

DAIRY MANURE TREATMENT USING SOLID-LIQUID SEPARATION AND MICROWAVE
ENHANCED ADVANCED OXIDATION PROCESS

by

SELINA KUUKUWA YAWSON

B.Sc., University of Ghana, 2000
MPhil., University of Ghana, 2004

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

MASTER OF APPLIED SCIENCE

in

The Faculty of Graduate Studies

(Civil Engineering)

THE UNIVERSITY OF BRITISH COLUMBIA
(Vancouver)

October 2010

© Selina Kuukuwa Yawson, 2010

Abstract

Dairy manure treatment, using solid-liquid separation and microwave enhanced advanced oxidation process (MW/H₂O₂-AOP), was investigated. The objectives of the research were to determine: 1) the nutrient and metal composition of solid and liquid fractions of raw dairy manure following solid-liquid separation, 2) the effects of MW/H₂O₂-AOP operating factors of temperature, hydrogen peroxide (H₂O₂) dosage, acid concentration and heating time on sugar production and nutrient release from solid dairy manure.

Solid-liquid separation of raw dairy manure, using a 1mm laboratory sieve, showed that solid fractions had a higher composition of TS and volatile solids (VS), while the liquid fractions were richer in nutrients and metals. Laboratory separation by screening alone was not effective in removing high amounts of nutrients and solids from the raw manure.

Screening experiments were conducted using cellulose fibers to study the effects of temperature, acid concentration, H₂O₂ dosage and heating time on sugar production, with the aim of applying the results to dairy manure lignocellulosic material. Sugar production increased when acid concentration was increased from 1% to 3%, but decreased with an increase to 10%. More sugar was produced at 160°C compared to 120°C. Sugar production decreased with increasing time.

Microwave irradiation of solid dairy manure at pH 2, temperatures of 80, 120 and 160°C, H₂O₂ dosages of 0 to 0.50 mL, and heating times of 10 to 20 min, showed that more sugars were released at higher temperatures. Temperature and hydrogen peroxide dosage were identified as the most important factors affecting solubilization of phosphorus and ammonia. Subsequently, a two-stage acid hydrolysis process, using MW/H₂O₂-AOP, was used to investigate sugar production and solubilization of phosphorus and ammonia from solid dairy manure at: 3% acid concentration, 120 and 160°C, 0 and 2 mL H₂O₂ and

heating times of 20 and 60min. To enhance sugar production from solid dairy manure, the microwave should be operated at higher temperatures and shorter heating times with no H_2O_2 . For ammonia and phosphorus solubilization, higher temperatures and longer heating times, in the presence of H_2O_2 , would be advantageous.

MW/ H_2O_2 -AOP is therefore an efficient means for treating dairy manure for nutrient recovery.

Table of contents

Abstract	ii
Table of contents.....	iv
List of tables	vii
List of figures	viii
Acknowledgements	x
Dedication.....	xi
1.0 Introduction	1
1.1 Background	1
1.2 Research objectives	4
1.3 Literature review	5
1.3.1 Solid-liquid separation.....	5
1.3.2 Principles of microwave heating	6
1.3.3 Advanced oxidation processes (AOPs)	8
1.3.4 Microwave enhanced advanced oxidation process (MW/H ₂ O ₂ -AOP)	8
1.3.5 Microwave enhanced advanced oxidation process in wastewater treatment.....	8
1.3.6 Sugar production from solid dairy manure using dilute acid hydrolysis	10
1.3.7 Nutrient recovery.....	10
1.3.7.1 Orthophosphate.....	11
1.3.7.2 Ammonia	12
1.3.7.3 Volatile fatty acids.....	13
1.3.7.4 Chemical oxygen demand	13
1.4 Materials and methods.....	14
1.4.1 Substrates.....	14
1.4.2 Microwave apparatus.....	14
1.4.3 Sample analysis	16
1.4.4 Statistical analysis	18
1.4.4.1 JMP-IN statistical software	18
2.0 Solid-liquid separation of raw dairy manure.....	20
2.1 Summary	20
2.2 Introduction	20
2.3 Materials and methods.....	21
2.3.1 Substrate	21
2.3.2 Experimental design	21
2.4 Results and discussion.....	23
2.4.1 Composition and properties of the separated solid and liquid fractions	23
2.4.2 Comparison of solid and liquid fractions versus raw unseparated dairy manure	26
2.4.3 Removal of solids, nutrients and metals from raw dairy manure by solid-liquid separation	28
3.0 Sugar and nutrient release from solid dairy manure at pH 2 using the microwave enhanced advanced oxidation process	31
3.1 Summary	31
3.2 Introduction	31
3.3 Materials and methods.....	32
3.3.1 Substrate	32

3.3.2	Experimental design	33
3.4	Results and discussion	34
3.4.1	Sugar production	35
3.4.2	Nutrient release.....	39
3.4.2.1	Orthophosphate.....	39
3.4.2.2	Ammonia	42
3.4.3	Solids disintegration	46
4.0	Factors affecting sugar production from cellulose using the microwave enhanced advanced oxidation process	50
4.1	Summary	50
4.2	Introduction	50
4.3	Experimental design	51
4.4	Results and discussion.....	52
4.4.1	Sugar production	52
4.4.2	Solids disintegration	54
5.0	Sugar production from cellulose fibers at 1, 3 and 10% sulfuric acid using the microwave enhanced advanced oxidation process	55
5.1	Summary	55
5.2	Introduction	55
5.3	Materials and methods.....	56
5.3.1	Substrate	56
5.3.2	Experimental design	56
5.4	Results and discussion.....	57
5.4.1	Sugar production	57
5.4.2	Solids disintegration	61
6.0	Two-stage dilute acid hydrolysis of solid dairy manure for sugar and nutrient release using the microwave enhanced advanced oxidation process	62
6.1	Summary	62
6.2	Introduction	62
6.3	Materials and methods.....	64
6.3.1	Substrate and sample preparation	64
6.3.2	Experimental design	64
6.4	Results and discussion.....	67
6.4.1	Stage 1	67
6.4.1.1	Sugar production	67
6.4.1.2	Nutrient release.....	70
6.4.1.3	Solids disintegration	72
6.4.2	Stage 2	74
6.4.2.1	Sugar production	75
6.4.2.2	Nutrient release.....	76
6.4.2.3	Solids disintegration	78
7.0	Conclusions	80
7.1	Solid-liquid separation.....	80
7.2	Sugar and nutrient release from solid dairy manure at pH 2 using the microwave enhanced advanced oxidation process.....	80
7.3	Factors affecting sugar production from cellulose using the microwave enhanced advanced oxidation process.....	81
7.4	Two-stage dilute acid hydrolysis of solid dairy manure for sugar and nutrient	

release using the microwave enhanced advanced oxidation process.....	82
7.5 Recommendations for follow-up research.....	83
References	84

List of tables

Table 2.1	Characteristics of dairy manure used	22
Table 2.2	Dairy manure samples used for solid-liquid separation	22
Table 2.3	Proportion of solid and liquid fractions in relation to initial raw dairy manure sample.....	23
Table 2.4	Composition of the solid and liquid fractions of raw dairy manure with various dilutions after solid-liquid separation	24
Table 2.5	Chemical oxygen demand results for liquid and solid fractions	25
Table 2.6	Removal of solids, COD, nutrients and metals from raw unseparated dairy manure using a 1mm laboratory scale sieve	29
Table 3.1	Characteristics of solid dairy manure	32
Table 3.2	Experimental design	33
Table 3.3	Overview of results	34
Table 4.1	Characteristics of the cellulose	51
Table 4.2	Experimental design	52
Table 4.3	Overview of results	53
Table 5.1	Characteristics of the cellulose	56
Table 5.2	Experimental design	57
Table 5.3	Overview of results	58
Table 6.1	Characteristics of the dairy manure	64
Table 6.2	Experimental design for first stage of hydrolysis	66
Table 6.3	Experimental design for second stage of acid hydrolysis.....	67
Table 6.4	Overview of results for first stage of dairy manure acid hydrolysis	68
Table 6.5	Table 6.5 Overview of results for second stage of dairy manure acid hydrolysis.....	74

List of figures

Figure 1.1	Microwave oven digestion system.....	15
Figure 1.2	Polytetrafluoroethylene (PTFE) teflon digestion vessels.....	16
Figure 1.3	System controller with an LCD screen control panel	16
Figure 2.1	TS (%) in separated solid and liquid fractions versus raw dairy manure.....	26
Figure 2.2	VS (%) in separated solid and liquid fractions versus raw dairy manure	27
Figure 2.3	TKN (% of dry matter) in separated solid and liquid fractions versus raw dairy manure	27
Figure 2.4	TP (% of dry matter) in separated solid and liquid fractions versus raw dairy manure.....	28
Figure 3.1a	Surface profile showing sugar release with respect to heating time and H ₂ O ₂ dosage.....	35
Figure 3.1b	Surface profile showing sugar release with respect to temperature and heating time.....	36
Figure 3.1c	Surface profile showing sugar release with respect to temperature and H ₂ O ₂ dosage	36
Figure 3.1d	Pareto plot for sugar release factors	37
Figure 3.2	Prediction profiler showing the variation of VFA, ammonia, sugar and PO ₄ -P with the MW/H ₂ O ₂ -AOP operating factors	38
Figure 3.3a	Surface profile for orthophosphate release with respect to heating time and H ₂ O ₂ dosage ..	40
Figure 3.3b	Surface profile for orthophosphate release with respect to temperature and heating time ...	40
Figure 3.3c	Surface profile for orthophosphate release with respect to treatment temperature and H ₂ O ₂ dosage.....	41
Figure 3.3d	Pareto plot for orthophosphate release factors	42
Figure 3.4a	Surface profile for ammonia release with respect to heating time and H ₂ O ₂ dosage	43
Figure 3.4b	Surface profile for ammonia release with respect to temperature and heating time	43
Figure 3.4c	Surface profile for ammonia release with respect to temperature and H ₂ O ₂ dosage.....	45
Figure 3.4d	Pareto plot for ammonia release factors.....	45
Figure 3.5a	Surface profile for VFA release with respect to heating time and H ₂ O ₂ dosage	46
Figure 3.5b	Surface profile for VFA release with respect to temperature and heating time	47
Figure 3.5c	Surface profile for VFA release with respect to temperature H ₂ O ₂ dosage.....	48
Figure 3.5d	Pareto plot for VFA release factors.....	48
Figure 4.1	Prediction profiler showing the response of sugar, SCOD and VFA to the MW/H ₂ O ₂ -AOP operating parameters	53
Figure 4.2	Pareto plot for sugar release factors	54
Figure 4.3	Pareto plot for VFA release factors.....	54
Figure 4.4	Pareto plot for SCOD release factors	54
Figure 5.1	Sugar production at different acid concentrations	59

Figure 5.2	Sugar production at different treatment temperatures.....	60
Figure 5.3	Sugar production at different heating times	60
Figure 6.1	Procedure for the two-stage acid hydrolysis of dairy manure.....	65
Figure 6.2	Sugar release from first stage of dairy manure acid hydrolysis	69
Figure 6.3	Ammonia release from first stage of dairy manure acid hydrolysis.....	70
Figure 6.4	Orthophosphate release from first stage of dairy manure acid hydrolysis	71
Figure 6.5	SCOD release from first stage of dairy manure acid hydrolysis.....	72
Figure 6.6	VFA release from first stage of dairy manure acid hydrolysis	73
Figure 6.7	Sugar release from second stage of dairy manure acid hydrolysis	76
Figure 6.8	Ammonia release from second stage of dairy manure acid hydrolysis.....	77
Figure 6.9	Orthophosphate release from second stage of dairy manure acid hydrolysis	78
Figure 6.10	SCOD release from second stage of dairy manure acid hydrolysis	79
Figure 6.11	VFA release from second stage of dairy manure acid hydrolysis.....	79

Acknowledgements

I would like to express gratitude to my Research Supervisor, Dr. Victor Lo, Department of Civil Engineering, under whose diligent supervision and guidance this research and thesis have been successfully completed. I would also like to thank Dr. Ping Huang Liao, Research Fellow, Department of Civil Engineering, for his contributions, advice and fruitful discussions which were essential in the structuring of experiments and analysis of data. My sincere appreciation goes to Winnie Chan, Research Assistant, Department of Civil Engineering for her invaluable support, instruction and direction in the laboratory. I would like to acknowledge and thank NSERC for funding this research. My thanks go to Paula Parkinson and Tim Ma, Environmental Engineering Laboratory, Department of Civil Engineering, whose support contributed immensely to the timely completion of laboratory analysis. Special thanks go to my colleagues, Isabel Londono, Sahar Kosari, Kerry Black, Ryan Thoren and Chad Novotny for their support during my time in Civil Engineering. Finally, I would like to express my heartfelt gratitude to my husband for his constant motivation, patience and endless support through the course of my program.

Dedication

To Almighty God, for his countless blessings;

To my husband, Kudjo, who is my pillar of strength and source of encouragement;

To my parents, who support me through prayer;

To my beautiful daughters, Nadine and Candace, who are my inspiration.

1. Introduction

1.1 Background

Manure residues from livestock industries have been identified as a major source of environmental pollution (Gebrezgabher et al., 2010). Large, concentrated animal operations have caused great environmental concern because of the large amount of animal manure produced at these facilities (Wen et al., 2004). Current manure management practices are often detrimental to the environment and potentially hazardous to human and animal health (Masse' et al., 2007). Animal manure is rich in nutrients and land application of manure has been the traditional standard practice on many farms (Qureshi et al., 2008a), with a small amount being composted (Wen et al., 2004). While utilization of dairy manure offers benefits such as increase of soil fertility and quality, improper use can produce air quality and odor concerns and impair water quality. Thus, there is major public interest to develop and demonstrate best control technologies that can lessen or eliminate the disposal problem of large amounts of dairy wastewater (Garcia et al., 2009). In addition, the increasingly stringent requirements for pollution control at animal operations are challenging the scientific community to develop new waste management strategies (Wen et al., 2004).

A simple technology that has the potential to reduce nutrient loads in dairy wastewater is solid–liquid separation (Garcia et al., 2009). Physical separation of the wastewater into fractions (solid and liquid) with different properties optimizes the methane potential recovery and material and nutrient flow of the digested material (Kaparaju and Rintala 2008). The optimum use of solid and liquid fractions from manure separation is affected by the variation in chemical and biochemical composition. Dry matter (DM), ash and organic carbon (C) are important parameters for process efficiency during composting, combustion or anaerobic treatment. The biochemical composition (soluble compounds, hemicellulose, cellulose and lignin) of plant materials has a major bearing on decomposition, Nitrogen (N) release patterns and C and N turnover in soils (Jensen et al., 2005). Information on N and phosphorus (P)

concentrations in the solids are important for estimating the fertilizer value of the untreated solids (Jørgensen and Jensen 2009). Solid-liquid separation makes handling of the manure easier and reduces the costly and environmentally damaging transport of raw manure over long distances by decreasing its weight and volume (Jørgensen and Jensen 2009). Separated solids may be used for composting, refeeding or generating biogas (methane) (Mukhtar et al., 1999). The remaining, nutrient-rich, separated liquid can be used in land application or reused on the farm as flushing water (Garcia et al., 2009). This gives farmers in areas with highly intensive livestock production an opportunity to reduce their overall environmental impact (Jørgensen and Jensen, 2009).

Another alternative for treatment and disposal is to convert animal manure from a disposal problem to a bioresource for value-added products (Wen et al., 2004). Animal manure is an underutilized biomass resource containing a large amount of organic carbon that is often wasted with the existing manure disposal practices (Chen et al., 2005). Animal manure as a feedstock has a great potential for producing value-added chemicals such as mono-sugars from manure fiber (Liao et al., 2006). Dairy manure contains 22% cellulose, 12% hemicelluloses and 13% lignin (Liao et al., 2007). As the major resource component of manure is fiber, converting fiber into biochemicals via a sugar platform provides an approach for this new level of manure utilization (Chen et al., 2005) and could effectively reduce the environmental liabilities related to manure management and disposal as well as provide an economic stimulus to the dairy farm (Liao et al, 2004). Fiber as a major component in dairy manure has been known for its recalcitrant nature. In general, manure fiber is “tougher” than other lignocelluloses, as the easily hydrolyzed part might have been digested by the cattle (Jin et al., 2009). Therefore a number of thermochemical and biochemical processing steps are necessary to convert these polymers to monomeric sugars (Bower et al, 2008). The purpose of the pretreatment is to remove lignin and hemicellulose, reduce cellulose crystallinity, and increase the porosity of the materials (Sun and Cheng, 2002). Cellulose can then be hydrolytically broken down into glucose either enzymatically by cellulases or chemically by

sulfuric or other acids (Mosier et al., 2005). Once in monomeric form, the sugars may be converted by fermentative microorganisms into ethanol or other products (Bower et al, 2008).

Dairy manure nutrients, such as phosphorus and nitrogen, can also be separated from other waste components so that they can be recycled as fertilizer or ingredients in other valuable products (de-Bashan and Bashan, 2004). The removal of nitrogen and phosphorus is critical in reducing and preventing eutrophication of sensitive inland and coastal waters (Doyle and Parsons, 2002). Phosphate can be precipitated as calcium phosphate and struvite, under conditions of high pH and with sufficient excess of calcium (Ca^{2+}), magnesium (Mg^{2+}) and ammonium (NH_4^+) ions (Valsami-Jones, 2001). Struvite is a white crystalline substance consisting of magnesium, ammonium and phosphorus in equal molar concentrations (Doyle and Parsons, 2002). The slow-release behaviour of struvite is ideal for coastal agriculture, since it reduces nutrient run-off and thus reduces the impact of nitrification on coastal waters. Further, when struvite is used as a fertilizer, mining of phosphate rocks can be reduced (Shu et al., 2006). The primary requirement for struvite crystallization is the presence of magnesium, ammonium and phosphate in the soluble form. The microwave-enhanced advanced oxidation process (MW/ H_2O_2 -AOP), helps release ammonia and orthophosphate in solution, to be used in struvite crystallization (Doyle and Parsons, 2002; Kenge, 2008).

Studies have indicated that microwave-assisted thermochemical pretreatment is effective in the breaking down of manure fiber (Jin et al., 2009). The application of microwave (MW) heating is not a new concept. Domestically, the microwave oven is a common household appliance used extensively for purposes of heating food materials (de la Hoz et al., 2005). The microwave-assisted heating method has proved more efficient than conventional methods due to its volumetric and rapid nature (de la Hoz et al., 2005). The application of MW irradiation (a closed-vessel MW digestion system, 2450 MHz, 1000 W), in combination with H_2O_2 for sewage sludge treatment, has been developed as a novel microwave-enhanced

advanced oxidation process (MW/H₂O₂-AOP) (Liao et al., 2005a). Microwave-based thermochemical pretreatment enhances manure anaerobic digestibility (through fiber degradation) and struvite precipitation (through phosphorus solubilization) (Jin et al., 2009). Microwave-based thermochemical (sodium hydroxide, calcium oxide, sulfuric acid or hydrochloric acid) pretreatment enhances chemical oxygen demand (COD) solubilization, glucan/xylan degradation as well as phosphorus and ammonium solubilization (Jin et al., 2009). Previous studies have proven that microwave temperature, hydrogen peroxide dosage and acid addition are the most significant factors affecting the MW/H₂O₂-AOP (Wong et al., 2007). The microwave irradiation was used as a generator agent of oxidizing radicals, as well as a heating source in the process.

Based on this background, the purpose of this research was to investigate the solids, nutrient and metal distribution in the solid and liquid fractions of dairy manure; the effects of the MW/H₂O₂-AOP operating conditions of temperature, hydrogen peroxide dosage, acid concentration and heating time on sugar production and nutrient release from solid dairy manure were studied.

1.2 Research objectives

This research studied the nutrient and metal balance of raw dairy manure following solid-liquid separation and investigated the effects of the MW/H₂O₂-AOP operating conditions of temperature, hydrogen peroxide (H₂O₂) dosage, acid concentration and heating time, on sugar production, nutrient release (expressed in terms of orthophosphate and ammonia) and solids disintegration (expressed in terms of soluble COD and volatile fatty acids) from solid dairy manure. To achieve, this several MW/H₂O₂-AOP experiments were conducted using dairy manure and cellulose substrates:

- In Chapter 2 the results of experiments conducted to determine
 - the solids, nutrient and metal composition of the solid and liquid fractions of raw dairy manure, following solid-liquid separation, are discussed.

- the removal efficiencies of solids, nutrients and metals from raw dairy manure, following solid-liquid separation.
- Chapter 3 reports on the investigation of sugar production, nutrient release and solids disintegration of solid dairy manure at pH 2, using microwave digestion both with and without the aid of an oxidizing agent (hydrogen peroxide). This was a follow up to previous experiments conducted within a pH range of 3.5 to 4.6 (Kenge, 2008).
- In Chapter 4, the results of experiments conducted to investigate the effects of the MW/H₂O₂-AOP operating conditions (temperature, hydrogen peroxide dosage, acid concentration and heating time) on sugar production from cellulose are presented and discussed. The aim was to apply the results to solid dairy manure substrate in subsequent experiments.
- In Chapter 5, the effects of increasing acid concentrations on sugar production, using cellulose at 1%, 3% and 10% sulfuric acid concentration are discussed.
- Experiments were conducted to investigate sugar production, nutrient release and solids disintegration from solid dairy manure, using a 2-stage dilute acid hydrolysis process at 3% sulfuric acid concentration. These results are presented and discussed in Chapter 6.

1.3 Literature review

1.3.1 Solid-liquid separation

Solid-liquid separation is the partial removal of organic and inorganic solids from a mixture of animal manure, open-lot runoff and process-generated wastewater, also known as liquid manure (Mukhtar et al., 1999). The most commonly used separation techniques are based on simple technological solutions where solids are mechanically separated from the liquid, e.g. by screw pressing, centrifugation, filtration or sieving (Burton, 2007). Separation of liquid and solid fractions of the wastewater is a desirable upstream operation in the treatment process (Rico et al., 2007) as separating the solids from the liquid manure helps

to avoid clogging (Cantrell et al., 2008) and makes the liquids easier to pump and handle. It also helps reduce the amount of organic material (organic loading) in treatment lagoons, odors in storage and treatment facilities and build-up of solids in primary lagoons (Mukhtar et al., 1999). Manure separation can contribute to reduced nutrient leaching from farmland by facilitating better distribution of the nutrients (Sorensen and Thomsen, 2005).

As a pre-storage procedure, separation of liquid manure can produce a liquid fraction containing soluble components such as mineral nitrogen (N), and potassium (K), and a solid dry matter (DM)-rich fraction containing the majority of the organic matter, including a significant proportion of the phosphorus (P) (Jørgensen and Jensen, 2009). The high methane potential fraction could be used for energy extraction (e.g. by recycling to the digester) while the low methane fraction could be directed elsewhere. Correspondingly, the nutrient rich fraction could be directed for fertilizing purposes (Kaparaju and Rintala 2008). The effect of solid–liquid separation to obtain an optimum feed stock for energy or nutrient extraction has been studied by several researchers with different manures. Lo et al., 1993 reported that when the separated solid fractions have an adequate total solids (TS) content and volatile solids (VS)/TS ratio, then they are suitable for production of compost. Pretreatment by separation also produces fractions of the manure with higher gas potential in terms of volume, since the water can be drained from the solids, thus creating fractions with a higher VS concentration (Møller et al., 2004).

1.3.2 Principles of microwave heating

Microwaves fall in the region of the electromagnetic spectrum between millimeter waves (0.01 m) and radio waves (1 m), corresponding to frequencies between 30 and 0.3 GHz (Hong et al., 2004). Heating applications generally use a frequency of 2450 MHz with a wavelength of 12.24 cm and energy of 1.02×10^{-5} eV. Frequencies around 900 MHz, which can provide up to 100kW and longer wavelengths (37.24

cm), are used for larger process heating applications where deeper penetration into material is necessary (Eskicioglu et al., 2007).

In a microwave oven, the waves generated are tuned to frequencies that can be absorbed by the polar materials. The polar material simply absorbs the energy and gets warmer (Hong et al., 2004). Industrial use of microwave (MW) heating as an alternative to conventional heating (CH) in chemical reactions is becoming popular mainly due to dramatic reductions in reaction times (Eskicioglu et al., 2007). The main advantages of microwave heating are: 1) the uniformity of heating throughout the object being heated; 2) precise control of the process temperature and heating time; and 3) much shorter heating times than that of the conventional conduction heating (Liao et al., 2005b).

Numerous studies have been carried out to analyze the effects of MW irradiation on both biological and chemical systems by using different MW and CH units, experimental techniques and approaches (Eskicioglu et al., 2007). Also, thermal and non-thermal effects of electromagnetic energy have been debated for many years (Hong et al., 2004). Eskicioglu et al., 2006 hypothesized that interactions which bind the biopolymers of sludge together can be disrupted by dipole rotation or orientation effects of MW-irradiation.

In previous studies, MW-irradiated microbial cells showed greater damage than CH cells at similar temperatures (Hong et al., 2004). Similarly, in some of the CH applications, a clear enhancement of reaction rate with MW heating compared to CH was observed indicating a non-thermal effect other than only dielectric heating of the materials (Gedye et al., 1986). It is believed that the orientation (athermal) and subsequent heating (thermal) effects break the polymeric network of sludge ending with the release of mainly extracellular and possibly intracellular materials such as polysaccharides, proteins, DNA and RNA (Eskicioglu et al., 2006).

1.3.3 Advanced oxidation processes (AOPs)

The generation of highly reactive oxygen radicals without the addition of metal catalysts is defined as advanced oxidation process (Liao et al., 2005a). The hydroxyl radicals (OH) generated by advanced oxidation processes (AOPs) accelerate an oxidative degradation of numerous organic compounds dissolved in wastewater (Han et al., 2004). AOPs include several processes such as ultraviolet/ozone (UV/O₃), ultraviolet/hydrogen peroxide (UV/H₂O₂) and ozone/hydrogen peroxide (O₃/H₂O₂) (Han et al., 2004). Hydrogen peroxide is one of the most powerful oxidizers (Liao et al., 2005a). From the thermodynamic point of view, H₂O₂ is stronger than chlorine (Cl₂) and chlorine dioxide (ClO₂), as the standard redox potential of H₂O₂ is greater than Cl₂ and ClO₂ (Eskicioglu et al., 2008). Through catalysis or irradiation, H₂O₂ can be converted into highly reactive hydroxyl radicals that possess a higher oxidation potential than the H₂O₂ itself (Liao et al., 2005a). A mixture of H₂O₂ and Fe²⁺ (Fenton reaction), generates hydroxyl radicals that are strong enough to oxidize and destroy recalcitrant organic compounds (Liao et al., 2005a). The activity or rate of decomposition of H₂O₂ is dependent on the temperature (Eskicioglu et al., 2008).

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

The oxidation power of H₂O₂ can be enhanced via a number of treatment scenarios including O₃ / H₂O₂, UV/H₂O₂, H₂O₂/ultrasound and H₂O₂/ thermal process. Heating increases decomposition of H₂O₂ into hydroxyl radicals and therefore enhances the oxidation process when H₂O₂ is applied simultaneously with conventional or microwave (MW) heating (Eskicioglu et al., 2008). Several studies have proved that microwaves can lead to the improvement of several types of oxidation processes (Han et al., 2004).

1.3.5 Microwave enhanced advanced oxidation process in wastewater treatment

The use of microwave ovens in laboratories has increased markedly in recent years. Using both completely closed and pressure-relief types of vessels, microwave digestion is steadily replacing most

classical wet digestion procedures for a wide variety of matrices, especially biological and geological materials (Jardim and Rohwedder (1989). Recent studies have suggested significant potential for use of MW irradiation in the environmental engineering field as well (Eskicioglu et al., 2007). A fast and effective physical-chemical digestion process, such as microwave digestion, can be of much assistance to nutrient recovery technologies (Qureshi et al., 2008b).

In wastewater treatment, microwave irradiation solubilizes primary sludge by interaction of the electromagnetic field with polar particles in sludge, which leads to a temperature increase in the irradiated sample (Zheng et al., 2009). Microwave-based pretreatment is also beneficial to the solubility of complex manure particles. The comparison of microwave and conventional-heating treatment demonstrated that microwave pretreatment was more effective in facilitating manure solubilization and digestibility (Jin et al., 2009). The benefit of microwave heating was due to the unique feature of microwave irradiation (de la Hoz et al., 2005).

Hydrogen peroxide, a powerful oxidizing agent and a potent source of free radicals, is an ecologically desirable pollution control agent, since it yields only water and/or oxygen upon decomposition. Thus, it has been used in increasingly greater quantities for environmental applications such as wastewater and sewage effluent treatment, industrial liquid and gaseous effluent detoxification (Kang et al., 1999). Liao et al., 2005a reported that the AOP process, using a combination of H_2O_2 /microwave heating, could facilitate release of phosphate from sewage sludge and also provide the release of a large quantity of sludge-bound phosphorus. In a study by Eskicioglu et al., (2008), the concentration of organic compounds (TS, COD, proteins, sugars and humic acid) present in thickened waste activated sludge (TWAS) samples decreased further when H_2O_2 was combined with MW irradiation especially at temperatures above 80° C.

1.3.6 Sugar production from solid dairy manure using dilute acid hydrolysis

Acid catalyzed processes can be divided in two general approaches, based on concentrated acid/low temperature and dilute acid/ high temperature hydrolysis (Girio et al., 2010). Dilute acid processes have been viewed primarily as a means of pretreatment for the hydrolysis of hemicelluloses rendering the cellulose fraction more amenable for further enzymatic treatment. Both cellulose and hemicellulose components can also be hydrolyzed using dilute acid catalyzed processes but in this case a two step-hydrolysis is required (Girio et al., 2010). Upon hydrolysis, the hemicelluloses are broken down into their monomers such as xylose, arabinose, mannose, galactose, rhamnose, uronic acids and acetyl groups (Girio et al., 2010).

Studies by Liao et al., (2007) found acid concentration to be the most influential factor affecting the accumulation of cellulose in dairy manure. Acid hydrolysis, particularly sulfuric acid hydrolysis, has been used to treat lignocellulosic materials to obtain mono-sugars (Choi and Mathews, 1996). Compared to the concentrated acid hydrolysis, one of the advantages of dilute acid hydrolysis is the relatively low acid consumption, limited problems associated with equipment corrosion and less energy demand for acid recovery. Under controlled conditions, the levels of the degradation compounds generated can also be low (Girio et al., 2010). Liao et al., (2007) further reported the optimal conditions for cellulose accumulation to be a reaction time of 2.80 h, temperature of 140°C, and acid concentration of 1% and concluded that with the proper dilute acid treatment, dairy manure could provide a substantial cellulose resource for the next step of enzymatic hydrolysis to produce glucose.

1.3.7 Nutrient recovery

Dairy farm effluents contain a large reserve of plant nutrients (Bolan et al, 2004). Sprayfield application of the wastewater has the advantage of on-site recycling of nutrients, but presents a nutrient and waste management dilemma (Harris et al., 2008). Anaerobic treatment of domestic and agro-industrial

wastewater releases large amounts of phosphorus (P) and nitrogen (N) into wastewater (de-Bashan and Bashan 2004). The disposal of nutrients (N and P) directly from wastewater plants or indirectly from agriculture runoff and leaching from sludge deposited in landfill and fields causes eutrophication of water bodies which is a major, global environmental problem (de-Bashan and Bashan 2004). Recovery of sufficient amounts of P and N from dairy wastes in a form that can be managed conservatively by dairy farmers would help resolve conflicting agricultural and environmental interests.

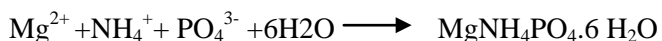
1.3.7.1 Orthophosphate

Phosphorus appears in wastewater as orthophosphate, polyphosphate and organically bound phosphorus, the last two components accounting usually for up to 70 percent of the influent phosphorus (Sotirakou et al., 1999). Anaerobic treatment of domestic and agro-industrial wastewater releases large amounts of phosphorus and nitrogen into wastewater (de-Bashan and Bashan 2004). Phosphorus removal from domestic and industrial wastewater has become one of the objectives of wastewater treatment in order to minimize eutrophication problems in natural water bodies (Chanona et al., 2006).

Global reserves of high-quality mined phosphate deposits are being gradually depleted. It is estimated that there are seven billion tons of phosphate rock as P_2O_5 remaining in reserves that could be economically mined (Shu et al., 2006). The presently known reserves will be depleted within about 50 years, and the remainder of the reserve base will be depleted within the next 100 years (Herring and Fantel, 1993).

Currently, the methods applied to remove P from wastewater are based on the formation of phosphate precipitates. Phosphate can be precipitated as calcium phosphate and struvite under conditions of high pH and with sufficient excess of Ca^{2+} , Mg^{2+} , and NH_4^+ ions (Valsami-Jones, 2001). Recovering phosphorus in the form of struvite is an effective way to reduce phosphorus discharge to ecological systems (Jin et al., 2009) and is also a sustainable strategy to conserve P resources (Harris et al., 2008). Struvite (magnesium

ammonium phosphate) is a crystalline solid which can serve as slow releasing fertilizer due to its lower solubility (Jin et al., 2009). Struvite forms according to the general reaction:



(Doyle and Parsons, 2002).

In general, dairy manure contains organic phosphorus and polyphosphate; converting them into a soluble orthophosphate is crucial for successful struvite formation (Jin et al., 2009). Recovery of phosphorus from waste streams has potential to recover more than 90% of dissolved phosphorus from digester supernatant as struvite (Shu et al., 2006). A microwave-assisted sulfuric acid and/or hydrogen peroxide pretreatment has been used to treat dairy manure with a high phosphorus release (Pan et al., 2006; Qureshi et al., 2008 a). Microwave pretreatment has also been used for phosphorus solubilization in municipal sewage sludge (Jin et al., 2009). Orthophosphate release from sewage sludge was higher than those from dairy manure (Liao et al., 2005a). The low release efficiency attributes to the complex structure of dairy manure (Jin et al., 2009).

1.3.7.2 Ammonia

Nitrogen appears in wastewater as ammonia, nitrite, nitrate and organic nitrogen. Organic nitrogen is decomposed to ammonia, which is assimilated to bacterial cells, thus leading to net growth, or oxidized to nitrite and nitrate. The nitrate is converted to gaseous nitrogen and is removed from the wastewater (Sotirakou et al., 1999). Agriculture is heavily dependent on industrial nitrogen fertilizers. In addition, N is added to agricultural systems through the use of animal manures. The expanded use of both N sources has resulted in a greater potential for NH_3 volatilization from improper use (Termeer and Warman, 1993) with potentially detrimental impacts on the environment (Misselbrook et al., 2005) such as soil acidification and eutrophication (Portejoie et al., 2003). Ecologically sound manure management on farms

is vital to minimize losses of valuable plant nutrients and to prevent nutrient contamination of the surrounding watershed (Mulbury et al., 2005).

1.3.7.3 Volatile fatty acids

Anaerobic digestion of organic matter to methane and carbon dioxide is done by the coordinated action of various groups of microorganisms and goes through several intermediate stages (Aguilar et al., 1995). Hydrolysis and acidification can convert complex organic substances in sludge flocs into volatile fatty acids (VFAs) and other low molecule weight soluble carbon compounds (Elefsiniotis and Oldham, 1994). The primary driver for a successful nutrient removal, in tertiary treatment, is the availability of a suitable carbon source, mainly in the form of VFA (Yu et al., 2008). The soluble organic products of hydrolysis and acidification can be used as energy and carbon sources for biological nutrients removal (Barnard, 1983). In the past, volatile fatty acids have been used quite frequently as performance indicators of anaerobic digestion of animal manures (Hill and Holmberg, 1988). In the biological enhanced phosphate removal (BEPR) process the key to efficient performance lies in the adequate availability of low molecular mass volatile fatty acids in the anaerobic zone (specifically acetate), since VFAs are needed for efficient biological phosphate removal (Chu et al., 1994).

1.3.7.4 Chemical oxygen demand

Chemical oxygen demand (COD) is widely used for determining the strength of waste streams (Baker et al., 1999) and is one of the most commonly used measurable parameters in assessing water quality (Zhang et al., 2009). Suspended substances, nutrients and organic load as COD contribute major pollutants in rivers, lakes and ponds. Removal of these contaminants in waste water is one of the fundamental goals in waste treatment (Ashan et al., 2001). COD is an important index for the control and operation of wastewater treatment plants and is one of the critical parameters to determine the treatment efficiency of reactors (Mohan and Sunny 2008; Zhang et al., 2009). COD solubilization and fiber degradation result in

more digestible compounds such as volatile fatty acids in the pretreated manure slurry (Jin et al., 2009). While good COD balances are expected in aerobic and aerobic-anoxic systems, systems incorporating anaerobic zones (i.e. BEPR systems) tend to exhibit low COD balances (less than 80%). This "loss" of COD apparently is associated with the fermentation processes occurring in the anaerobic zone of BEPR systems treating municipal wastewater (Barker and Dold, 1995).

1.4 Materials and methods

1.4.1 Substrates

All dairy manure samples used in this research were obtained from the University of British Columbia (UBC) Dairy Education and Research Centre in Agassiz, British Columbia, Canada. Raw (unseparated) dairy manure was used for experiments on solid-liquid separation. For all MW/H₂O₂-AOP experiments, solid dairy manure, obtained after field solid –liquid separation of raw dairy manure was used. Manure samples were stored at 4°C until further use. The dairy manure contained a lot of sand particles and though significant amounts were removed by allowing the sand to settle and decanting the manure slurry, some sand still remained in the manure samples. Whatman cellulose powder (medium length fibers) for column chromatography was used as the substrate (see Chapters 4 and 5).

1.4.2 Microwave apparatus

A closed-vessel microwave digestion system was used in this study (Liao et al., 2005a). The detailed description of the system setup has previously been reported (Wong, 2006; Kenge 2008). In brief, microwave heating was conducted using the Milestone Ethos Advanced Microwave Labstation (Milestone Inc., USA) (Figure 1.1), which operates at a frequency of 2450 MHz and has a maximum power output of 1000 W. The system has dual independent magnetrons with a rotating microwave diffuser for homogenous microwave distribution. The microwave oven holds 12 polytetrafluoroethylene (PTFE) Teflon digestion vessels (Figure 1.2), including one reference vessel, each with a capacity of approximately 100 mL in a single run. The vent and reseal design of the system allows for the maximum

operating temperature and pressure of the microwave system to be 220°C and pressures of up to 435 psig respectively. During each run, a thermowell, which holds a thermocouple, is placed in the reference vessel containing the sample, thereby providing real time temperature feedback. A system controller, with an LCD screen control panel (Figure 1.3), connected to the microwave system is used to program the ramp time, heating time and operating temperature for each run. For all MW/H₂O₂-AOP experiments, ramp time was set at a fixed rate of 20°C per minute. Magnetic stirrers were used to stir all samples during microwave heating. Hydrogen peroxide (30wt%) was used for all MW/H₂O₂-AOP experiments in this study.



Figure 1.1 Microwave oven digestion system



Figure 1.2 Polytetrafluoroethylene (PTFE) teflon digestion vessels



Figure 1.3 System controller with an LCD screen control panel

1.4.3 Sample analysis

Following microwave treatment, dairy manure samples were allowed to cool to room temperature. For all initial untreated samples and microwave treated samples, a portion of the total fraction was used for total chemical oxygen demand (TCOD), total phosphate (TP) and total Kjeldahl nitrogen (TKN) analysis. The remaining portions of the samples were centrifuged at 4000 rpm for 10 mins in a Thermo IEC CL30 rotor and the supernatant filtered using 4.5 μm fiberglass filter to separate the liquid from the solid. The filtrate was analyzed for total sugar, soluble chemical oxygen demand (SCOD), volatile fatty acids (VFAs), orthophosphate ($\text{PO}_4\text{-P}$) and ammonia-nitrogen ($\text{NH}_4\text{-N}$) content. In experiments where cellulose

was used as the substrate, the total fraction was analyzed for TCOD only while the filtrate was analyzed for total sugars, SCOD and VFAs where applicable.

All analysis, except TS, VS, sugar, COD and metals, were conducted at the Environmental Engineering Laboratory of the Department of Civil Engineering, UBC using flow injection analysis (Lachat QuikChem 8000 Automated Ion Analyzer). The TS content was determined after a 24-h drying period at 105°C. Calcium (Ca), magnesium (Mg) and potassium (K) were determined using a Varian Spectra 220 Fast Sequential Atomic Absorption Spectrometer. VFA was measured with a Hewlet Packard (HP) 6890 Series Gas Chromatograph System equipped with a flame ionization detector (FID). COD was determined colorimetrically using a Hach DR/2000 direct reading spectrophotometer at 600nm.

Analysis for TS, VS, COD, VFA, Ortho-P, Ammonia, TP, TKN, Ca, Mg and K were determined according to procedures described in Standard Methods (APHA, 1998). Total sugar was measured using the anthrone carbohydrate method (Raunkjaer et al., 1994) with some modifications to remove H₂O₂ residue which causes interference with this method. 1 mL samples in mini centrifuge tubes were spun in a Thermo IEC Multi rotor at 6500 rpm for 15 min and dried at 60°C for 3 days. The dried samples were cooled to room temperature and 1 mL of ice-cold ethanol added to each sample to precipitate the carbohydrates. The samples were then spun again at 6500 rpm for 15 min and dried at 60°C for 3 days. The dried samples were resolubilized with 1 mL distilled water and then mixed with 2mL of anthrone reagent in glass vials with Teflon caps and incubated at 105°C for 15 min. Absorbance was measured at 625nm using a Hach DR/2000 direct reading spectrophotometer. Glucose solutions ranging from 25 to 600 mg/L were used as standards.

1.4.4 Statistical analysis

1.4.4.1 JMP-IN statistical software

Experimental designs

Screening and response surface designs were used to generate experiments aimed at determining conditions that maximize sugar production, nutrient solubilization and solids disintegration from solid dairy manure. Experiments were run based on the conditions in the design matrix. After analysis the data was interpreted using surface plots, prediction profiles and Pareto plots.

Screening design

Screening designs are pre-formulated designs which examine many factors to determine which have the greatest effect on the results of a process. Screening experiments involve many factors. Screening factors can be continuous or categorical with two or three levels. To economize on the number of runs, each factor is usually set at only two levels and response measurements are not taken for all possible combinations of levels. Screening designs are a prelude to further experiments (Sall et al., 2005).

Response surface design

The Response Surface Methodology (RSM) is a pre-formulated design which focuses on finding the optimal response within the specified ranges of factors. The Response Surface designer in JMP lists well-known RSM designs for two to eight continuous factors (Sall et al., 2005). The Box-Behnken design was used in this study. This design is constructed by combining two-level factorial designs with incomplete block designs in such a way as to avoid extreme vertices and to present an approximately rotatable design with only three levels per factor (Sall et al., 2005). The design screens the maximum number of effects in the least number of experimental runs and is therefore economical and particularly useful when it is expensive to perform the necessary experimental runs.

Surface plots

This sequential plot fits a smoothed surface to each data point. Plotted in three dimensions, surface plots indicate the response of one or more variable as two input variables are adjusted with the others held constant.

Prediction profiles

A prediction profile for a dependent variable consists of a series of graphs, one for each independent variable, of the predicted values for the dependent variable at different levels of one independent variable. Predicted values for the dependent variables can either be inspected at the actual levels at which the independent variables were set during the experiment, or at levels other than the actual levels of the independent variables used during the experiment, to see if there might be intermediate levels of the independent variables that could produce even more desirable responses.

Pareto plots

The purpose of the Pareto plot is to highlight the most important among a large set of factors. In Pareto plots, factors are displayed in the order of their severity or significance, using bars that are in descending order of values, thus visually emphasizing the most important parameters.

2. Solid-liquid separation of raw dairy manure

2.1 Summary

Three sets of manure samples with different strengths (undiluted, 1:1 water dilute and 2:1 water diluted), prepared from raw dairy manure with a TS content of 8.0% were each separated into two fractions, solid and liquid, using a laboratory scale 1mm sieve. The screening separated 42%, 36% and 47% of the initial mass of manure as solids for the undiluted, 1:1 diluted and 2:1 diluted manure samples respectively. A comparison of the separated fractions indicated that the solid fractions had a higher TS and VS content compared to the liquid fractions. The VS/TS ratio was 0.94 in the raw unseparated dairy manure, 0.95 in the liquid fraction and 0.97 in the solid fraction. The liquid fractions had a higher composition (as % of the total solids) of ammonia, TKN, $\text{PO}_4\text{-P}$ and TP and metals. A comparison of the properties of the separated fractions with the raw unseparated manure revealed that solid–liquid separation produced solid fractions that had a higher TS and VS content, compared to the original manure and liquid fractions, which had a higher composition of TKN and TP than the raw dairy manure. Removal efficiencies for nutrients were 40.4 %, 34.8%, 79.5% and 50.6% for ammonia, TKN, $\text{PO}_4\text{-P}$ and TP respectively. 55.3% of TS and 54.8% of VS was removed from the liquid fraction, upon solid-liquid separation.

2.2 Introduction

Since the modern farming trend towards large operations leads to a surplus of nutrients in nearby cropland, there is a need for better distribution of these nutrients. Solid–liquid separation of livestock effluents into various fractions with different properties is a good option to concentrate these nutrients in the separated fractions and easily transport them for land application or other uses such as composting or bioenergy production (Garcia e al., 2009). This study was focused on the laboratory separation of the solid and liquid fractions of raw dairy manure. The objective was to investigate the distribution of solids, nutrients and metals in the separated solid and liquid fractions and compare with the raw undiluted

manure. Removal efficiencies of nutrients, metals and solids using the laboratory screening, were also determined.

2.3 Materials and methods

2.3.1 Substrate

Raw dairy manure from the UBC Dairy Research and Education Center was used for this set of experiments. Raw dairy manure with a TS content of 8.0% was used. The TKN contained 51.7% of inorganic nitrogen in the form ammonia. The TP also contained 32% of $\text{PO}_4\text{-P}$. Results obtained for the composition of metals were quite high (28.9% for Ca; 11.5% for Mg; 57% of the dry matter). The reason for these high values is unclear and likely due to experimental errors. The initial characteristics of the manure are presented in Table 2.1.

2.3.2 Experimental design

3 sets of manure samples, with different strengths /dilutions as presented in Table 2.2, were prepared from the raw dairy manure and separated into liquid and solid portions by passing the samples through a 1mm U.S.A standard testing laboratory scale sieve. The separated solid and liquid fractions were weighed and stored at 4°C before further use. The solid fractions were diluted with distilled water and mixed at 130 rpm for one hour, with a laboratory shaker, to facilitate extraction of nutrients and metals. The solid and liquid fractions were analyzed for TS, COD, $\text{PO}_4\text{-P}$, $\text{NH}_4\text{-N}$, TP, TKN, Ca, Mg and K. 9 replicates were run for each set of experiments.

Table 2.1 Characteristics of dairy manure used

TS (%)	VS (%)	Ca (% of dry matter)	Mg (% of dry matter)	K (% of dry matter)	PO ₄ -P (% of dry matter)	TP (% of dry matter)	NH ₃ -N (% of dry matter)	TKN (% of dry matter)	SCOD (g/L)	TCOD (g/L)
8.0	7.5±0.2	28.9±2.1	11.5±0.4	57.0±5.0	0.2±0.0	0.8±0.1	1.8±0.1	3.4±0.2	31.4±12.7	87.2±15.6

Data represents arithmetic mean of 9 replicates ± standard deviation

Table 2.2 Dairy manure samples used for solid-liquid separation

Set no.	Dairy manure sample
1	No dilution
2	1:1 water diluted
3	2:1 water diluted

2.4 Results and discussion

2.4.1 Composition and properties of the separated solid and liquid fractions

Table 2.3 Proportion of solid and liquid fractions in relation to initial raw dairy manure sample

Set no.	Raw dairy manure sample	Total weight (g)	Weight of liquid fraction (g)	Weight of solid fraction (g)	Liquid fraction (%)	Solid fraction (%)
1	No dilution	1075	628	447	58	42
2	1:1 water diluted	1246	796	450	64	36
3	2:1 water diluted	1136	599	537	53	47

For all the 3 sets of manure samples, percentage composition and weights of the solids fraction was lower than the liquid fractions (Table 2.3). The screening separated 42%, 36% and 47% of the initial mass of manure as solids, for sets 1, 2 and 3 respectively (Table 2.3). Low weight and volume (and thereby high TS contents) are preferable and economical, if recycling of the solids requires transport over long distances to remote crop lands that could utilize the organic nitrogen and phosphorus (Jørgensen and Jensen, 2009; Chastain et al., 2001).

Solid-liquid separation of the 3 sets of manure samples resulted in solid and liquid fractions that had different properties. The solid fractions had a higher percentage composition of TS and VS compared to the liquid fractions (Table 2.4). A high dry matter content of the solid fraction is necessary for high energy recovery during combustion such as in combined heat and power plants (Jørgensen and Jensen, 2009). Møller et al., 2004, explains that pre-treatment of manure by separation results in fractions of manure with higher gas potential in terms of volume, since the water can be drained from the solids thus creating fractions with a higher VS concentration, making them favourable for combustion or anaerobic digestion.

Table 2.4 Composition of the solid and liquid fractions of raw dairy manure with various dilutions after solid-liquid separation

Set no.	Sample description	TS (%)	VS (%)	Ca (% of dry matter)	Mg (% of dry matter)	K (% of dry matter)	PO ₄ -P (% of dry matter)	TP (% of dry matter)	NH ₃ -N (% of dry matter)	TKN (% of dry matter)
1a	LF (no dilution)	3.57±0.14	3.40±0.16	1.52±0.09	1.83±0.07	12.18±1.48	0.11±0.03	0.84±0.03	2.38±0.28	5.04±0.69
1b	SF (no dilution)	9.98±1.3	9.66±1.46	0.67±0.04	0.39±0.03	3.90±0.72	0.12±0.08	0.52±0.01	0.87±0.22	3.33±0.36
2a	LF (1:1 water diluted)	2.39±0.15	2.28±0.14	1.36±0.25	2.20±0.58	11.32±1.76	0.22±0.01	0.92±0.02	2.04±0.08	5.28±0.12
2b	SF (1:1 water diluted)	8.59±0.34	8.28±0.45	0.72±0.08	0.36±0.05	4.32±1.52	0.08±0.01	0.39±0.02	0.49±0.04	2.33±0.15
3a	LF (2:1 water diluted)	3.28±0.17	3.14±0.16	1.67±0.02	1.65±0.05	9.94±1.17	0.14±0.01	0.87±0.06	1.60±0.13	4.82±0.50
3b	SF (2:1 water diluted)	8.74±0.26	8.20±0.38	0.78±0.13	0.37±0.02	3.78±0.71	0.10±0.03	0.44±0.02	0.64±0.02	2.65±0.16

Data represents arithmetic mean of 9 replicates ± standard deviation

LF = Liquid fraction

SF = Solid fraction

% of dry matter = $\frac{\text{concentration (mg/L)}}{\text{TS (mg/L)}} \times 100$

When dairy manure is separated into solid and liquid fractions, the VS/TS ratio diminishes indicating an increase in the percentage of inorganic compounds (Rico et al., 2007). Also, when separated solid fractions have an adequate TS content and VS/TS ratio, then they are suitable for production of compost (Lo et al., 1993). In the present study, the VS/TS ratio was 0.94 in the raw unseparated dairy manure, 0.95 in the liquid fraction and 0.97 in the solid fraction. These results are higher than those obtained by Rico et al., (2007), which reported VS/TS ratio of 0.78 for dairy manure, 0.87 for solid fraction and 0.72 for screened manure.

Comparing the liquid fractions to the solid fractions, it was determined that for all the manure sets investigated, the separated liquid fractions had a higher composition (as % of the total solids) of ammonia, TKN, PO₄-P and TP and metals, compared with the solid fractions (Table 2.4).

Set 1a had the highest SCOD results (Table 2.5). Set 2a (1:1 water diluted dairy manure) had approximately 59% of the SCOD in set 1a, while set 3a (2:1 water diluted dairy manure) had approximately 72% of the SCOD in set 1a. Table 2.5 presents the chemical oxygen demand results for the separated liquid and solid fractions.

Table 2.5 Chemical oxygen demand results for liquid and solid fractions

Set no.	Separated manure sample	SCOD (g/L)	TCOD (g/L)
1a	LF (no dilution)	23.4 \pm 4.4	-
1b	SF (no dilution)	-	112.7 \pm 8.0
2a	LF (1:1 water diluted)	13.9 \pm 0.5	-
2b	SF (1:1 water diluted)	-	124.4 \pm 24.2
3a	LF (2:1 water diluted)	16.8 \pm 2.5	-
3b	SF (2:1 water diluted)	-	123.0 \pm 39.6

Data represents arithmetic mean of 9 replicates \pm standard deviations

LF = Liquid fraction SF = Solid fraction

2.4.2 Comparison of solid and liquid fractions versus raw unseparated dairy manure

Physical separation of the wastewater also results in fractions (solids and liquid) with different properties (Kaparaju and Rintala 2008) compared to the initial raw unseparated manure. Figures 2.1 to 2.4 present a comparison of the solids, nutrient and metal composition of the separated solids and liquid fractions with that of the initial unseparated raw dairy manure. For all the 3 different manure strengths, solid –liquid separation produced solid fractions that had a higher TS content and VS % compared to the original manure (Figures 2.1 and 2.2 respectively), with set 1(undiluted manure sample) having the highest % composition of TS and VS. The liquid fractions had a higher composition of TKN and TP than the raw initial manure, with set 2 (1:1 water diluted manure) having the highest % composition. In terms of chemical oxygen demand, the separated liquid fractions had lower SCOD concentrations as compared to the SCOD of the initial dairy manure. However, TCOD values of the separated solids were all higher than that of the initial dairy manure (Tables 2.1, 2.5).

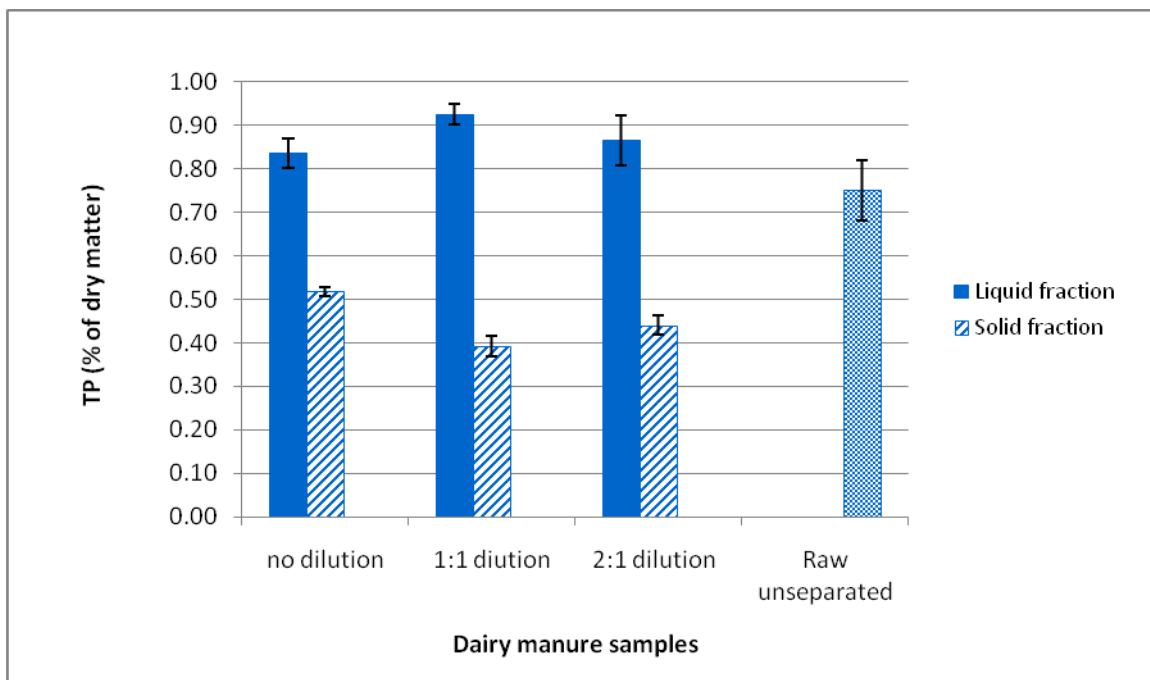


Figure 2.1 TS (%) in separated solid and liquid fractions versus raw dairy manure

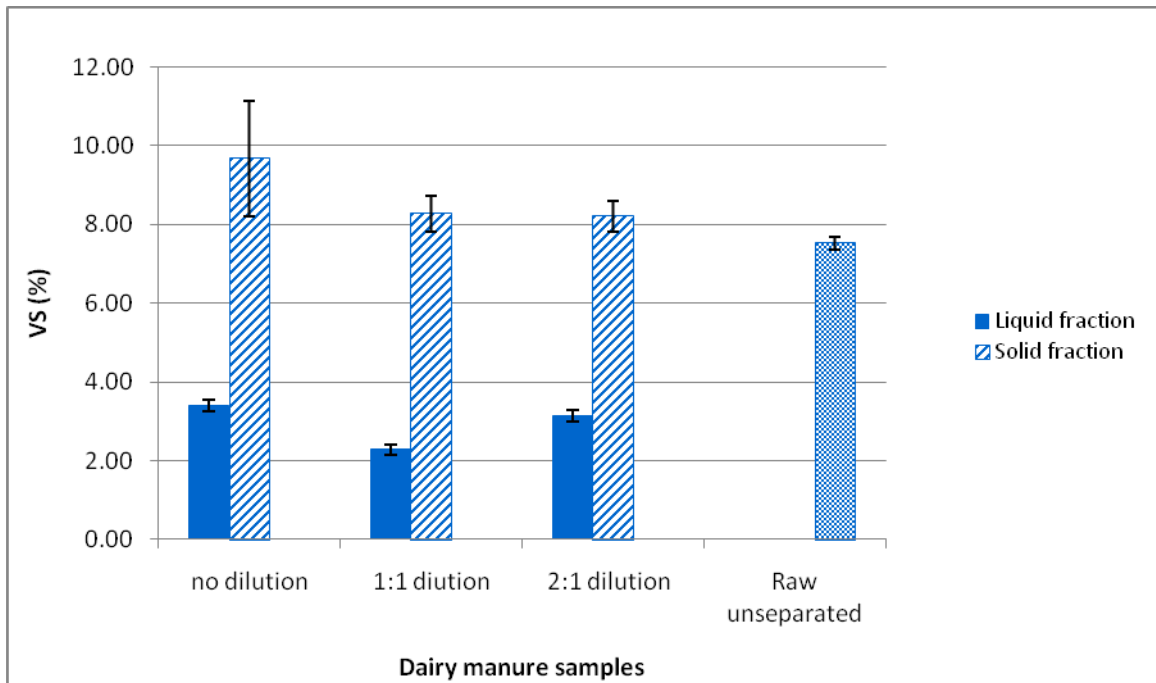


Figure 2.2 VS (%) in separated solid and liquid fractions versus raw dairy manure

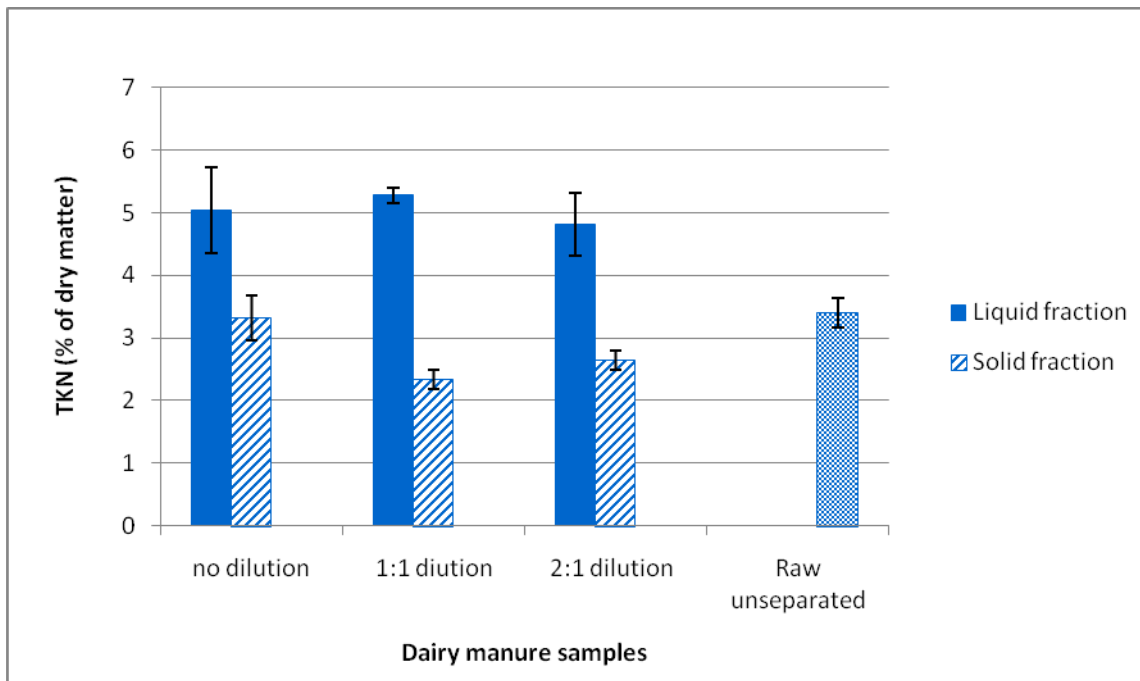


Figure 2.3 TKN (% of dry matter) in separated solid and liquid fractions versus raw dairy manure

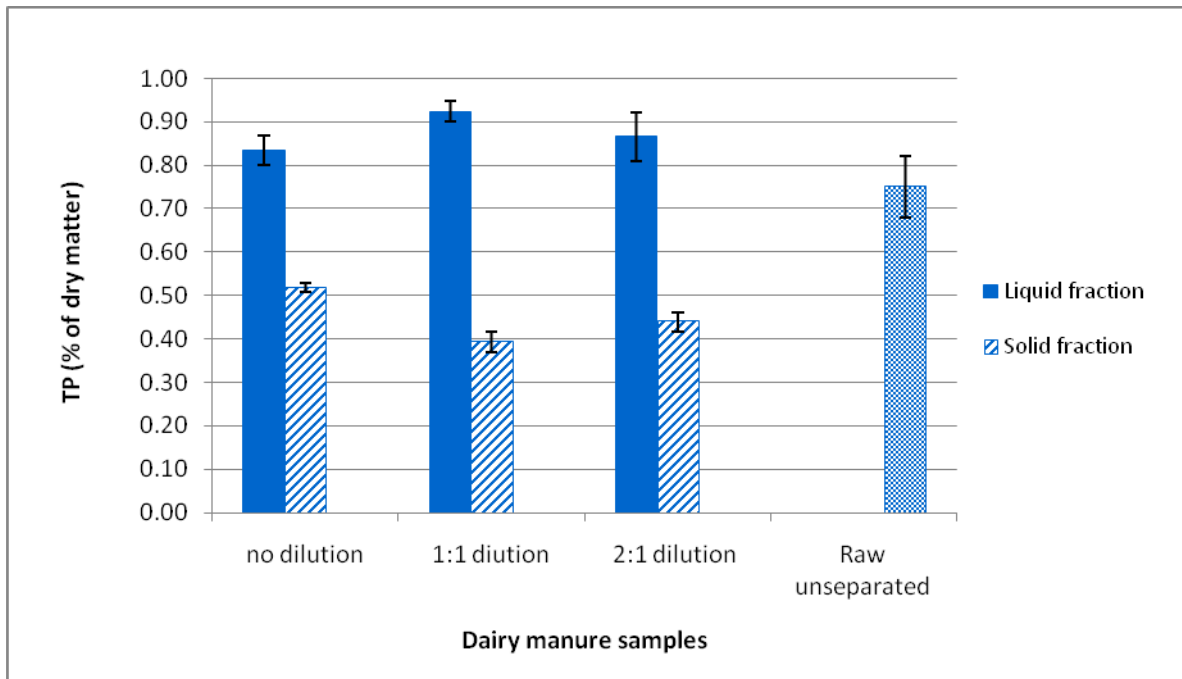


Figure 2.4 TP (% of dry matter) in separated solid and liquid fractions versus raw dairy manure

2.4.3 Removal of solids, nutrients and metals from raw dairy manure by solid-liquid separation

Table 2.6 presents the removal efficiencies of solids, nutrients, metals and COD, from raw dairy manure by a 1mm laboratory scale sieve. Effectiveness of the screening treatment was determined by the difference between the solids, nutrient and metal concentrations in the effluent passing the screen and the initial raw unseparated dairy manure sample before screening. The amount removed was calculated by the equation:

$$\frac{\text{Concentration in raw unseparated dairy manure} - \text{Concentration in liquid fraction slurry}}{\text{Concentration in raw unseparated dairy manure}} \times 100$$

Table 2.6 Removal of solids, COD, nutrients and metals from raw unseparated dairy manure using a 1mm laboratory scale sieve

	Raw unseparated dairy manure	*Liquid fraction	Amount removed (%)
Total solids (g/L)	79.9 \pm 0.9	35.7 \pm 1.4	55.3
Volatile solids (g/L)	75.3 \pm 1.6	34.0 \pm 1.6	54.8
Chemical oxygen demand (g/L)	87.2 \pm 15.6	23.4 \pm 4.4	73.2
NH ₃ -N (mg/L)	1422 \pm 84	847 \pm 63	40.4
TKN (mg/L)	2750 \pm 190	1793 \pm 214	34.8
PO ₄ -P (mg/L)	188 \pm 5	38 \pm 10	79.5
TP (mg/L)	603 \pm 60	298 \pm 6	50.6
Ca (mg/L)	23050 \pm 1638	544 \pm 48	97.6
K (mg/L)	45550 \pm 4019	4337 \pm 425	90.5
Mg (mg/L)	9159 \pm 311	653 \pm 21	92.9

Data represents arithmetic mean of 9 replicates \pm standard deviation

*after screening through 1mm laboratory scale sieve

The highest removal efficiencies (97.6% for Ca; 90.5% for K; 92.9% for Mg) were obtained for metals. Chastain et al., (2001) reported 48.8%, 50.8% and 50.2% removal efficiencies for Ca, K and Mg, respectively. Removal of nutrients was 40.4 % for ammonia and 79.5% for PO₄-P. During manure separation fractionation transfers organic N to the dry-matter-rich fraction, while the dissolved NH₄-N stays in the liquid fraction (Kaparaju and Rintala, 2008). Ammonia is soluble and cannot be screened; thus, a removal efficiency of 40.4% is considered relatively high and could be due to enhanced volatilization (Chastain et al., 2001). Bedding particles could also absorb a large amount of moisture and soluble nutrients such as ammonia, thereby accentuating its removal (Chastain et al., 2001). Chastain et al., 2001, using a 1.5mm sieve and dairy manure with TS content of 3.83 % reported 45.7% of ammonia removal.

Removal efficiencies for TKN and TP in this study were 34.8% and 50.6%, respectively. These are lower compared to Chastain et al., 2001 which reported removal efficiencies of 49.2 % for TKN and 53.1% for TP. In other studies, McKenney, (1998) reported removal efficiencies of 31-41% for TKN and 69-75% for phosphorus, using dairy manure with TS content of 5.4-8.3% while Garcia et al., (2009) reported lower removal efficiencies of 22% and 26 % for TKN and TP, respectively. Large reductions in the P and N in the liquid fraction would allow for better management of the P and N, since irrigation of the liquid fraction onto cropland adjacent to dairy farms would be more feasible (Chastain et al., 2001).

55.3% of TS and 54.8% of VS was removed from the liquid fraction compared to 60.9% and 62.6 %, respectively obtained by Chastain et al., (2001). McKenney, (1998), also reported TS removal efficiencies of 71-78%. Therefore, in this study, as well as in Chastain et al., (2001) and McKenney, (1998) the solid fractions retained greater proportions of the TS and VS. Large removals of VS and TS onsite on dairy farms would greatly reduce the required treatment volume for an anaerobic lagoon and the rate of sludge buildup. A large amount of VS removal would also make lagoon design, at lower loading rates, more economical and would reduce the potential for strong odour (Chastain et al., 2001).

3. Sugar and nutrient release from solid dairy manure at pH 2 using the microwave enhanced advanced oxidation process

3.1 Summary

Solid dairy manure with a TS concentration of 4.9% was adjusted to pH 2 and treated at 3 different temperatures (80, 120 and 160°C) with hydrogen peroxide dosages of 0 to 0.50 mL and heating times of 10 to 20 min, to investigate the release of sugar, solubilization of orthophosphates and ammonia and the disintegration of manure solids. The highest sugar yield of 7.4% was obtained at 160°C, 0 mL H₂O₂, and 15 min heating time. Irrespective of the heating time and dosage, more sugars were released at higher temperatures, compared to the lower temperatures. Temperature and hydrogen peroxide dosage were identified as the most important factors affecting the solubilization of orthophosphates, ammonia and VFA. Following microwave treatment, there was a maximum of 96% and 196% increase in orthophosphates and ammonia concentration, respectively. These results were both obtained at 160°C, 0.5mL hydrogen peroxide and 15 min heating time.

3.2 Introduction

Currently, the disposal of manure is predominately done through land application, which causes greenhouse gas emissions, ecological system eutrophication, and groundwater contamination (Wen et al., 2004). Increasingly stringent requirements as well as a lack of land availability are limiting the farmers' ability to use their land for direct manure disposal, requiring the development of new animal waste management strategies and alternatives, such as processes to turn the manure into saleable high value chemical products (Liao et al., 2006). Converting animal manure into value-added products also provides a potential alternative for treatment and disposal (Wen et al., 2004).

Previous research using the MW/H₂O₂-AOP to enhance sugar production from solid dairy manure was based on a pH range of 3.5 to 4.6 (Kenge, 2008). H₂O₂ was used in all the experiments. At this pH range the highest sugar yield was obtained at 160°C, 12 mL H₂O₂ and 7.5 minutes reaction time and pH of 4.2.

Kenge, (2008) reported that overall ammonia concentration was affected mainly by heating time and microwave temperature; higher ammonia concentration was obtained at a higher operating temperature with a longer heating time. Temperature and hydrogen peroxide dosage were key factors for orthophosphate release. High orthophosphate release could be obtained either at a low hydrogen peroxide dosage with a longer heating time, or at a higher hydrogen peroxide dosage with a shorter heating time. Recommendations were made to investigate the effects of increasing acid concentration on sugar production and nutrient release.

In this chapter, microwave digestion of solid dairy manure at pH 2 was investigated for the release of sugar and solubilization of nutrients, such as orthophosphates and ammonia-nitrogen, both with and without the aid of an oxidizing agent (hydrogen peroxide).

3.3 Materials and methods

3.3.1 Substrate

Solid dairy manure from the UBC Dairy Education and Research Centre in Agassiz, British Columbia, Canada was diluted to a TS concentration of 4.9 %. The pH was adjusted to two by adding concentrated sulfuric acid. The initial characteristics of the solid dairy manure substrate are presented in Table 3.1.

Table 3.1 Characteristics of solid dairy manure

Substrate	TS (%)	SCOD (mg/L)	TCOD (g/L)	VFA (mg/L)	Sugar (mg/L)	TP (mg/L)	TKN (mg/L)	PO ₄ -P (mg/L)	NH ₄ -N (mg/L)
Solid dairy manure	4.9	577 \pm 97	53.2 \pm 13.1	22 \pm 15.0	149 \pm 10	142 \pm 8	758 \pm 89	53 \pm 2.2	64 \pm 10

Data represents arithmetic mean of 3 replicates \pm standard deviation

3.3.2 Experimental design

In this study, a hydrogen peroxide dosage range of between 0 to 0.5 mL was used. Heating temperatures of 80, 120 and 160°C and heating times of 10, 15 and 20 min were selected. Based on this range of factors, 15 sets of experiments were generated by the JMP-IN statistical software using a response surface design. The experimental design is presented in Table 3.2. Sample volumes of 30 mL were used in each set. 3 replicates were run for each set of experiments.

Table 3.2 Experimental design

Set no.	Temperature (°C)	Heating time (min)	H ₂ O ₂ dosage	
			(mL)	(gH ₂ O ₂ /g dry solids)
1	120	15	0.25	0.051
2	160	20	0.25	0.051
3	120	15	0.25	0.051
4	80	10	0.25	0.051
5	80	15	0	0.000
6	160	15	0.5	0.201
7	160	15	0	0.000
8	80	20	0.25	0.051
9	160	10	0.25	0.051
10	120	10	0	0.000
11	120	15	0.25	0.051
12	80	15	0.5	0.102
13	120	20	0	0.000
14	120	20	0.5	0.102
15	120	10	0.5	0.102

3.4 Results and discussion

Table 3.3 Overview of results

Set no.	Sugar (mg/L)	Sugar (% of dry matter)	SCOD (g/L)	TCOD (g/L)	NH ₄ -N (mg/L)	NH ₄ -N (% increase)	PO ₄ -P (mg/L)	PO ₄ -P (% increase)	VFA (mg/L)
1	843±144	1.72	1.4±0.9	50.0±9.8	114±6	78	69±13	29	135±15
2	2453±308	5.01	13.0±0.8	51.5±25.6	160±8	150	104±9	96	265±78
3	659± 96	1.34	2.0±0.2	47.6±7.3	120±5	87	70±9	32	209±8
4	136±21	0.28	1.2±0.1	38.1±6.7	81±4	27	49±6	-8	109±10
5	191± 29	0.39	0.7±0.1	41.6±2.3	76±2	19	47±4	-12	51±4
6	2261±189	4.62	12.9±1.1	43.9±12.5	189±12	196	104±14	96	387±37
7	3623±513	7.39	17.4±2.0	49.1±4.3	117±6	83	84±10	58	197±73
8	145±19	0.29	1.3±0.1	44.7±4.9	84±3	82	52±4	-2	53±34
9	2836±438	5.79	15.7±1.6	47.4±5.0	150±6	134	98±11	84	226±97
10	154±30	0.31	1.2± 0.1	53.5±14.4	80±7	25	55±11	3	103±7
11	819±217	1.67	2.4±0.5	56.1±5.4	116±8	81	73±7	38	264±44
12	100±27	0.2	2.0±0.3	48.6±9.9	74±3	15	54±4	2	119±79
13	890±76	1.82	2.6±0.9	54.9±3.6	88±4	38	55±4	5	124±24
14	1066±113	2.18	10.1±0.8	49.7±3.6	141±7	121	84±10	58	249±43
15	512±204	1.05	2.2±0.4	54.6±16.0	140±10	119	77±6	46	323±9

Data represents arithmetic mean of 3 replicates ± standard deviation

$$\% \text{ increase of nutrients} = \frac{(\text{Final concentration (mg/L)} - \text{Initial concentration (mg/L)})}{\text{Initial concentration (mg/L)}} \times 100$$

3.4.1 Sugar production

Sugar yields ranged from 0.20 to 7.39% of dry matter (Table 3.3). The highest sugar yield was obtained for set 7, at 160°C, 0 mL H₂O₂ and 15 min heating time, while the lowest yield was obtained for set 12, at 80°C, 0.5 mL H₂O₂ and 15 min heating time. Figures 3.1a, 3.1b and 3.1c show surface plots of sugar production with respect to temperature, hydrogen peroxide dosage and heating time.

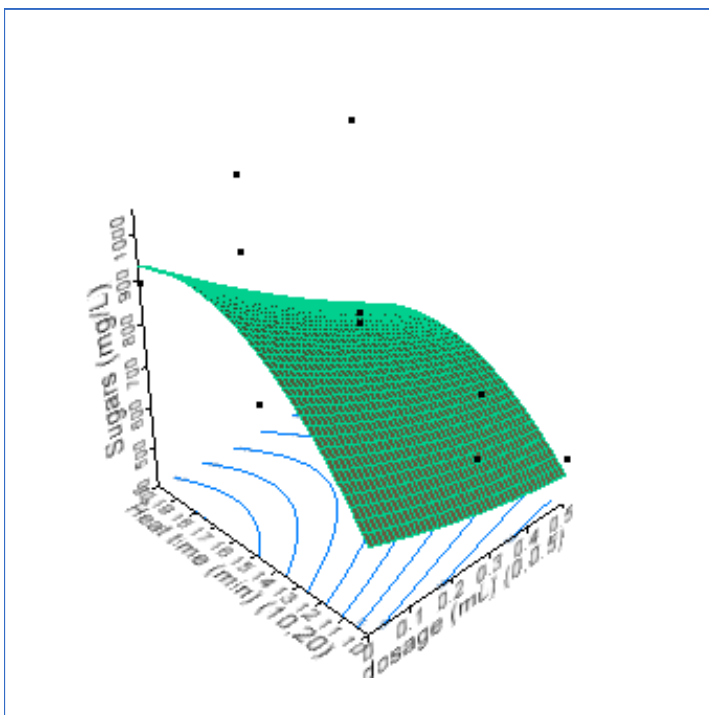


Figure 3.1a Surface profile showing sugar release with respect to heating time and H₂O₂ dosage

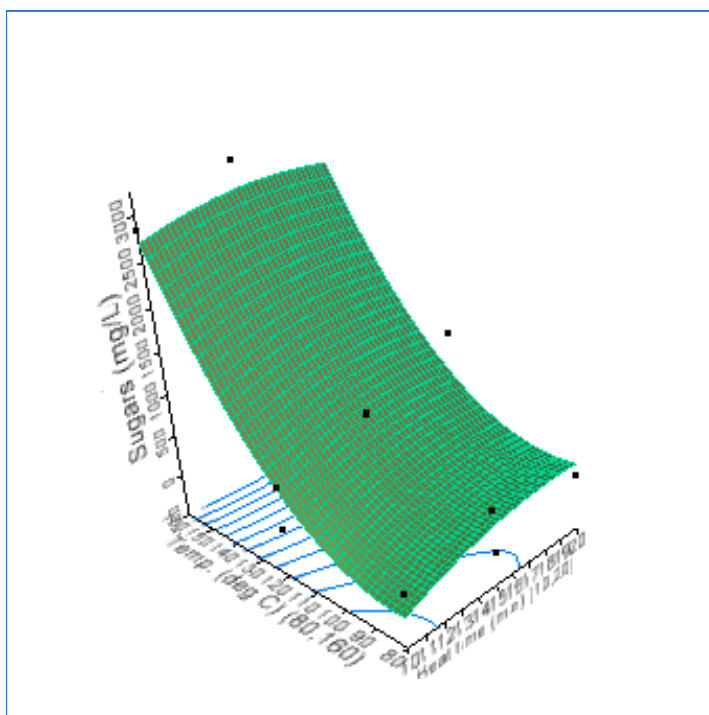


Figure 3.1b Surface profile showing sugar release with respect to temperature and heating time

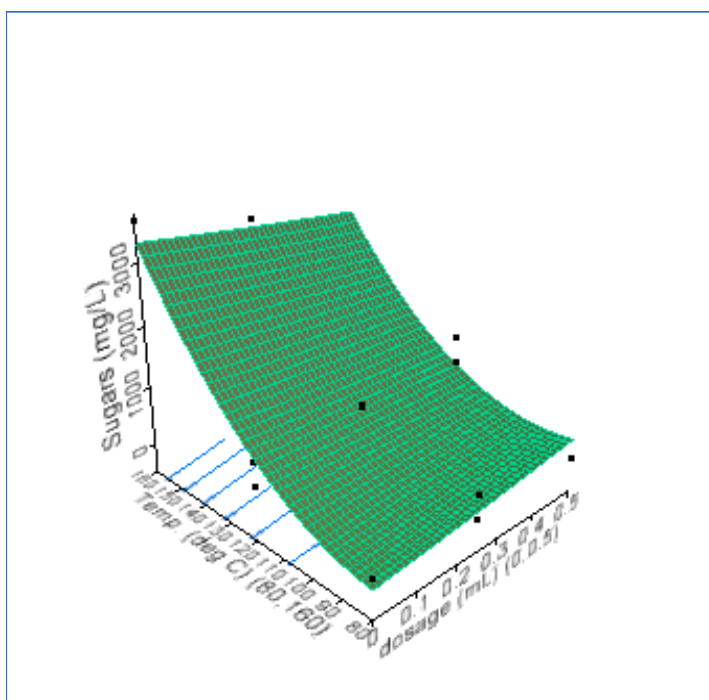


Figure 3.1c Surface profile showing sugar release with respect to temperature and H_2O_2 dosage

Figure 3.1a presents the combined effects of heating time and dosage on sugar production. Sugar production seemed to increase with an increase in time. Increasing dosage resulted in lower yields of sugar. In Kenge, (2008) however, where much higher hydrogen peroxide doses (6-12 mL) were used, an increase in dosage resulted in an increase in sugar production. Figure 3.1b shows the combined effects of temperature and heating time. Sugar production increased with increasing temperature. This observation is consistent with results obtained by Kenge, (2008). This is also consistent with results obtained by Liao et al., (2006), who demonstrated that low temperature under dilute acid condition did not convert much cellulose and hemicelluloses to sugars. Irrespective of the heating time, more sugars were released at higher temperatures compared to the lower temperatures. The combined effects of temperature and dosage are presented in Figure 3.1c. Irrespective of dosage, more sugars were released at higher temperatures compared to the lower temperatures. For Kenge, (2008) however, an increase of hydrogen peroxide dosage also increased sugar yield at lower temperatures, while sugar yield remained relatively constant at higher temperature. Temperature seems to be the most significant factor for sugar release followed by hydrogen peroxide dosage (Figures 3.1d and 3.2).

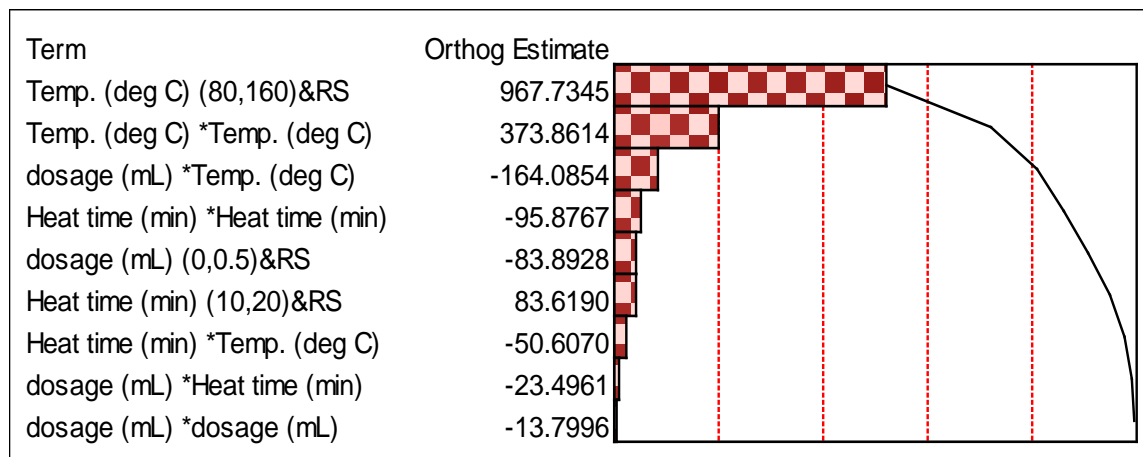


Figure 3.1d Pareto plot for sugar release factors

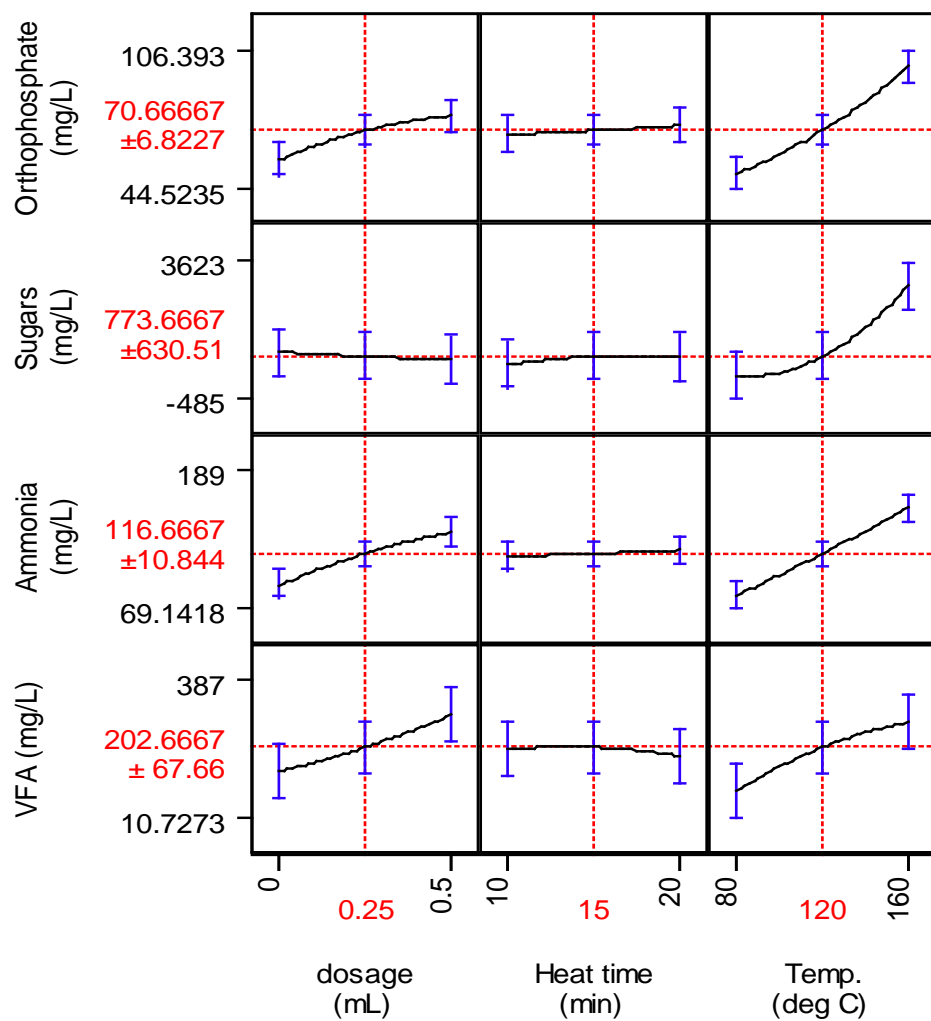


Figure 3.2 Prediction profiler showing the variation of VFA, ammonia, sugar and PO₄-P with the MW/H₂O₂-AOP operating factors

3.4.2 Nutrient release

3.4.2.1 Orthophosphate

Results are shown in Figures 3.3 a-d. The highest percentage increase in $\text{PO}_4\text{-P}$ concentration (96 %) was observed in both sets 2 (160°C , 0.25 mL H_2O_2 , 20 min) and 6 (160°C , 0.5 mL H_2O_2 , 15 min) (Table 3.3). Sets 4, 5 and 8, all operated at a temperature of 80°C , showed a decrease in $\text{PO}_4\text{-P}$ concentration after microwave treatment (8, 12 and 2% respectively). This could be due to the formation of polyphosphates at this low temperature, thereby making orthophosphate release temperature dependent. In a similar study by Kenge, (2008) at pH 4.1, the highest $\text{PO}_4\text{-P}$ increase was also obtained at 160°C , H_2O_2 dosage of 9 mL and 7.5 mL heating time, while the lowest percentage increases were generally observed at low temperatures of 60 and 80°C . A comparison of sets 2 and 8 indicated that more orthophosphate was released at temperatures of 160°C , than 80°C , given the same dosage and time (0.25 mL and 20 min). Figures 3.2 and 3.3d show that temperature is clearly the most important factor affecting $\text{PO}_4\text{-P}$ release, followed by hydrogen peroxide dosage. Kenge, (2008) also identified temperature and hydrogen peroxide dosage as the most important factors affecting $\text{PO}_4\text{-P}$ release. The results in this study indicate that operating temperatures below 120°C are not feasible for the purpose of orthophosphate release. For significant releases of $\text{PO}_4\text{-P}$, the microwave enhanced advanced oxidation process should be conducted at temperatures above 120°C (Liao et al., 2005a).

Figures 3.3a, 3.3b and 3.3c show the effects of temperature, hydrogen peroxide dosage and heating time on $\text{PO}_4\text{-P}$ release. Orthophosphate release increases with dosage (Figure 3.3a) but seems to remain constant with time (Figure 3.3a; 3.3b). However, when higher heating time is combined with higher dosage, more $\text{PO}_4\text{-P}$ is released as compared to when low heating time and high dosage are combined. In Kenge, (2008) however, more $\text{PO}_4\text{-P}$ was released at lower H_2O_2 and shorter heating time. The combined effects of temperature and heating time on the release of orthophosphates are presented in Figure 3.3b. At

any given heating time, more $\text{PO}_4\text{-P}$ is released when higher temperatures are employed, compared to lower temperatures.

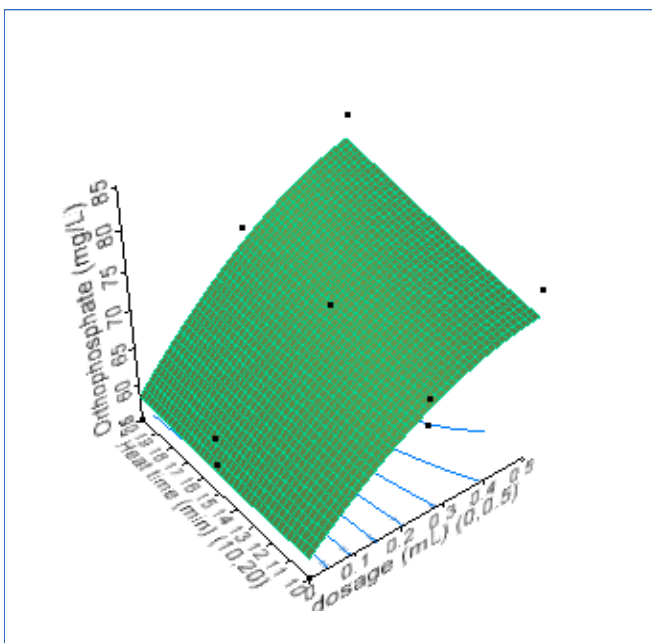


Figure 3.3a Surface profile for orthophosphate release with respect to heating time and H_2O_2 dosage

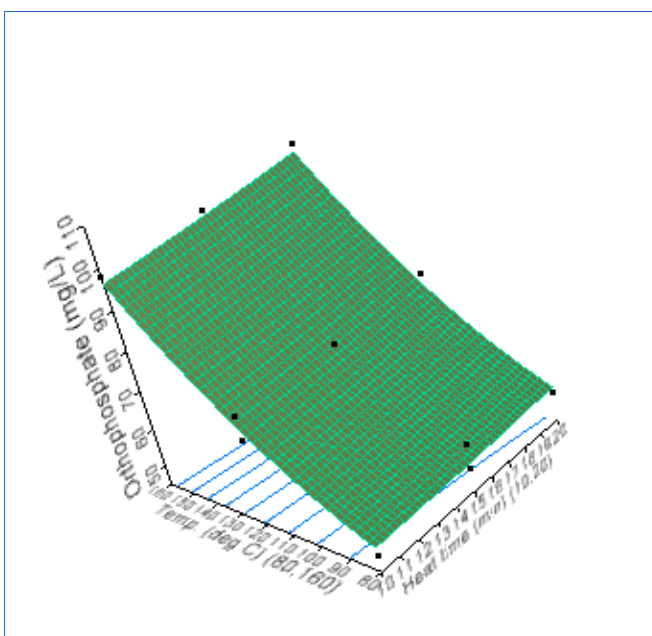


Figure 3.3b Surface profile for orthophosphate release with respect to temperature and heating time

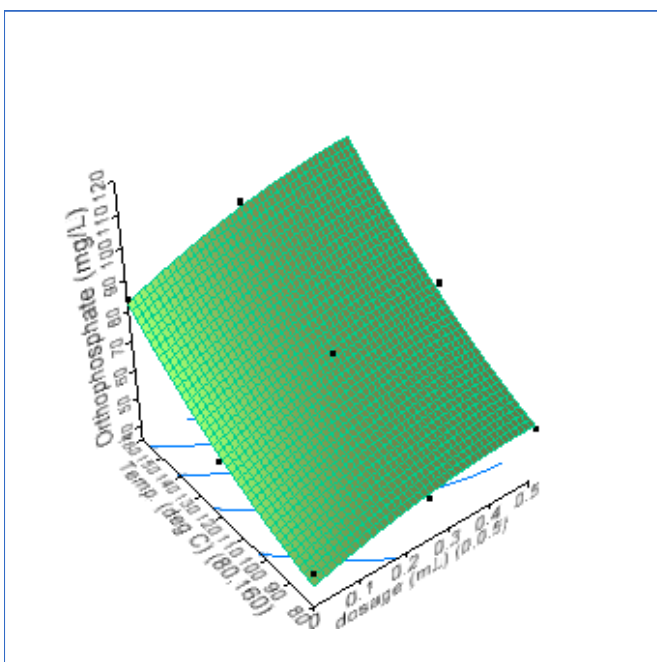


Figure 3.3c Surface profile for orthophosphate release with respect to treatment temperature and H₂O₂ dosage

When the effects of temperature and dosage are combined (Figure 3.3c), it is observed that more PO₄-P is released at higher dosage and higher temperatures as compared to lower dosage and high temperatures. Wong, (2006) confirms that the combined effects of hydrogen peroxide dosage and temperature contributes to the breakdown of polyphosphates. The importance of hydrogen peroxide is ascertained by comparing sets 5 and 12; 6 and 7; 10 and 15; 13 and 14. Although the results of these sets stress the importance of hydrogen peroxide in releasing more PO₄-P, they also show that PO₄-P can be solubilized by microwave treatment, even in the absence of hydrogen peroxide.

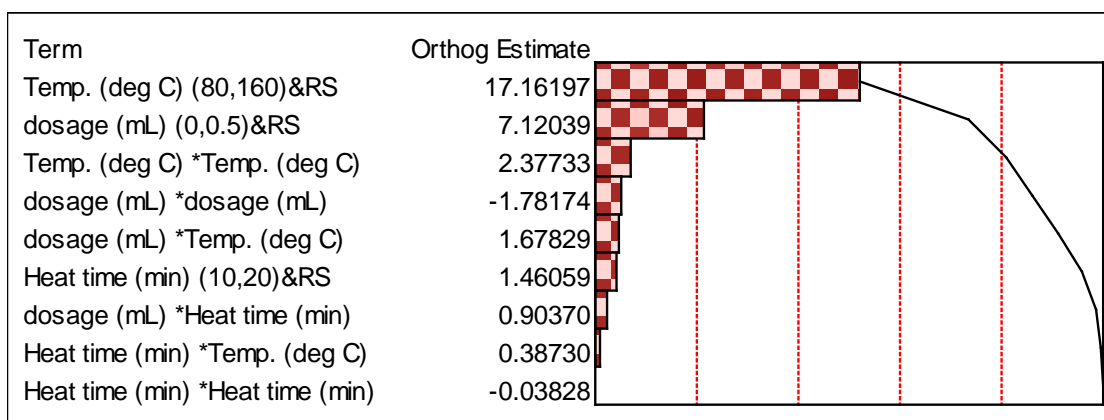


Figure 3.3d Pareto plot for orthophosphate release factors

3.4.2.2 Ammonia

Results are shown in Figures 3.4a-d. The highest percentage increase in ammonia concentration (196 %) was observed in set 6 (160°C, 0.5 mL H₂O₂, 15 min) (Table 3.3). The lowest percentage was observed in set 12 (80°C, 0.5 mL H₂O₂, 15 min.). At pH 4.2, Kenge, (2008) reported a maximum of 297 % increase in ammonia following microwave treatment at 160°C, 12 mL hydrogen peroxide dosage and 7.5 minutes heating time. Figures 3.2 and 3.4d show that ammonia release is most affected by treatment temperature, followed by dosage. Kenge, (2008) confirms the importance of temperature and dosage in ammonia release. Figures 3.4a, 3.4b, and 3.4c show the combined effects of temperature, hydrogen peroxide dosage and heating time on ammonia release.

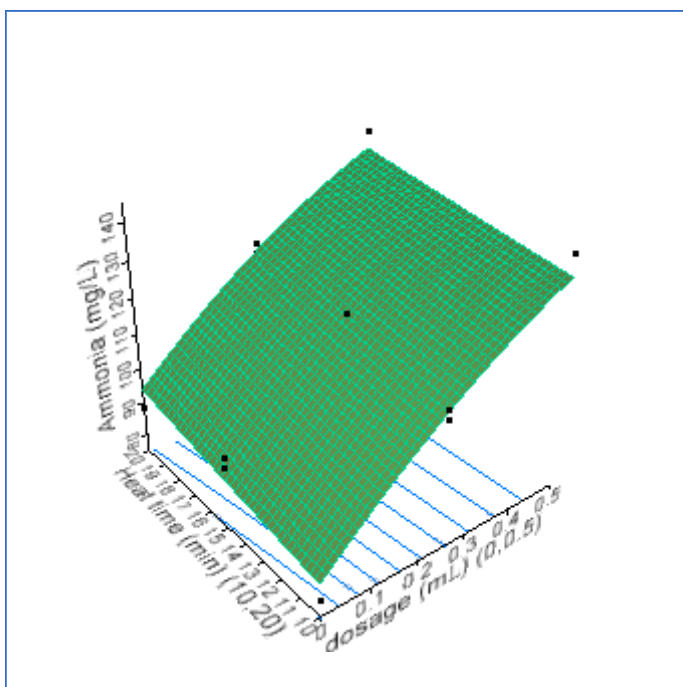


Figure 3.4a Surface profile for ammonia release with respect to heating time and H₂O₂ dosage

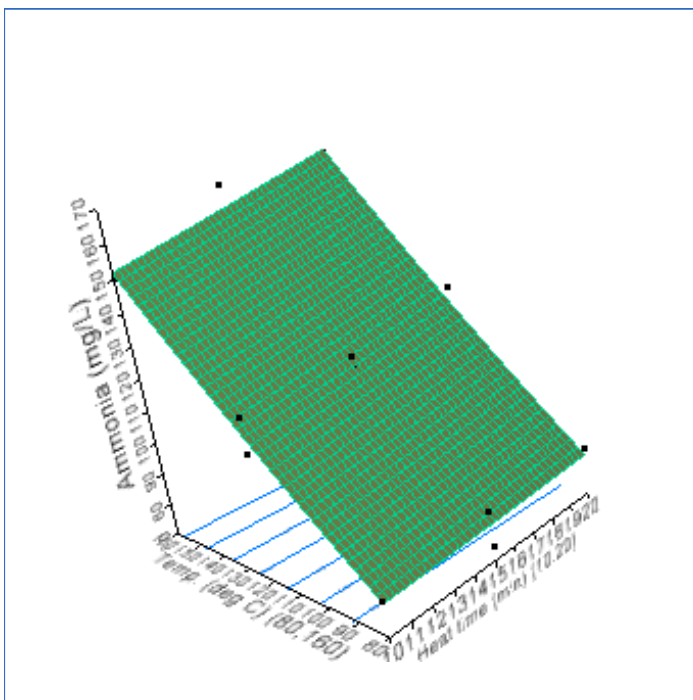


Figure 3.4b Surface profile for ammonia release with respect to temperature and heating time

Ammonia release increased with increasing dosage, while it remains seemingly constant with time (Figure 3.4a). It should be noted that though ammonia was solubilized using the microwave process alone, with no dosage, there was a further increase in the solubilization when the MW process was combined with H_2O_2 . This is evidenced by comparing sets 6 and 7; 10 and 15; 13 and 14. This confirms the importance of the H_2O_2 dosage on the solubilization of ammonia and is consistent with Qureshi et al., (2008a) who reports that hydrogen peroxide addition (MW/ H_2O_2 -AOP) resulted in higher soluble ammonia concentration.

An increase in temperature also increased ammonia release, irrespective of the heating time. This is clearly illustrated in Figure 3.4b. The combined effects of temperature and dosage (Figure 3.4c) indicated that more ammonia was released when the process was carried out at higher dosages and higher temperatures, compared to lower dosages and higher temperatures; this emphasizing the importance of higher dosages and temperatures on ammonia release. Kenge, (2008) also reported that a higher hydrogen peroxide dosage, at lower temperatures, did not appear to have aided in ammonia solubilization, and even decreased its concentration in the solution.

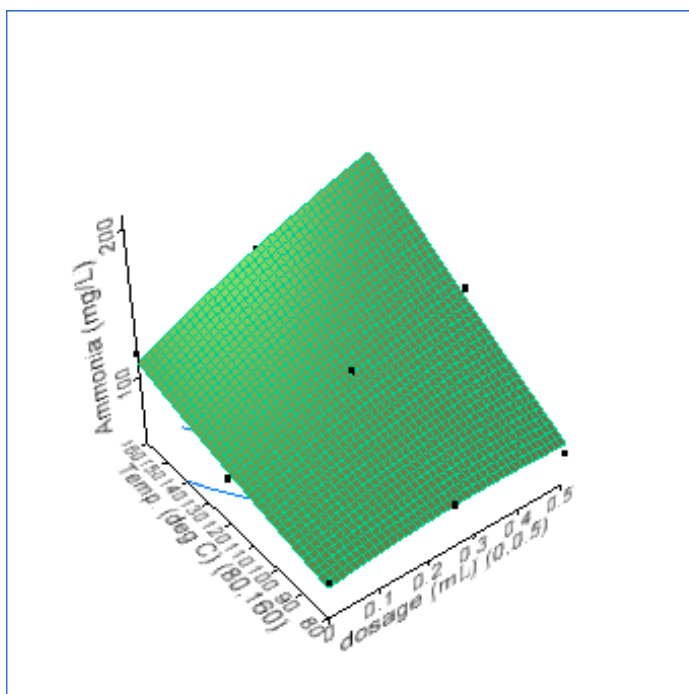


Figure 3.4c Surface profile for ammonia release with respect to temperature and H₂O₂ dosage

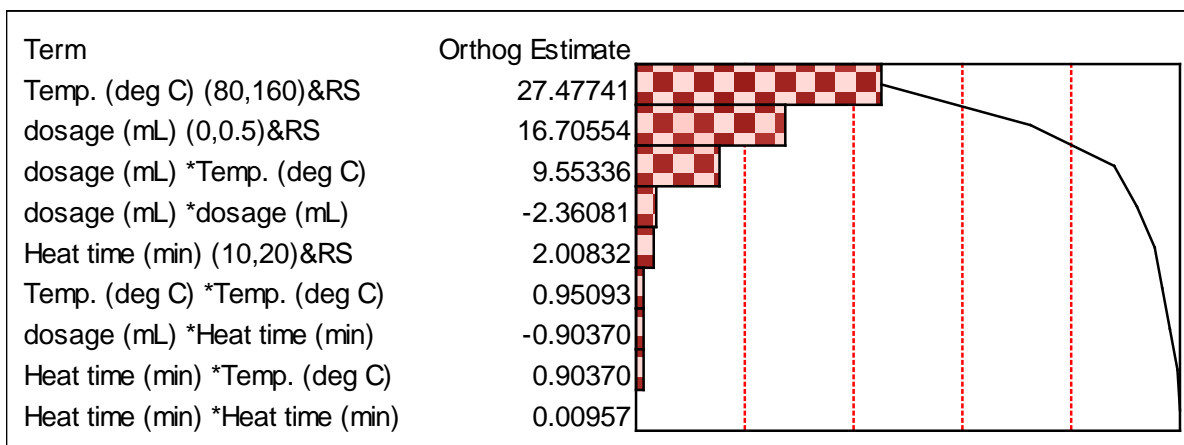


Figure 3.4d Pareto plot for ammonia release factors

3.4.3 Solids disintegration

Results are presented in Figures 3.5a-d. The disintegration of sludge solids can be expressed in terms of SCOD and VFAs (Kenge, 2008). The VFA in the treated samples consisted mainly of acetic and propionic acids. All VFA results were converted to equivalent concentrations of acetic acid. The highest concentration of VFAs and SCOD was released in set 6 (160 °C, 0.5 mL H₂O₂, 15 min). Figures 3.5a, 3.5b and 3.5c present variation of VFAs with the combined effects of time, dosage and temperature. Heating time seems to slightly affect the release of VFA (Figures 3.5a). This is evidenced by the flat slope of time in Figure 3.5 b. The effects of time on VFA release can be further investigated by comparing sets 2 and 9, 4 and 8, 15 and 14. A decrease in VFA release is observed when the heating time is increased from 10 to 20 min, with the temperatures and dosage being held constant.

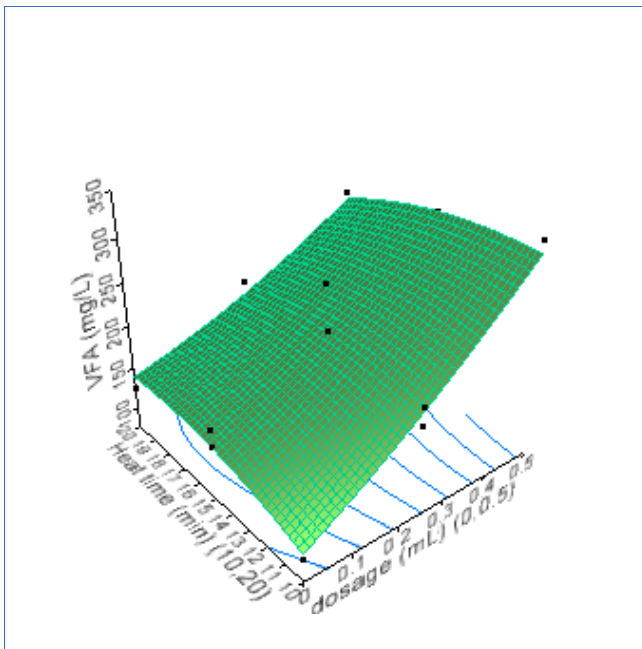


Figure 3.5a Surface profile for VFA release with respect to heating time and H₂O₂ dosage

Increasing the dosage increases the VFA. For example, at 80 degrees, set 5 (80 °C, 0mL, 15min) yielded 51mg/L while set 12 (80 °C, 0.5mL, 15 min) yielded 119 mg/L. At 120 °C, set 10 (120 °C, 0mL, 10 min)

yielded 103mg/L while set 15(120 °C, 0.5 mL, 10 min) yielded 323 mg/L. Also, at 160 °C, set 6 (160°C, 0.5mL, 15 min) yielded 387mg/L while set 7 (160 °C, 0mL, 15 min) yielded 197mg/L. Thus, in this study dosage seemed to be an important factor in VFA release. Although VFAs are produced using the MW process alone, further increase in VFA is observed when the microwave process is combined with H₂O₂. This can be confirmed by comparing sets 5 and 12; 6 and 7; 10 and 15; 13 and 14. In contrast, Kenge, (2008) identified heating time and temperature as the prime factors affecting VFA release. VFAs increased with an increase in temperature. This is seen by comparing sets 5 and 7, 8 and 2, 4 and 9, 6 and 12. In these sets, when heating time and dosage were kept constant, there was an increase in VFA production with an increase in temperature. The combined effects of high temperatures and high dosages yielded more VFAs compared to the combined effects of high temperatures and low dosages (Figure 3.5c). Figure 3.5d shows that temperature is the most important factor for VFA release followed by dosage.

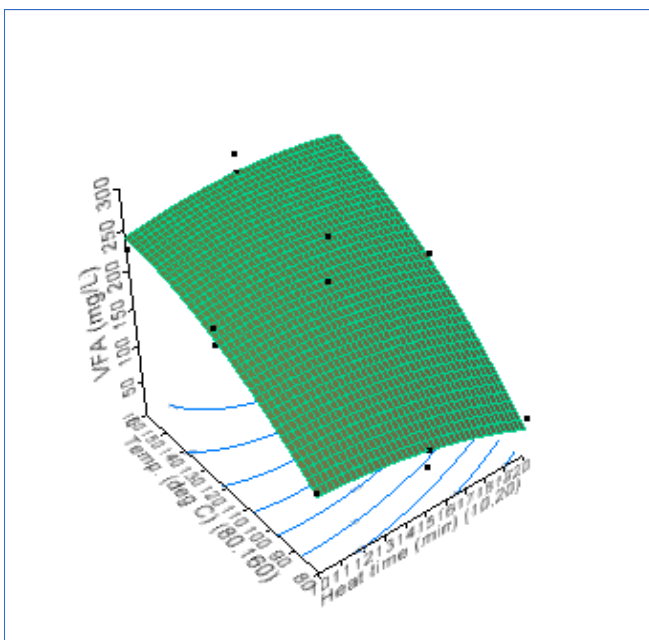


Figure 3.5b Surface profile for VFA release with respect to temperature and heating time

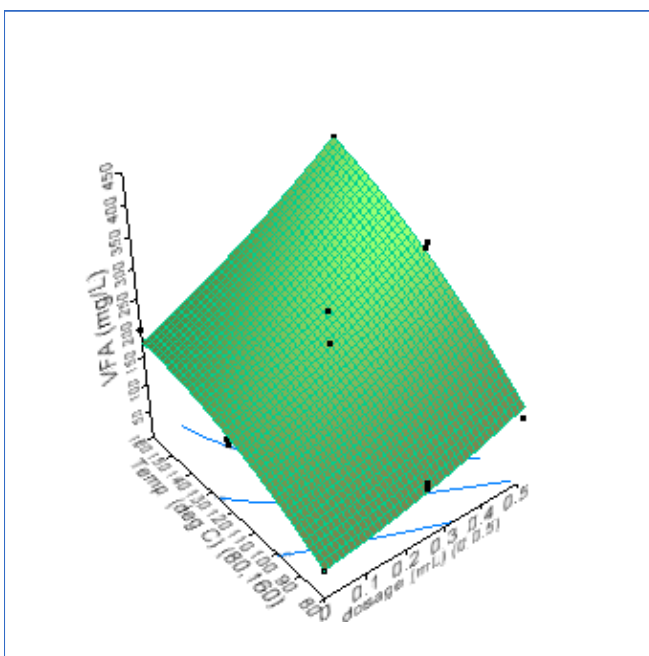


Figure 3.5c Surface profile for VFA release with respect to temperature H₂O₂ dosage

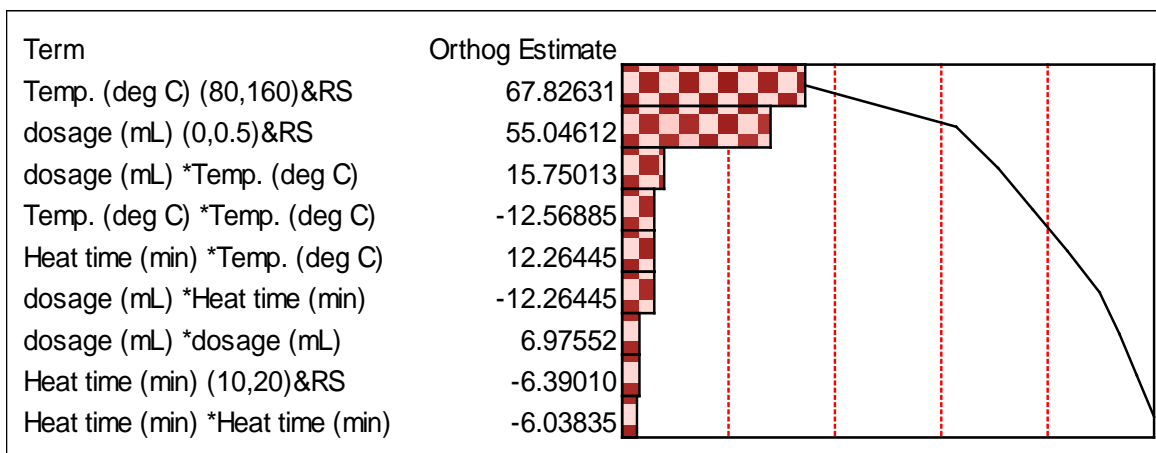


Figure 3.5d Pareto plot for VFA release factors

The higher the temperature the more SCOD was released. The highest SCOD concentrations were obtained at 160°C. Given the same heating time and dosage (15 min and 0 mL) set 7 at 160°C had the highest SCOD release (17.4 g/L) while set 5 at 80°C had the lowest SCOD release (0.7 g/L). The same trend exists when sets 2 and 8, 4 and 9, and 6 and 12 are observed. Elevated microwave temperatures

(>80°C) increased the decomposition of H₂O₂ into OH radicals and enhances both oxidation and particulate COD disintegration (Eskicioglu et al., 2008).

Significantly more SCOD was released when H₂O₂ was combined with the microwave process and hydrogen peroxide dosage was increased from 0 to 0.5 mL. This was, however, only observed at temperatures of 80 and 120°C. For example, a comparison of sets 5 and 12; 10 and 15; 13 and 14; showed an increase in SCOD when dosage was increased from 0 to 0.5 mL in the presence of constant temperature and time. This indicates that although COD was solubilized using the MW process alone, a combination of the MW process with H₂O₂ resulted in a further increase in COD solubilization. This trend was not observed at 160°C. At 160°C, there was a decrease in SCOD when dosage was increased from 0 mL to 0.5 mL (Table 3.3). The effects of time on SCOD release can be investigated by comparing sets 2 and 9; 4 and 8; 15 and 14. An increase in SCOD concentration was observed when the heating time was increased from 10 to 20 min, with the temperatures and dosage being held constant.

4. Factors affecting sugar production from cellulose using the microwave enhanced advanced oxidation process

4.1 Summary

A screening design generated by the JMP-IN statistical software was used to investigate the effects of microwave temperature, acid concentration, hydrogen peroxide dosage and heating time on the release of sugar from cellulose fibers. A temperature range of 80 to 160°C, acid concentration of 0.1 to 1%, hydrogen peroxide dosage of 0 to 0.5 g/g dry solids and heating time of 10 to 30 min was used for the MW/H₂O₂-AOP. The results indicated that sugar production was influenced by all the 4 factors investigated. The conditions under which sugar production were enhanced was 160°C, 1% acid, 0 mL hydrogen peroxide and 10 min heating time. Under these conditions, the corresponding sugar release was 3.1 % of dry matter. The results indicate that operating the microwave at high temperature and shorter heating times, in the absence of hydrogen peroxide, enhances the production of sugar. VFA was most influenced by acid concentration and temperature, while SCOD was most affected by hydrogen peroxide dosage.

4.2 Introduction

Lignocellulosics is a major component of animal manure (Wen et al., 2004). Dairy manure contains 22% cellulose, 12% hemicellulose and 13% lignin (Liao et al., 2007). Cellulose and hemicellulose in lignocellulosic feedstocks are a source of renewable sugars that could be converted to a variety of products. Jin et al., (2009) reported that the reduction of glucan/xylan of treated manure indicated that microwave-based thermochemical pretreatment facilitates the degradation of cellulose and hemicelluloses contained in manure fiber. Lignocellulosic materials are an attractive feedstock because they are available in large quantities at a relatively low cost (von Sivers and Zacchi 1996).

In the previous chapter, which was a follow up to Kenge, (2008), experiments conducted at pH 2 resulted in a low yield of sugar (7.4 % of dry matter) at 160 °C, 0 mL hydrogen peroxide and 15 min heating time. The low sugar yields could be attributed to the complex structure of the dairy manure. It should also be noted that dairy manure contains a higher percentage of cellulose (22%), compared to hemicellulose (12%) and lignin (13%). Since cellulose crystallinity has been identified as the most important structural feature affecting hydrolysis efficiency (Gan et al., 2003), experiments were conducted in this chapter to investigate sugar release from cellulose using the MW/H₂O₂-AOP. Four factors (temperature, heating time, H₂O₂ dosage and acid concentration) were chosen for a screening experiment to determine the effectiveness of the MW/H₂O₂-AOP for sugar production from cellulose fibers. The aim was to subsequently apply the results of the study to dairy manure lignocellulosic material, to enhance sugar production.

4.3 Experimental design

Whatman cellulose powder (medium length fibers) for column chromatography was used for these experiments. 30g of cellulose was diluted in 1L of distilled water. The initial characteristics of the cellulose substrate are presented in Table 4.1.

Table 4.1 Characteristics of the cellulose

Substrate	TS (%)	SCOD (mg/L)	TCOD (g/L)	VFA (mg/L)	Sugar (mg/L)
Cellulose	3	53 ± 0	46.5 ± 5.8	0 ± 0	0 ± 0

Data represents arithmetic mean of 3 replicates ± standard deviation

Two acid concentrations (1% and 0.1%, v/ v representing strong and weak acid respectively), were studied at three H₂O₂ dosages (0.0, 0.25 and 0.5g/g of dry solids), three treatment temperatures (80, 120 and 160°C) and three heating times (10, 20, and 30 min). Using a screening design, the JMP-IN statistical software was used to generate 9 experimental runs. The experimental design is presented in Table 4.2.

Table 4.2 Experimental design

Set no.	Temperature (°C)	H ₂ SO ₄ conc. (%)	H ₂ O ₂ dosage (g/g dry solids)	Heating time (min)
1	80	1	0.5	10
2	160	0.1	0	30
3	160	0.1	0.5	10
4	120	0.1	0.25	20
5	80	1	0	30
6	160	1	0.5	30
7	80	0.1	0.5	30
8	160	1	0	10
9	80	0.1	0	10

4.4 Results and discussion

4.4.1 Sugar production

Data is presented in Figures 4.1-4.4 and a summary of the results is given in Table 4.3. Sugar production is affected by all the four operating conditions of temperature, H₂O₂ dosage, acid concentration and heating time (Figure 4.1 and 4.2). Sugar production decreases within creasing H₂O₂ dosage or heating time. On the other hand, increasing acid concentration or temperature increases sugar production. Following microwave treatment, sugar increased from 0mg/L in the initial cellulose substrate to a maximum of 939 mg/L (corresponding to a yield of 3.13 % of dry matter) was obtained for set 8 (160°C, 1% acid, 0 mL H₂O₂, 10 min). The lowest yield, 0.06% was obtained for sets 3 and 5 (160°C, 0.1% acid, 0.5 mL H₂O₂, 30 min and 80°C, 1% acid, 0 mL H₂O₂, 30 min respectively). Higher temperatures and shorter heating times were, therefore, beneficial for increasing sugar yields. This conclusion is consistent with studies by Liao et al., (2006).

Table 4.3 Overview of results

Set no.	Sugar (mg/L)	Sugar (% of dry matter)	SCOD (g/L)	TCOD (g/L)	VFA (mg/L)
1	117±91.8	0.39	7.7±1.5	42.7±5.3	13±4.7
2	295±125	0.98	1.4±0.0	46.0±4.2	19±3.6
3	19 ±11.5	0.06	4.9±2.2	37.5±4.4	22±3.3
4	20 ±8	0.07	5.6±0.8	56.21±6.2	3±1.6
5	17±2.3	0.06	0.1±0.0	45.8±2.5	3±0.6
6	24±10	0.08	4.5±0.9	46.4±1.2	77±33.3
7	53±25.3	0.18	9.5±0.2	72.6±4.6	10±1.2
8	939±21.2	3.13	4.8±0.7	46.4±1.6	78±12.2
9	42±7.2	0.14	0.1±0.0	49.4±1.9	2±0.3

Data represents arithmetic mean of 3 replicates ± standard deviation

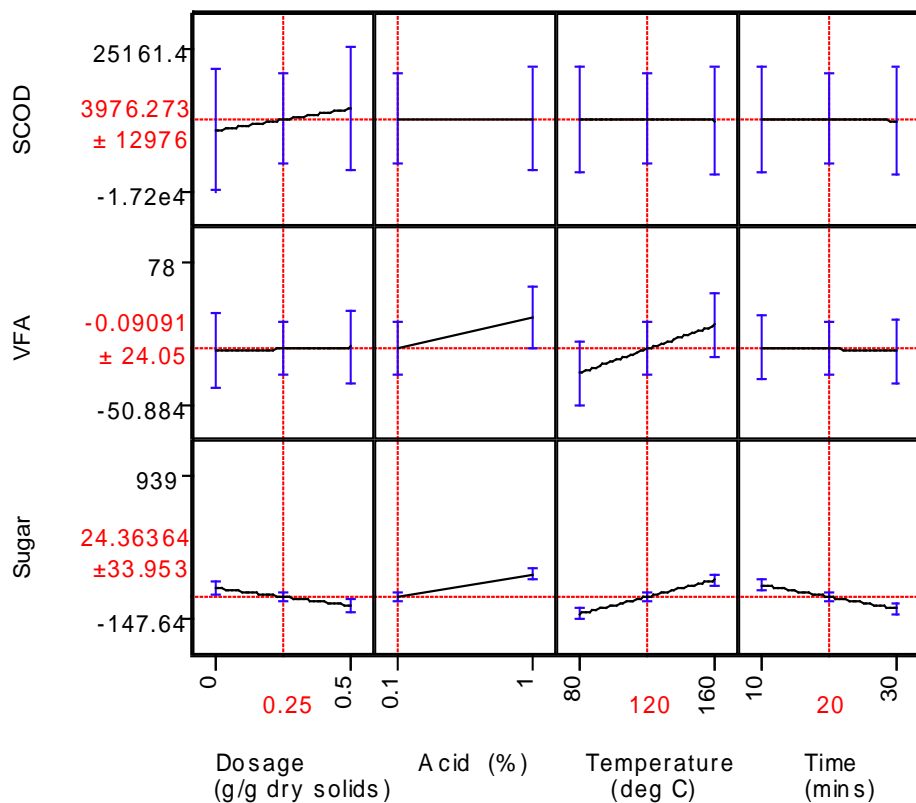


Figure 4.1 Prediction profiler showing the response of sugar, SCOD and VFA to the MW/H₂O₂-AOP operating parameters

4.4.2 Solids disintegration

SCOD appears only to be most affected by hydrogen peroxide dosage (Figures 4.1 and 4.4). Increasing the hydrogen peroxide dosage increases the SCOD concentration. Acid concentration, temperature and heating time do not seem to have significant influence on the solubilization of COD. Therefore the solubilization of COD in cellulose fibers seems to be is mainly an oxidative process and not due to thermal decomposition. While increasing acid concentration and temperature increases the formation of VFAs, dosage and time do not seem to have significant influence on VFA production (Figure 4.1 and 4.3). VFAs in the MW/H₂O₂-AOP treated cellulose comprised mainly of acetic acid.

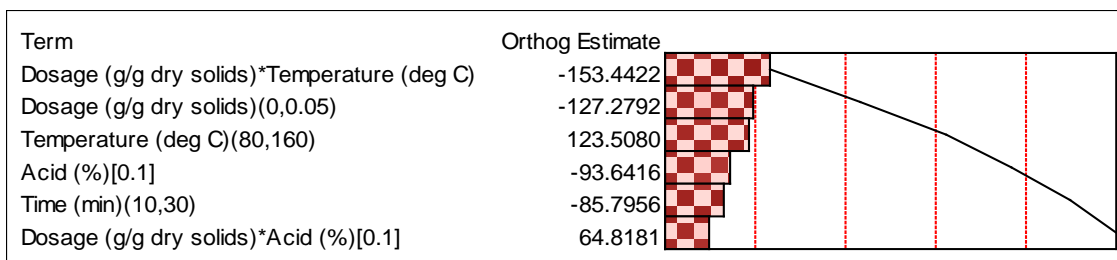


Figure 4.2 Pareto plot for sugar release factors

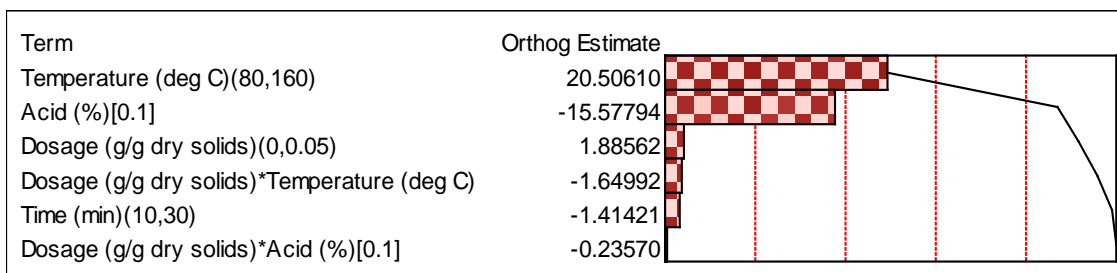


Figure 4.3 Pareto plot for VFA release factors

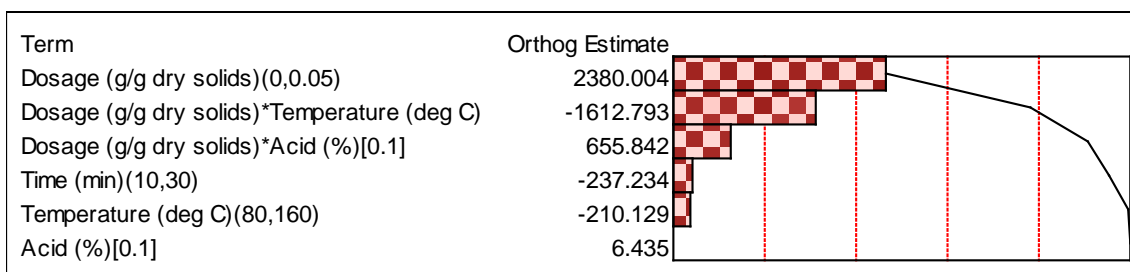


Figure 4.4 Pareto plot for SCOD release factors

5. Sugar production from cellulose fibers at 1, 3 and 10% sulfuric acid using the microwave enhanced advanced oxidation process

5.1 Summary

Cellulose fibers with a TS content of 3.0% was treated at three different sulfuric acid concentrations (1, 3 and 10% v/v), two heating times (20 and 60 min) and two temperatures (120 and 160 °C) using the MW/H₂O₂-AOP. The aim of the experiments was to study the effects of increasing acid concentrations on sugar production from cellulose fibers. The results indicated that sugar concentration increased when the acid concentration was increased from 1% to 3%, but decreased when the concentration was increased to 10%. The highest sugar yield (14.7%) was at 160 °C, 20 min and 3% acid. More sugar was produced at 160 °C compared to 120 °C. At 1 and 3% acid sugar production was higher at 20 min heating time, compared to 60 min. For 10%, however, increasing the heating time to 60 min increased the sugar production.

5.2 Introduction

In Chapter 4, sugar production from cellulose was affected by all four MW/H₂O₂-AOP operating factors of temperature, heating time, H₂O₂ dosage and acid concentration. The results indicated that increasing acid concentration or temperature increases sugar production. However, at the range of acid concentrations used (that is, between 0.1% and 1%), sugar yields were very low; the highest being 3.13 % of dry matter. Therefore, in this present study, experiments were conducted as a follow up to chapter 4 to further investigate the possibility of enhancing sugar yields from cellulose by increasing acid concentration. Three acid concentrations were selected at 1, 3 and 10% v/v for further experiments, to study the effects of increasing acid concentrations on sugar production.

5.3 Materials and methods

5.3.1 Substrate

Medium length cellulose fibers with TS concentration of 3% was used for these sets of experiments. The initial characteristics of the cellulose are presented in Table 5.1

Table 5.1 Characteristics of the cellulose

Substrate	TS (%)	SCOD (mg/L)	TCOD (g/L)	VFA (mg/L)	Sugar (mg/L)
Cellulose	3	53 \pm 0	46.5 \pm 5.6	0 \pm 0	0 \pm 0

Data represents arithmetic mean of 3 replicates \pm standard deviation

5.3.2 Experimental design

The effects of increasing acid concentrations (1, 3 and 10% v/v) on sugar production from cellulose, using the MW/H₂O₂ – AOP, was studied at constant treatment temperature of 120°C and heating time of 20 min. Samples at the three different acid concentrations were also treated at 60 min heating time and 120°C and compared to those previously treated at 20 min and 120°C, to study the effects of different heating times on sugar production. Finally, to study the effects of changing temperatures on the process, samples at 3 and 10 % acid were then treated at 160°C and 20 min and compared to those previously treated at 120°C and 20 min. For all the experiments, the H₂O₂ dosage was maintained constant at 0.3 mL. The experimental design is presented in Table 5.2.

Table 5.2 Experimental design

Set no.	Acid concentration (%)	Temperature (°C)	H ₂ O ₂ dosage (mL)	Heating time (min)
1	1	120	0.3	20
2	1	120	0.3	60
3	3	120	0.3	20
4	3	120	0.3	60
5	3	160	0.3	20
6	10	120	0.3	20
7	10	120	0.3	60
8	10	160	0.3	20

5.4 Results and discussion

5.4.1 Sugar production

Figures 5.1, 5.2, and 5.3 present the trends of sugar production with respect to different acid concentrations, temperatures and heating times. Sets 1, 3 and 6 were compared to investigate the variation of sugar production with the different acid concentrations of 1, 3 and 10% respectively and the results presented in Figure 5.1. The operating conditions at which this trend was investigated was 120°C, 20 min and 0.3mL H₂O₂. At 1%, the sugar concentration was 29 mg/L doubling up to 59 % following an increase of the acid concentration to 3%. Therefore, sugar concentration increased with increasing acid concentration from 1% to 3% (Figure 5.1). At 10% acid concentration, sugar production decreased to 12 mg/L (Table 5.3). As a result of this observation, coupled with the added benefit of the environmental benefits of using a lower acid concentration (Liao et al., 2006), a 3% acid concentration was selected for the rest of the studies in this research involving acid hydrolysis of dairy manure.

Table 5.3 Overview of results

Set no.	Sugar (mg/L)	Sugar (% of dry matter)	SCOD (g/L)	TCOD (g/L)
1	29 \pm 16	0.1+0.05	3.2 \pm 0.2	46.6 \pm 2.8
2	11 \pm 2	0.04+0.01	3.4 \pm 0.9	46.9 \pm 3.8
3	59 \pm 37	0.2+0.12	4.3 \pm 1.6	50.6 \pm 3.6
4	25 \pm 7	0.08+0.02	2.5 \pm 0.1	45.5 \pm 3.2
5	4413 \pm 356	14.7+1.19	9.4 \pm 1.7	41.8 \pm 3.4
6	12 \pm 6	0.04+0.02	3.6 \pm 0.2	40.3 \pm 2.9
7	46 \pm 25	0.15+0.08	3.5 \pm 0.7	39.3 \pm 1.5
8	54 \pm 4	0.18+0.01	6.0 \pm 1.1	44.3 \pm 4.1

Data represents arithmetic mean of 3 replicates \pm standard deviation

Sets 3 and 6, representing microwave treatment at 120°C for 3 and 10 %, respectively were compared to sets 5 and 8, representing microwave treatment at 160°C degrees for 3 and 10 %, respectively, to investigate the variation of sugar production with temperature at 120°C and 160°C. The results are presented in Figure 5.2. The operating conditions at which this trend was investigated were 20 min and 0.3 mL H₂O₂. Sugar production increased when temperature was increased from 120 to 160°C. This result is consistent with Liao et al., (2006) who indicated that low temperature, under dilute acid conditions did not convert much cellulose and hemicelluloses to sugars. The authors point out however, that the higher the temperature, the more rapid the sugars are consumed by side reactions such as dehydration reaction and a browning reaction; the latter referring to the caramelization of sugars at very high temperatures. Figure 5.2 also confirmed that more sugar was produced at 3% than at 10%. Figure 5.2 also confirmed that more sugar was produced at 3% than at 10%.

Sets 1, 3, 6 representing microwave treatment at 20 min for 1, 3 and 10%, respectively were compared to sets 2, 4 and 7, representing treatment at 60 min for 1, 3 and 10%, respectively, to investigate the

variation of sugar production with heating time. The results are presented in Figure 5.3. The operating condition at which this trend was investigated was 120°C and 0.3 mL H₂O₂. At 1 and 3% acid concentration, sugar production was higher at 20 min heating time compared to 60 min. For 10% however, increasing the heating time to 60 min increased the sugar production.

Highest sugar yield (14.7% of dry matter) was at 160°C, 20 min and 3% acid, indicating that, for enhanced sugar production from cellulose, the MW/H₂O₂-AOP should be operated at higher temperatures and shorter run times. A study by Liao et al., (2006) concluded that as a result of the side reactions, such as dehydration and browning reactions, shorter time and higher temperature were beneficial for increasing sugar yields.

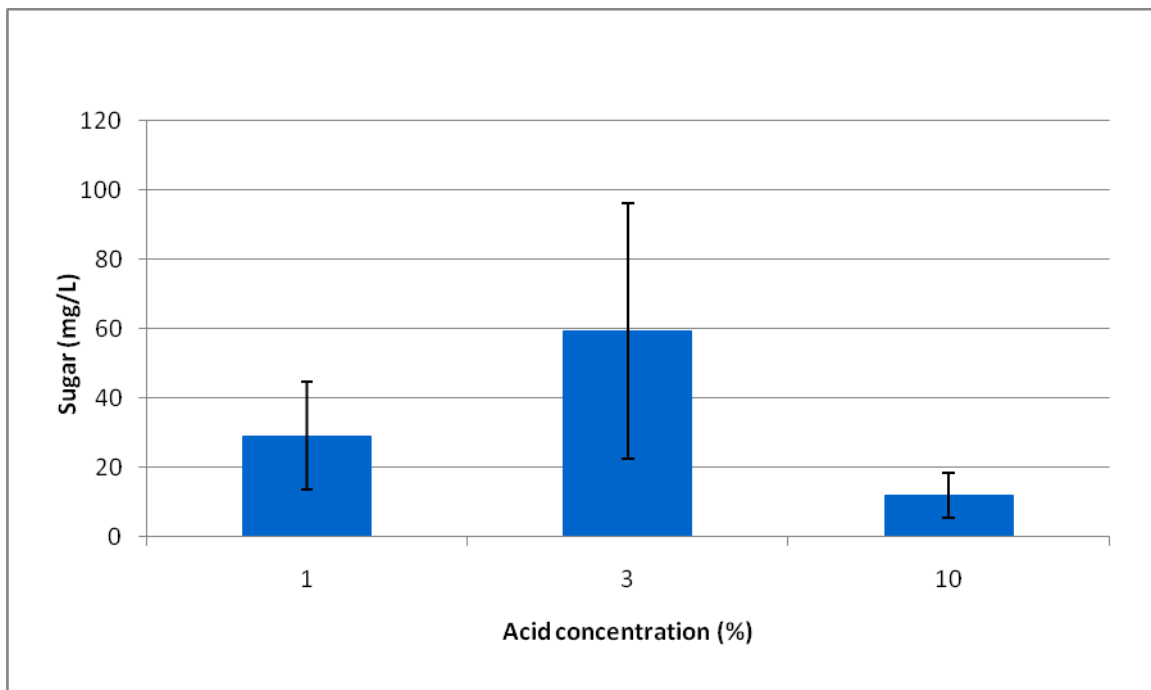


Figure 5.1 Sugar production at different acid concentrations

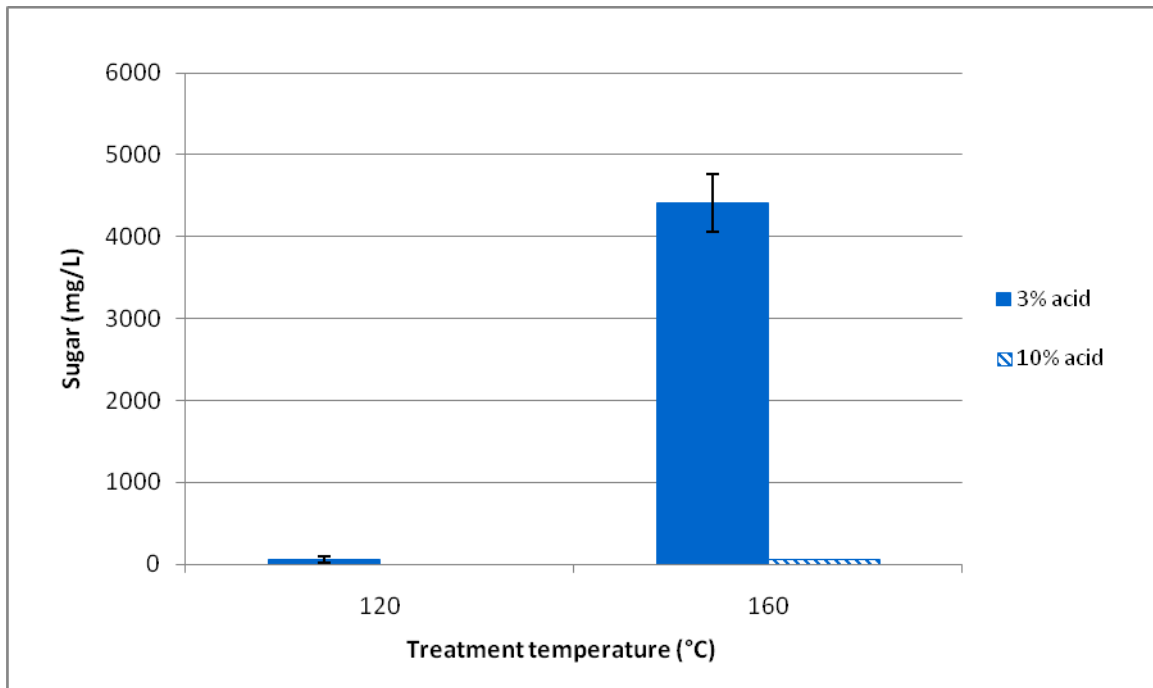


Figure 5.2 Sugar production at different treatment temperatures

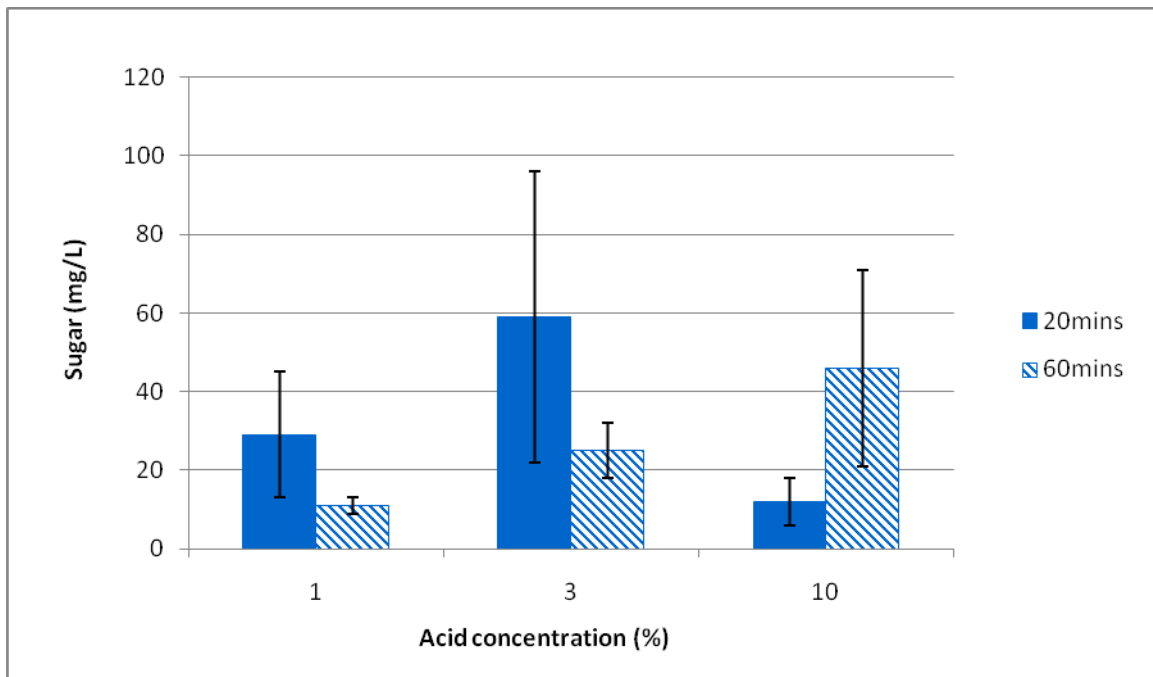


Figure 5.3 Sugar production at different heating times

5.4.2 Solids disintegration

Generally, SCOD released was higher at 160°C compared to 120°C. Similar to the trends observed in sugar production, SCOD concentration increased when acid concentration was increased from 1 to 3 % but decreased with an increase to 10 % (Table 5.3). More SCOD is released at higher temperatures of 160°C, compared to 120°C. At 120°C and 1% acid concentration, there was no significant difference between the release of SCOD at 20 and 60 min. A similar trend is observed at 120°C and 10% acid concentration. However, at 120°C and 3% acid concentration, more SCOD (almost double) is released at 20 min than at a 60 min heating time.

6. Two-stage dilute acid hydrolysis of solid dairy manure for sugar and nutrient release using the microwave enhanced advanced oxidation process

6.1 Summary

A two-stage, acid hydrolysis process, combining advanced oxidation process and microwave heating, was used for the release of sugar and solubilization of $\text{PO}_4\text{-P}$ and $\text{NH}_4\text{-N}$ from solid dairy manure with TS of 5.4%, TP of 355 mg/L and TKN of 1420 mg/L. For the first stage, solid dairy manure, with a sulfuric acid concentration of 3%, was treated at two temperatures (120 and 160°C), two hydrogen peroxide dosages (0 and 2 mL) and two heating times (20 and 60 min). Operating conditions of 160°C, 0 mL H_2O_2 and 20 min gave the highest sugar yields at 15.5% of the total dry matter, while the lowest yield was observed at 160°C, 2 mL H_2O_2 and 60 min. A maximum of 41 % of total phosphorus was released as $\text{PO}_4\text{-P}$ at 160°C, 0 mL H_2O_2 , 60 min, and 160, 2 mL, 60 min. 13% of TKN was released as ammonia at 160°C, 2 mL, 20 min. The lowest $\text{PO}_4\text{-P}$ and ammonia concentrations were released at 120, 0 mL and 20 min. In the second stage, solid residues from the first stage were treated at 3% acid, 160°C, hydrogen peroxide dosages of 0 and 2 mL and a constant temperature of 5 min. There was a further release of a maximum of 4% of sugar from acid hydrolysis of the residues (1.7%TS) previously treated at 120, 0 mL and 20 min. The results of this set of experiments indicated that it would be advantageous to operate the microwave at higher temperatures and shorter times, in the absence of hydrogen peroxide, to enhance sugar production from solid dairy manure; for nutrient release, it would be preferable to run the MW/ H_2O_2 -AOP at higher temperatures, longer run times and in the presence of hydrogen peroxide dosage.

6.2 Introduction

Manure lignocellulosics represents a large potential source of carbohydrates capable of being converted to useable mono-sugars (Liao, 2004). The sugars produced from the dairy manure lignocellulosic material can subsequently be fermented into fuel ethanol or organic acids or by yeasts or bacteria (Wen et al., 2004). Because lignocellulosic biomass is naturally resistant to breakdown to its component sugars, a pretreatment step is needed to open up the structure of the material (Wyman, 1994). Acid hydrolysis is a

typical process used to convert lignocellulosic material to sugars. In general, concentrated acid hydrolysis is much more effective than dilute acid hydrolysis (Harris, 1949). However, concentrated acid hydrolysis has a major drawback in its use of highly concentrated acid that could cause serious environmental concerns (Sun and Cheng, 2002). Acids or hemicellulases hydrolyze the hemicellulose polymer to release its component sugars (Mosier et al., 2005), leaving a porous structure of primarily cellulose and lignin that is more accessible to enzymatic or chemical action by sulfuric or other acids (Wyman, 1994; Mosier et al., 2005). The sugars produced from the dairy manure lignocellulosic material can be fermented into fuel ethanol or organic acids or by yeasts or bacteria (Wen et al., 2004). Conventional acid hydrolysis of lignocellulosic materials in dairy manure for sugar production has included one-stage hydrolysis with decrystallization, one stage hydrolysis, two-stage hydrolysis, two-stage hydrolysis with alkaline extraction and two-stage hydrolysis with decrystallization (Chen et al., 2005). Two-stage acid hydrolysis processes have been proven to produce more sugars than one stage hydrolysis procedures (Chen et al., 2005; Choi and Mathews 1996).

All tertiary wastewater facilities eliminate phosphorus (either by chemical or biological removal) as a non-recyclable material (de-Bashan and Bashan, 2004). Reducing phosphorus released in wastewater has important environmental implications, as the phosphorus released into water bodies from wastewater treatment plants can have a range of effects, including algal blooms, which reduce light penetration and available oxygen in the water body (Shu et al., 2006). Recovering phosphorus in the form of struvite is an effective way to reduce phosphorus discharge to ecological systems. To successfully recover phosphorus from animal manure via struvite crystallization, pretreatment processes are required to render phosphorus, ammonium and magnesium into a soluble form (Pan et al., 2006; Doyle and Parsons, 2002; Kenge, 2008).

Microwave-based thermochemical pretreatment enhances manure anaerobic digestibility (through fiber degradation) and struvite precipitation (through phosphorus solubilization) (Jin et al., 2009). In this

chapter, solid dairy manure samples were acid hydrolyzed at 3% sulfuric acid concentration using the MW/H₂O₂ – AOP and a two-stage hydrolysis process. The objective was to investigate conditions that would maximize sugar production, as well as nutrient release, from solid dairy manure.

6.3 Materials and methods

6.3.1 Substrate and sample preparation

Field separated solid dairy manure was used as the substrate for the first stage. The remaining solids from the first stage were used as the substrate for the second stage. For the first stage, the solid dairy manure sample was diluted with distilled water to 5.4% total solids. Manure samples were characterized for their basic composition. The initial characteristics of the manure are presented in Table 6.1.

Table 6.1 Characteristics of the dairy manure

TS (%)	SCOD (g/L)	TCOD (g/L)	VFA (mg/L)	Sugar (mg/L)	TP (mg/L)	PO ₄ -P (mg/L)	TKN (mg/L)	NH ₄ -N (mg/L)
5.4	5.7±1.0	66.0±6.6	0±0	898±415	355±21	48±1.0	1420±60	92±2.4

Data represents arithmetic mean of 3 replicates ± standard deviation

6.3.2 Experimental design

Based on the results obtained in chapter 5, two treatment temperatures, 120 and 160° C and two heating times 20 and 60 min, were selected for the first stage of the dilute acid hydrolysis process. H₂O₂ dosages of zero (0) and 2.0 mL were selected to determine the effects of the presence or absence of H₂O₂ on the process (Table 6.2). The samples were then acidified to a concentration of 3% H₂SO₄ and treated. Total sample volume for each set was 30 mL. Six replicates were used in each set of experiments. Following microwave treatment, the solids remaining from each sample from the first stage were dried at 40° C for a week and used as the substrate for the second stage of the dilute acid hydrolysis process. Figure 6.1

presents a schematic of the procedures used for the two-stage acid hydrolysis process. Table 6.3 presents the detailed experimental design for the second stage.

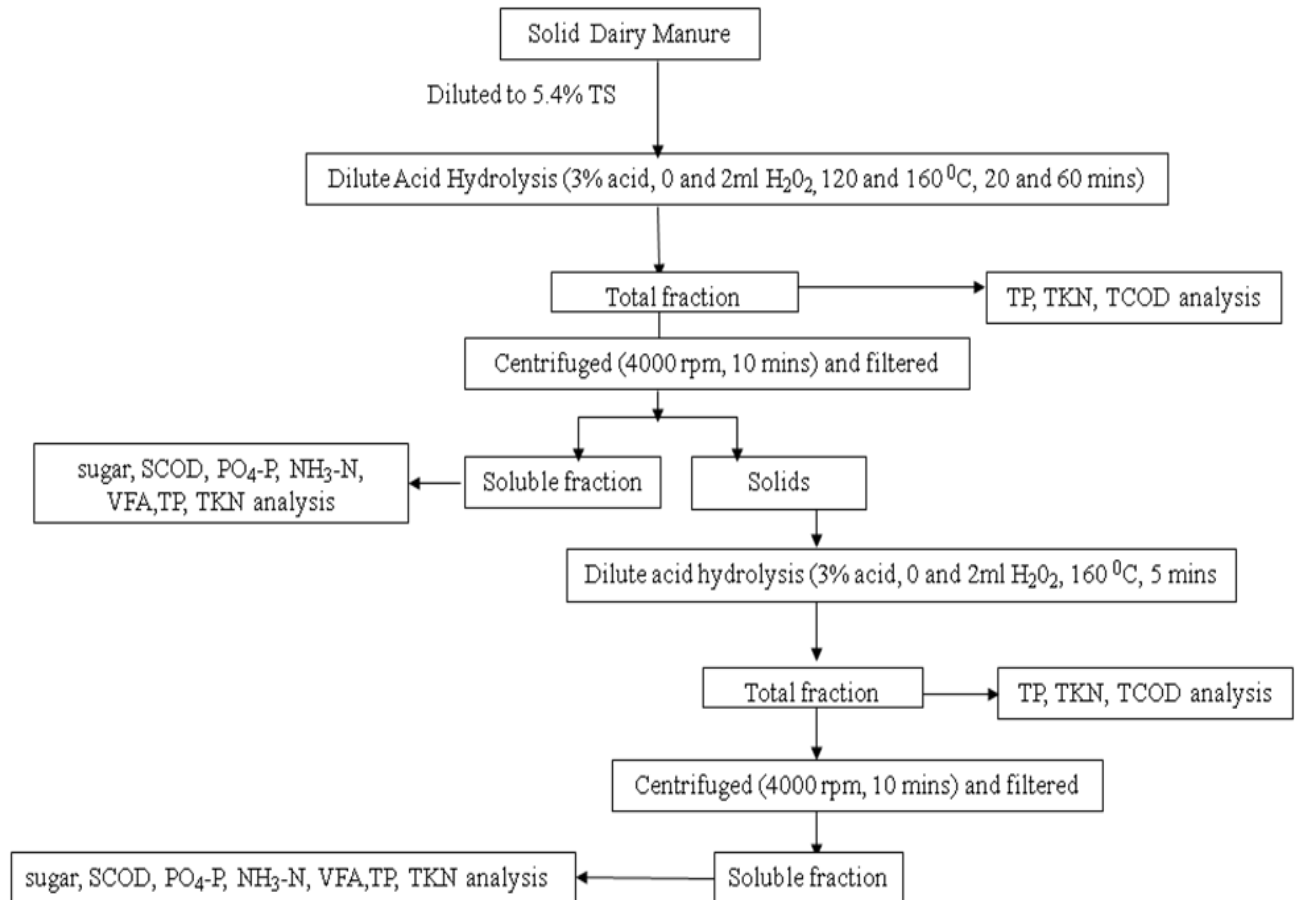


Figure 6.1 Procedure for the two-stage acid hydrolysis of dairy manure

Table 6.2 Experimental design for first stage of hydrolysis

Set no.	TS (%)	Temperature (°C)	H ₂ O ₂ dosage (mL)	Heating time (min)
1	5.4	120	0	20
2	5.4	120	2	20
3	5.4	120	0	60
4	5.4	120	2	60
5	5.4	160	0	20
6	5.4	160	2	20
7	5.4	160	0	60
8	5.4	160	2	60

For the second stage of the hydrolysis process, 0.5g of solids residue (representing 1.7% TS) from each set in stage 1 was treated with 3% acid. A high temperature of 160°C was selected to facilitate the breakdown of dairy manure fibers. Since, from previous experiments in Chapters 4 and 5, it was determined that long heating times decreased the production of sugars at higher temperatures, a heating time of 5 min was used. Solids previously treated at 0 mL H₂O₂ in the first stage were treated at 0 mL H₂O₂ in the second stage; similarly, substrates treated at 2 mL H₂O₂ in the first stage were treated at 2 mL H₂O₂ in the second stage. Total sample volume for each set was 30 mL. Six replicates were used in each set of experiments.

Table 6.3 Experimental design for second stage of acid hydrolysis

Set no.	Sample description (Solid residues from manure samples previously treated at the following conditions in stage 1)	Temperature (°C)	H ₂ O ₂ dosage (mL)	Heating time (min)
1	120 °C, 0mL H ₂ O ₂ , 20min	160	0	5
2	120 °C, 2mL H ₂ O ₂ , 20min	160	2	5
3	120 °C, 0mL H ₂ O ₂ , 60min	160	0	5
4	120 °C, 2mL H ₂ O ₂ , 60min	160	2	5
5	160 °C, 0mL H ₂ O ₂ , 20min	160	0	5
6	160 °C, 2mL H ₂ O ₂ , 20min	160	2	5
7	160 °C, 0mL H ₂ O ₂ , 60min	160	0	5
8	160 °C, 2mL H ₂ O ₂ , 60min	160	2	5

6.4 Results and discussion

6.4.1 Stage 1

6.4.1.1 Sugar production

The MW/H₂O₂-AOP operating conditions that gave the highest sugar yield, 15.5%, was 160 °C, 0 mL H₂O₂, and shorter run times of 20 min, while the lowest yield was obtained at 160 °C, 2 mL H₂O₂, and longer run times of 60 min (Table 6.4). Chen et al., (2005) reported that dilute acid treatment could hydrolyze most of hemicelluloses and reported up to 104% of sugar yield from the first stage of acid hydrolysis. However, in this study, the low yields of sugar indicate that the experimental conditions were not effective in producing sugar, as very little of the manure lignocelulosic material was converted to sugars in the first stage of acid hydrolysis. The low sugar yields could be due to the formation of sugar degradation products, such as hydroxymethylfurfural and furfural, during the acid hydrolysis process.

Table 6.4 Overview of results for first stage of dairy manure acid hydrolysis

Set no.	Sugar (mg/L)	Sugar (% of dry matter)	SCOD (g/L)	SCOD increase (%)	TCOD (g/L)	VFA (mg/L)	TKN (mg/L)	NH ₄ -N (mg/L)	NH ₄ -N released (%)	NH ₄ -N increase (%)	TP (mg/L)	PO ₄ -P (mg/L)	PO ₄ -P release (%)	PO ₄ -P increase (%)
1	8150±996	15.1	21.4±1.6	277	59.7±9.4	1489±131	1117±107	140±9	3	53	260±14	128±2	22	169
2	3806±745	7.0	22.4±1.7	293	57.2±4.4	970±244	1187±46	208±6	8	126	248±5	140±7	26	195
3	5032±723	9.3	21.9±1.0	284	68.3±4.4	962±241	1250±87	148±8	4	61	265±7	132±5	24	178
4	3690±880	6.8	23.0±0.6	304	65.2±9.0	697±266	1165±23	224±10	9	144	242±5	148±10	28	211
5	8356±2987	15.5	28.2±0.8	396	73.0±8.1	687±150	1194±55	172±10	6	87	254±6	171±7	35	259
6	5124±519	9.5	30.9±1.7	444	67.1±3.7	319±158	1163±7	254±11	11	176	254±8	180±9	37	279
7	4801±597	8.9	28.4±1.5	398	63.0±7.7	414±239	1206±91	209±43	8	127	259±12	192±6	41	305
8	2538±631	4.7	28.0±3.3	391	62.7±8.1	291±63	1028±45	271±49	13	195	237±9	194±9	41	307

Data represents arithmetic mean of 6 replicates ± standard deviation

% NH₄-N and % Ortho-P released were calculated based on the percentage of the total TKN and TP, respectively, in the initial dairy manure

Figure 6.2 presents the effects of temperature, heating time and dosage on sugar production at 3% H_2SO_4 . When heating time and dosage are maintained at a constant, a temperature increase from 120 to 160°C does not seem to result in a significant difference in sugar production. For example, at 120, 0 mL H_2O_2 , 20 min (set 1) and 160, 0 mL H_2O_2 , 20 min (set 5) the sugar released was 15.1 and 15.5%, respectively. When the temperature is maintained constant, increasing the heating time results in a decrease in sugar production. For example, a comparison of sets 1 (120°C, 0 mL, 20 min) and 3 (120°C, 0 mL, 60 min) results in sugar yields of 15.1 and 9.3%, respectively. Thus, the longer heating times of 60 min result in reduced sugar production. Irrespective of the temperature and heating times, more sugar was released at 0 mL hydrogen peroxide dosage than at 2 mL dosage (Figure 6.2). Thus, the presence of hydrogen peroxide seems to suppress the breakdown of manure lignocellulosic material into sugars. It could also be due to the fact that, in the presence of excess hydrogen peroxide, sugars produced are further oxidized into CO_2 and other oxidation products, such as carbonyl compounds and VFAs.

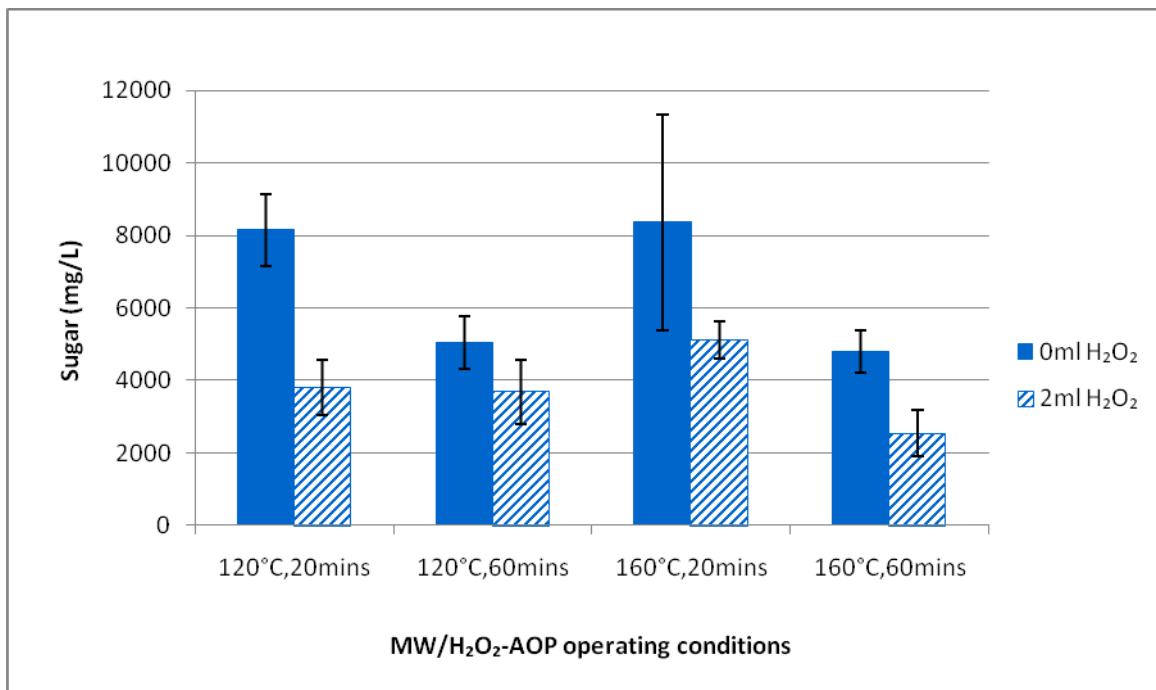


Figure 6.2 Sugar release from first stage of dairy manure acid hydrolysis

6.4.1.2 Nutrient release

MW/H₂O₂-AOP operating conditions that increase nutrient release are higher temperatures of 160°C, the presence of H₂O₂ dosage, and longer run times (60 min). Percentage increase in nutrient concentrations following microwave treatment were as high as 195%, for ammonia and 307% for orthophosphate; these results were obtained at 160°C, 2 mL H₂O₂, 60 min (Table 6.4). The lowest percentage increases for both NH₄-N and PO₄-P, that is 53% and 169 %, respectively, were obtained at 120°C, 0 mL H₂O₂ and 20 min. Up to 13% of the TKN and 41% of the TP was released as soluble ammonia and orthophosphate respectively, at 160°C, 2 mL H₂O₂ and 60 min. Similarly, previous studies by Jin et al., (2009), aimed at enhancing anaerobic digestibility and phosphorus recovery of dairy manure through microwave-based thermochemical pretreatment, resulted in the release of 20-40% soluble phosphorus and 9–14% ammonium (Jin et al., 2009). Pan et al., (2006), however, reported that the AOP process could achieve up to 85% of total phosphate release at 120°C. The orthophosphate to total phosphorus ratio of the manure increased from 13.5% in the initial untreated dairy manure to a maximum of 82% with 160, 2 mL and 60 min of microwave treatment. Under these conditions, ammonia to TKN ratio also increased from 6.5% to 26%.

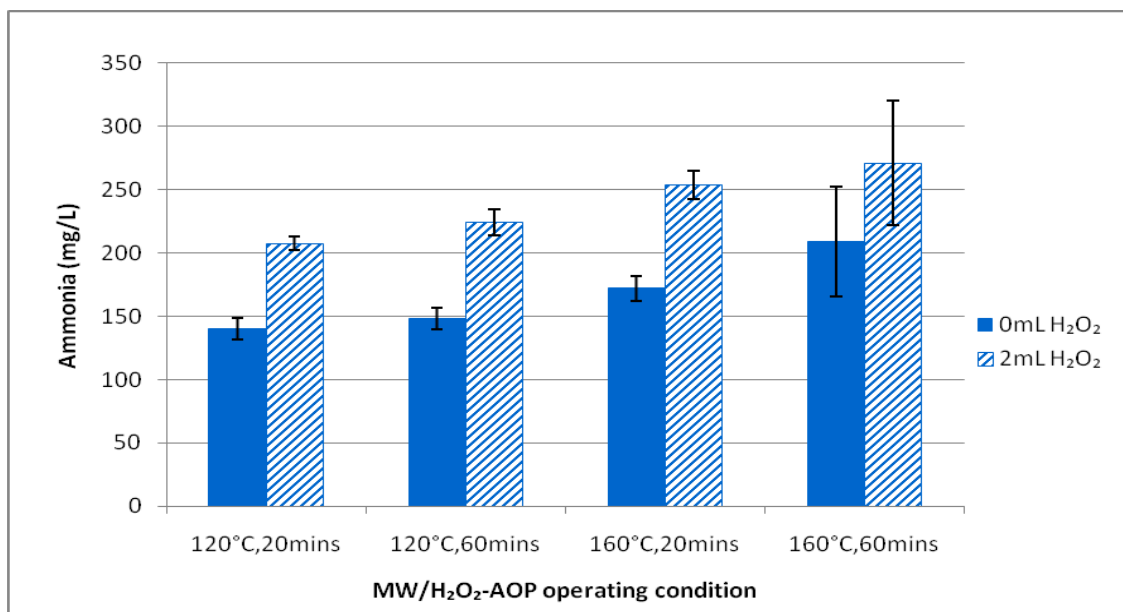


Figure 6.3 Ammonia release from first stage of dairy manure acid hydrolysis

Generally, trends for ammonia and orthophosphate release were similar. More ammonia and orthophosphate were solubilized at 160°C compared to 120°C (Figures 6.3, 6.4). This is consistent with other studies (Qureshi et al., 2008a; Kenge, 2008). The combined effects of temperature and time also resulted in more nutrients being released. That is, at 120°C and 160°C, more ammonia and orthophosphate was released at the longer run time of 60 min compared to 20 min. Also, higher hydrogen peroxide dosages increased the amount of ammonia and orthophosphate solubilized into solution (Figures 6.3, 6.4). It can be observed that although both ammonia and orthophosphate are influenced by temperature and run time, ammonia seems to be more sensitive to the solubilizing effects of hydrogen peroxide, compared to orthophosphate.

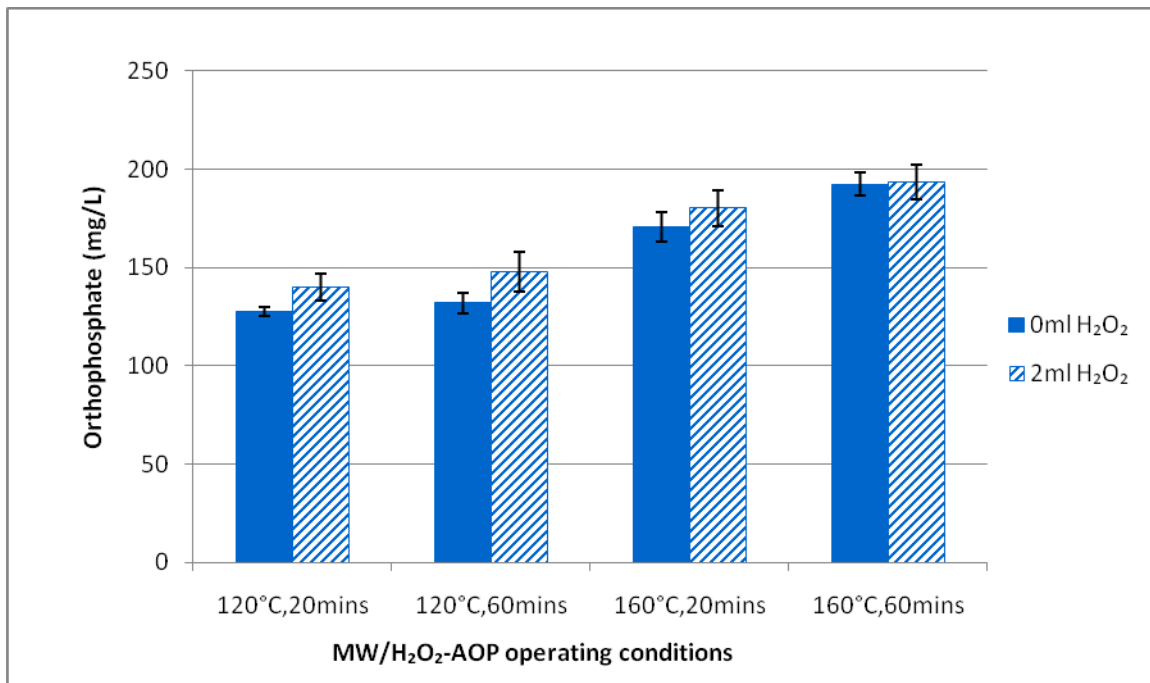


Figure 6.4 Orthophosphate release from first stage of dairy manure acid hydrolysis

It can therefore be concluded in this study that the most important factors for ammonia and PO₄-P release were temperature and H₂O₂ dosage. This observation is consistent with Kenge, (2008).

6.4.1.3 Solids disintegration

The MW/H₂O₂-AOP not only solubilizes orthophosphate and ammonia, but also reduces TSS (Qureshi et al., 2008a).

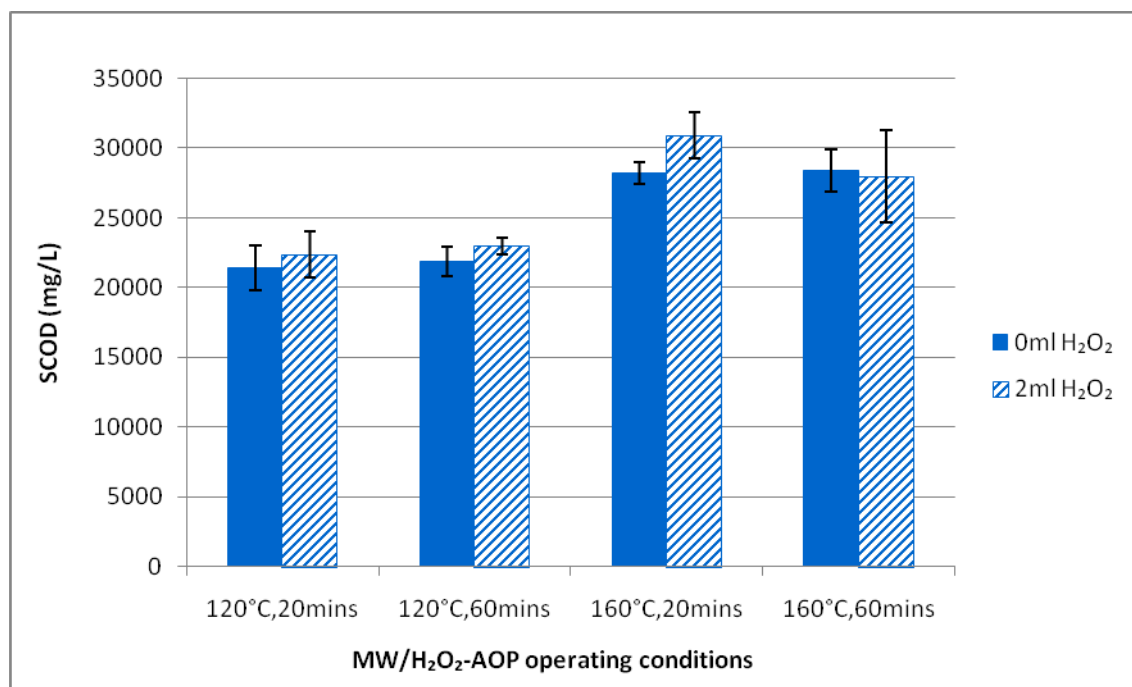


Figure 6.5 SCOD release from first stage of dairy manure acid hydrolysis

SCOD release was enhanced at higher temperatures. Increasing the dosage also seemed to favour a slight increase in SCOD release. Operating conditions that favoured manure treatment (in terms of solids reduction) are higher temperatures of 160°C, the presence of H₂O₂ dosage and longer run times (60 min) (Figure 6.5). At 160°C, 2 mL and 20 min microwave treatment, there was a maximum of 444% increase in SCOD. SCOD did not seem to be very sensitive to changes in heating time. To obtain the best yield of SCOD, the reaction should be undertaken at a shorter reaction time and a high temperature.

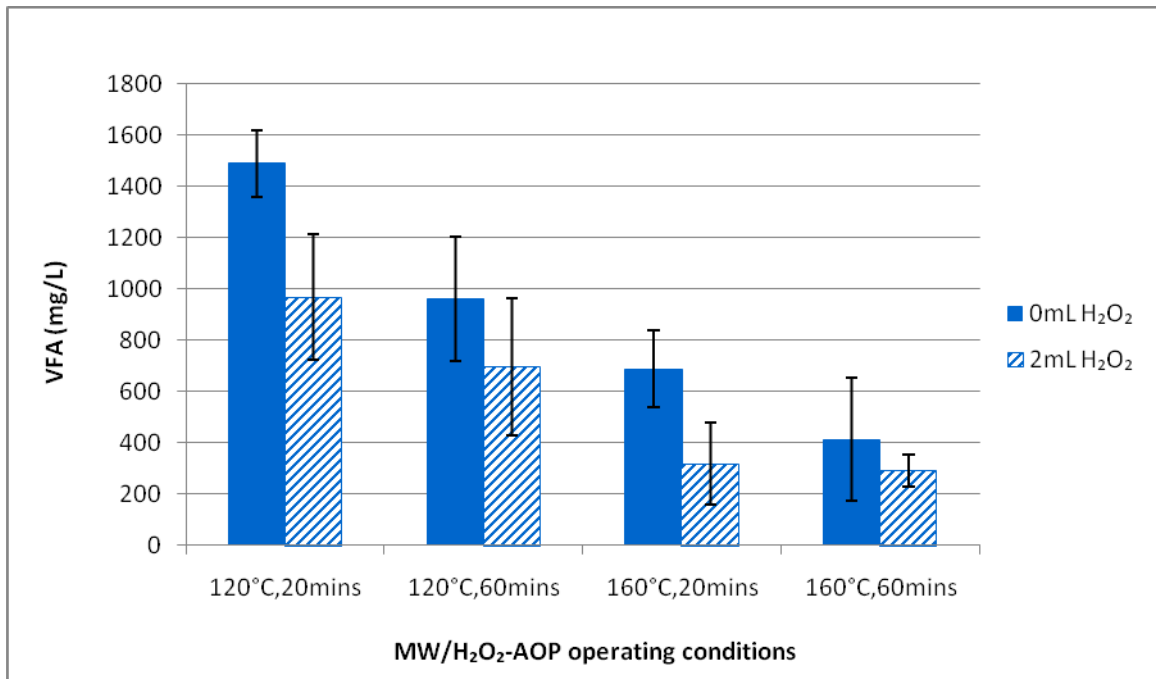


Figure 6.6 VFA release from first stage of dairy manure acid hydrolysis

In this study, VFA existed mainly as acetic acid, and some propionic, butyric and heptanoic acids. The highest VFA release was at 120, 20, 0 mL. VFA seems to decrease with increase in temperature, dosage and time (Figure 6.6). The decrease in VFAs with temperature and time could be due to vaporization of VFAs produced at higher operating temperatures (Kenge, 2008). Qureshi et al., (2008a) further explains that the reduction of VFAs at higher temperatures suggest that at higher temperatures, CO₂ was generated as the end product, while at lower operating temperatures, VFAs were the end product. In the presence of excess hydrogen peroxide and at longer heating times, VFAs could be oxidized to CO₂, resulting in low concentrations of VFA. To obtain the best yield of VFA, the MW/H₂O₂-AOP should be operated at low temperature of 120°C, a shorter heating time and no hydrogen peroxide.

6.4.2 Stage 2

Table 6.5 presents an overview of the second stage database. Subsequent sections discuss specific details for targeted parameters.

Table 6.5 Overview of results for second stage of dairy manure acid hydrolysis

Set no.	Sugar (mg/L)	Sugar yield (% of dry matter)	SCOD (g/L)	TCOD (g/L)	VFA (mg/L)	TKN (mg/L)	NH ₄ -N (mg/L)	NH ₄ -N (% of dry matter)	TP (mg/L)	PO ₄ -P (mg/L)	PO ₄ -P (% of dry matter)
1	667±154	4	2.6±0.3	14.9±0.1	26±1	193±22	35±3	0.21	20±2	20±1	0.12
2	129±104	0.77	1.7±0.6	11.2±0.3	200±89	176±14	126±3	0.75	19±2	25±2	0.15
3	319±106	1.91	2.1±0.4	16.4±0.5	51±35	156±25	26±2	0.16	22±4	23±2	0.14
4	25±18	0.15	1.0±0.2	13.7±0.3	125±49	151±22	131±5	0.79	20±2	26±2	0.16
5	299±94	1.79	1.9±0.2	24.8±0.3	21±0	137±21	27±2	0.16	20±2	23±1	0.14
6	2±1.7	0.01	0.9±0.3	19.8±0.5	93±27	177±20	112±7	0.67	20±1	23±2	0.14
7	29±23	0.18	0.8±0.0	19.9±0.2	0±0	173±7	31±1	0.18	24±2	29±9	0.17
8	1.5±1.0	0.01	0.8±0.0	16.9±0.2	98±20	180±5	114±7	0.68	21±2	26±2	0.16

Data represents arithmetic mean of 3 replicates ± standard deviation

Sugar yield was calculated as a percentage of the initial dairy manure dry mass

6.4.2.1 Sugar production

Pretreatment of lignocellulosic biomass with dilute sulfuric acid at high temperatures, can effectively solubilise the hemicelluloses; reducing the cellulose crystallinity increases the digestibility of cellulose in residual solids (Esteghlalian et al., 1997; Grous et al., 1986). After investigating several procedures of acid hydrolysis, Chen et al., (2005) reported that, in terms of cellulose conversion, two-stage hydrolysis with decrystallization converted almost 90% cellulose into sugars, while the cellulose sugar yield of all the other procedures was less than 35%. Chen et al., (2005) goes on to explain that the back-bone structure of manure, composed of cellulose, could only be degraded after decrystallization by concentrated acid.

At microwave operating conditions of 3% acid concentration, 160°C and 5 min heating time, sugar yields (% as dry mass) from the 2nd stage of dilute acid hydrolysis ranged from 0.01% to 4% (Table 6.5). The substrate that gave the highest sugar yield was dairy manure that had previously been treated at 120°C, 0 mL H₂O₂, 20 min (set 1). The lowest yields were from substrate previously treated at 160°C, 2 mL H₂O₂, 20 min, (set 6) and 160°C, 2 mL, 60 min (set 8) (Figure 6.7). Therefore, sets that had been previously treated with hydrogen peroxide in the first stage, released a lesser amount of sugar in the second stage. The low yields obtained in the second stage of the acid hydrolysis could be due to the low TS content (1.67%) of the residual dairy manure solids. The lower yields obtained in this stage, compared to the first stage, indicate that the crystal structure of manure cellulose is the most difficult part of manure lignocellulosics to break down and is a critical factor influencing sugar yields during acid hydrolysis. Considering that the cellulose content of manure (22%) is much higher than hemicelluloses (12%), the priority of dilute acid hydrolysis should be to degrade manure cellulose (Liao et al., 2006; Liao et al., 2007).

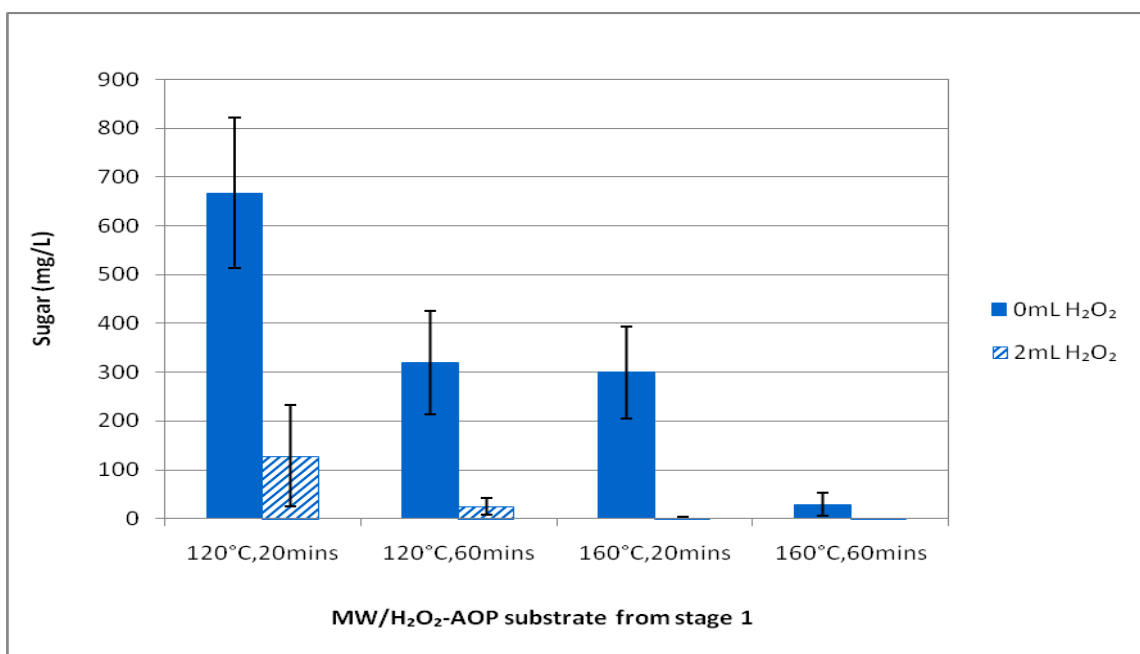


Figure 6.7 Sugar release from second stage of dairy manure acid hydrolysis

Previous research has studied sugar yields from lignocellulosic materials at very short reaction times. Poplar and switchgrass, treated at temperatures between 170 to 180°C, acid concentrations greater than 0.9% and reaction times between 0.5 and 1 min resulted in reasonably high (80%) sugar yields (Esteghlalian, 1997). Similarly, Liao et al., (2006), after investigating glucose yield from dairy manure at a range of temperatures and reaction times, reported that the optimal conditions for dilute acid hydrolysis were 135 °C and short reaction time of 10 min, giving the highest glucose yield of 84%. However, results obtained from this present study, at a reaction time of 5 minutes, yielded such low levels of sugar probably due to the recalcitrant and complex nature of dairy manure lignocellulosics (Jin et al., 2009).

6.4.2.2 Nutrient release

Hydrogen peroxide addition favoured the release of nutrients from the dairy manure solid residues from the first stage, with more ammonia and orthophosphate being released from the solids treated with 2 mL, compared to 0 mL hydrogen peroxide. The substrate that gave the highest sugar yield was dairy manure

solids that had previously been treated at 120°C, 0 mL H₂O₂ and 20 min. A maximum of 0.16% of the dry matter was solubilized as orthophosphates, while a maximum of 0.79% of ammonia was further released. As mentioned in the first stage, the effects of hydrogen peroxide in solubilizing ammonia are more pronounced than for the solubilization of phosphorus. Therefore, ammonia is very sensitive to oxidative processes (Figures 6.8, 6.9).

Although low nutrient yields were obtained in this study, previous studies have proved that considerably high nutrient release for sewage sludge can be achieved with a heating time of 5 minutes (Wong et. al., 2006). Also, Pan et al., (2006), studying the effects of microwave heating time on orthophosphate release from dairy manure, reported that it took only 5 min of microwave heating to achieve a very high rate of phosphorus release. There was a slight increase in soluble phosphorus following an increase of reaction time from 5 to 10 min; however, this was not statistically significant (Pan et al., 2006).

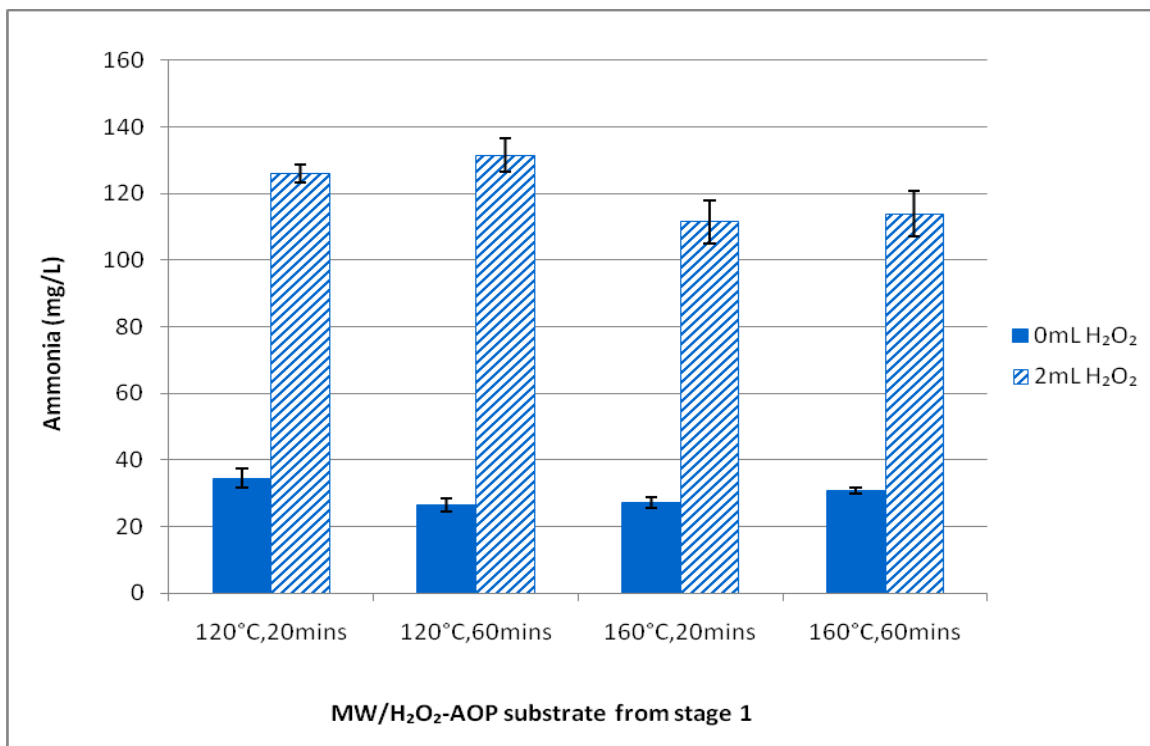


Figure 6.8 Ammonia release from second stage of dairy manure acid hydrolysis

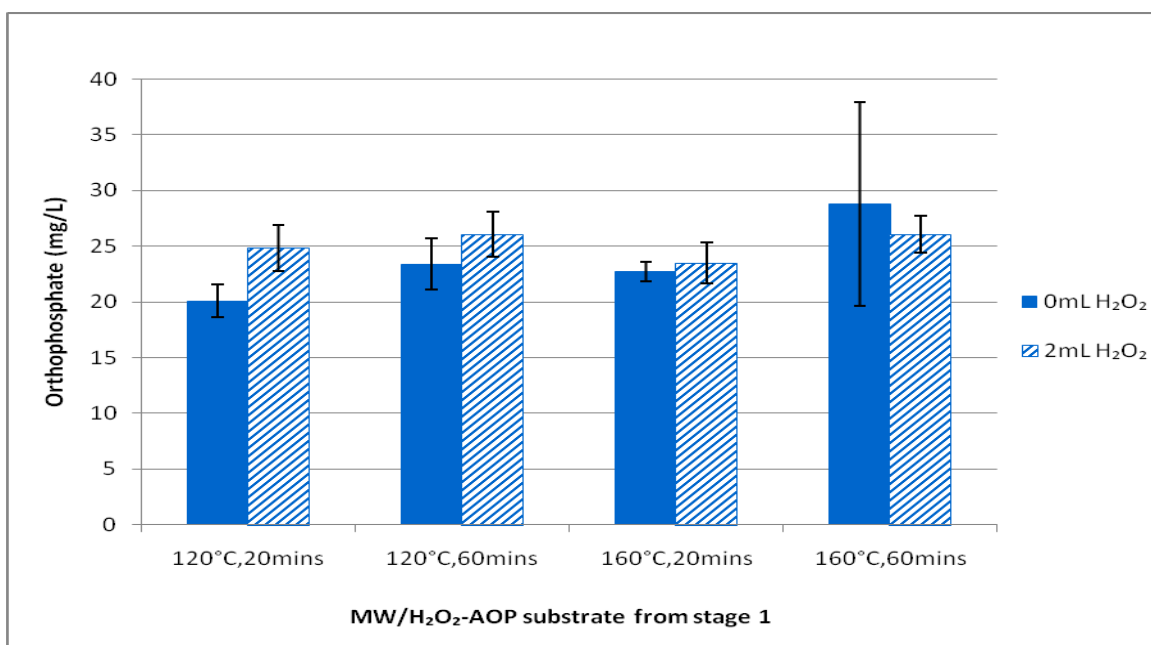


Figure 6.9 Orthophosphate release from second stage of dairy manure acid hydrolysis

6.4.2.3 Solids disintegration

The solubilization of COD and formation of VFAs seem to be influenced to a large extent by hydrogen peroxide dosage (Figures 6.10, 6.11), hence oxidative processes. The presence of hydrogen peroxide resulted in less amounts of COD being solubilized. Solid residues previously treated at lower temperatures (120°C) and shorter heating times (20 min), with no hydrogen peroxide, released more SCOD compared to residues previously treated at higher temperatures (160°C) and longer heating times (60 min). This could be due to the conversion of all soluble organics in this substrate to CO₂ at the higher temperatures of 160°C.

The presence of hydrogen peroxide resulted in an increased formation of VFAs. Solid residues previously treated at lower temperatures (120°C) released more VFAs, compared to residues previously treated at higher temperatures (160°C). There were no clear trends for the release of VFA with respect to heating time.

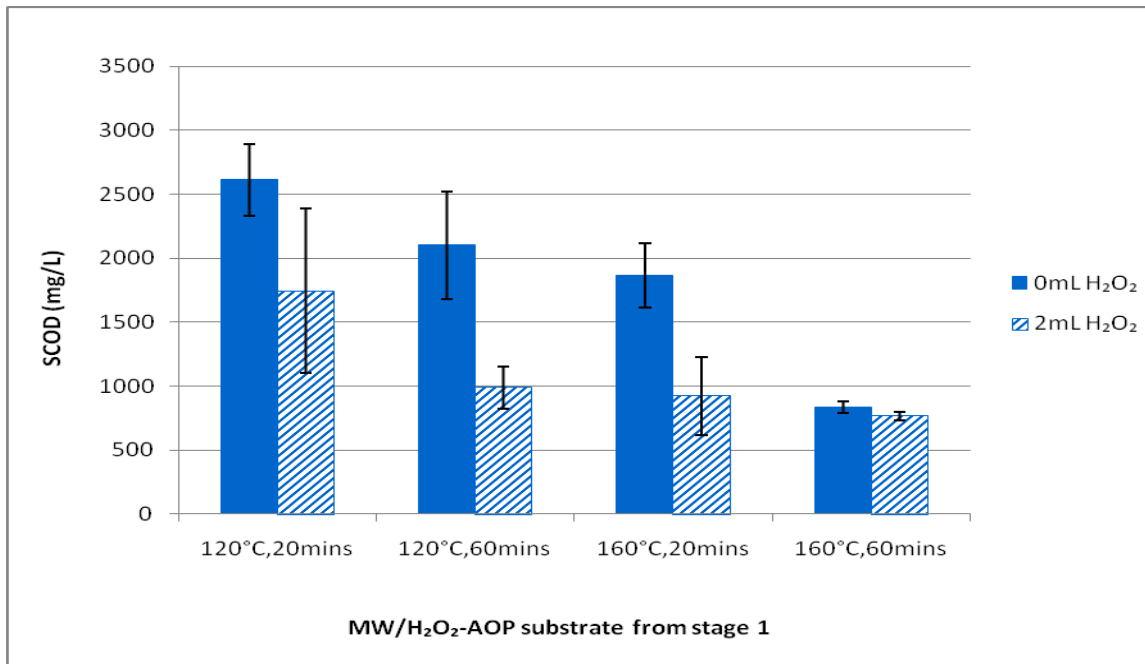


Figure 6.10 SCOD release from second stage of dairy manure acid hydrolysis

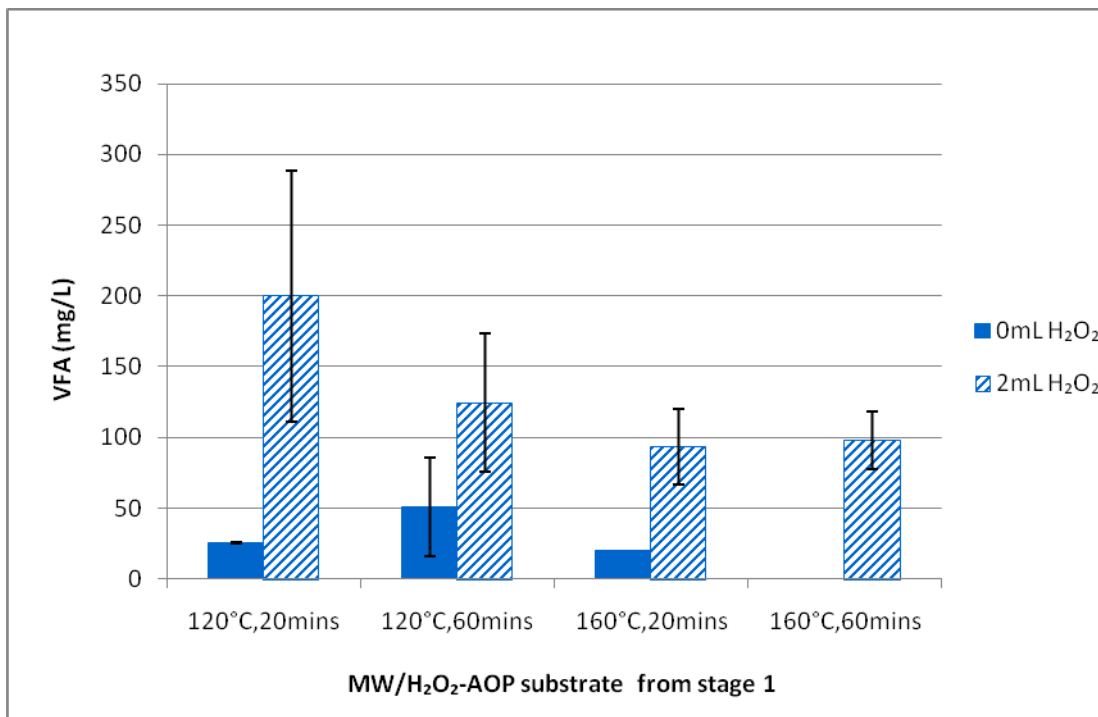


Figure 6.11 VFA release from second stage of dairy manure acid hydrolysis

7. Conclusions

The impact of dairy farms on the environment has come under closer scrutiny in recent years. The development of best control technologies can lessen or eliminate the disposal problem of large amounts of dairy wastewater. Several studies have been conducted on nutrient removal and nutrient recovery from dairy manure, to reduce the overall environmental impact on vulnerable water bodies and also for the production of value added products. In this research, solid-liquid separation and MW/H₂O₂-AOP for dairy manure treatment were investigated. Based on the results and discussions from this research, the following conclusions and recommendations were arrived at:

7.1 Solid-liquid separation

Solid-liquid separation of raw dairy manure resulted in solid and liquid fractions that had different properties. The solid fractions were richer in TS and VS content, while the liquid fractions were richer in nutrients and metals. Separation also resulted in solid fractions that had higher composition of dry matter and VS and liquid fractions that had higher nutrients and metals, compared to the initial raw unseparated dairy manure. Generally, removal efficiencies achieved for TS, VS and TP were just a little over 50%, while less than 50% removal was achieved for ammonia and TKN. Therefore, laboratory separation by screening alone was not effective in removing high amounts of nutrients and solids from the raw manure. This is in agreement with observations made by Garcia et al., (2009), whose study concluded that simple screening was rather ineffective in removing solids and nutrients (N and P) from dairy manure, compared to the addition of a chemical flocculant.

7.2 Sugar and nutrient release from solid dairy manure at pH 2 using the microwave enhanced advanced oxidation process

In an attempt to enhance sugar production from dairy manure, solid dairy manure was treated at pH 2. Temperature was clearly the most important factor affecting sugar production. Sugar production was enhanced by increasing temperatures and low hydrogen peroxide dosages. Longer run times and higher

H₂O₂ dosage decreased sugar yields. The generally low sugar yields obtained in this present study (maximum of 7.39% of dry matter) could be attributed to the complex structure of the dairy manure. Hydrogen peroxide dosage and temperature were both important for the solubilization of PO₄-P and NH₄-N. Therefore, although orthophosphate and ammonia were solubilized using the microwave process alone, there was a further increase in their concentrations when the MW process was combined with H₂O₂. It would also be advantageous for the MW/H₂O₂-AOP process to be operated at a higher temperature and a longer heating time, to achieve a higher orthophosphate and ammonia release. A decrease in VFA release was observed when the heating time was increased from 10 to 20 min. An increase in temperature and dosage increased VFA production. VFA was produced using the MW process alone; however, a further increase in VFA was observed when the microwave process is combined with H₂O₂. The higher the temperature the more SCOD was released. At temperatures of 80°C and 120°C, significantly more SCOD is released when H₂O₂ was combined with the microwave process and the dosage was increased from 0 to 0.5 mL. Therefore, temperature and H₂O₂ dosage are clearly the factors that most affect the solubilization of all the parameters; sugar, VFA, ammonia and orthophosphate.

7.3 Factors affecting sugar production from cellulose using the microwave enhanced advanced oxidation process

Sugar production was affected by all the 4 microwave operating conditions of temperature, acid concentration, hydrogen peroxide dosage and heating time. An increase in acid concentration, from 1% to 3%, resulted in an increase in sugar production. A subsequent increase in acid concentration to 10%, however, resulted in a decrease in the sugar yield from the dairy manure. An increase in time decreased sugar production. The enhancement of sugar production, with shorter heating times, corresponds to lesser energy demands. The fact that more sugar is produced at 3%, compared to 10%, also has significant implications for the protection of the environment, since it removes the concerns associated with using acids of higher concentrations. SCOD release was influenced by dosage, while VFA production was sensitive to acid concentration and temperature.

7.4 Two-stage dilute acid hydrolysis of solid dairy manure for sugar and nutrient release using the microwave enhanced advanced oxidation process

Sugar yield from the two-stage acid hydrolysis process was enhanced by MW/H₂O₂-AOP operating conditions of shorter run times (20 min) and the absence of hydrogen peroxide. When the microwave process was combined with hydrogen peroxide, sugar yields decreased. Temperature change from 120°C to 160°C did not seem to influence the amount of sugars produced from the dairy manure fibers. Similar concentrations of sugars were produced at 120°C and 160°C, under the same conditions. The longer heating times of 60 min also resulted in reduced sugar production.

In the first stage of the hydrolysis process, the MW/H₂O₂-AOP operating conditions that increased nutrient release were higher temperatures of 160°C, presence of H₂O₂ dosage, and longer run times (60 min). Though both ammonia and orthophosphate were influenced by temperature and run time, ammonia seems to be more sensitive to the solubilizing effects of hydrogen peroxide, compared to orthophosphate. SCOD release was enhanced at higher temperatures. Increasing the dosage and longer heating times seemed to favour a slight increase in SCOD release. SCOD did not seem to be very sensitive to changes in heating time. VFA decreased with increase in temperature, dosage and time.

In the second stage of acid hydrolysis, heating time of 5 min did not provide a good solubilization of dairy manure cellulose for sugar production. The substrate that gave the highest sugar yield (4%) was dairy manure that had previously been treated at 120°C, 0 mL H₂O₂, 20 min. Sets that had been previously treated with hydrogen peroxide in the first stage released less amount of sugar in the second stage. Hydrogen peroxide addition favoured the release of more ammonia and orthophosphate from the dairy manure solid residues from the first stage. The presence of hydrogen peroxide resulted in less amounts of COD being solubilized, but an increase in the formation of VFAs.

Generally, the results indicate that, to enhance sugar formation, the microwave process should be operated at low dosage and shorter heating times. The important factors for COD solubilization are higher temperatures and higher hydrogen peroxide dosages. To increase ammonia and orthophosphate release, the process should be run at higher temperatures, higher hydrogen peroxide dosages and longer heating times. VFA formation can be improved at lower temperatures, lower hydrogen peroxide dosages and shorter heating times.

The MW/H₂O₂-AOP operating conditions that maximized sugar yields from dairy manure were not the same as conditions that maximized nutrient yields. Thus, it is imperative to define the objectives of the treatment regime, prior to embarking on a process flow scheme.

7.5 Recommendations for follow-up research

- A decrystallization step should be included in the two-stage acid hydrolysis procedure, for possible increase in sugar production.
- In subsequent studies, the reaction time for the second stage should be increased from 5 minutes to 7.5 or 10 mins, for potential increase in sugar yields.
- Other methods for hydrolysis of dairy manure lignocellulosic material (such as alkaline extraction) should be investigated using the MW/H₂O₂-AOP.

References

Aguilar, A., Casas, C. and Lema, J.M. Degradation of volatile fatty acids by differently enriched methanogenic cultures: kinetics and inhibition. *Water Research*. **1995**, 29 (2), 505-509

Ahsan, S., Kaneco, S., Ohta, K., Mizuno, T. and Kani, K. Use of some natural and waste materials for waste water treatment. *Water Research*. **2001**, 35 (15), 3738–3742

American Public Health Assoc., “Standard Methods for the Examination of Water and Wastewater 20th Edition. American Public Health Association, Washington, D.C. **1998**

Baker, J.R., Milke, M.W. and Mihelcic, J.R. Relationship between chemical and theoretical oxygen demand for specific classes of organic chemicals. *Water Research*. **1999**, 33 (2), 327-334

Barker, P. S. and Dold, P. L. COD and nitrogen mass balances in activated sludge systems. *Water Research*. **1995**, 29 (2) 633-643

Barnard, J.L. Background to biological phosphorus removal. *Water Sci. Technol*. **1983**, 15 (3–4), 1–13.

Bolan, N.S., Wong, L. and Adriano, D.C. Nutrient removal from farm effluents. *Bioresource Technology*. **2004**, 94, 251–260

Bower, S., Wickramasinghe, R., Nagle, N. J. and Schell, D.J. Modeling sucrose hydrolysis in dilute sulfuric acid solutions at pretreatment conditions for lignocellulosic biomass. *Bioresource Technology*. **2008**, 99, 7354–7362

Burton, C.H. The potential contribution of separation technologies to the management of livestock manure. *Livestock Science*. **2007**, 112, 208–216.

Cantrell, K.B., Ducey, T., Ro, K.S. and Hunt, P.G. Livestock waste-to-bioenergy generation opportunities. *Bioresource Technology*. **2008**, 99 (17), 7941–7953

Chanona, J., Ribes, J., Seco, A. and Ferrer, J. Optimum design and operation of primary sludge fermentation schemes for volatile fatty acids production. *Water Research*. **2006**, 40, 53 – 60

Chastain, J.P., Vanotti, M.B. and Wingfield, M.M. Effectiveness of liquid-solid separation for treatment of flushed dairy manure: a case study. *Applied Engineering in Agriculture*. **2001**, 17 (3), 343-354

Chen, S., Wen, Z., Liao, W., Liu, C., Kincaid, R. L., Harrison, J.H., Elliot, D.C., Brown, M.D. and Stevens, D.J. Studies into using manure in a biorefinery concept. *Applied Biochemistry and Biotechnology*. **2005**, 121-124, 999-1015

Choi, C.H. and Mathews, A.P. Two-step acid hydrolysis process kinetics in the saccharification of low-grade biomass: 1. Experimental studies on the formation and degradation of sugars. *Bioresource Technology*. **1996**, 58, 101–106.

Chu, A., Mavinic, D.S., Kelly, H.G. and Ramey, W.D. Volatile fatty acid production in thermophilic aerobic digestion of sludge. *Water. Research*. **1994**, 28 (7), 1513-1522

de-Bashan, L.E. and Bashan, Y. Recent advances in removing phosphorus from wastewater and its future use as fertilizer (1997–2003). *Water Research*. **2004**, 38, 4222–4246

Doyle, J.D. and Parsons, S.A. Struvite formation, control and recovery. *Water Research*. **2002**, 36, 3925–3940

de la Hoz, A., Diaz-Ortiz, A., Moreno, A., 2005. Microwaves in organic synthesis. Thermal and non-thermal microwave effects. *Chemical Society Reviews* 34 (2), 164–178.

Elefsiniotis, P. and Oldham, W.K. Anaerobic acidogenesis of primary sludge: the role of solids retention time. *Biotechnol. Bioeng*. **1994**, 44 (1), 7–13.

Eskicioglu, C., Kennedy, K.J., Droste, R.L. Characterization of soluble organic matter of waste activated sludge before and after thermal treatment. *Water Research*. **2006**, 40, 3725 – 3736

Eskicioglu, C., Terzian, N., Kennedy, K.J., Droste, R.L. and Hamoda, M. Athermal microwave effects for enhancing digestibility of waste activated sludge. *Water Research*. **2007**, 41, 2457 – 2466

Eskicioglu, C., Prorot, A., Marin, J., Droste, R.L. and Kennedy, K.J. Synergetic pretreatment of sewage sludge by microwave irradiation in presence of H₂O₂ for enhanced anaerobic digestion. *Water Research*. **2008**, 42, 4674 – 4682

Esteghlalian, A., Hashimoto, A.G., Fenske, J.J. and Penner, M.H. Modeling and optimization of the dilute sulfuric-acid pretreatment of corn stover, poplar and switchgrass. *Bioresource Technology*. **1997**, 59, 129-136

Gan, Q., Allen, S.J. and Taylor, G. Kinetic dynamics in heterogeneous enzymatic hydrolysis of cellulose: an overview, an experimental study and mathematical modeling. *Process Biochem*. **2003**, 38, 1003–1018.

- Garcia, M.C., Szogi A.A., Vanotti, M.B., Chastain, J.P. and Millner, P.D. Enhanced solid–liquid separation of dairy manure with natural flocculants. *Bioresource Technology*. **2009**, *100*, 5417–5423
- Gebrezgabher, S.A., Meuwissen, M.P.M., Prins, B.A.M. and Oude Lansink, A.G.J.M. Economic analysis of anaerobic digestion—A case of Green power biogas plant in The Netherlands. *NJAS -Wageningen Journal of Life Sciences*. **2010**, *57*, 109–115
- Gedye, R.N., Smith, F.E., Westaway, K.C., Ali, H., Baldisera, L.L. and Rousell, J. The use of microwave ovens for rapid organic synthesis. *Tetrahedron Lett*. **1986**, *27*, 279–282.
- Girio, F.M., Fonseca, C., Carvalheiro, F., Duarte, L.C., Marques, S. and Bogel-Lukasik, R. Hemicelluloses for fuel ethanol: A review. *Bioresource Technology*. **2010**, *101*, 4775–4800
- Grous, W.R., Converse, A.O. and Grethlein, H.E. Effect of steam explosion pretreatment on pore size and enzymatic hydrolysis of poplar. *Enzyme and Microbial Technology*. **1986**, *8*, 274–280.
- Harris, E.E. Wood Saccharification. *Advances in Carbohydrate Chemistry*. **1949**, *4*, 150–188.
- Harris, W.G., Wilkie, A.C., Cao, X. and Sirengo, R. Bench-scale recovery of phosphorus from flushed dairy manure wastewater. *Bioresource Technology*. **2008**, *99*, 3036–3043
- Hill, D. T. and Holmberg, R. D. Long chain volatile fatty acid relationships in anaerobic digestion of swine waste. *Biological Wastes*. **1988**, *23*, 195–214
- Han, D-H., Cha, S-Y., Yang, H-Y. Improvement of oxidative decomposition of aqueous phenol by microwave irradiation in UV/H₂O₂ process and kinetic study. *Water Research*. **2004**, *38* 2782–2790
- Herring, J.R. and Fantel, R.J. Phosphate rock demand into the next century: Impact on world food supply. *Natural Resources Research*. **1993**, *2* (3) 226–246)
- Hong, S.M., Park, J.K and Lee, Y.O. Mechanisms of microwave irradiation involved in the destruction of fecal coliforms from biosolids. *Water Research*. **2004**, *38*, 1615–1625
- Jardim, W. F. and Rohwedder, J. R. Chemical oxygen demand (COD) using microwave digestion. *Water Research*, **1989**, *23* (8), 1069–1071
- Jensen, L.S., Salo, T., Palmason, F., Breland, T.A., Henriksen, T.M., Stenberg, B., Pedersen, A., Lundstrom, C. and Esala, M. Influence of biochemical quality on C and N mineralisation from a broad variety of plant materials in soil. *Plant and Soil*. **2005**, *273*, 307–326.

Jin, Y., Hu, Z. and Wen, Z. Enhancing anaerobic digestibility and phosphorus recovery of dairy manure through microwave-based thermochemical pretreatment. *Water Research*. **2009**, 43, 3493–3502

Jørgensen, K. and Jensen, L.S. Chemical and biochemical variation in animal manure solids separated using different commercial separation technologies. *Bioresource Technology*. **2009**, 100, 3088–3096

Kang, Y.W., Cho, M. and Hwang, K. Correction of hydrogen peroxide interference on standard chemical oxygen demand test. *Water Research*. **1999**, 33 (5), 1247-1251

Kaparaju, P.L.N. and Rintala, J.A. Effects of solid–liquid separation on recovering residual methane and nitrogen from digested dairy cow manure. *Bioresource Technology*. **2008**, 99, 120–127

Kenge, A.A. Enhancing nutrient solubilization from organic waste using the microwave technology. MSc. Thesis . University of British Columbia. **2008**

Liao, P.H., Wong, W.T. and Lo, K.V. Advanced oxidation process using hydrogen peroxide/microwave system for solubilization of phosphate. *Journal of Environmental Science and Health Part a-Toxic/Hazardous Substances & Environmental Engineering*. **2005a**, 40 (9), 1753–1761

Liao, P.H.; Wong, W.T. and Lo, K.V. Release of phosphorus from sewage sludge using microwave technology. *Journal of Environmental Engineering and Science* **2005b**, 4, 77–81.

Liao, W., Liu, Y., Liu, C. and Chen, S. Optimizing dilute acid hydrolysis of hemicelluloses in a nitrogen-rich cellulosic material—dairy manure. *Bioresource Technology*. **2004**, 94, 33–41

Liao, W., Liu, Y., Wen, Z., Frear, C. and Chen, S. Studying the effects of reaction conditions on components of dairy manure and cellulose accumulation using dilute acid treatment. *Bioresource Technology*. **2007**, 98, 1997-1999.

Liao, W., Liu, Y., Liu, C., Wen, Z., and Chen, S. Acid hydrolysis of fibers from dairy manure. *Bioresource Technology*, **2006**, 97, 1687-1695

Lo, K.V., Lau, A. and Liao, P.H. Composting of separated solid swine wastes. *J. Agric. Eng. Res.* **1993**, 54 (4), 307–317.

Masse', D.I., Croteau, F. and Masse L. The fate of crop nutrients during digestion of swine manure in psychrophilic anaerobic sequencing batch reactors. *Bioresource Technology*. **2007**, 98, 2819–2823

McKenney, L.A. Dewatering dairy manure using polymer and belt press technology. In: Proc. Manure Management in Harmony with the Environment Conf. **1998**, 354–358, Soil and Water Conservation Society, Ames, Iowa, USA, 10–12 Feb. Ames, Iowa: SWCS.

Misselbrook, T.H., Nicholson, F.A. and Chambers, B.J. Predicting ammonia losses following the application of livestock manure to land. *Bioresource Technology*. **2005**, *96*, 159–168

Mohan, S. and Sunny, N. Study on biomethonization of waste water from jam industries. *Bioresource Technology*. **2008**, *99*, 210–213

Møller, H.B., Sommer, S.G. and Ahring, B.K. Methane productivity of manure, straw and solid fractions of manure. *Biomass Bioenergy*. **2004**, *26*, 485–495.

Møller, H.B., Sommer, S.G. and Ahring, B.K. Separation efficiency and particle size distribution in relation to manure type and storage conditions. *Bioresource Technology*. **2002**, *85*, 189–196.

Mosier, N., Wyman, C., Dale, B., Elander, R., Lee, Y.Y., Holtzapple, M. and Ladisch, M. Features of promising technologies for pretreatment of lignocellulosic biomass. *Bioresource Technology*. **2005**, *96*, 673–686

Mukhtar, S., Sweeten, J. M. and Auvermann, B. W. Solid-Liquid Separation of Animal Manure and Wastewater. Bulletin E-13. Texas Agricultural Extension Service. The Texas A & M University System. **1999**.

Mulbry, W., Westhead, E.K., Pizarro, C., Sikora, L. Recycling of manure nutrients: use of algal biomass from dairy manure treatment as a slow release fertilizer. *Bioresource Technology*. **2005**, *96*, 451–458

Pan, S.H., Lo, K.V., Liao, P.H. and Schreier, H. Microwave pretreatment for enhancement of phosphorus release from dairy manure. *Journal of Environmental Science and Health Part B-Pesticides Food Contaminants and Agricultural Wastes*. **2006**, *41* (4), 451–458

Portejoie, S., Martinez, J., Guiziou, F. and Coste, C.M. Effect of covering pig slurry stores on the ammonia emission processes. *Bioresource Technology*. **2003**, *87*, 199–207

Qureshi, A., Lo, K.V. and Liao, P.H. Microwave treatment and struvite recovery potential of dairy manure. *Journal of Environmental Science and Health Part B-Pesticides Food Contaminants and Agricultural Wastes*. **2008a**, *43* (4), 350–357

Qureshi, A., Victor Lo, K.V., Liao, P.H. and Mavinic, D.S. Real-time treatment of dairy manure: Implications of oxidation reduction potential regimes to nutrient management strategies. *Bioresource Technology*. **2008b**, 99, 1169–1176

Raunkjaer, K., Hvitved-Jacobsen, T., and Nielsen, P.H. Measurement of pools of protein, carbohydrate and lipid in domestic wastewater. *Water Research*. **1994**, 28 (2) 251-262

Rico, J.L., Garcia, H., Rico, C. and Tejero, I. Characterisation of solid and liquid fractions of dairy manure with regard to their component distribution and methane production. *Bioresource Technology*. **2007**, 98, 971–979

Sall, J., Creighton, L. and Lehman, A. “JMP Start Statistics: A Guide to Statistics and Data Analysis using JMP and JMP IN Software”. Third Edition. Brooks/Cole-Thomson Learning. Belmont, California, **2005**.

Shu, L., Schneider, P., Jegatheesan, V. and Johnson, J. An economic evaluation of phosphorus recovery as struvite from digester supernatant. *Bioresource Technology*. **2006**, 97, 2211–2216

Sørensen, P., Thomsen, I.K. Separation of Pig Slurry and Plant Utilization and Loss of Nitrogen-15-labeled Slurry Nitrogen. *Soil Sci. Soc. Am. J.* **2005**, 69, 1644-1651

Sotirakou, E., Kladitis, G., Diamantis, N. and Grigoropoulou, H. Ammonia and Phosphorus removal in wastewater treatment plant with extended aeration. *Global Nest: the Int. J.* **1999**, 1,(1) 47-53

Sun, Y. and Cheng, J. Hydrolysis of lignocellulosic materials for ethanol production: a review. *Bioresource Technology*. **2002**, 83, 1–11

Termeer, W. C. and Warman, R. R. Use of mineral amendments to reduce ammonia losses from dairy-cattle and chicken-manure slurries. *Bioresource Technology*. **1993**, 44, 217-222

Valsami-Jones, E. Mineralogical controls on phosphorus recovery from wastewaters. *Mineralogical Magazine*. **2001**, 65 (5), 611–620.

von Sivers, M. and Zacchi, G. Ethanol from lignocellulosics: a review of the economy. *Bioresource Technology*. **1996**, 56, 131-140

Wen, Z., Wei Liao, W., and Chen, S. Hydrolysis of animal manure lignocellulosics for reducing sugar production. *Bioresource Technology*. **1994**, 91, 31–39

Wong, W.T. Applications of microwave technology to wastewater treatment. MSc. Thesis. University of British Columbia. **2006**

Wong, W.T., Chan, W.I., Liao, P.H., Lo, K.V. and Mavinic, D.S. "Exploring the role of hydrogen peroxide in the microwave advanced oxidation process: solubilization of ammonia and phosphates". J. Environmental Engineering and Science. **2006**, 5(6): 459-465

Wong, W.T. Lo, K.V. and Liao, P.H. Factors affecting nutrient solubilization from sewage sludge in microwave advanced oxidation process. J. Environ. Science and Health-Part A, **2007**, 42 (6), 825-829

Wyman, C.E. Ethanol from lignocellulosic biomass: technology, economics, and opportunities. Bioresource Technology. **1994**, 50, 3-16

Yu, G-H., He, P-J., Shao, L.M. and He, P.P. Toward understanding the mechanism of improving the production of volatile fatty acids from activated sludge at pH 10.0. Water Research. **2008**, 42, 4637 – 4644

Zhang, J., Zhou, B., Zheng, Q., Li, J., Bai, J., Liu, Y. and Cai, W. Photoelectrocatalytic COD determination method using highly ordered TiO₂ nanotube array. Water Research. **2009**, 43, 1986 – 1992

Zheng, J. Kennedy, K.J. and Eskicioglu, C. Effect of low temperature microwave pretreatment on characteristics and mesophilic digestion of primary sludge. Environmental Technology. **2009**, 30 (4), 319-327