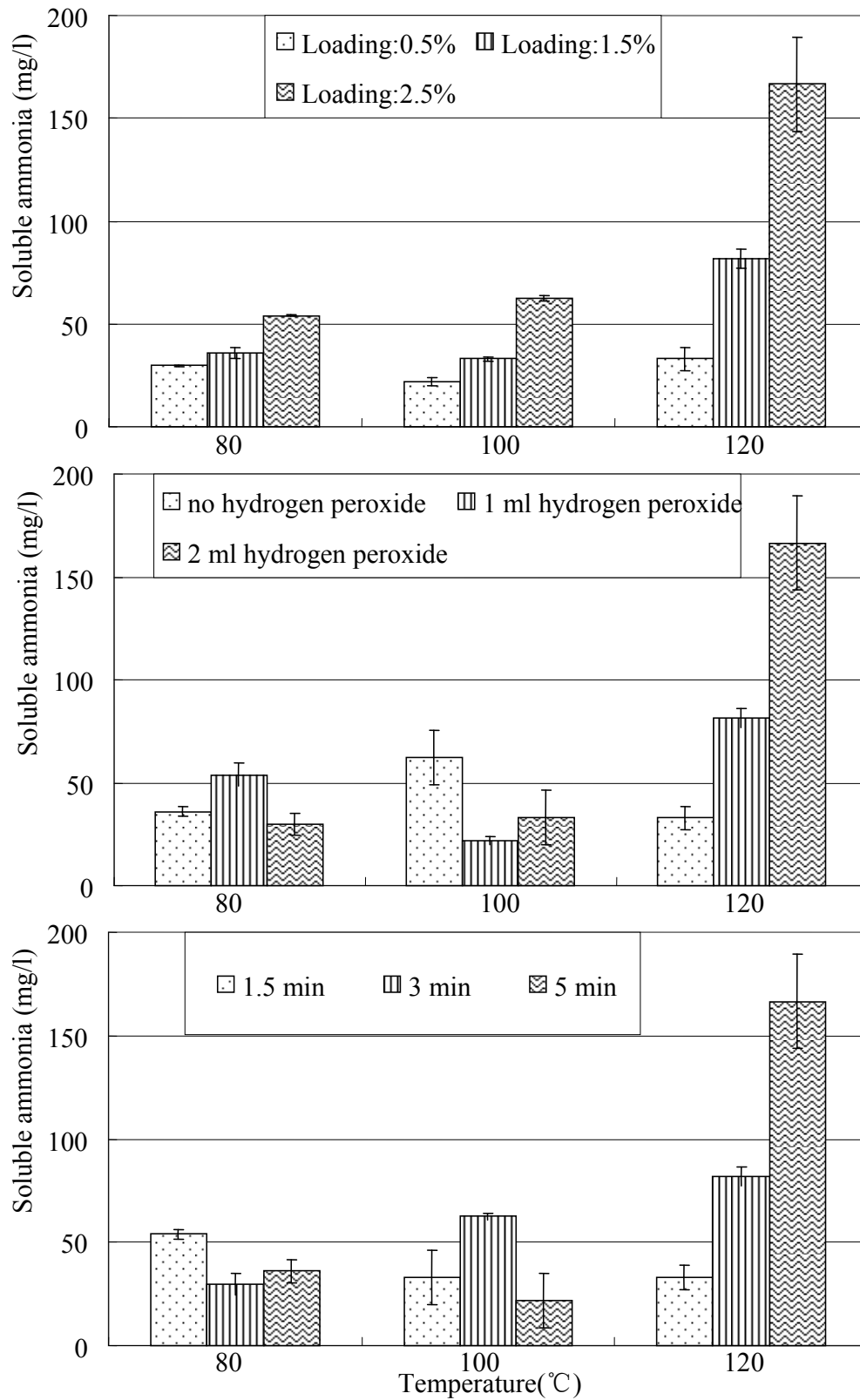


Figure 2.9 Comparison of soluble ammonia among different conditions

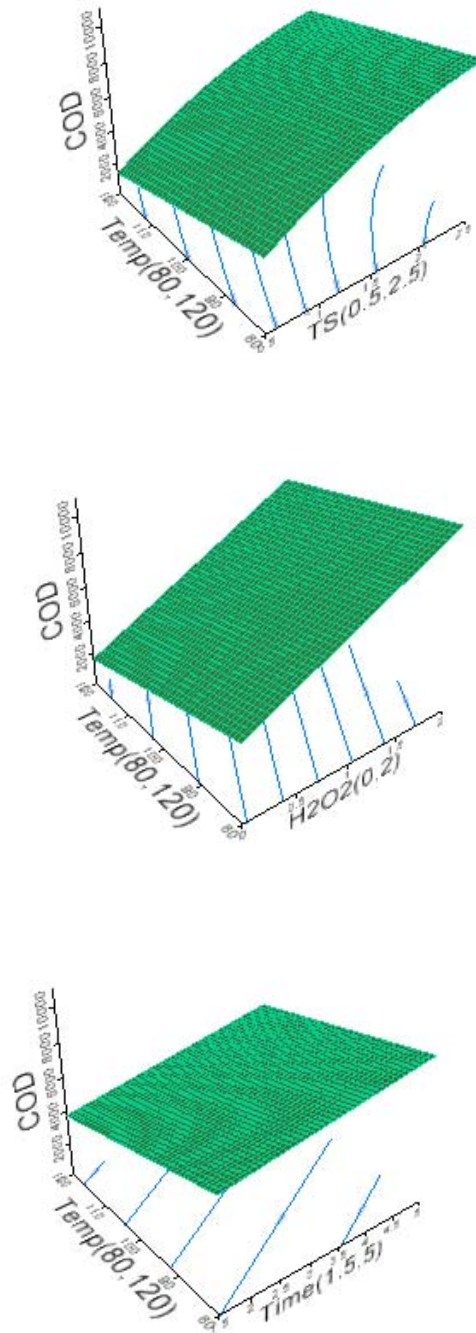


Figure 2.10 Comparison of soluble COD among different conditions by surface profiler

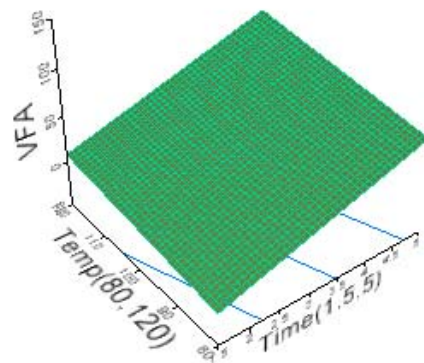
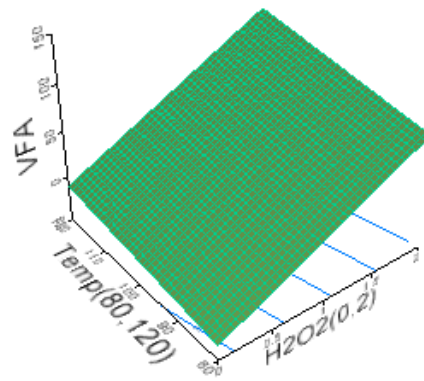
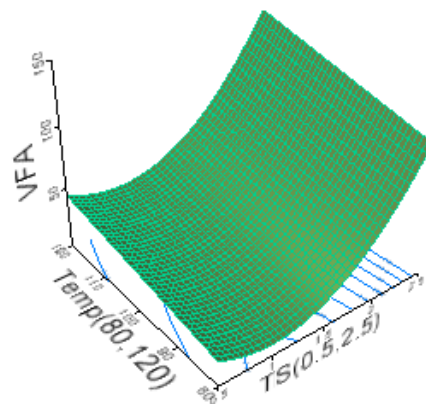


Figure 2.11 Comparison of VFA among different conditions by surface profiler

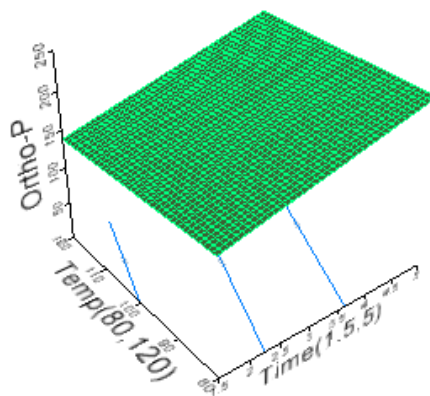
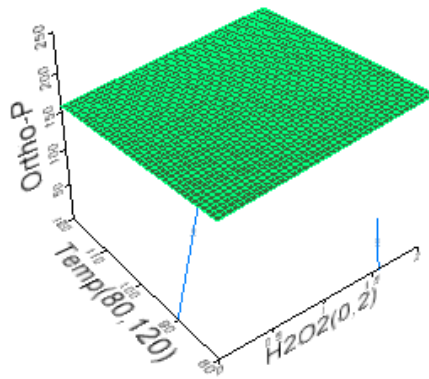
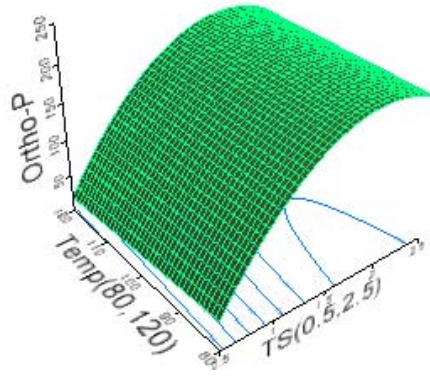


Figure 2.12 Comparison of soluble ortho-P among different conditions by surface profiler

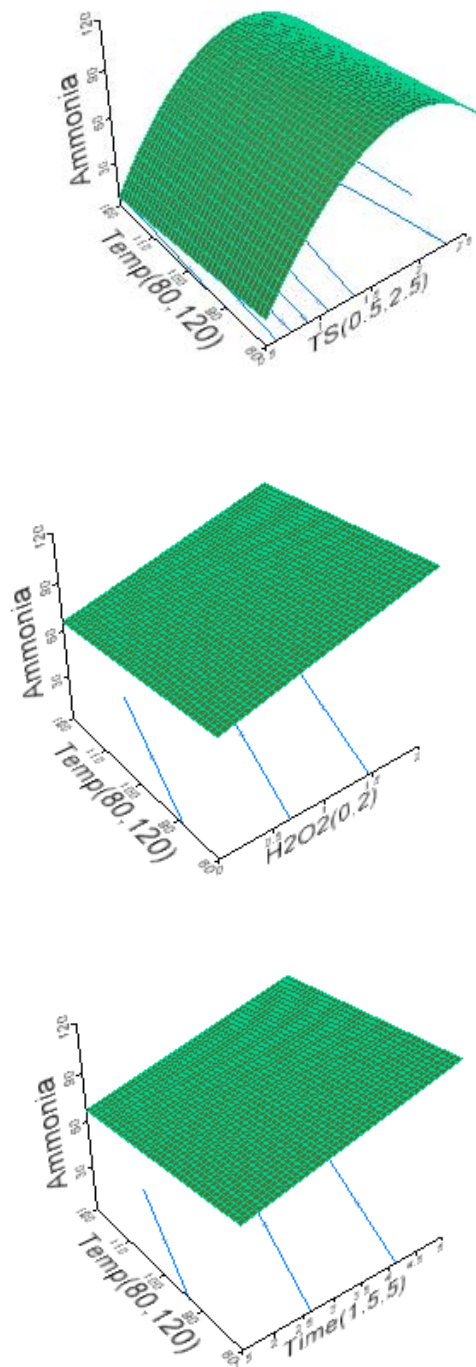


Figure 2.13 Comparison of soluble ammonia among different conditions by surface profiler

Table 2.1 Summary of experiments

| Set | Temp (°C) | Heating time (mins) | Sludge loading (%) | Reaction medium | | H ₂ O ₂ dosage (by weight %) |
|-----|--------------|------------------------|-----------------------|-----------------|---------------------------------------|---|
| | | | | Sludge (ml) | H ₂ O ₂ (ml) | |
| 1 | 80 | 1.5 | 2.5 | 29 | 1 | 1 |
| 2 | 80 | 3 | 0.5 | 28 | 2 | 2 |
| 3 | 80 | 5 | 1.5 | 30 | 0 | 0 |
| 4 | 100 | 1.5 | 1.5 | 28 | 2 | 2 |
| 5 | 100 | 3 | 2.5 | 30 | 0 | 0 |
| 6 | 100 | 5 | 0.5 | 29 | 1 | 1 |
| 7 | 120 | 1.5 | 0.5 | 30 | 0 | 0 |
| 8 | 120 | 3 | 1.5 | 29 | 1 | 1 |
| 9 | 120 | 5 | 2.5 | 28 | 2 | 2 |

Table 2.2 Characteristics of aerobic sludge used in this study

| Parameters | Secondary | | Concentrated Sludge 1 | | Concentrated Sludge 2 | |
|--------------------------|-----------------|----------------|-----------------------|-----------------|-----------------------|-----------------|
| | Concentration | Range | Concentration | Range | Concentration | Range |
| TS | 0.51±0.01 % | 0.51-0.51% | 1.34±0.03 % | 1.30-1.37% | 2.30±0.13 % | 2.21-2.39% |
| pH | 6.11 | 6.10-6.11 | — | — | — | — |
| Total COD | 6.87±0.04 g/l | 6.84-6.92 g/l | 14.68±0.68 g/l | 13.94-15.28 g/l | 22.63±0.34 g/l | 22.23-22.82 g/l |
| Total Phosphorus | 149±1 mg/l | 148-150 mg/l | 259±13 mg/l | 248-277 mg/l | 382±19 mg/l | 337-442 mg/l |
| Total Kjehldah Nitrogen | 340±7 mg/l | 335-346 mg/l | 636±37 mg/l | 581-659 mg/l | 863±106 mg/l | 722-964 mg/l |
| Initial Ortho-phosphates | 0.22±0.09 mg/l | 0.15-0.32 mg/l | — | — | — | — |
| Initial Ammonia | 2.22 ±0.34 mg/l | 1.73-2.63 mg/l | — | — | — | — |

Table 2.3 Summary of experimental results

| Set | O-PO ₄ (mg P/l) | Percentage of soluble O-PO ₄ (%) | NH ₃ (mg N/l) | Percentage of soluble NH ₃ (%) | Soluble COD (g /l) | Total COD of study material (g /l) | Percentage of soluble COD (%) ¹ | VFA (mg /l) |
|-----|-------------------------------|--|-----------------------------|--|--------------------------|---|---|----------------|
| 1 | 141±26 | 36 | 54±5 | 6 | 8.48±0.62 | 22.63±0.34 | 37 | 46±13 |
| 2 | 41±5 | 28 | 30±0.4 | 9 | 5.99±1.32 | 6.87±0.04 | 87 | 37±13 |
| 3 | 162±8 | 62 | 36±2 | 6 | 3.53±0.45 | 14.68±0.68 | 24 | 10±2 |
| 4 | 112±4 | 44 | 33±1 | 5 | 4.53±0.42 | 14.68±0.68 | 31 | 59±15 |
| 5 | 164±10 | 42 | 62±13 | 10 | 3.93±0.44 | 22.63±0.34 | 17 | 17±7 |
| 6 | 43±5 | 28 | 33±6 | 10 | 3.60±0.46 | 6.87±0.04 | 52 | 41±18 |
| 7 | 50±6 | 34 | 32±5 | 10 | 1.12±0.68 | 6.87±0.04 | 16 | 11±3 |
| 8 | 166±7 | 64 | 82±5 | 13 | 4.48±0.61 | 14.68±0.68 | 30 | 38±7 |
| 9 | 288±31 | 76 | 166±23 | 19 | 13.77±0.34 | 22.63±0.34 | 61 | 273±111 |

Chapter 3 An Ozone/Hydrogen Peroxide/Microwave Enhanced Advanced Oxidation Process for Sewage Sludge Treatment

3.1 Introduction

The large volume of sludge as an end product from the biological activated sludge (AS) process poses one of the biggest challenges to the wastewater treatment industry (Metcalf and Eddy, 2003). Treatment and disposal of sewage sludge from wastewater treatment plants can account for up to 50-60 % of the total cost of wastewater treatment (Davis and Hall, 1997). Currently, the residual sludge is digested, incinerated, deposited in landfills, or used as fertilizer through agricultural land application (Odegaard, et al., 2002).

There is an urgent need to develop more viable methods for handling and treating sludge to reduce the costs of treatment and disposal, and to recover and reuse nutrients contained in the sludge. A microwave enhanced advanced oxidation process (MW/H₂O₂-AOP) for sludge treatment has been developed at the University of British Columbia (Liao, et al., 2005a; Liao, et al., 2005b; Wong, et al., 2006; Wong, et al., 2007). Most of sludge suspended solids was disintegrated at temperatures at 80 °C and above. A significant amount of nutrients and metals were also released into the solution.

Ozone is a very reactive oxidant, and it does not produce harmful byproducts, but only H₂O and O₂. Hydroxyl radicals can be formed when ozone enters into water. Since hydroxyl radical has a very high oxidation potential, it is a much more effective oxidant than ozone itself. Ozone would also help dissociate H₂O₂ to form hydroxyl radical too.

This study is a part of our research group's continuing efforts to improve upon the MW/H₂O₂-AOP process. It was expected that by using a combination of ozone and

hydrogen peroxide in the process (designated as MW/H₂O₂/O₃-AOP), the efficacy of the treatment could be improved. This chapter reports the preliminary results of the different processes studied using ozone (O₃), hydrogen peroxide (H₂O₂), their combination (H₂O₂/O₃), microwave (MW), microwave with ozone (MW/O₃), microwave with hydrogen peroxide (MW/H₂O₂), and microwave with hydrogen peroxide and ozone (MW/H₂O₂/O₃).

3. 2 Materials and methods

3.2.1 Ozonation

The schematic flow diagram of the ozonation process is presented in Figure 3.1. The system includes a reaction flask, an ozone generator, a flow meter, and an exhaust gas collection system. The ozonation experiments were conducted in a 500 ml flask reactor. Ozone was produced from oxygen using an ozone generator (Azcozon VMUS-4, AZCO Ind., Canada). The flow rate was set at 1 l min⁻¹ by a flow meter. Exhaust ozone gas was monitored, and excess amounts were destroyed by reacting with potassium iodide (KI) solution (2% w/w).

3.2.2 Microwave heating

The microwave digestion system— Ethos TC Digestion Labstation 5000, Milestone Inc., U.S.A. was used in this study.

3.2.3 Experimental design

Conventional oxidation and AOP processes, plus microwave treatment without oxidant, were conducted in this study. Either hydrogen peroxide or ozone was used in the conventional oxidation process, while the combined oxidation processes, H₂O₂/O₃,

MW/O₃, MW/H₂O₂ and MW/H₂O₂/O₃, are grouped into the AOP. It was expected that by combining two oxidants, the oxidation capacity would further increase, and the treatment would be more efficient than that from a single oxidant. Microwave heating alone, without any oxidant, as a thermal destruction process, served as the control.

Seven sets of experiments were carried out, each with at least three replicates, to explore the effects of ozone, hydrogen peroxide and microwave heating on the solubilization of secondary sewage sludge. The conditions of these experiments are summarized in Table 3.1. The first three sets of experiments (Sets 1, 2 and 3) were performed at ambient temperature. The second four sets of experiments (Sets 4 to 7) were subjected to microwave treatments at a temperature of 100 °C. Results from our previous studies revealed that lowest amounts of solubilized nutrients were obtained at this temperature (Liao, et al., 2005a; Liao, et al., 2005b; Wong, et al., 2006); hence this temperature was selected, as it would depict the worst scenario for nutrient-solubilization. Based on the results from chapter 2, large amounts of solubilized nutrients were obtained at the heating time of 3 minutes compared with those obtained at the heating time of 5 minutes. Therefore 3 minutes of heating time was selected in this experiment. The sludge volumes with or without ozone treatment were not the same, because the experiments involved in ozonation needed more sludge volumes. However, the ratio of sludge to hydrogen peroxide was kept the same.

3.2.4 Ozonation/Microwave process and sampling

Secondary aerobic sludge was obtained from the pilot-scale wastewater treatment facilities located at the University of British Columbia (UBC) campus. The characteristics of the secondary aerobic sludge over the course of the study were

presented in Table 3.2. Fresh sludge samples were collected daily for the duration of the experiments. A total of 90 ml of sludge, with or without the combination of microwave heating and 1 ml H₂O₂ (30 wt %), was bubbled through ozone for 20 minutes at the flow rate of 1 l min⁻¹. During the microwave heating, the heating time and ramp time (an increase of 20°C per minutes) were kept constant at 3 and 4 minutes, respectively.

Samples were taken from the ozonation reactor and subjected to microwave heating immediately. The mixed liquors from all samples were spun in a centrifuge at 4000 rpm for 15 minutes. The resulting supernatants were filtered through Whatman No.4 filters and analyzed. Total solids (TS), ammonia, orthophosphate (ortho-P), total phosphate (TP), total Kjeldahl nitrogen (TKN) and chemical oxygen demand (COD) were determined according to the procedures described in Standard Methods (APHA, 1995). All analyses, except for the determinations of TS and COD, were conducted using the flow injection analysis (Lachat Quick-Chem 8000 Automated Ion analyzer, Lachat Instruments, U.S.A). Samples collected before treatments were also measured for TS, TP, TKN, ortho-P, ammonia and total COD. All supernatant samples were analyzed for ortho-P, ammonia and soluble COD (SCOD).

A Hewlett Packard 5890 Series II gas chromatograph equipped with a flame ionization detector (FID) was used to measure volatile fatty acids (VFA).

3. 3 Results and discussion

3.3.1 Nutrients release

The results of phosphate solubilized from various oxidation processes are presented in Figure 3.2. All oxidation processes showed good phosphate release. The soluble

phosphate ranged from 150 to 188 mg P /l, about 24 - 31 % of total phosphate. The minimum release of ortho-phosphate (150 mg P /l) was obtained in oxidation processes using either ozone or hydrogen peroxide alone (Sets 1 and 2) at ambient temperature. Even though the oxidation potentials are quite different for these two oxidants, 2.1 V for ozone verse 1.8 V for hydrogen peroxide, there are no difference for the yield. It seemed that the oxidation potential of the oxidants did not play an important role in the conventional oxidation process. This probably depended on the amount of oxidant used and also the reaction period. If a sufficient amount of oxidant is present in the reaction medium, it would be very effective to release phosphate from the sludge. For Set 3, a combination of ozone and hydrogen peroxide together at ambient temperature yielded a better result than that of a single oxidant. This might be because of the combination of hydrogen peroxide and ozone in the solution, resulting in the generation of hydroxyl radicals, which had a very high oxidation potential. It might be also due to a larger total amount of oxidants used in the process.

The thermal destruction process (microwave heating alone without any oxidant) also resulted in a substantial increase of soluble phosphates, at 185 mg P /l in the solution (Set 4). It was reported that a simple heating process could release orthophosphate from the activated sludge process (Kuroda, et al., 2002). Microwave irradiation only facilitated the release process (Liao, et al., 2005a; Liao, et al., 2005b).

The microwave enhanced treatments with oxidants (Sets 5, 6 and 7) also gave high orthophosphates (176-187 mg P /l). The maximum release of 188 mg P /l of orthophosphate occurred in the MW/H₂O₂/O₃-AOP at 100 °C (Set 7). The results were consistent with our previous works (Liao, et al., 2005a; Liao, et al., 2005b; Wong, et al.,

2006). The AOP process was found to have a slight improvement in the phosphate release over that of the microwave heating alone at temperatures below 120 °C. Hydrogen peroxide used in the MW-AOP was not the most significant factor affecting phosphorus release, while microwave temperature was the most significant factor (Wong, et al., 2007). It should be noted that polyphosphates, which can easily be converted into orthophosphate by treating with an acid, contributed a large portion of the soluble phosphate in the treated solution (Wong, et al., 2006; Kuroda, et al., 2002; Chan, et al., 2006).

The ammonia concentrations in the solution are shown in Figure 3.3. At the ambient temperature, only small amounts of ammonia (7-15 mg /l) were obtained, regardless of oxidants used in the processes. No clear trend was observed for Sets 1, 2 and 3. Microwave thermal destruction also released small amounts of ammonia (Set 4).

There was not a significant increase of soluble nitrogen in the MW/O₃-AOP treatment (Set 5). However, a significant amount of soluble nitrogen occurred in the MW/H₂O₂-AOP and the MW/H₂O₂/O₃-AOP (Sets 6 and 7). The highest ammonia concentration was obtained in the MW/H₂O₂/O₃-AOP (Fig. 3.3). The results indicated that hydrogen peroxide is a better oxidant than ozone for the MW-AOP process. There was an advantage to use a combination of H₂O₂ and O₃ in the MW-AOP.

The ammonia solubilization result from the MW/H₂O₂-AOP was also similar to the previous studies (Wong, et al., 2006; Wong, et al., 2007). Unlike the phosphate release, hydrogen peroxide played an important role for the release of ammonia in the MW/H₂O₂-AOP. It was found that ammonia release was dependent on the following factors, from most significant to least significant: (1) hydrogen peroxide addition, (2) temperature and

(3) acid addition.^[8] This also implied that amounts of total oxidants are very important. Set 7 (MW/H₂O₂/O₃-AOP) had the largest amount of oxidant in the process, therefore, it produced the highest amount of soluble ammonia among the treatments.

3.3.2 Destruction of sludge solids

The results of COD solubilization are showed in Figure 3.4. While all of the treatments were able to achieve certain sludge solids destruction, the efficacy varied over a wide range. Very little sludge suspended solids were destroyed by using ozone and hydrogen peroxide at ambient temperature (Sets 1 and 2). Therefore, very low SCOD concentrations were obtained in the solutions, i.e., 0.8 and 2.6 g /l for Sets 1 and 2, respectively. As expected, a higher concentration of SCOD (3.5 g /l) was observed for Set 3 (H₂O₂/O₃ at ambient temperature). Also, the microwave thermal destruction treatment yielded 4.9 g /l of SCOD. This was the highest amounts among the Sets (Sets 1, 2, 3 and 4). Thermal destruction treatment could yield a substantial amount of SCOD was reported previously (Metcalf and Eddy, 2003; Liao, et al., 2005a).

Very low volatile acids concentrations were obtained at ambient temperature. The VFA for Sets 1, 2, 3 and 4 were 20, 33, 38 and 19 mg /l, respectively (Table 3.3). The results indicated that it was very useful to use a combination of H₂O₂ and O₃ for the VFA production. The lowest value of pH, contributing from the VFA production, was also observed in Set 3.

There was a significant increase of SCOD for all of the MW-AOP treatments (MW/O₃, MW/H₂O₂ and MW/H₂O₂/O₃). The SCOD concentrations were 6.3, 9.7 and 9.9 g /l for Sets 5, 6 and 7, respectively. The MW/O₃-AOP process (Set 5) had a 27% more SCOD than that from the microwave thermal treatment (Set 4). The highest COD concentration

was obtained in the MW/H₂O₂/O₃-AOP (Set 7), where about 37% of the total COD was released. This might be due to the highest total amounts of oxidants used among all the treatments. The COD results were very comparable to previous works (Wong, et al., 2007). It also showed that the SCOD concentration in the treated solution was affected by hydrogen peroxide.

A similar trend was also obtained in the resulting VFA (Table 3.3). The highest concentration of 122 mg /l was obtained in the MW/H₂O₂/O₃-AOP (Set 7). The MW/H₂O₂-AOP (Set 6) also produced a significant amount of VFA. The pH for both Sets decreased to less than 4.5 (Table 3.3). This indicated that more final oxidation products were present in the treated solutions for the AOP than those in the convention oxidation processes. The VFA results were also consistent with our previous works (Liao, et al., 2005b; Wong, et al., 2006).

The overall results indicated that the MW-AOP would increase the destruction of solids particles in sewage sludge, and it would also increase nutrient solubilization. It was also advantageous to have both ozone and hydrogen peroxide in the MW-AOP; as both are powerful oxidants, which can generate hydroxyl radicals in the solution. It seems that hydrogen peroxide is a better oxidant than ozone for the process (Fig. 3.4). If only one oxidant is to be used, hydrogen peroxide should be the preferred one. The AOP processes using hydrogen peroxide and/or ozone are safe and environmental friendly, as there would not produce harmful residues.

3.4 Conclusions

The results indicated that both conventional oxidation process and the AOP process could be used to release nutrients and to reduce suspended solids from sewage sludge. The AOP process was superior to the conventional oxidation process for sludge treatment. The best result, in terms of nutrients release and solids reduction, was obtained in the MW/H₂O₂/O₃-AOP, where hydrogen peroxide and ozone were both used. More than 30% of TP and 20% of TKN, and 37% of total COD, were released into the solution. The amount of oxidants would affect the release of ammonia and the destruction of suspended solids; however, the soluble phosphate in the solution was affected by the operating temperature. The microwave thermal destruction process alone would also be able to release phosphate, and reduce suspended solids from sewage sludge.

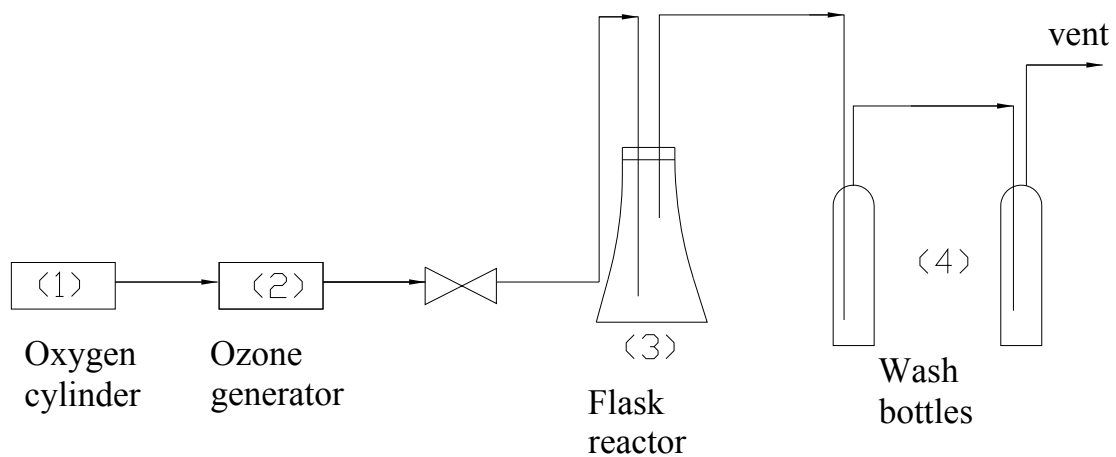


Figure 3.1 Schematic diagram of the ozonation process

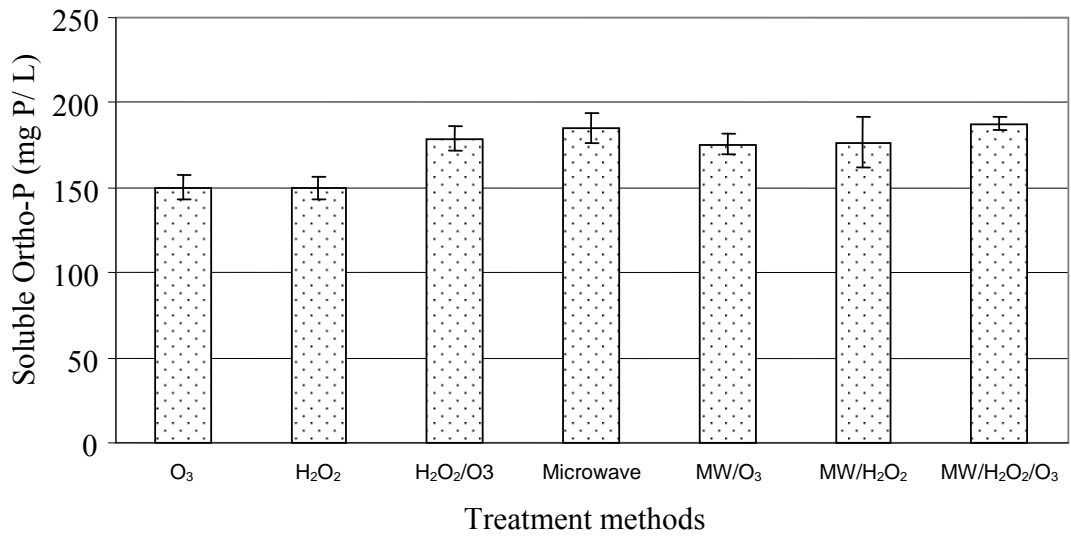


Figure 3.2 Comparison of soluble Ortho-P among different treatment methods

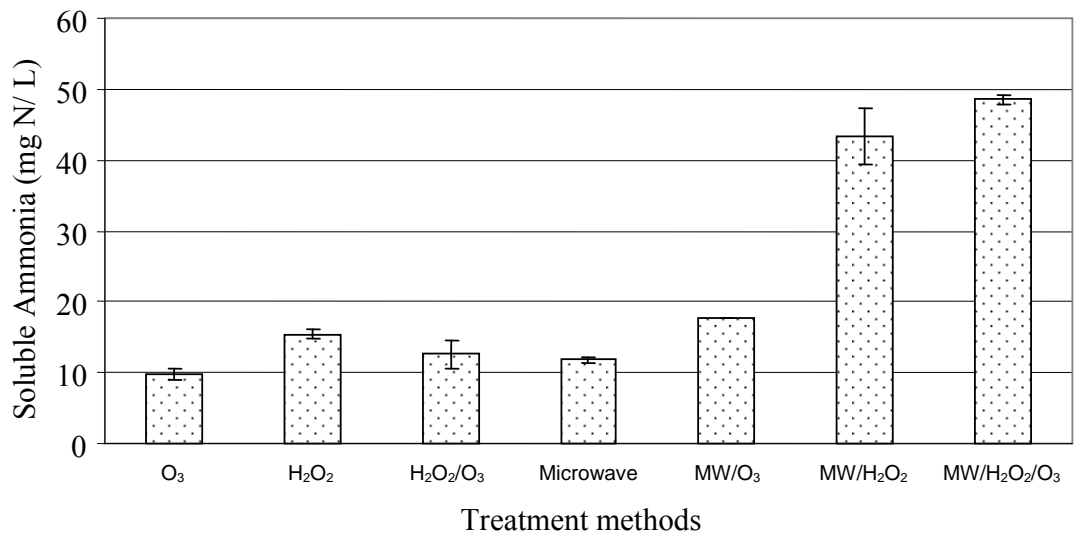


Figure 3.3 Comparison of soluble Ammonia among different treatment methods

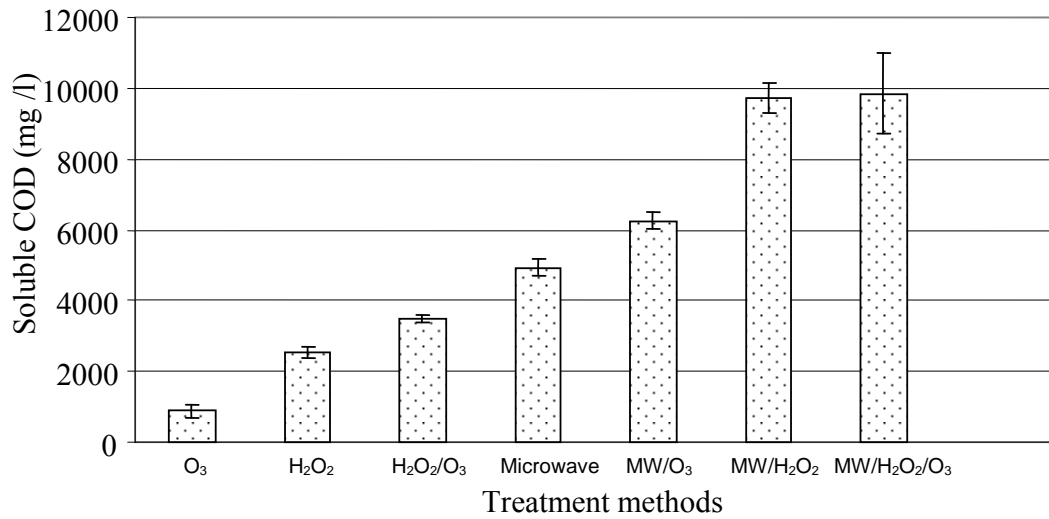


Figure 3.4 Comparison of soluble COD among different treatment methods

Table 3.1 Summary of experiments

| Set | Treatment | Sludge (ml) | H ₂ O ₂ (ml) | Temp (°C) | Reaction time | Bubble time (min) |
|-----|---|----------------|---------------------------------------|--------------|---------------|----------------------|
| 1 | O ₃ | 90 | 0 | Ambient | 4 hrs | 20 |
| 2 | H ₂ O ₂ | 29 | 1 | Ambient | 4 hrs | 0 |
| 3 | H ₂ O ₂ / O ₃ | 87 | 3 | Ambient | 4 hrs | 20 |
| 4 | MW | 30 | 0 | 100 | 3 mins | 0 |
| 5 | MW/ O ₃ | 90 | 0 | 100 | 3 mins | 20 |
| 6 | MW/H ₂ O ₂ | 29 | 1 | 100 | 3 mins | 0 |
| 7 | MW/H ₂ O ₂ /O ₃ | 87 | 3 | 100 | 3 mins | 20 |

Table 3.2 Characteristics of secondary aerobic sludge

| Parameters | Concentration | Range |
|--------------------------|-----------------|----------------|
| TS | 2.93% | 2.88-2.98% |
| pH | 6.11 | 6.10-6.11 |
| Total COD | 26900 mg/l | |
| Total Phosphorus | 614±129 mg/l | 474-860 mg/l |
| Total Kjehldah Nitrogen | 1051 ±339 mg/l | 768-1730 mg/l |
| Initial Ortho-phosphates | 0.22±0.09 mg/l | 0.15-0.32 mg/l |
| Initial Ammonia | 2.22 ±0.34 mg/l | 1.73-2.63 mg/l |

Table 3.3 Volatile fatty acids and pH of sludge after treatment

| Treatment methods | VFA (mg/l) | pH |
|--|-----------------|-----------|
| O ₃ | 19.5±2.9 mg/l | 6.47±0.11 |
| H ₂ O ₂ | 33.4±10.9 mg/l | 6.77±0.01 |
| H ₂ O ₂ / O ₃ | 35.7±7.5 mg/l | 5.44±0.19 |
| MW | 19.0±4.2 mg/l | 6.42±0.05 |
| MW/ O ₃ | 42.3±6.2 mg/l | 4.90±0.16 |
| MW/H ₂ O ₂ | 93.1±4.0 mg/l | 4.46±0.05 |
| MW/H ₂ O ₂ /O ₃ | 122.3±27.9 mg/l | 3.64±0.01 |

Chapter 4 Microwave Enhanced Advanced Oxidation Process for Sewage Sludge Treatment

4.1 Introduction

One of the most challenging tasks for the wastewater sector is the management of the excess sludge from wastewater treatment plants. A thermal/chemical method has been used as an effective sludge disintegration technology for sludge minimization (Odegaard et al. 2002). The method involves heating the sludge to a temperature, normally 160°C, at which cells are disintegrated and lysis takes place. Chemical addition is often used to facilitate the process.

Advanced oxidation process (AOP) involves the generation of the highly reactive hydroxyl radicals, which can be used as an efficient means for sludge disintegration and nutrient release. The most common AOP methods are combinations of ozone, hydrogen peroxide and ultraviolet (UV) radiation. The microwave enhanced AOP with an addition of hydrogen peroxide (MW/H₂O₂-AOP) has been used for phosphorus release and reduction of suspended solids from sewage sludge at the University of British Columbia (Liao et al. 2005a, Liao et al. 2005b, Wong et al. 2006a). At temperatures of 80 °C and above, most of the suspended solids in the sewage sludge were disintegrated by the MW/H₂O₂-AOP (Wong et al. 2006a). The microwave process was also found to limit microbial activity, and with the addition of hydrogen peroxide, pasteurization or sterilization of pathogens in the solution can be achieved (Liao et al. 2005b). It is also more efficient than the conventional heating process, i.e., the microwave enhanced reactions can be completed in a much shorter period.

It was supposed that the efficiency of the MW/H₂O₂-AOP could be further enhanced by adding ozone to combine the effects of ozone and hydrogen peroxide (MW/H₂O₂/O₃-AOP). Ozone is also a very reactive oxidant, and hydroxyl radicals can be formed when it is fed into water. It could also help dissociate H₂O₂ to further form hydroxyl radicals. A preliminary study of the MW-AOP using hydrogen peroxide, ozone, and a combination of both was reported in a previous paper (Yin et al. 2007). These microwave enhanced advanced oxidation processes, designated respectively, as MW/O₃-AOP, MW/H₂O₂-AOP and MW/H₂O₂/O₃-AOP, were conducted at 100 °C. Thermal destruction using microwave alone without an oxidant, served as the control, was also conducted. Results from the study indicated that the MW/H₂O₂/O₃-AOP yielded the highest soluble nutrient and soluble COD in the solution. The efficiency of the process was improved by an addition of ozone.

In this study, the performance of the MW-AOP process using various amounts of hydrogen peroxide and ozone was further explored. This chapter reports the effects of ozone addition on the MW-AOPs, and also the significant factors that affect nutrient solubilization and sludge disintegration.

4.2 Materials and methods

4.2.1 Ozonation

The schematic flow diagram of ozonation process is presented in Figure 4.1. The system includes a glass column contactor (80cm h x 2.8cm d), an ozone generator, a flow meter, and an exhaust gas collection system. The picture of setup can be seen in Figure 4.2.

Ozone concentration used in the process was determined by ozone demand-semi batch process (Standard Method, 1995).

4.2.2 Microwave

The microwave digestion system— Ethos TC Digestion Labstation 5000, Milestone Inc., U.S.A. was used in this study.

4.2.3 Experimental design

Based on the previous studies, key factors were microwave temperature, amounts of oxidants and heating time (Liao, et al., 2005b; Wong et al., 2006a). More than 80% of sludge solids were reduced at a heating period of three minutes. Therefore, heating time was set for three minutes. In order to determine the effects of oxidants on the sludge treatment, a computer software package (JMP IN[®] 5.1) was used. Various amounts of oxidants and microwave temperatures were thus selected in this study, and are showed in Table 4.1. A total of thirteen runs were carried out. The resulting data were incorporated into the screening design to identify the most significant factors.

4.2.4 Ozonation/Microwave process and sampling

Secondary aerobic sludge was obtained from the pilot-scale wastewater treatment facilities located at the University of British Columbia (UBC) campus. The characteristics of the secondary aerobic sludge over the course of the study were presented in Table 4.2. Fresh sludge samples were collected daily for the duration of the experiments. First, ozone was introduced into sludge at a flow rate of 1l/min for 3, 6 and 9 minutes, respectively. Subsequently, hydrogen peroxide was also added into samples. Finally, samples were subjected to the microwave heating. Heating time was kept for three minutes, however, various ramp times (an increase of 20°C per minutes) were used. Samples were taken from the ozonation reactor and microwave immediately after treatment. Each set of samples with three replicates was then kept for total phosphate

(TP), total kjeldahl nitrogen (TKN) and total chemical oxygen demand (TCOD) analyses. The other samples of three replicates were spun in a centrifuge at 4000 rpm for 15 minutes. The resulting supernatants were filtered through Whatman No.4 filters and analyzed. Samples collected before treatments were also measured for TS, TP, TKN, ortho-phosphate, ammonia and total COD. All supernatant samples were analyzed for ortho-phosphate, ammonia and soluble COD.

The percentage of soluble phosphate and ammonia are based on TP and TKN of the starting material, respectively. Two percentage SCOD (%) units are used; one is based on TCOD of the starting materials, another is calculated from TCOD of the resulting solution.

4.3 Results and discussion

MW/H₂O₂-AOP process has been proven very useful for solubilizing nutrient for sewage sludge treatment (Liao et al., 2005b). Efforts have been made to evaluate the effects of the O₃/H₂O₂ system on the solubilization of nutrient and solids reduction. Hydroxyl radical is formed when ozone enters into water. Since hydroxyl radical has a very high oxidation potential, it is therefore a much more effective oxidant than ozone itself. It would also help dissociate H₂O₂ to form hydroxyl radical too.

As mentioned earlier, ozone was introduced into each solution first. The ozone dosages in solutions were between 0.89 and 5.28 mg/ml in this study. The results of soluble phosphate, ammonia, COD and VFA are presented in Table 4.3. The data presented in Table 4.3 were input into the JMP-IN statistical package to determine the significant factors affecting solubilization and solids reduction.

4.3.1 Solubilization of phosphorus and nitrogen

Figure 4.3 shows a Parelo plot based on the results, which is a bar chart that is used to compare the relative significance of the effects with respect to one another. It can be seen that most significant factors for maximizing orthophosphate yield is in the following order, from most to least significant: (1) microwave heating temperature, (2) ozone dosage (3) the combined effect of temperatures and (4) the combined effect of hydrogen peroxide and temperature. Microwave heating temperature and ozone dosage were found to be the dominating factors for the release of phosphate from the sewage sludge.

Figure 4.4 shows the soluble phosphate concentration at various experimental conditions. It clearly indicated that a higher yield of phosphate occurred at a higher temperature. For Sets 4, 7 and 1, they were operated with similar ozone dosages at 80, 100 and 120°C, respectively. Soluble phosphate increased with an increase of microwave heating temperature. A higher amount of soluble phosphate was obtained with an increase amount of oxidant used. As indicated in Table 4.3 and Figure 4.4, the maximum solubilization of phosphate was obtained with additions of 2 % hydrogen peroxide (wt) and 5.09 mg/ml of ozone, and operating at 120 °C (Set 13). It was operated at highest microwave heating temperature in this study. As indicated in Pareto plot, temperature is the dominant factor for maximizing phosphate release. However, amounts of oxidants used in the reaction are also an important factor for phosphate yield. In this set, the highest concentration of oxidants was also used.

A higher phosphate was yielded with an increase of ozone dosage (5.01 mg/ml), even though the microwave heating temperature was set at 60°C (Set 1). Similar results were obtained from Sets 10 and 11. About 307 mg/l of phosphate was occurred at Set 11 with

an addition of 3.16 mg/ml of ozone, while it only produced 215 mg/l of phosphate with 0.89 mg/ml of ozone for Set 10.

The lowest yield of soluble phosphate was obtained at 80°C with the lowest ozone dosage of 1.20 mg/ml (Set 4). No hydrogen peroxide was added in this experiment set.

It can be seen in Figure 4.5 that significant factors affecting soluble ammonia are in the following order, from most to least significant: (1) hydrogen peroxide addition, (2) the combined effect of hydrogen peroxide and temperature, (3) temperature, and (4) ozone. It indicated that hydrogen peroxide play a very important role of solubilization of ammonia. A higher amount of oxidants used in the reaction would produce more ammonia into solution. Hydrogen peroxide addition would have more pronounced effect than ozone dosage. Temperature also affected the yield of ammonia. However, ammonia tended to be easily escaped into air when it was operated at a higher temperature. It would make a higher variation in the yield of soluble ammonia. Figure 4.6 shows the soluble ammonia concentration in various treatment conditions. The highest soluble ammonia concentration of 313 mg/l was obtained at 120°C, with 2 % of H₂O₂ and 5.09 mg/ml of O₃ (Set 13). The highest amount of oxidants was used in this experimental set. It also operated at the highest temperature selected in this study. Therefore, it produced most of ammonia in the solution. The lowest ammonia concentration of 10.8 mg/l was occurred at Set 4. This set used the least oxidants (only 1.08 mg/ml of O₃) among all experiments conducted in this study. About 122 mg/l of ammonia was obtained with a dosage of 5.01 mg/ml of O₃ at 60°C. Other experimental sets (2 and 3), which were operated at 60°C, also produced fair amounts of ammonia. It should be noted that the yield of ammonia was affected by total amount of oxidants used in the reaction. As indicated in Pareto plot,

hydrogen peroxide would have more pronounced effect on ammonia solubilization than ozone.

4.3.2 Reduction of sludge solids

The initial sludge had TS concentration of 2.63%, and it contained very little SCOD concentration. Sludge solids were reduced after the MW-AOP treatment. As a result, the SCOD concentration for the treated solution was increased. The COD results are presented at Table 4.3 and Figure 4.7.

The significant factors for reduction of sludge solids in the solution are in the following orders, from the most to least significant: (1) hydrogen peroxide, (2) the combined effect of hydrogen peroxide and temperature, (3) temperature and (4) ozone dosage (Figure 7).

It can be seen in Figure 4.7 that the most significant factor affecting the SCOD concentration is hydrogen peroxide addition. Without an addition of hydrogen peroxide, the reduction of sludge solids was relative low. The SCOD concentrations were in a range of 3643 to 4527 mg/l. With an addition of 1 % of hydrogen peroxide, the SCOD concentration increased with an increase of temperature. The SCOD concentration was increased from 6355 to 11834 mg/l as temperature increased from 60 to 120°C. However, the resulting SCOD concentrations remained very steady with an addition of 2 % of hydrogen peroxide. The highest SCOD concentration was obtained at the following operating conditions: 2 % of H₂O₂, 3.02 mg/ml of O₃ and microwave temperature of 100°C. The SCOD concentrations did not increase with an increase of microwave heating temperature. At a high microwave heating temperature (120 °C), some of sludge solids was oxidized to form CO₂, and then was escaped into air. Therefore, SCOD concentrations were remained relatively steady (Sets 12 and 13). As indicated in Table

4.3, SCOD/TCOD ratios based on resulting solution for Set 12 and 13 were 73 and 74 %, respectively. The ratios based on the starting material were 45 % for both sets. The results were consistent with our previous study (Wong, et al., 2006).

The VFA results are presented in Table 4.3 and Figure 4.9. The production of the VFA is dependent on the microwave operating temperature and amounts of oxidant used. A higher operating temperature and more oxidant used in the reaction favor VFA yields. The highest acetic acid of 448 mg/l was obtained at 120 °C, and with 2 % H₂O₂ and 5.09 mg/ml of O₃.

4.3.3 The benefits and drawbacks of using ozone

In general, ozone is a very reactive oxidant, and is very useful for treating sludge. Ozone does not produce harmful byproducts, but only H₂O₂ and O₂. However, Ozone production requires a large amount of electric energy and oxygen, and high capital costs related to the equipment. Another drawback is poor solubility of ozone in water, leading to mass transfer limitations.

In the MW/H₂O₂-AOP process, a drawback in the usage of H₂O₂ is an interference that it imposes in COD analysis after treatment (Sreeram, et al. 1998). If H₂O₂ were added in slight excess that left over, it would contribute to a higher COD value of the sample. Excess amounts of ozone can be used to overcome this problem. Ozone itself is a strong oxidant, combining with hydrogen peroxide would give a better treatment results as indicated in this study.

4.4 Conclusions

The results indicated that The AOP process combined with the use of ozone could be used not only to release nutrients, but also to reduce suspended solids from sludge. The best result, in terms of the release of phosphate and ammonia, and solids reduction, was obtained with additions of 2 % hydrogen peroxide by weight and ozone dosage of 5.09 mg/ml, and operating at 120°C. About 95%, 32% and 78% of TP, TKN and COD were released into the solution, respectively. It showed that an addition of ozone improved the AOP process. Ozone could be used as an efficient source of the hydroxyl radical in solution and therefore be employed in advanced oxidation processes.

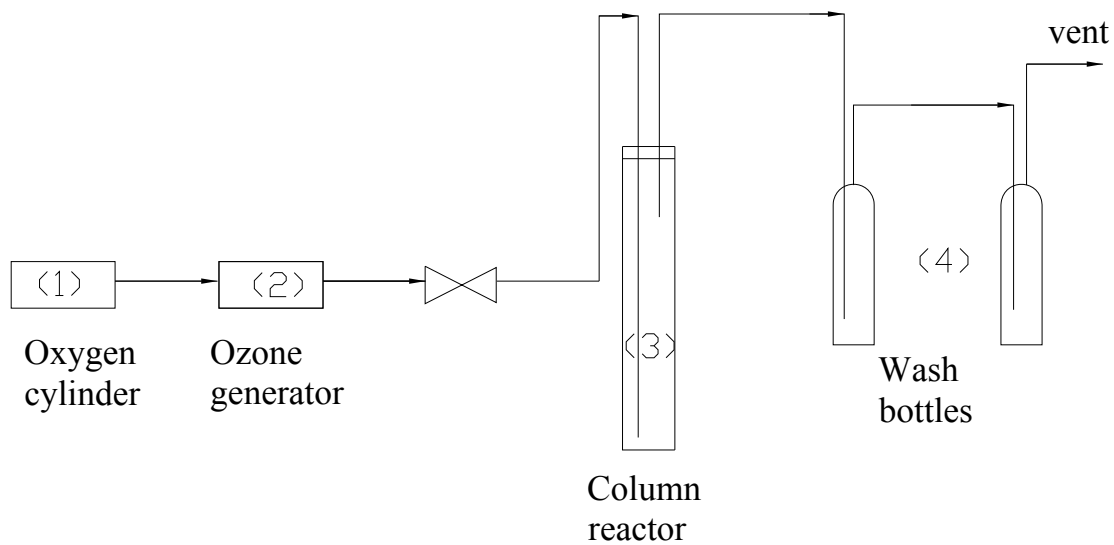


Figure 4.1 Schematic diagram of the ozonation process



Figure 4.2 The picture of the ozonation process setup

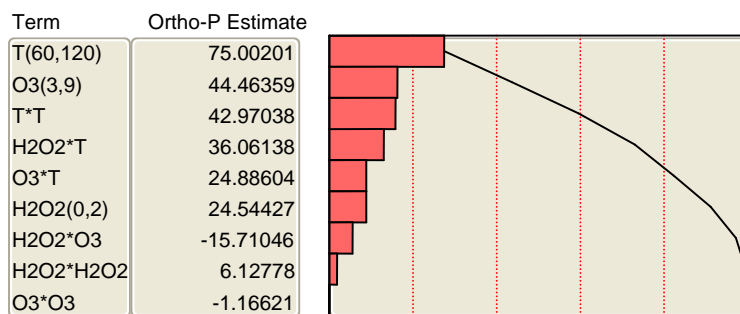


Figure 4.3 Pareto plot of significant factors examined for orthophosphate solubilization

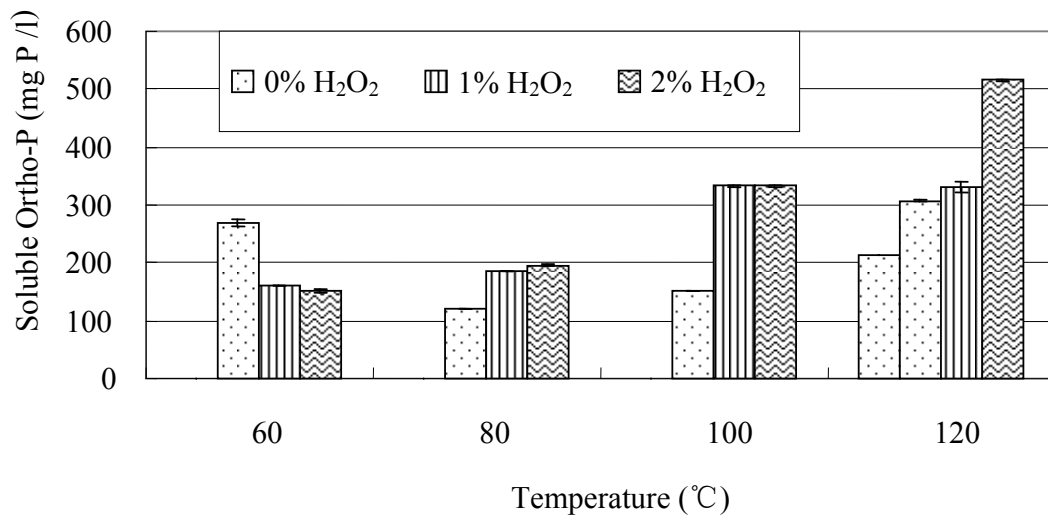


Figure 4.4 Comparison of soluble Ortho-P among different treatment methods

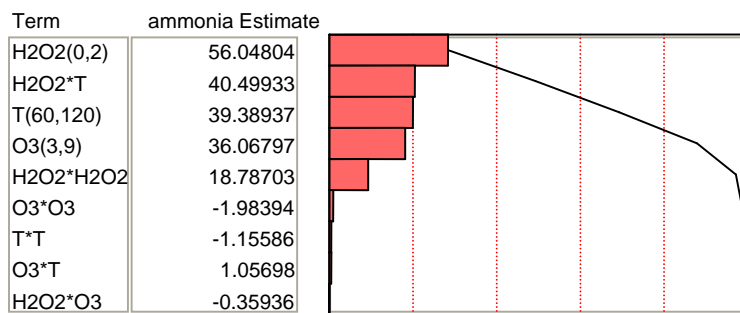


Figure 4.5 Pareto plot of significant factors examined for ammonia solubilization

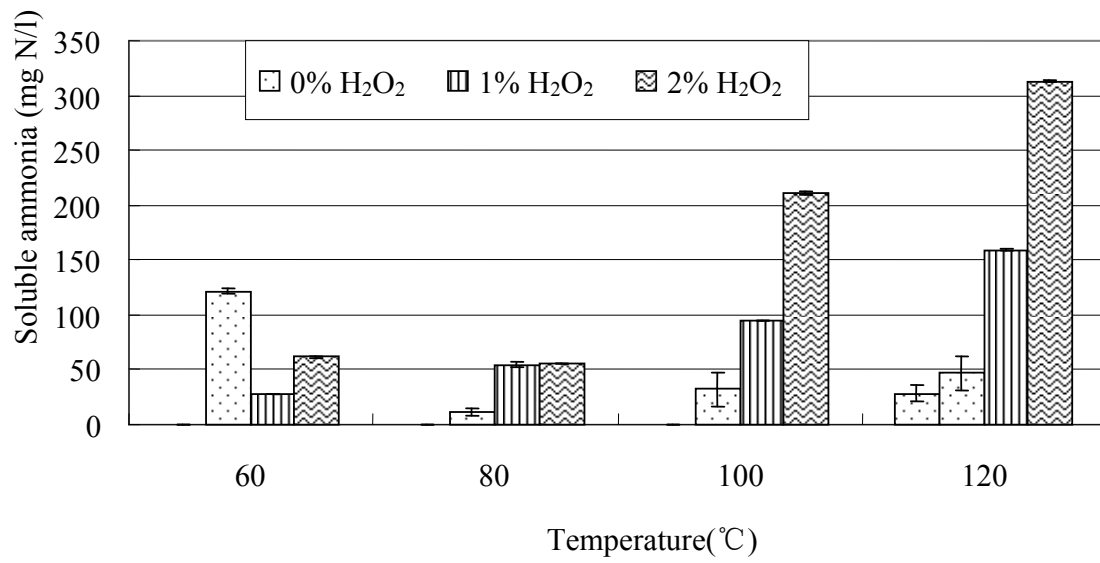


Figure 4.6 Comparison of soluble ammonia among different treatment conditions

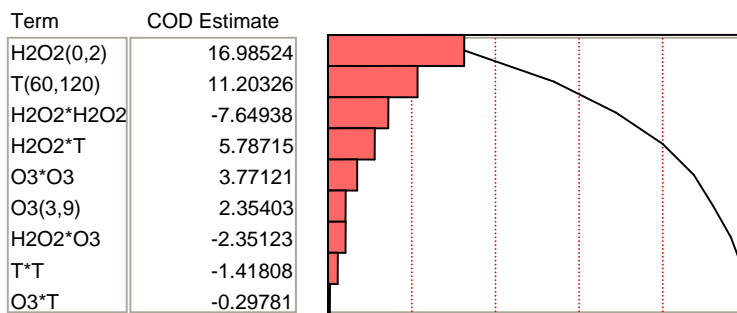


Figure 4.7 Pareto plot of significant factors examined for COD solubilization

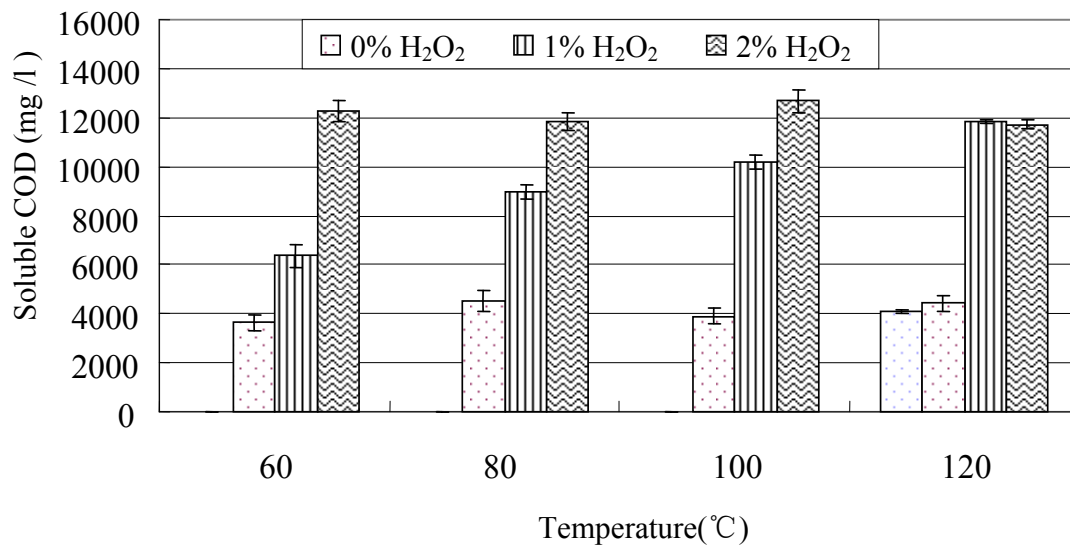


Figure 4.8 Comparison of soluble COD among different treatment methods

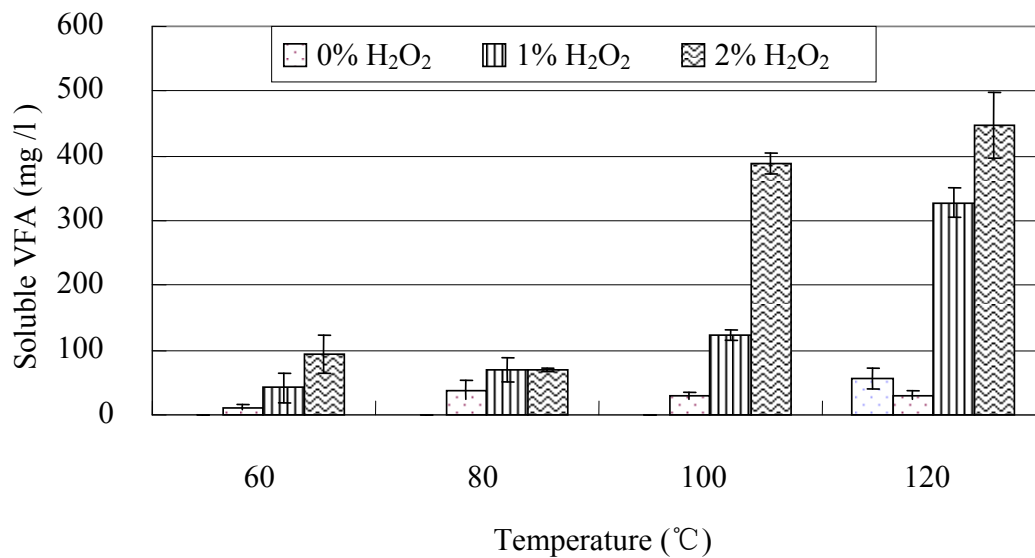


Figure 4.9 Comparison of VFA among different treatment conditions

Table 4.1 Summary of experiments

| Set | Temp (°C) | Heating time (mins) | Sludge (ml) | H ₂ O ₂ (ml) | H ₂ O ₂ dosage (by weight %) | Bubble time (mins) | Ozone dosage (mg•m/l) |
|-----|--------------|------------------------|----------------|---------------------------------------|--|-----------------------|--------------------------|
| 1 | 60 | 3 | 120 | 0 | 0 | 9 | 5.01±0.07 |
| 2 | 60 | 3 | 87 | 3 | 1 | 6 | 3.43±0.01 |
| 3 | 60 | 3 | 84 | 6 | 2 | 3 | 1.64±0.01 |
| 4 | 80 | 3 | 120 | 0 | 0 | 3 | 1.08±0.01 |
| 5 | 80 | 3 | 87 | 3 | 1 | 9 | 5.10±0.03 |
| 6 | 80 | 3 | 84 | 6 | 2 | 6 | 3.62±0.05 |
| 7 | 100 | 3 | 120 | 0 | 0 | 3 | 1.20±0.10 |
| 8 | 100 | 3 | 87 | 3 | 1 | 9 | 5.28±0.03 |
| 9 | 100 | 3 | 84 | 6 | 2 | 6 | 3.02±0.02 |
| 10 | 120 | 3 | 120 | 0 | 0 | 3 | 0.89±0.01 |
| 11 | 120 | 3 | 120 | 0 | 0 | 6 | 3.16±0.02 |
| 12 | 120 | 3 | 87 | 3 | 1 | 3 | 1.08±0.05 |
| 13 | 120 | 3 | 84 | 6 | 2 | 9 | 5.09±0.01 |

Table 4.2 Characteristics of secondary aerobic sludge

| Parameters | Concentration | Range |
|--------------------------|-----------------|------------------|
| TS | 2.63±0.16 % | 2.42-2.80% |
| pH | 6.11 | 6.10-6.11 |
| Total COD | 26157±3010 mg/l | 21149-28912 mg/l |
| Total Phosphorus | 541±54 mg/l | 443-640 mg/l |
| Total Kjehldah Nitrogen | 968 ±111 mg/l | 850-1250 mg/l |
| Initial Ortho-phosphates | 0.22±0.09 mg/l | 0.15-0.32 mg/l |
| Initial Ammonia | 2.22 ±0.34 mg/l | 1.73-2.63 mg/l |

Table 4.3 Summary of experimental results

| Set | O-PO ₄ (mg P/l) | Percentage of soluble O-PO ₄ (%) | NH ₃ (mg N/l) | Percentage of soluble NH ₃ (%) | Soluble COD (mg/ L) | Total COD of study material (mg/l) | Percentage of soluble COD (%) ¹ | Total COD after treatment (mg/l) | Percentage of soluble COD (%) ² | VFA (mg/l) |
|-----|-------------------------------|--|-----------------------------|--|---------------------------|---|---|--|---|---------------|
| 1 | 268±6.8 | 44 | 122±2.2 | 13 | 3643±320 | 26157±3010 | 14 | 30085±1150 | 12 | 12±4 |
| 2 | 161±0.5 | 26 | 28±0.5 | 3 | 6355±441 | 26157±3010 | 24 | 24770±377 | 26 | 42±22 |
| 3 | 152±1.8 | 28 | 62±1.0 | 6 | 12265±411 | 26157±3010 | 47 | 29030±154 | 42 | 94±30 |
| 4 | 120±0.3 | 22 | 11±3.1 | 1 | 4527±420 | 26157±3010 | 17 | 25495±292 | 18 | 39±14 |
| 5 | 186±0.7 | 34 | 54±2.3 | 6 | 8994±284 | 26157±3010 | 34 | 222324±1465 | 40 | 69±19 |
| 6 | 196±0.2 | 36 | 56±0.4 | 6 | 11845±376 | 26157±3010 | 45 | 27150±249 | 44 | 70±2 |
| 7 | 152±0.1 | 28 | 32±15.7 | 3 | 3901±300 | 26157±3010 | 15 | 24025±2629 | 16 | 30±6 |
| 8 | 333±2.0 | 62 | 95±0.4 | 10 | 10213±298 | 26157±3010 | 39 | 18120±669 | 56 | 124±8 |
| 9 | 333±1.9 | 62 | 211±1.3 | 22 | 12674±490 | 26157±3010 | 49 | 26312±735 | 48 | 388±16 |
| 10 | 215±0.5 | 40 | 29±6.6 | 3 | 4071±60 | 26157±3010 | 16 | 24574±2736 | 17 | 57±16 |

| Set | O-PO ₄ (mg P/l) | Percentage of soluble O-PO ₄ (%) | NH ₃ (mg N/l) | Percentage of soluble NH ₃ (%) | Soluble COD (mg/ L) | Total COD of study material (mg/l) | Percentage of soluble COD (%) ¹ | Total COD after treatment (mg/l) | Percentage of soluble COD (%) ² | VFA (mg/l) |
|-----|-------------------------------|--|-----------------------------|--|---------------------------|---|---|--|---|---------------|
| 11 | 307±1.4 | 57 | 47±15.4 | 5 | 4422±313 | 26157±3010 | 17 | 20164±511 | 22 | 31±7 |
| 12 | 330±9.1 | 61 | 159±0.8 | 16 | 11834±61 | 26157±3010 | 45 | 16170±262 | 73 | 328±22 |
| 13 | 516±1.9 | 96 | 313±0.9 | 32 | 11731±159 | 26157±3010 | 45 | 14965±166 | 78 | 448±51 |

1. Based on the study material

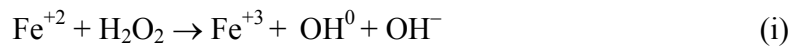
2. Based on the treated sludge

Chapter 5 Sewage Sludge Treatment Using Microwave Enhanced Advanced Oxidation Process With and Without Ferrous Sulfate Addition

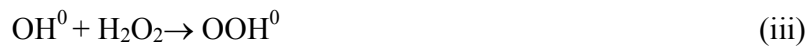
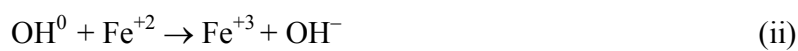
5.1 Introduction

The thermal/chemical process has been reported as an effective sludge disintegration technology for sludge minimization (Odegaard, et al., 2002). Among various thermal/chemical methods, advanced oxidation processes (AOP) have been used for nutrient release and sludge disintegration (Liao, et al., 2005a; Wong, et al., 2006a). The AOP process involves the generation of highly reactive hydroxyl radical species. The most common AOPs are Fenton reagent, and/or combinations of ozone, hydrogen peroxide and ultraviolet (UV) radiation.

Fenton reagent is a mixture of H₂O₂ and ferrous iron, which generates hydroxyl radical according to the following equation:



There are also other reactions involved in the Fenton's process:



The ferrous iron initiates the decomposition of H₂O₂, resulting in the generation of hydroxyl radical (Kitis, et al., 1999). If a hydroxyl radical is not trapped by species that can react with it, another Fe⁺² will react with it to form another Fe⁺³ and another OH⁻ as indicated in Equation (ii). On the other hand (Kolthoff and Medalia, 1949), the hydroxyl radicals formed can also react with hydrogen peroxide, as in equation (iii), thus

generating perhydroxyl radicals, OOH^0 , which can react with ferric ions present in the reaction media to give off oxygen gas as the byproduct, Equation (iv). The Haber-Weiss cycle, which consists of equations (ii), (iii) and (iv), is inclusive of the Fenton reactions. Whether or not a Fenton reaction becomes a Haber-Weiss cycle depends on the stoichiometries of the reactants. If there is a lot of hydrogen peroxide and little Fe^{+2} , then the Haber-Weiss cycle is more likely to take place, whereas, if there is very little hydrogen peroxide and lots of Fe^{+2} , then Fenton reaction alone takes place.

Most of the works involving Fenton's reaction were operated at temperatures between 20 to 40 °C. The rate of reaction increased with an increase of temperature. However, the efficiency of H_2O_2 utilization declined as temperatures increased above 40–50 °C (Walling, 1975). The time needed to complete Fenton reactions depends on the catalyst dosage and the wastewater strength. In general, the reactions could take from 30 minutes to several hours to complete.

In a study on the treatment of synthetic phenol solutions and of surfactant wastewaters, the effects of the Fenton reaction to that of a microwave enhanced AOP (MW-AOP) were compared (Sanz, et al., 2003). However, microwave irradiation was not applied to the Fenton reaction. There have been no literatures reported on the use of a combination of microwave irradiation and Fenton reagent in the AOP, hereby, abbreviated as MW/ H_2O_2 / Fe^{+2} -AOP. It has been known that microwave heating would facilitate the oxidation process (Liao, et al., 2005a). It was expected that a combination of both microwave irradiation and Fenton reagent would increase the efficiency of the overall MW-AOP. Therefore, this study was conducted as a part of our research group's continuous efforts to improve upon the microwave/hydrogen peroxide enhanced advance

oxidation process (MW/H₂O₂-AOP) developed at the University of British Columbia. This chapter reports the results of the two MW-AOP systems, i.e., MW/H₂O₂-AOP and MW/H₂O₂/Fe⁺²-AOP, applied to treat the secondary aerobic sludge.

5. 2 Materials and methods

5.2.1 Experimental design

In our research group's previous studies (Wong, et al., 2006a; Liao, et al., 2005b), microwave heating temperature, amount of oxidants, and heating time were identified as key factors in the MW/H₂O₂-AOP. Since more than 75 % of the sludge solids could be reduced at a microwave heating period of three minutes, this same heating time was selected for this preliminary study. As we talked before, most of the works involving Fenton's reaction were operated at temperatures between 20 to 40 °C. It was expected that by using the combination of both microwave irradiation and Fenton reagent, the best MW-AOP working temperature range could be decreased. Therefore, microwave heating temperatures of 40, 60 and 80 °C were selected (Table 5.1).

Six sets of experiments, each with six replications, were carried out in this study. The experiments were setup in two categories, wherein Sets 1, 3 and 5 are in the MW/H₂O₂-AOP and Sets 2, 4 and 6 are in the MW/H₂O₂/FeSO₄-AOP (Table 5.1). For Sets 1, 3, and 5, samples consisted of 29 ml of secondary aerobic sludge with 1 ml of H₂O₂ (30 %). According to the process (Fenton's process) reported previously (Kitis, et al., 1999; Kolthoff and Medalia, 1949), H₂O₂ to FeSO₄ ratio of 10 would give the best result in terms of the generation of highly reactive hydroxyl radical species. In order to have a ratio of H₂O₂ to FeSO₄ at about 10 in the samples, 28 ml of sludge sample, 1 ml of H₂O₂, and 1 ml of FeSO₄ (145 g /l) were used for Sets 2, 4 and 6.

5.2.2 Microwave apparatus

The microwave digestion system— Ethos TC Digestion Labstation 5000, Milestone Inc., U.S.A. was used in this study.

5.2.3 Microwave process and sampling

Secondary aerobic sludge was obtained from the pilot-scale wastewater treatment facilities located at the University of British Columbia (UBC) campus. The characteristics of the secondary aerobic sludge over the course of the study were presented in Table 5.2. Fresh sludge samples were collected daily for the duration of the experiments. Samples were subjected to the microwave heating. Heating time was kept at three minutes, however, various ramp times (an increase of 20 °C per minutes) were used as needed to reach the desired heating temperatures.

Each set of samples was divided into two subsets with three replications each. Samples in one subset were kept for total phosphate (TP), total Kjeldahl nitrogen (TKN) and total chemical oxygen demand (TCOD) analyses. Samples in the other subset were spun in a centrifuge at 4000 rpm for 15 minutes. The resulting supernatants were filtered through Whatman No.4 filters and analyzed. Samples collected before treatments were also measured for TS, TP, TKN, orthophosphate, ammonia and total COD. All supernatant samples were analyzed for orthophosphate, ammonia and soluble COD.

A Hewlett Packard 5890 Series II gas chromatograph equipped with a flame ionization detector (FID) was used to measure volatile fatty acids (VFA).

5.3 Results and discussion

5.3.1 Nutrient solubilization

The results of solubilization of phosphate, ammonia are presented in Table 5.3. Figure 5.1 shows the soluble orthophosphate concentrations at three temperatures for both AOP processes.

For the MW/H₂O₂-AOP, the orthophosphate result is consistent with those from previous reports (Wong, et al., 2006a; Kuroda, et al., 2002; Liao, et al., 2005b). The orthophosphate release increased from 20 mg/l to 81 mg/l, as temperature increased from 40 to 60 °C, it then decreased to 45 mg/l as temperature increased to 80 °C. The highest yield of soluble orthophosphate (81 mg/l) at 60 °C represented a solubilization efficiency of approximately 41%, as the original secondary sludge had a soluble phosphorus content of less than 0.1 percent. The low orthophosphate in the solution at 80 °C was due to the presence of intermediate products of soluble polyphosphates; a greater amount of orthophosphate was released in the solution after the acid hydrolysis step (Wong, et al., 2006a). It was also reported (APHA, 1995) that the rate and extent of polyphosphates in the solution were dependent on the heating temperature. A majority of soluble phosphorus was in the form of polyphosphates at intermediate temperatures between 70 to 80 °C. This is also consistent with the results from our previous study that the microwave heating temperature was the most significant factor for phosphate release (Wong, et al., 2006b).

Unlike that in the MW/H₂O₂-AOP, orthophosphate release decreased with an increase of temperature in the case of MW/H₂O₂/Fe⁺²-AOP. The highest yield of soluble orthophosphate, at 88 mg/l, was obtained at 40 °C, reflecting a solubilization of

approximately 50%. Very low orthophosphate concentrations were obtained at the temperature range of 60 to 80 °C. This might be due to the accelerated decomposition of H₂O₂ into oxygen and water, and/or the Haber-Weiss cycle became a dominant reaction pathway. As a result, less phosphate was soluble in the solution. It should be noted that most of the Fenton's reactions were operated at temperatures between 20 to 40 °C. The rate of reaction increased with an increase of temperature. The efficiency of H₂O₂ utilization, however, declined as temperatures increased above 40 to 50 °C (Walling, 1975). The time needed to complete the Fenton reactions would depend on the catalyst dose and the wastewater strength; it would take from 30 minutes to several hours. In this study, with microwave irradiation, these reactions were allowed to take place in three minutes.

Figure 5.2 shows the amounts of ammonia released into the solutions of the two processes at different microwave heating temperatures. The results of the two processes exhibited a sharp contrast. For the MW/H₂O₂-AOP, an increase of heating temperature resulted in increased soluble ammonia concentrations, from 8.9 mg /l at 40 °C to 35 mg /l at 80 °C. On the contrary, for the MW/H₂O₂/Fe⁺²-AOP, an increase of heating temperature resulted in decreased soluble ammonia concentrations, from 23 mg /l at 40 °C to 10 mg /l at 80 °C. This might be either due to the decomposition of H₂O₂ or the Fenton reaction becoming the Haber-Weiss cycle at the higher operating temperatures. The ammonia concentration in the solution was found to be very sensitive to the hydrogen peroxide concentration. At all experimental temperatures, a higher hydrogen peroxide dosage gave a higher ammonia concentration in the solution (Wong, et al., 2006a). It was also found that the most significant among factors affecting ammonia

solubilization was the hydrogen peroxide dosage (Wong, et al., 2006b). The solubilization efficiency in both processes was relatively low, 7.2% for the MW/H₂O₂-AOP at 80 °C and 7.1% for the MW/H₂O₂/Fe⁺²-AOP at 40 °C.

5.3.2 Reduction of sludge solids

Using the MW-AOP processes, particulate organic substrates are also solubilized (in terms of soluble COD and VFA). In this study, the initial sludge had a TS concentration of 1.0%, and it contained very little soluble COD concentration. The results are presented in Table 5.3, and in Figures 5.3 and 5.4.

Figure 5.3 shows that the soluble COD (SCOD) increased with increased temperature for the MW/H₂O₂-AOP, from 833 mg /l at 40 °C to 1954 mg /l at 80 °C. It clearly indicated that temperature was an important factor affecting sludge disintegration in this process. The maximum COD release, about 18% of the initial COD concentration, occurred at 80 °C. The result is consistent with our previous report (Wong, et al., 2006b) that the most significant factor for maximizing SCOD concentration was temperature for the MW/H₂O₂-AOP.

The SCOD concentration for the MW/H₂O₂/Fe⁺²-AOP remained steady in the range of temperatures tested, indicating that temperature was not an important factor for the reduction of suspended solids when ferrous sulfate was added. The results seemed to suggest that at a low temperature regime, the MW/H₂O₂/Fe⁺²-AOP had an advantage, just as in a typical Fenton reaction. However, this might also suggest that microwave enhancement at this low temperature range were not beneficial to the solubilization of organic substrates. More studies will be required to further explore the optimal regime of MW-AOP in solids reduction and nutrients release from sludge.

As shown in Figure 5.4, the production of the VFA was dependent on the microwave heating temperature for both processes, though again the trend differed. In the MW/H₂O₂/Fe⁺²-AOP, a higher operating temperature favored the production of the VFA. The maximum yield of VFA, expressed as acetic acid, was 83 mg /l at 80 °C. However, for the MW/H₂O₂-AOP, the highest yield of acetic acid occurred at 40 °C. The yield of VFA was affected by the pH of the solution. It was reported (Liao, et al., 2006a) that a higher accumulation of VFA occurred at a low pH environment. For the MW/H₂O₂-AOP, pH values were 6.1, 6.4 and 6.4 for 40, 60 and 80 °C, respectively. For the MW/H₂O₂/Fe⁺²-AOP, pH values remained steady at 3.1.

5.3.3 Implications

While the results obtained in this preliminary study are limited in scope, certain implications could be drawn. The MW-AOP is a simple oxidation process which can be used to recover valuable products from sewage sludge, such as orthophosphate, ammonia, metals, and VFA. It can also be used to reduce odour, pathogen content, and levels of organic contaminants in treated sludge. Hydrogen peroxide in the AOP is a very powerful oxidizer which breaks down into oxygen and water; no harmful products are produced. This process is clean, efficient, and can be classified as one of the green technologies for treatment of sludge.

Even though iron is a non-toxic element, in the case of the MW/H₂O₂/Fe⁺²-AOP, treated sludge residue may be classified as a chemical sludge due to its iron contamination. On the other hand, this process can produce sludge with reduced heavy metal content. Levels of copper, zinc, cadmium, lead, mercury, chromium and nickel can all be reduced to those found naturally in soils (Andrews, et al., 2006).

Due to the higher yields, in terms of orthophosphate, ammonia and SCOD obtained at higher treatment temperatures, the MW/H₂O₂-AOP is recommended to be operated at a higher temperature regime, 60 to 80 °C. The MW/H₂O₂/Fe⁺²-AOP, on the other hand, should be operated at temperatures of 40 °C or below.

Over the range of temperature tested, the MW/H₂O₂-AOP generally out-performed the MW/H₂O₂/Fe⁺²-AOP in terms of solubilization of orthophosphate, ammonia and SCOD. The pH values of the resulting solutions were 6.1 and 3.1, respectively for the MW/H₂O₂-AOP and the MW/H₂O₂/Fe⁺²-AOP. It is advantageous to use the MW/H₂O₂-AOP, as the resulting solution can easily be used in a subsequent process such as, anaerobic digestion for biogas production, or crystallization for struvite recovery. No neutralization treatment is required.

5. 4 Conclusions

The results indicated that the MW-AOP process could be used not only to release nutrients, but also to reduce solids from the secondary sludge

For the MW/H₂O₂-AOP, higher yields in terms of soluble orthophosphate, ammonia and COD were obtained at elevated temperatures (60 to 80 °C), with the best performance of solids reduction at 80 °C. However, the best results were obtained at 40 °C for the MW/H₂O₂/Fe⁺²-AOP.

Overall, at temperatures of 60 °C or above, the MW/H₂O₂-AOP performed better solubilization than that of the MW/H₂O₂/Fe⁺²-AOP. At temperatures of 40 °C or below, the MW/H₂O₂/Fe⁺²-AOP performed better than the MW/H₂O₂ -AOP in terms of nutrients release and solids reduction.

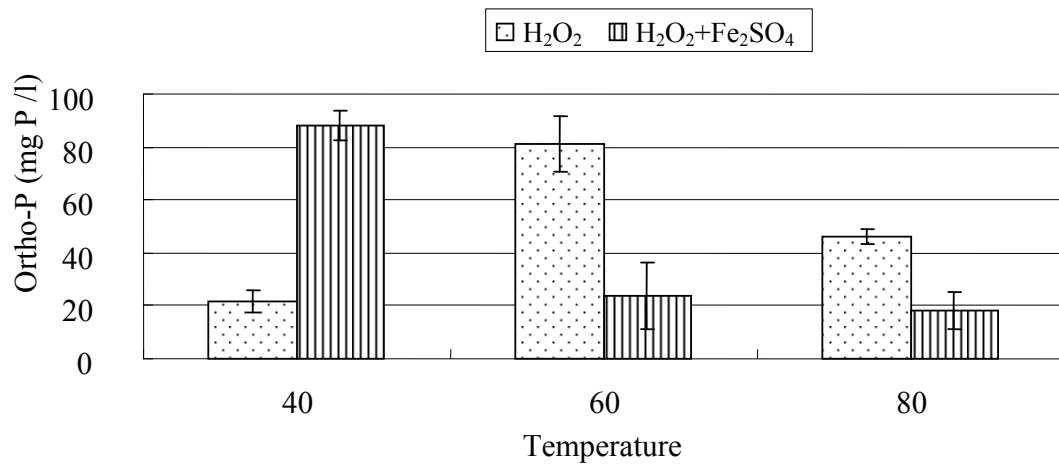


Figure 5.1 Comparison of soluble Ortho-P between different treatment methods

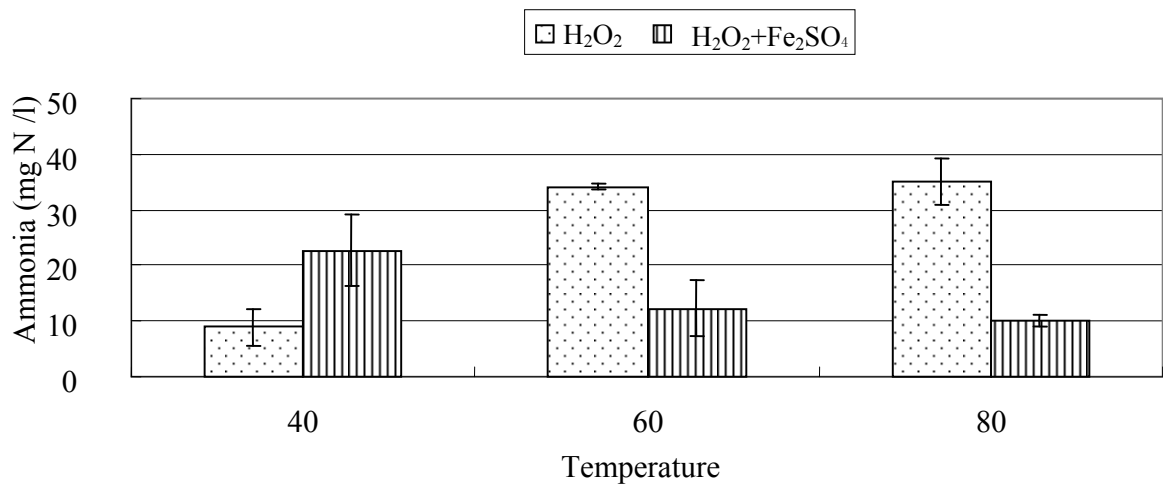


Figure 5.2 Comparison of soluble ammonia between different treatment conditions

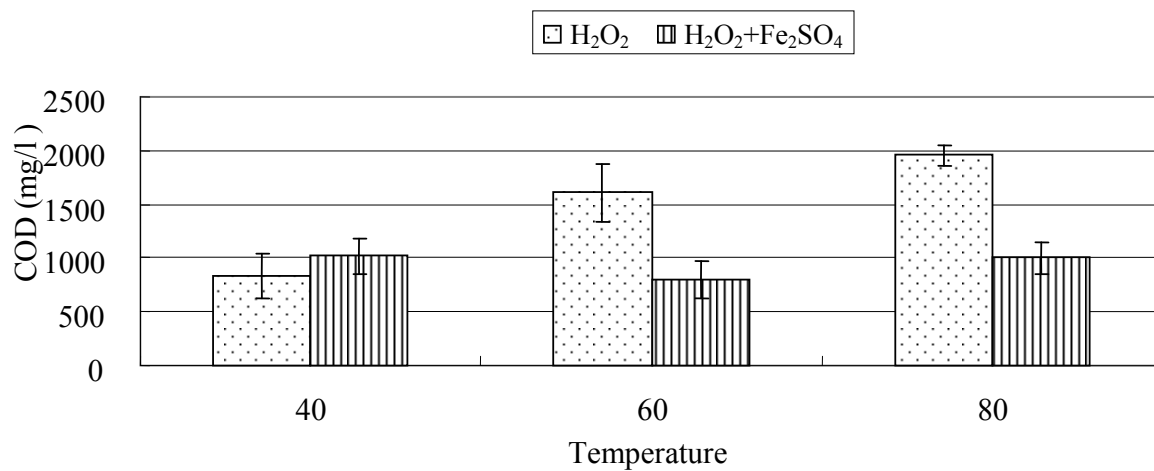


Figure 5.3 Comparison of soluble COD between different treatment methods

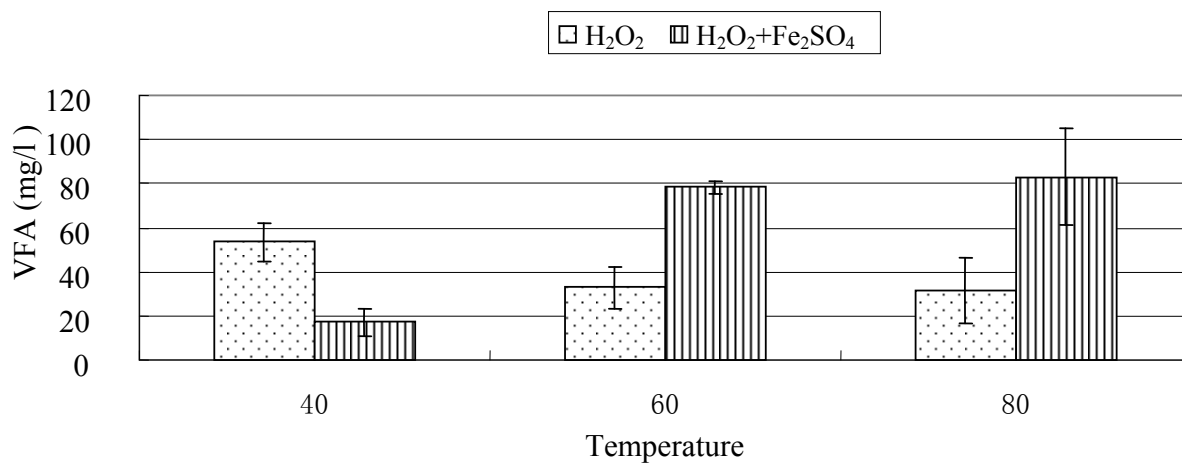


Figure 5.4 Comparison of VFA between different treatment conditions

Table 5.1 Summary of experiments

| Set ¹ | Temp (°C) | Heating time (mins) | Sludge (ml) | H ₂ O ₂ (ml) | H ₂ O ₂ dosage ² (by weight %) | FeSO ₄ (ml) | FeSO ₄ dosage ² (g/l) |
|------------------|--------------|------------------------|----------------|---------------------------------------|--|---------------------------|--|
| 1 | 40 | 3 | 29 | 1 | 1 | 0 | 0 |
| 2 | 40 | 3 | 28 | 1 | 1 | 1 | 4.75 |
| 3 | 60 | 3 | 29 | 1 | 1 | 0 | 0 |
| 4 | 60 | 3 | 28 | 1 | 1 | 1 | 4.75 |
| 5 | 80 | 3 | 29 | 1 | 1 | 0 | 0 |
| 6 | 80 | 3 | 28 | 1 | 1 | 1 | 4.75 |

1. Sets 1, 3 and 5 are MW/H₂O₂-AOP; Sets 2, 4 and 6 are MW/H₂O₂/Fe⁺⁺-AOP

2. Dosage means the concentration after diluted in 30ml samples.

Table 5.2 Characteristics of secondary aerobic sludge

| Parameters | Concentration | Range |
|------------------------|----------------|------------------|
| TS | 1.00±0.02 % | 0.98-1.02% |
| pH | 6.71 | 6.70-6.71 |
| Total COD | 10699±328 mg/l | 10467-10931 mg/l |
| Total Phosphorus | 197±13 mg/l | 186-212 mg/l |
| Total Kjeldah Nitrogen | 481 ±13 mg/l | 466-492 mg/l |

Table 5.3 Summary of experimental results

| Set* | Temp (°C) | O-PO ₄ (mg P/l) | NH ₃ (mg N/l) | Soluble COD (mg/ L) | VFA (mg /l) |
|------|--------------|-------------------------------|-----------------------------|------------------------|----------------|
| 1 | 40 | 21.6±4.1 | 8.9±3.3 | 833±206 | 54±9 |
| 2 | 40 | 88.1±5.7 | 22.7±6.6 | 1022±166 | 17±6 |
| 3 | 60 | 81.1±10.5 | 34.1±0.5 | 1606±269 | 33±10 |
| 4 | 60 | 23.8±12.6 | 12.3±4.9 | 799±166 | 78±3 |
| 5 | 80 | 46.0±3.0 | 35.0±4.2 | 1954±88 | 31±15 |
| 6 | 80 | 18.2±7.0 | 10.1±1.1 | 1005±149 | 83±22 |

*. Sets 1, 3 and 5 are MW/H₂O₂-AOP; Sets 2, 4 and 6 are MW/H₂O₂/F_e⁺⁺-AOP

Chapter 6 General Conclusion and Recommendations

6.1 General conclusion

This thesis investigated the significant factors affecting the MW/H₂O₂-AOP that would yield maximum soluble substrates and the effects of combination of microwave treatment and oxidative reagents on solids destruction and nutrients release. The yields of the nutrient release and solid reduction under various operating conditions were therefore investigated and reported. Experiments were performed at sludge solids content of 0.5, 1.5 and 2.5%, heating temperature of 80, 100 and 120 °C, heating time of 1.5, 3 and 9 minutes, and hydrogen peroxide dosage of 0, 1 and 2% by weight, respectively. The initial sludge TS content and hydrogen peroxide dosage were the most significant factors for the solubilization of COD. The initial sludge TS content was the most significant factor for the nutrient release. Therefore, a thickened sludge will be more suitable for the MW/H₂O₂ –AOP. The results showed that the microwave heating time was not a significant factor as TS concentration, microwave temperature and hydrogen peroxide dosage. It could achieve the release of most soluble substrates within a heating time of five minutes. Even with a heating period of 1.5 minutes, the yield was estimated to be about 70% of that of the 5-minute heating. With a heating period of 3 minutes, the yield was increased to be about 80% of that of the 5-minute heating.

Two kinds of oxidants, ozone and ferrous sulphate, were investigated to determine the effects of combination of microwave treatment and oxidative reagents on solids destruction and nutrients release. The results indicated that an addition of ozone was helpful for MW-AOP process. The best result was obtained in the MW/H₂O₂/O₃-AOP in

terms of nutrients release and solids reduction. A further study was conducted to test the effects of the dosage of ozone on the release of nutrients and the destruction of suspended solids. Three factors including microwave heating temperature, hydrogen peroxide dosage, and ozone were selected and examined. About 95%, 32% and 78% of TP, TKN and COD were released into the solution under the experiments condition of 2 % hydrogen peroxide by weight, ozone dosage of 5.09 mg/ml and 120°C. Two MW-AOP systems, i.e., MW/H₂O₂-AOP and MW/H₂O₂/Fe⁺²-AOP, were applied to treat the secondary aerobic sludge. At temperatures of 60 °C or above, the MW/H₂O₂-AOP performed better than the MW/H₂O₂/Fe⁺²-AOP in terms of nutrients release and solids reduction. At temperatures of 40 °C or below, the MW/H₂O₂/Fe⁺²-AOP performed better than the MW/H₂O₂ –AOP.

6.2 Recommendations

The presented research provided an effective method of releasing the nutrients and reducing solids stored in sewage sludge using microwave irradiation and chemical addition. The implementation of this research for the industrial applications requires some more research to better elaborate various aspects of the developed treatment process and prepare it for commercialization. Briefly, the following areas of research would prove useful in future studies based on the results of this research:

- Performing further optimization studies for nutrient solubilization and solids reduction via microwave irradiation. For instance, it is worthwhile to find out whether a better mixing, or longer heating time (9 to 20 minutes) at low

temperature (60 °C to 80 °C) can improve the performance of microwave treatment with respect to nutrients release and solids reduction.

- Optimizing the process of using the combination of ozone or Fenton's reagent and microwave treatment. Finding the optimum conditions under these processes, including oxidative reagents dosage, hydrogen peroxide dosage, reaction time, heating time, heating temperature, etc.
- Developing a continuous microwave treatment process to evaluate the performance for nutrients release and sludge breakdown; comparing the process efficiency between a batch and continuous microwave treatment process, further optimizing the continuous microwave treatment process.
- Performing scale-up studies for microwave treatment of sludge, either as a batch or continuous process, or both.
- Performing cost-effective analysis between microwave treatment process and traditional wastewater treatment process.

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Appendix A – Raw Data

A1 Sewage Sludge Treatment Using Microwave Enhanced Advanced Oxidation Process

Table A1.1 Sample TP&TKN concentration

| TS (%) | | Replicate (mg P or N/l) | | | Average (mg P or N/l) | S.D. (mg P or N/l) |
|--------|-----|-------------------------|-----|-----|-----------------------|--------------------|
| | | 1 | 2 | 3 | | |
| 0.5 | TP | 148 | 150 | — | 149 | 1 |
| | TKN | 335 | 346 | — | 340 | 7 |
| 1.5 | TP | 248 | 259 | 252 | 253 | 5 |
| | TKN | 648 | 659 | 654 | 654 | 5 |
| 2.5 | TP | 337 | 432 | 379 | 383 | 24 |
| | TKN | 920 | 964 | 847 | 910 | 59 |

Table A1.2 soluble COD concentration

| Set | Experimental Conditions | | | | Replicate (mg/l) | | | | | | Average (mg/l) | S.D (mg/l) |
|-----|-------------------------|--------|-------------|------------------------------------|------------------|-------|-------|-------|-------|-------|----------------|------------|
| | Temp (°C) | TS (%) | Time (mins) | H ₂ O ₂ (ml) | 1 | 2 | 3 | 4 | 5 | 6 | | |
| 1 | 80 | 0.5 | 3 | 2 | 3365 | 6176 | 6176 | 6842 | 6842 | 6546 | 5991 | 1320 |
| 2 | 80 | 1.5 | 5 | 0 | 3957 | 2773 | 3365 | 3957 | 3661 | 3439 | 3525 | 445 |
| 3 | 80 | 2.5 | 1.5 | 1 | 8248 | 8248 | 8248 | 8618 | 9653 | 7878 | 8482 | 620 |
| 4 | 100 | 0.5 | 5 | 1 | 3661 | 3365 | 3661 | 3365 | 3661 | 3069 | 3414 | 459 |
| 5 | 100 | 1.5 | 1.5 | 2 | 6694 | 7434 | 7730 | 6694 | 2255 | 6028 | 6139 | 1996 |
| 6 | 100 | 2.5 | 3 | 0 | 3439 | 4401 | 3809 | 4105 | 3439 | 4401 | 3932 | 441 |
| 7 | 120 | 0.5 | 1.5 | 0 | 776 | 1590 | 2181 | 258 | 1072 | 1885 | 1294 | 723 |
| 8 | 120 | 1.5 | 3 | 1 | 4401 | 5067 | 5363 | 4105 | 4105 | 3809 | 4475 | 610 |
| 9 | 120 | 2.5 | 5 | 2 | 13574 | 14388 | 13574 | 13944 | 13574 | 13574 | 13772 | 336 |

Table A1.3 soluble ortho-P concentration

| Set | Experimental Conditions | | | | Replicate (mg P/l) | | | | | | Average (mg P/l) | S.D (mg P/l) |
|-----|-------------------------|-----------|----------------|---------------------------------------|--------------------|-----|-----|-----|-----|-----|---------------------|-----------------|
| | Temp (°C) | TS (%) | Time (mins) | H ₂ O ₂ (ml) | 1 | 2 | 3 | 4 | 5 | 6 | | |
| 1 | 80 | 0.5 | 3 | 2 | 49 | 37 | 40 | 37 | 39 | 46 | 41 | 5 |
| 2 | 80 | 1.5 | 5 | 0 | 165 | 165 | 165 | 151 | 154 | 172 | 162 | 8 |
| 3 | 80 | 2.5 | 1.5 | 1 | 181 | 153 | 144 | 126 | 136 | 104 | 141 | 26 |
| 4 | 100 | 0.5 | 5 | 1 | 37 | 42 | 40 | 40 | 44 | 53 | 43 | 5 |
| 5 | 100 | 1.5 | 1.5 | 2 | 109 | 120 | 113 | 108 | 112 | 112 | 112 | 4 |
| 6 | 100 | 2.5 | 3 | 0 | 152 | 171 | 163 | 179 | 152 | 166 | 164 | 10 |
| 7 | 120 | 0.5 | 1.5 | 0 | 47 | 45 | 48 | 60 | 60 | 47 | 50 | 6 |
| 8 | 120 | 1.5 | 3 | 1 | 162 | 170 | 177 | 159 | 169 | 159 | 166 | 7 |
| 9 | 120 | 2.5 | 5 | 2 | 255 | 268 | 268 | 325 | 327 | 283 | 288 | 31 |

Table A1.4 soluble ammonia concentration

| Set | Experimental Conditions | | | | Replicate (mg N/l) | | | | | | Average (mg N/l) | S.D (mg N/l) |
|-----|-------------------------|-----------|----------------|---------------------------------------|--------------------|-----|-----|-----|-----|-----|---------------------|-----------------|
| | Temp (°C) | TS (%) | Time (mins) | H ₂ O ₂ (ml) | 1 | 2 | 3 | 4 | 5 | 6 | | |
| 1 | 80 | 0.5 | 3 | 2 | 30 | 30 | 29 | 30 | 29 | 30 | 30 | 0 |
| 2 | 80 | 1.5 | 5 | 0 | 36 | 33 | 35 | 36 | 36 | 40 | 36 | 2 |
| 3 | 80 | 2.5 | 1.5 | 1 | 50 | 54 | 61 | 50 | 49 | 60 | 54 | 5 |
| 4 | 100 | 0.5 | 5 | 1 | 37 | 20 | 24 | 20 | 22 | 23 | 22 | 2 |
| 5 | 100 | 1.5 | 1.5 | 2 | 33 | 34 | 34 | 32 | 31 | 34 | 33 | 1 |
| 6 | 100 | 2.5 | 3 | 0 | 77 | 66 | 57 | 55 | 77 | 43 | 62 | 13 |
| 7 | 120 | 0.5 | 1.5 | 0 | 33 | 32 | 31 | 25 | 31 | 29 | 33 | 6 |
| 8 | 120 | 1.5 | 3 | 1 | 86 | 84 | 86 | 74 | 82 | 79 | 82 | 5 |
| 9 | 120 | 2.5 | 5 | 2 | 144 | 152 | 184 | 192 | 141 | 185 | 166 | 23 |

Table A1.5 VFA concentration

| Set | Experimental Conditions | | | | Replicate (mg /l) | | | | | | Average | S.D |
|-----|-------------------------|-----------|----------------|---------------------------------------|-------------------|-----|-----|-----|-----|-----|---------|---------|
| | Temp (°C) | TS (%) | Time (mins) | H ₂ O ₂ (ml) | 1 | 2 | 3 | 4 | 5 | 6 | (mg /l) | (mg /l) |
| 1 | 80 | 0.5 | 3 | 2 | 16 | 44 | 35 | 32 | 44 | 52 | 37 | 13 |
| 2 | 80 | 1.5 | 5 | 0 | 10 | 8 | 13 | 9 | 13 | 7 | 10 | 2 |
| 3 | 80 | 2.5 | 1.5 | 1 | 31 | 37 | 40 | 54 | 47 | 68 | 46 | 13 |
| 4 | 100 | 0.5 | 5 | 1 | 32 | 41 | 34 | 75 | 41 | 25 | 41 | 18 |
| 5 | 100 | 1.5 | 1.5 | 2 | 51 | 51 | 76 | 78 | 42 | 53 | 59 | 15 |
| 6 | 100 | 2.5 | 3 | 0 | 31 | 15 | 12 | 12 | 16 | 16 | 17 | 7 |
| 7 | 120 | 0.5 | 1.5 | 0 | 12 | 15 | 14 | 7 | 12 | 8 | 11 | 3 |
| 8 | 120 | 1.5 | 3 | 1 | 39 | 45 | 46 | 27 | 37 | 37 | 38 | 7 |
| 9 | 120 | 2.5 | 5 | 2 | 192 | 205 | 191 | 414 | 418 | 218 | 273 | 111 |

A2 An Ozone/Hydrogen Peroxide/Microwave Enhanced Advanced Oxidation Process for Sewage Sludge Treatment

Table A2.1 Sample TP&TKN concentration

| TS (%) | | Replicate (mg P or N/l) | | | | | | Average | S.D. |
|-----------|-----|-------------------------|------|-----|-----|-----|------|------------------|------------------|
| | | 1 | 2 | 3 | 4 | 5 | 6 | (mg P or N/l) | (mg P or N/l) |
| 0.5 | TP | 139 | 146 | 153 | 180 | 185 | 184 | 165 | 21 |
| | TKN | 268 | 262 | 275 | 328 | 320 | 338 | 299 | 34 |
| 3.0 | TP | 590 | 474 | 489 | 594 | 634 | 660 | 574 | 76 |
| | TKN | 873 | 1210 | 768 | 774 | 933 | 1070 | 938 | 174 |

Table A2.2 soluble COD concentration

| Set | Treatment | Replicate (mg/l) | | | Average (mg/l) | S.D. (mg/l) |
|-----|--|------------------|-------|-------|-------------------|----------------|
| | | 1 | 2 | 3 | | |
| 1 | 3% material | 28050 | 26688 | 25962 | 26900 | 1060 |
| 2 | H ₂ O ₂ | 2460 | 2732 | 2460 | 2550 | 157 |
| 3 | MW | 5091 | 4638 | 4910 | 4933 | 228 |
| 4 | O ₃ | 1099 | 736 | 554 | 804 | 277 |
| 5 | H ₂ O ₂ / O ₃ /MW | 8750 | 11010 | 9777 | 9846 | 1132 |
| 6 | H ₂ O ₂ / O ₃ | 3509 | 3406 | 3612 | 3509 | 103 |
| 7 | H ₂ O ₂ /MW | 9880 | 9263 | 10085 | 9743 | 428 |
| 8 | O ₃ /MW | 5975 | 6386 | 6386 | 6249 | 237 |

Table A2.3 soluble ortho-P concentration

| Set | Treatment | Replicate (mg P/l) | | | Average (mg P/l) | S.D. (mg P/l) |
|-----|--|--------------------|-----|-----|---------------------|------------------|
| | | 1 | 2 | 3 | | |
| 1 | H ₂ O ₂ /MW | 193 | 165 | 171 | 176 | 15 |
| 2 | H ₂ O ₂ / O ₃ | 170 | 182 | 184 | 179 | 7 |
| 3 | O ₃ /MW | 169 | 181 | 177 | 176 | 6 |
| 4 | H ₂ O ₂ / O ₃ /MW | 183 | 189 | 191 | 188 | 4 |
| 5 | H ₂ O ₂ | 142 | 152 | 148 | 150 | 5 |
| 6 | MW | 140 | 176 | 185 | 174 | 24 |
| 7 | O ₃ | 159 | 141 | 147 | 148 | 9 |

Table A2.4 soluble ammonia concentration

| Set | Treatment | Replicate (mg N/l) | | | Average (mg N/l) | S.D. (mg N/l) |
|-----|--|--------------------|-----|-----|---------------------|------------------|
| | | 1 | 2 | 3 | | |
| 1 | H ₂ O ₂ /MW | 193 | 165 | 171 | 176 | 15 |
| 2 | H ₂ O ₂ / O ₃ | 170 | 182 | 184 | 179 | 7 |
| 3 | O ₃ /MW | 169 | 181 | 177 | 176 | 6 |
| 4 | H ₂ O ₂ / O ₃ /MW | 183 | 189 | 191 | 188 | 4 |
| 5 | H ₂ O ₂ | 142 | 152 | 148 | 150 | 5 |
| 6 | MW | 140 | 176 | 185 | 174 | 24 |
| 7 | O ₃ | 159 | 141 | 147 | 148 | 9 |

Table A2.5 VFA concentration

| Set | Treatment | Replicate (mg N/l) | | | Average (mg N/l) | S.D. (mg N/l) |
|-----|--|--------------------|-----|-----|---------------------|------------------|
| | | 1 | 2 | 3 | | |
| 1 | H ₂ O ₂ /MW | 95 | 89 | 96 | 93 | 4 |
| 2 | H ₂ O ₂ / O ₃ | 29 | 44 | 35 | 36 | 7 |
| 3 | O ₃ /MW | 49 | 40 | 37 | 42 | 6 |
| 4 | H ₂ O ₂ / O ₃ /MW | 102 | 111 | 154 | 122 | 28 |
| 5 | H ₂ O ₂ | 44 | 35 | 22 | 33 | 11 |
| 6 | MW | 24 | 16 | 17 | 19 | 4 |
| 7 | O ₃ | 22 | 20 | 16 | 19 | 3 |

A3 Microwave Enhanced Advanced Oxidation Process for Sewage Sludge Treatment

Table A3.1 Sample TP&TKN concentration

| TS (%) | | Replicate (mg P or N/l) | | | | | | Average | S.D. |
|--------|-----|-------------------------|-----|------|-----|-----|------|---------------|---------------|
| | | 1 | 2 | 3 | 4 | 5 | 6 | (mg P or N/l) | (mg P or N/l) |
| 0.5 | TP | 151 | 142 | 141 | 153 | 155 | 157 | 149 | 7 |
| | TKN | 237 | 224 | 231 | 228 | 224 | 236 | 230 | 6 |
| 3.0 | TP | 540 | 615 | 590 | 535 | 565 | 575 | 570 | 30 |
| | TKN | 905 | 106 | 1075 | 895 | 965 | 1055 | 993 | 82 |

Table A3.2 soluble and total COD concentration

| Set | | Experimental conditions | | | Replicate (mg/l) | | | Average | S.D. |
|-----|------|-------------------------|-------------------------------|-------------|------------------|-------|-------|---------|--------|
| | | Temp | H ₂ O ₂ | Bubble | 1 | 2 | 3 | (mg/l) | (mg/l) |
| | | (°C) | (%) | time (mins) | | | | | |
| 1 | SCOD | 60 | 0 | 9 | 3401 | 4006 | 3521 | 3642 | 320 |
| | TCOD | | | | 30866 | 30624 | 28764 | 30085 | 1150 |
| 2 | SCOD | 60 | 1 | 6 | 6304 | 5941 | 6818 | 6355 | 441 |
| | TCOD | | | | 25179 | 24695 | 24437 | 24770 | 377 |
| 3 | SCOD | 60 | 2 | 3 | 11870 | 12233 | 12691 | 12265 | 411 |
| | TCOD | | | | 29051 | 29172 | 28867 | 29030 | 154 |
| 4 | SCOD | 80 | 0 | 3 | 4490 | 4127 | 4964 | 4527 | 420 |
| | TCOD | | | | 25663 | 25663 | 25158 | 25495 | 292 |
| 5 | SCOD | 80 | 1 | 9 | 8966 | 8724 | 9291 | 8994 | 284 |
| | TCOD | | | | 23606 | 22638 | 20728 | 23324 | 1465 |
| 6 | SCOD | 80 | 2 | 6 | 11628 | 11628 | 12279 | 11845 | 376 |
| | TCOD | | | | 27357 | 26873 | 27219 | 27150 | 249 |
| 7 | SCOD | 100 | 0 | 3 | 4248 | 3727 | 3727 | 3901 | 300 |
| | TCOD | | | | 25982 | 21037 | 25055 | 24025 | 2629 |

| Set | | Experimental conditions | | | Replicate (mg/l) | | | Average (mg/l) | S.D. (mg/l) |
|-----|------|-------------------------|-------------------------------|-------------|------------------|-------|-------|-------------------|----------------|
| | | Temp | H ₂ O ₂ | Bubble | 1 | 2 | 3 | | |
| | | (°C) | (%) | time (mins) | | | | | |
| 8 | SCOD | 100 | 1 | 9 | 10176 | 9934 | 10527 | 10213 | 298 |
| | TCOD | | | | 18767 | 18162 | 17431 | 18120 | 669 |
| 9 | SCOD | 100 | 2 | 6 | 12233 | 13201 | 12588 | 12674 | 490 |
| | TCOD | | | | 27115 | 26147 | 25673 | 26312 | 735 |
| 10 | SCOD | 120 | 0 | 3 | 4036 | 4036 | 4139 | 4071 | 59 |
| | TCOD | | | | 22994 | 22994 | 27734 | 24574 | 2736 |
| 11 | SCOD | 120 | 0 | 6 | 4369 | 4139 | 4758 | 4422 | 313 |
| | TCOD | | | | 20582 | 20315 | 19594 | 20164 | 511 |
| 12 | SCOD | 120 | 1 | 3 | 11870 | 11764 | 11867 | 11834 | 60 |
| | TCOD | | | | 16226 | 15885 | 16400 | 16170 | 262 |
| 13 | SCOD | 120 | 2 | 9 | 11870 | 11764 | 11558 | 11731 | 159 |
| | TCOD | | | | 14774 | 15061 | 15061 | 14965 | 166 |

Table A3.3 soluble ortho-P concentration

| Set | Experimental conditions | | | Replicate (mg P/l) | | | Average (mg P/l) | S.D. (mg P/l) |
|-----|-------------------------|-------------------------------|-------------|--------------------|-----|-----|---------------------|------------------|
| | Temp | H ₂ O ₂ | Bubble | 1 | 2 | 3 | | |
| | (°C) | (%) | time (mins) | | | | | |
| 1 | 60 | 0 | 9 | 261 | 263 | 264 | 263 | 1 |
| 2 | 60 | 1 | 6 | 161 | 162 | 161 | 161 | 1 |
| 3 | 60 | 2 | 3 | 154 | 151 | 151 | 152 | 2 |
| 4 | 80 | 0 | 3 | 120 | 120 | 119 | 120 | 0 |
| 5 | 80 | 1 | 9 | 187 | 185 | 186 | 186 | 1 |
| 6 | 80 | 2 | 6 | 196 | 197 | 196 | 196 | 0 |
| 7 | 100 | 0 | 3 | 152 | 151 | 151 | 152 | 0 |

| Set | Experimental conditions | | | Replicate (mg P/l) | | | Average (mg P/l) | S.D. (mg P/l) |
|-----|-------------------------|-------------------------------|-------------|--------------------|-----|-----|---------------------|------------------|
| | Temp | H ₂ O ₂ | Bubble | 1 | 2 | 3 | | |
| | (°C) | (%) | time (mins) | | | | | |
| 8 | 100 | 1 | 9 | 334 | 334 | 331 | 333 | 2 |
| 9 | 100 | 2 | 6 | 331 | 333 | 335 | 333 | 2 |
| 10 | 120 | 0 | 3 | 215 | 214 | 215 | 215 | 1 |
| 11 | 120 | 0 | 6 | 308 | 307 | 306 | 307 | 1 |
| 12 | 120 | 1 | 3 | 320 | 335 | 336 | 330 | 9 |
| 13 | 120 | 2 | 9 | 514 | 515 | 518 | 516 | 2 |

Table A3.4 soluble ammonia concentration

| Set | Experimental conditions | | | Replicate (mg N/l) | | | Average (mg N/l) | S.D. (mg N/l) |
|-----|-------------------------|-------------------------------|-------------|--------------------|-----|-----|---------------------|------------------|
| | Temp | H ₂ O ₂ | Bubble | 1 | 2 | 3 | | |
| | (°C) | (%) | time (mins) | | | | | |
| 1 | 60 | 0 | 9 | 120 | 122 | 124 | 122 | 2 |
| 2 | 60 | 1 | 6 | 28 | 27 | 27 | 27 | 0 |
| 3 | 60 | 2 | 3 | 61 | 62 | 63 | 62 | 1 |
| 4 | 80 | 0 | 3 | 14 | 10 | 8 | 11 | 3 |
| 5 | 80 | 1 | 9 | 57 | 53 | 52 | 54 | 2 |
| 6 | 80 | 2 | 6 | 56 | 56 | 56 | 56 | 0 |
| 7 | 100 | 0 | 3 | 18 | 49 | 31 | 32 | 16 |
| 8 | 100 | 1 | 9 | 95 | 94 | 95 | 95 | 0 |
| 9 | 100 | 2 | 6 | 210 | 212 | 210 | 211 | 1 |
| 10 | 120 | 0 | 3 | 22 | 35 | 28 | 29 | 7 |
| 11 | 120 | 0 | 6 | 55 | 57 | 29 | 47 | 15 |
| 12 | 120 | 1 | 3 | 160 | 158 | 159 | 159 | 1 |
| 13 | 120 | 2 | 9 | 314 | 312 | 314 | 313 | 1 |

Table A3.5 VFA concentration

| Set | Experimental conditions | | | Replicate (mg /l) | | | Average | S.D. |
|-----|-------------------------|-------------------------------|-------------|-------------------|-----|-----|---------|---------|
| | Temp | H ₂ O ₂ | Bubble | 1 | 2 | 3 | (mg /l) | (mg /l) |
| | (°C) | (%) | time (mins) | | | | | |
| 1 | 60 | 0 | 9 | 11 | 17 | 8 | 12 | 4 |
| 2 | 60 | 1 | 6 | 22 | 66 | 37 | 42 | 22 |
| 3 | 60 | 2 | 3 | 71 | 128 | 83 | 94 | 30 |
| 4 | 80 | 0 | 3 | 54 | 36 | 26 | 39 | 14 |
| 5 | 80 | 1 | 9 | 52 | 89 | 66 | 69 | 19 |
| 6 | 80 | 2 | 6 | 71 | 68 | 71 | 70 | 2 |
| 7 | 100 | 0 | 3 | 37 | 26 | 27 | 30 | 6 |
| 8 | 100 | 1 | 9 | 115 | 125 | 132 | 124 | 8 |
| 9 | 100 | 2 | 6 | 375 | 385 | 406 | 388 | 16 |
| 10 | 120 | 0 | 3 | 75 | 47 | 48 | 57 | 16 |
| 11 | 120 | 0 | 6 | 39 | 27 | 27 | 31 | 7 |
| 12 | 120 | 1 | 3 | 321 | 311 | 352 | 328 | 22 |
| 13 | 120 | 2 | 9 | 480 | 475 | 390 | 448 | 51 |

A4 Sewage sludge treatment using microwave enhanced advanced oxidation processes with and without ferrous sulphate addition

Table A4.1 Sample TP&TKN concentration

| | Replicate (mg P or N/l) | | | Average | S.D. |
|-----|-------------------------|-----|-----|---------------|---------------|
| | 1 | 2 | 3 | (mg P or N/l) | (mg P or N/l) |
| TP | 212 | 186 | 194 | 197 | 13 |
| TKN | 492 | 466 | 486 | 481 | 14 |

Table A4.2 Sample PH

| | Temperature (°C) | Treatment | Replicate | | Average |
|------------------|---------------------|--|-----------|------|---------|
| | | | 1 | 2 | |
| Before treatment | Ambient | Raw | 6.71 | — | 6.71 |
| | | Fe ₂ SO ₄ | 6.18 | — | 6.18 |
| | | H ₂ O ₂ | 3.05 | — | 3.05 |
| After treatment | 40 | H ₂ O ₂ | 6.11 | 6.07 | 6.09 |
| | | H ₂ O ₂ +FeSO ₄ | 3.15 | — | 3.15 |
| | 60 | H ₂ O ₂ | 6.37 | 6.48 | 6.42 |
| | | H ₂ O ₂ +FeSO ₄ | 3.13 | 3.05 | 3.09 |
| | 80 | H ₂ O ₂ | 6.38 | 6.44 | 6.41 |
| | | H ₂ O ₂ +FeSO ₄ | 3.13 | 3.16 | 3.14 |

Table A4.3 soluble and total COD concentration

| Set | | Experimental conditions | | | Replicate (mg/l) | | | Average (mg/l) | S.D. (mg/l) |
|-----|------|-------------------------|--------------------------------------|-------------------------|------------------|------|------|-------------------|----------------|
| | | Temp (°C) | H ₂ O ₂ (%) | FeSO ₄ (g/l) | 1 | 2 | 3 | | |
| 1 | SCOD | 40 | 1 | 0 | 1039 | 833 | 627 | 833 | 206 |
| | TCOD | | | | 8406 | 8921 | — | 8664 | 364 |
| 2 | SCOD | 40 | 1 | 4.75 | 833 | 1142 | 1091 | 1022 | 166 |
| | TCOD | | | | 8818 | 9540 | — | 9179 | 510 |
| 3 | SCOD | 60 | 1 | 0 | 1812 | 1812 | 1555 | 1606 | 269 |
| | TCOD | | | | 8458 | 8715 | — | 8586 | 182 |
| 4 | SCOD | 60 | 1 | 4.75 | 988 | 730 | 679 | 799 | 166 |
| | TCOD | | | | 9179 | 9179 | — | 9179 | 0 |

| Set | Experimental conditions | | | Replicate (mg/l) | | | Average (mg/l) | S.D. (mg/l) | |
|-----|-------------------------|-------------------------------|-------------------------|------------------|------|------|-------------------|----------------|-----|
| | Temp | H ₂ O ₂ | FeSO ₄ (g/l) | 1 | 2 | 3 | | | |
| | (°C) | (%) | | | | | | | |
| 5 | SCOD | 80 | 1 | 0 | 2070 | 1915 | 1967 | 1954 | 88 |
| | TCOD | | | | 8818 | 9024 | — | 8921 | 146 |
| 6 | SCOD | 80 | 1 | 4.75 | 1091 | 1091 | 833 | 1005 | 149 |
| | TCOD | | | | 8870 | 7994 | — | 8432 | 619 |

Table A4.4 soluble ortho-P concentration

| Set | Experimental conditions | | | Replicate (mg P/l) | | | Average (mg P/l) | S.D. (mg P/l) |
|-----|-------------------------|-------------------------------|-------------------------|--------------------|----|----|---------------------|------------------|
| | Temp | H ₂ O ₂ | FeSO ₄ (g/l) | 1 | 2 | 3 | | |
| | (°C) | (%) | | | | | | |
| 1 | 40 | 1 | 0 | 24 | 19 | — | 22 | 4 |
| 2 | 40 | 1 | 4.75 | 87 | 83 | 94 | 88 | 6 |
| 3 | 60 | 1 | 0 | 83 | 67 | 93 | 81 | 10 |
| 4 | 60 | 1 | 4.75 | 38 | 17 | 16 | 24 | 13 |
| 5 | 80 | 1 | 0 | 42 | 49 | 46 | 46 | 3 |
| 6 | 80 | 1 | 4.75 | 11 | 20 | 24 | 18 | 7 |

Table A4.5 soluble ammonia concentration

| Set | Experimental conditions | | | Replicate (mg N/l) | | | Average (mg N/l) | S.D. (mg N/l) |
|-----|-------------------------|-------------------------------|-------------------------|--------------------|----|----|---------------------|------------------|
| | Temp | H ₂ O ₂ | FeSO ₄ (g/l) | 1 | 2 | 3 | | |
| | (°C) | (%) | | | | | | |
| 1 | 40 | 1 | 0 | 14 | 8 | 7 | 9 | 3 |
| 2 | 40 | 1 | 4.75 | 18 | 20 | 30 | 23 | 7 |
| 3 | 60 | 1 | 0 | 35 | 34 | 34 | 34 | 1 |

| Set | Experimental conditions | | | Replicate (mg N/l) | | | Average (mg N/l) | S.D. (mg N/l) |
|-----|-------------------------|--------------------------------------|-------------------------|--------------------|----|----|---------------------|------------------|
| | Temp (°C) | H ₂ O ₂ (%) | FeSO ₄ (g/l) | 1 | 2 | 3 | | |
| 4 | 60 | 1 | 4.75 | 18 | 9 | 10 | 12 | 5 |
| 5 | 80 | 1 | 0 | 38 | 32 | — | 35 | 4 |
| 6 | 80 | 1 | 4.75 | 10 | 11 | 9 | 10 | 1 |

Table A4.6 soluble ammonia concentration

| Set | Experimental conditions | | | Replicate (mg/l) | | | Average (mg/l) | S.D. (mg/l) |
|-----|-------------------------|--------------------------------------|-------------------------|------------------|-----|----|-------------------|----------------|
| | Temp (°C) | H ₂ O ₂ (%) | FeSO ₄ (g/l) | 1 | 2 | 3 | | |
| 1 | 40 | 1 | 0 | 45 | 57 | 64 | 54 | 9 |
| 2 | 40 | 1 | 4.75 | 10 | 19 | 21 | 17 | 6 |
| 3 | 60 | 1 | 0 | 26 | 45 | 24 | 33 | 10 |
| 4 | 60 | 1 | 4.75 | 76 | 81 | 78 | 78 | 3 |
| 5 | 80 | 1 | 0 | 18 | 19 | 47 | 31 | 15 |
| 6 | 80 | 1 | 4.75 | 87 | 103 | 59 | 83 | 22 |