The University Of Sheffield.

Intensification of Anaerobic Digestion of Food Waste Due to Seeding with CO_2 Microbubbles and Simultaneous Microbubble Stripping to Study their Role in Alleviating Ammonia Inhibition

By
Ummul Hasanah Binti Haji Hassan

A thesis submitted as part of the requirements for the
Doctor of Philosophy degree

The University of Sheffield, Faculty of Engineering

Department of Chemical and Biological Engineering (CBE)

August 2023

Acknowledgements

Firstly, I would like to thank Allah the Almighty, the Most Gracious, and the Most Merciful for His blessings during my studies. May Allah's blessings be upon the last prophet Muhammad (peace be upon him), his family, and companions.

I would like to express my appreciation for the guidance and supervision I received from my supervisor, Professor William BJ Zimmerman, throughout my PhD program. I greatly appreciate the support provided by Perlemax Ltd (especially Dr. Pratik Desai and Mr Hamza Mohammed) as well as Viridor Waste Management Limited. I would like to thank the lab manager, Dr. Thomas D Holmes, for providing me with all the supplies I needed in order to conduct our experiments in the lab. Thank you to the technical staff at TUoS, Mario Dorna and Andrew, who assisted me in building the stripping rigs.

Gratitude is extended to the Government of His Majesty the Sultan and Yang Dipertuan of Brunei Darussalam and my employer, Universiti Teknologi Brunei, for providing me with a scholarship and for the opportunity to further my studies. Thank you to my fellow PhD students at the University of Sheffield, including Dr. Wahyu Nugroho, Dr. Aya Farag and Su Natasha, for their support and encouragement.

My husband, Mohamad Fauzi Haji Metali, deserves special recognition for his unconditional love, patience, and support throughout this journey, as well as my dear son, Muhammad Fayyadh Amsyar. Lastly, I would like to convey my sincere gratitude to my parents, my parents-in-law, and all other family members who have supported and encouraged us throughout this process.

Abstract

Recent studies have demonstrated that sparging CO_2 microbubbles directly into the digesters of food waste increased methane yields substantially. Anaerobic digestion produces ammonia from organic nitrogen, and anaerobic digesters can benefit from the presence of ammonia, which acts as a buffer. At higher concentrations of ammonia, however, the digestion process may be inhibited.

This work provides an insight into the application of microbubble stripping mediated by Desai-Zimmerman fluidic oscillators (DZFO) in anaerobic digestion, particularly the ones with microbubbles CO_2 sparging to prevent ammonia inhibition. The primary objective is to develop low-cost, low-energy alternatives that can be used to reduce ammonia levels in the anaerobic digestion of food waste with a low C/N value, which was sparged with CO_2 microbubbles. Microbubble stripping engendered by an energy-efficient fluidic oscillator, DZFO was utilized to strip ammonia from the digestate. In this way, ammonia inhibition could be alleviated.

Initially, three designs of Desai-Zimmerman (DZ) stripping rigs, including DZ lab-scale, recirculating and continuous DZ rigs, were evaluated for their potential to strip ammonia from highly concentrated liquids. A fluidic oscillator (DZFO) was used to generate microbubbles, and stripping was accomplished within a short period, at a moderate temperature, without adjusting the pH level. It was observed that the K_La values for these rigs were higher than those obtained in previous studies using conventional fine bubbles with a diameter typically ranging from 1 to 4 mm.

Additionally, the present study revealed that microbubbles of CO_2 injected into the AD is unlikely to reduce total ammonia nitrogen (TAN) from the system. By seeding the system with microbubble CO_2, the pH was lowered, which decreased the free ammonia nitrogen fraction (FAN). However, the concentration of TAN in the system remained unchanged. Hence, nitrogen gas was chosen as the stripping gas in the simultaneous ammonia removal from anaerobic digester in this work.

In the final experiment, DZ lab-scale stripping rig was coupled with AD using nitrogen as a stripping gas at the flow rate of 1 LPM and temperature of 70 ^{o}C. A 25 mL digestate was used for each stripping run with a duration of two minutes. During this process, 2 L of digestate was removed daily from the anaerobic digestion sparged (seeded) with CO_2 microbubbles, and the digestate was stripped in a batch operation before returning it to the digester immediately. For an unoptimized process, batch microbubble stripping successfully reduced TAN concentration by 51.4% while increasing methane production by 45.9%.

Table of Contents

List of Tables

List of Figures

Declaration

I, Ummul Hasanah Haji Hassan, hereby declare that the thesis submitted here is my own work and that the research presented here resulted from my efforts unless otherwise indicated. This work has not previously been submitted to this, or any other, university for an award.

Chapter 1 : Introduction

1.1 Research Background

1.1.1 Anaerobic digestion as a source of renewable energy

Global warming is an issue that exists for many years. Soil, air, and water pollution have been increasing due to the continuous use of fossil fuels as energy sources. Thus, it has become necessary to look for alternative fuel sources that are not harmful to the environment. There have been numerous anaerobic digestion applications worldwide, including sewage sludge treatment, organic fractions of municipal waste, and agricultural waste. This method minimizes the release of volatile organic compounds, stabilizes organic matter, produces an effluent with excellent fertilization properties, and recovers energy through the combustion of biogas. During anaerobic digestion, organic matter undergoes biological degradation in the absence of oxygen, yielding two main products, biogas and digestate (Dague et al., 1970; Lettinga, 1995). The biogas generated by these processes can generate renewable resources, while the digestate can be used for fertilization, as illustrated in Figure 1.1.

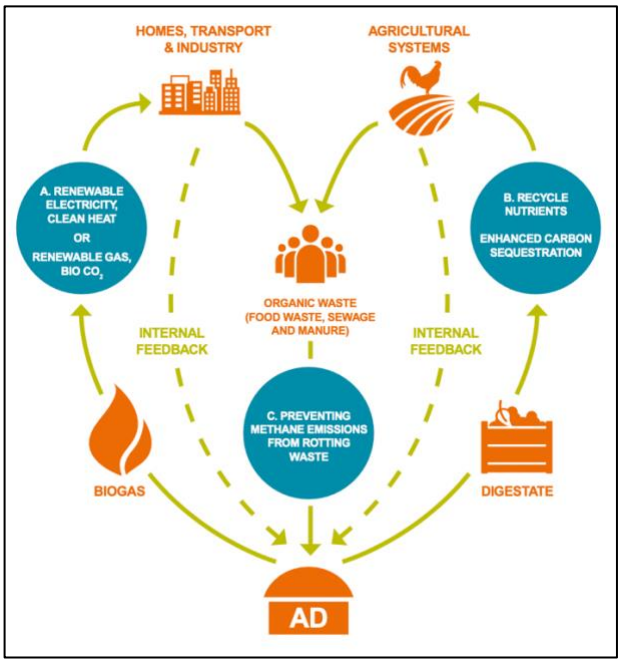

Figure 1.1: Key renewable resources produced by AD (ADBA, 2022)

Furthermore, the application of anaerobic bioreactors for organic waste eliminates the emission of greenhouse gases into the atmosphere. AD has thus become increasingly important as a means of disposing of organic waste and recovering energy (Ward *et al.*, 2008; ADBA, 2022).

1.1.2 Food waste

Approximately 931 million tonnes of food are wasted annually in the United States, of which 570 million tonnes are discarded by households according to the UNEP's Food Waste Index report (UNEP, 2021). As a result of its high decomposable organic compounds and moisture content, food waste poses challenges to waste management systems due to its rapid decomposition, odours, and health hazards. Additionally, food waste is disposed of in landfills, which is a major contributor to greenhouse gas emissions and global warming. It has been demonstrated that the anaerobic digestion of food waste is an effective method of reducing the amount of waste sent to landfills, thereby reducing pollution and odour problems associated with the disposal site (Ebrahimi-Nik *et al.*, 2018; Midgley *et al.*, 2021).

The moisture content of food wastes ranges between 70% and 80%, indicating a readily biodegradable organic substrate (Yaser *et al.*, 2022). Consequently, there is a reasonable expectation that all the methane that can be produced from this fraction will be captured and not released into the atmosphere. However, it is also necessary to address the issue of fugitive methane emissions. This depends on the digester's design, feeding system and operation. Even when an anaerobic digester is airtight, it may still emit some methane. These emissions may originate from fugitive emissions in the digester itself, from temporary storage during feeding of food waste, or from the digestate itself (El Mashad *et al.*, 2023). It has been reported that the biogas collection efficiency of anaerobic digesters in enclosed vessels was 99%, as opposed to the 70% efficiency of impermeable modular lagoons (EPA, 2009). The present work was conducted in a batch reactor with an enclosed tank, which minimized fugitive emissions as feeding occurred only at the beginning of the cycle.

1.1.3 AD intensification due seeding with CO_2 microbubbles

There have been numerous studies conducted to improve and increase the production of biogas from anaerobic digestion. The seeding (by sparging or injection) of carbon dioxide into anaerobic digesters had previously been suggested as an interesting method to improve the methane production from anaerobic digestion of organic waste and sludge (Bajón Fernández *et al.*, 2014, 2015; Al-Mashhadani *et al.*, 2016; Alibardi *et al.*, 2017). In comparison with the control reactor, carbon dioxide injection increased methane production by 20% (Bajón Fernández *et al.*, 2015; Koch *et al.*, 2015). In another study, a significant increase (about 100 - 110%) in the production of methane had been observed in the anaerobic digestion of food waste sparged with pure carbon dioxide gas (Al-Mashhadani *et al.*, 2016). There are several hypotheses regarding what causes the increase in methane production following the injection of exogenous CO_2, including the *in situ* stripping of inhibitor ammonia by CO_2 microbubbles within the digester in the bioreactor increases the degradation efficiency of the substrates (Al-Mashhadani, 2013).

1.1.4 Ammonia in AD

Anaerobic digestion also produces ammonia through the degradation of organic nitrogen. Ammonia is an essential nutrient for many organisms in the digester, and it also serves as a buffer. However, if ammonia concentration is excessive, it may inhibit digestion (Serna-Maza et al., 2017), specifically methanogenic activity and lead to VFA accumulation (Nielsen and Angelidaki, 2008). A decrease in biogas production will occur if ammonia and volatile fatty acids (VFAs) are accumulated in the digester. This will eventually result in the digester malfunctioning, particularly when using substrates with a low carbon-to-nitrogen ratio (details in Section 2.2.3).

Various approaches have been taken to overcome the inhibition caused by ammonia in order to maximize methane production. Despite being widely used as a low-energy industrial process, ammonia recovery by air stripping has the disadvantage of long processing time. Microbubbles can be utilised to influence chemical equilibrium to generate and strip ammonia. Accordingly, a recent study by Desai et al. (2021) showed that using microbubbles engendered

by an energy efficient fluidic oscillator can reduce the duration of the ammonia stripping process and increase the removal efficiency by up to 97% (Desai et al., 2021).

1.1.5 Removal of Ammonia from AD sparged with CO_2

Several studies have been performed on stripping ammonia from anaerobic digesters (Walker et al., 2011; Serna-Maza et al., 2017). However, no research has been conducted on removing ammonia from anaerobic digestion systems sparged with carbon dioxide microbubbles. This study examined the feasibility of stripping ammonia concentration from digestate in anaerobic digestion of food waste, sparged with carbon dioxide microbubbles, at a lower cost. The purpose of this is to maintain the ammonia concentration at a level that does not inhibit anaerobic digestion. This is performed by utilizing a fluidic oscillator in microbubble stripping. It also investigated whether it could increase methane production and reduce the costs associated with operation and maintenance.

1.2 Motivation, Aims and Objectives of the Research

A rise in food waste has led to increased landfills and greenhouse gas emissions. The anaerobic digestion process has the potential to manage food waste efficiently and generate renewable energy. In recent years, the sparging of CO_2 into the AD has demonstrated significant improvements in methane production. However, high ammonia levels in digestate inhibit the digestion process, resulting in a loss of capacity and slow production. Desai et al. (2021) reported that microbubbles created by Desai-Zimmerman (DZ) energy-efficient fluidic oscillators are capable of stripping ammonia at exceptionally fast rates. The present thesis is motivated to develop low-cost, low-energy alternatives that can be used to reduce ammonia levels in the anaerobic digestion of food waste with a low C/N value. A combination of CO_2 microbubbles sparging into the digester and ammonia microbubble stripping utilizing DZ energy-efficient fluidic oscillators as illustrated in Figure 1.2 below was used to further exploit AD's potential. In addition, the hypothesis of CO_2 sparging induced ammonia stripping in AD was also investigated.

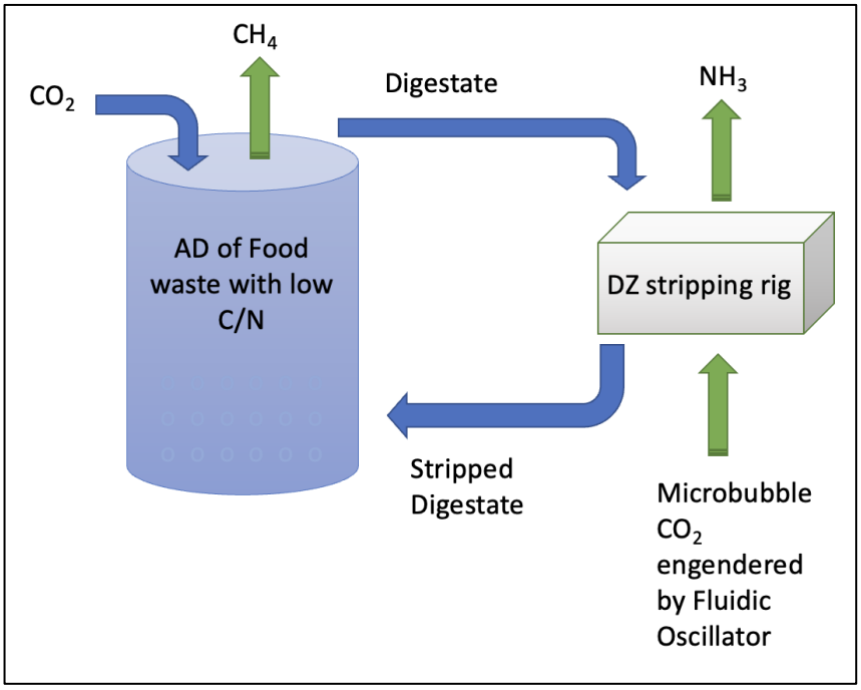

Figure 1.2: Illustration of combining microbubble CO_2 sparging and microbubble stripping utilizing DZ fluidic oscillator

The following objectives were identified in order to achieve the above aim: -

- Factors optimizing ammonia stripping
    - To study the performance of ammonia stripping using three different designs of rig utilizing microbubble engendered by fluidic oscillator. This is also to determine optimal operation parameters of the microbubble stripping to be coupled with the anaerobic digester.

- Investigation of *in situ* ammonia removal during CO_2 sparging
    - To investigate whether *in situ* ammonia stripping occur during the CO_2 microbubble sparging into the AD reactor and to identify the suitable gas medium for the batch ammonia stripping. In anaerobic digesters, methane production increased after sparging with microbubble CO_2, and it is thought that this occurs as a result of the CO_2 removing the ammonia inhibitors. An analysis about this has been presented in this study.

- Intensification of ammonia removal during AD
    - Finally, to investigate the feasibility of batch stripping with microbubbles engendered by a fluidic oscillator to reduce the TAN in a digester treating food waste to alleviate ammonia inhibition. Digesters were sparged with CO_2 microbubbles, and pH levels were not adjusted with additional chemicals.

The intention was originally to use a side-arm stripping system in anaerobic digestion, but there were many technical issues and limitations in addition to the pandemic that made it difficult to implement the system. Hence, microbubble stripping was carried out in a batch operation. This will serve as a starting point to point to demonstrate the feasibility of microbubble technology reducing the TAN in AD.

1.3 An overview of the thesis structure

Figure 1.3 illustrates the structure of the thesis, which consists of seven chapters. The current chapter outlines the background of the study, aims and objectives of the research. The second chapter provides a review of the literature, which analyses the literature to assess the key performance indicators for anaerobic digestions. The concept of anaerobic digestion, carbon dioxide seeding to anaerobic digesters, the issue ammonia in anaerobic digestion and its removal, and application of fluidic oscillator in stripping processes are discussed. Thereafter, Chapter 3 discussed the methodology and approaches used in the present study. This includes the methods and techniques employed in the analysis of the samples, design of the stripping rigs and anaerobic digesters, and the methods used for analysing the data.

The next three chapters are the experimental chapters. Chapter 4 assesses the performance of microbubble stripping engendered by fluidic oscillator using three different rigs. This was to identify their potential in ammonia stripping and the operating conditions for the simultaneous stripping from anaerobic digester in the present work. Chapter 5 investigates whether ammonia was removed during the CO_2 sparging in the digester and the capability of CO_2 microbubbles in removing ammonia from the digestate. This also examines which suitable gas for removing ammonia from the digestate in the anaerobic digester. Following the optimal performance for ammonia microbubble stripping and identifying the gas medium for batch stripping, Chapter 6 presents the investigation of microbubble batch stripping coupled with anaerobic digester. Finally, a summary of the conclusions and suggestions for further research work are presented in Chapter 7.

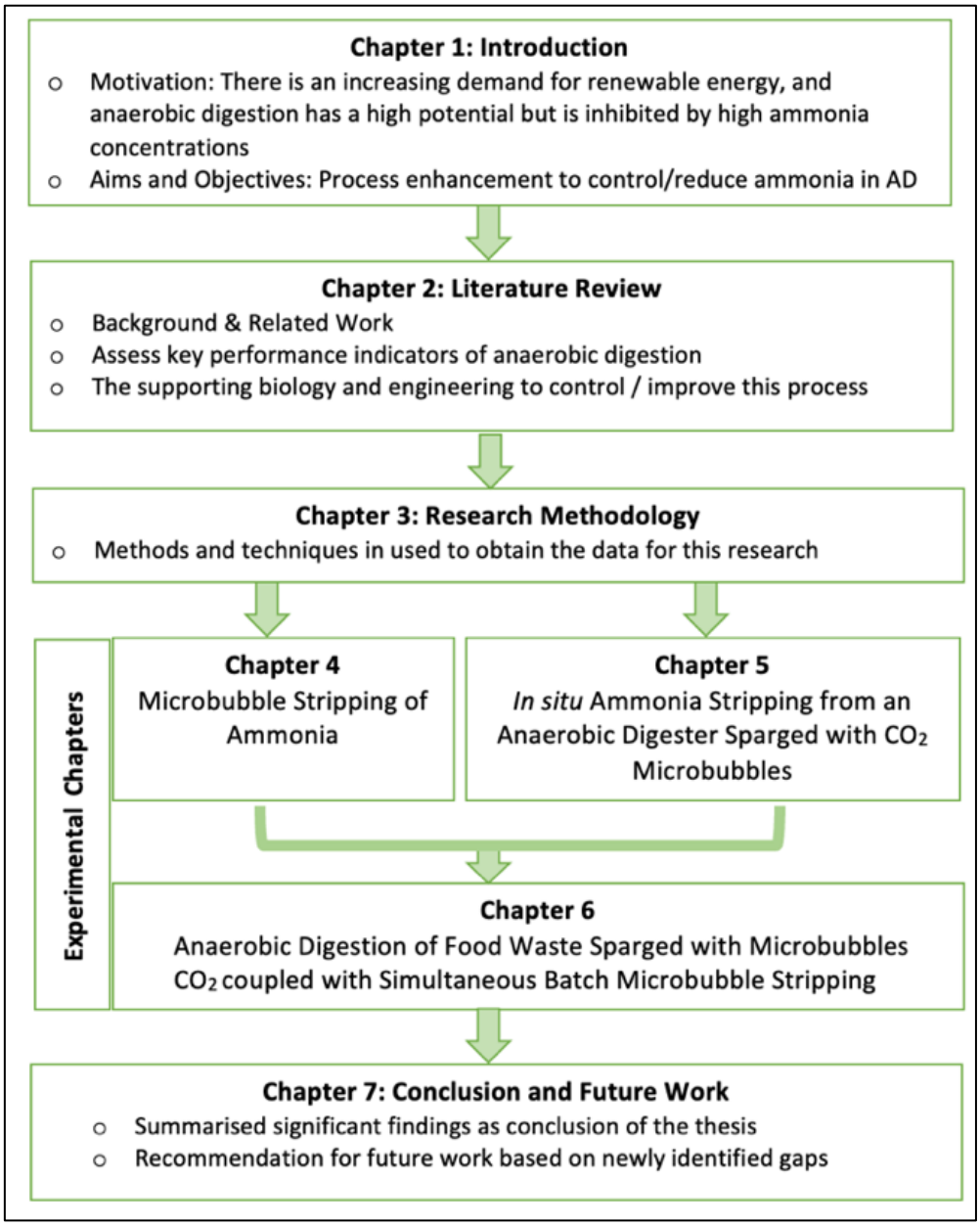

Figure 1.3: Approach and organisation of the present thesis

Chapter 2 : Literature Review

2.1 Introduction

It has been shown that anaerobic digestion is a viable alternative waste treatment method for the organic fraction of municipal solid waste, and it is a well-established technique that has gained widespread acceptance for its efficacy. Anaerobic digestion, AD is the breakdown of organic matter without the presence of oxygen, producing biogas and a residual effluent or digestate. The effectiveness of AD has been well documented for many decades. There are, however, a number of challenges that need to be addressed, in particular the issue of ammonia inhibition, which slows down the rate at which biogas is produced.

This chapter discusses several fundamental principles of anaerobic digestion and its status. Several topics are covered in this review, including ammonia inhibition and its removal, CO_2 sparging to AD, and fluidic oscillation. Accordingly, the specific research objectives for this project are determined considering the issues and gaps identified in this chapter.

2.2 Anaerobic Digestion: Principles and Applications

Figure 2.1 illustrates four stages of anaerobic digestion, which include hydrolysis, acidogenesis, acetogenesis, and methanogenesis. There are different microbial populations associated with each stage (Gujer and Zehnder, 1983).

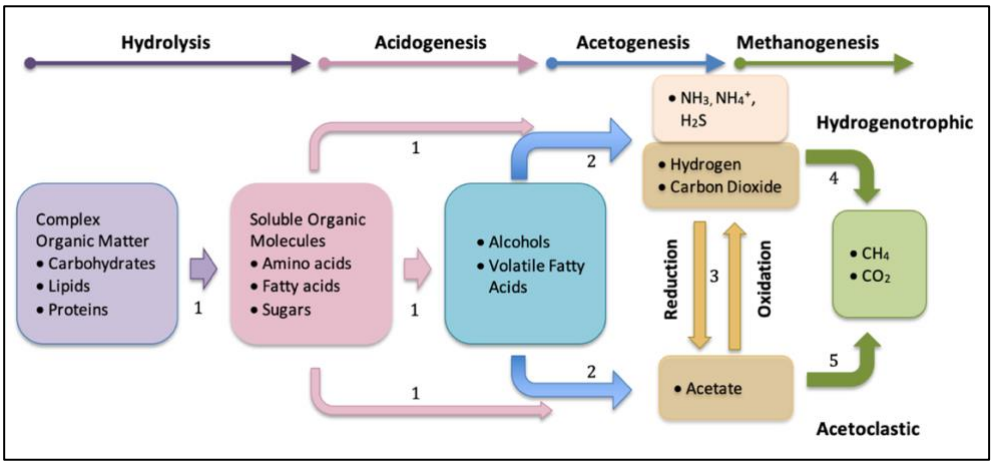

Figure 2.1: An overview of anaerobic digestion stages

There are several microorganism groups involved in this process (Saady, 2013), as indicated by the numbers:

1. Hydrolytic and Acidogenic bacteria
2. Acetogenic bacteria
3. Homoacetogenic bacteria
4. Hydrogenotrophic methanogens
5. Aceticlastic methanogens

During the first stage of hydrolysis, the heavier molecular weight carbohydrates, proteins, and fats are broken down into simpler and soluble polymers. These include simple sugars, amino acids, and fatty acids. Acid forming bacteria break down the soluble polymers into organic acids, alcohols, hydrogen, and carbon dioxide in acidogenesis. A variety of small organic compounds are also produced in this stage for instance, volatile fatty acids (acetate and higher organic acids including propionate and butyrate) along with ammonia and hydrogen sulphide. This is the most rapid step and the least prone to inhibition in the anaerobic digestion system (Koster and Lettinga, 1988; Robbins et al., 1989). In the subsequent stage (acetogenesis), hydrogen-producing bacteria reduce the alcohol and volatile fatty acids (VFAs) into acetate. Hydrogen, carbon dioxide, ammonia, and hydrogen sulphide are also produced during this process.

The final stage, methanogenesis involves the production of methane and carbon dioxide. Based on the pathway used to produce methane, methanogenic archaea can be classified into two groups. The acetoclastic pathway is the first pathway that produces methane and carbon dioxide directly from acetate by acetoclastic methanogens. A second pathway involves syntrophic acetate oxidation (SAO) and hydrogenotrophic methanogenesis, whereby acetate was oxidised to produce hydrogen and carbon dioxide, followed by methanogens that reduce carbon dioxide and hydrogen into methane (Yang *et al.*, 2018).

Anaerobic digestion has the main advantage of requiring no oxygen, thus resulting in lower operational costs than aerobic digestion. Anaerobic digestion produces biogas that can be

burned to generate heat or used to power a generator to create electricity. Waste and wastewater can be treated in an environmentally friendly manner that reduces the consumption of energy and the emission of greenhouse gases through anaerobic digestion. Moreover, the digestate (solid component) remaining can be used as soil conditioners to increase the organic content and as organic fertilisers to supply vital nutrient to soils. The digestate can also be an alternative to chemical fertilisers, as it requires less energy and cost to manufacture.

The performance of anaerobic digestion varies according to the type of substrate being digested as well as the configuration and operation of the anaerobic digestion unit. Research challenges remain in both areas. This thesis focuses primarily on the challenges involved in the second issue, improvement on the operation of the AD unit particularly on the ammonia inhibition.

2.2.1 Feedstock and inoculum

Most easily biodegradable biomass materials are suitable for use as anaerobic digestion feedstocks. Manure from livestock, food waste, and sewage sludge are the most commonly used feedstocks. Feedstock energy yields are subject to a number of factors such as their type, the degree of processing or pre-treatment, and the amount of biodegradable material that is present. Several different types of feedstocks can be used for anaerobic digestion, including food waste, agricultural waste, animal manure, wastewater sludge, and sewage. Compared to the other substrates, food waste has a high organic content, and anaerobic digestion is a feasible method of reducing treatment costs (incineration) and recovering renewable energy.

Food waste was used as the feedstock for AD in the present study. It can be quite challenging to dispose of kitchen food waste due to its bulk density as well as its biodegradability (Jouhara et al., 2017). However, the high calorific value and moisture content of kitchen food waste make it suitable for anaerobic treatment. In most cases, protein makes up a significant portion of food waste, which then degrades to produce a substantial amount of ammonia. As a result, the concentration of ammonia in the anaerobic digesters of food waste is generally higher than in other types of waste. Thus, the present study utilized food waste as the feedstock to

investigate the feasibility of simultaneous batch microbubble stripping to reduce the ammonia in the digestate and control the ammonia inhibition in the digester.

An essential step in the beginning or speeding up the process of anaerobic digestion is the application of inoculum to the feedstock (Staley et al., 2006; Vargas-García et al., 2007; Wang and Wu, 2008). Anaerobic digestion requires the presence of active microbial communities in inoculums. In the early stages of anaerobic digestion, organic matter concentration is sufficient, while microbial communities are limited. Therefore, seeding with various inocula and increasing microbial concentration during this phase will facilitate digestion. The inoculum used in the present study was obtained from the anaerobic digestion of food waste in previous work.

2.2.2 pH and Temperature

A high pH value may be detrimental to many anaerobes in anaerobic digestion, and this depends on the specific pH range and tolerance of the microorganisms involved (Lin *et al.*, 2022). For instance, fermentation bacteria can be active at pH levels ranging from 4 to 8.5 while methanogens can thrive at pH levels ranging from 6.5 to 7.2 (Braguglia et al., 2018). Therefore, pH has a vital role in the AD system to ensure stability and efficiency of anaerobic digestion processes. In addition to adversely affecting the growth of the microbial population, it also leads to the accumulation of substances that inhibit the process, including ammonia and volatile fatty acids (VFAs). Studies have shown that a pH range between 6.8 and 7.2 is optimal for mesophilic anaerobic digestion (Gerardi, 2003). Initially, the pH of an anaerobic digester will drop because volatile acids are produced. However, upon consumption of these acids by methanogens, alkalinity is created, which raises the pH of the digester and stabilizes it over time (Gerardi, 2003).

Similarly, the operating temperature of an anaerobic digestion system has a significant impact on microbial growth and ammonia accumulation. Anaerobic digestion can occur at a temperature below 20 ^{o}C (psychrophilic), but this process is slow. Heat is typically required to accelerate the process, increasing the feedstock's temperature, and enhancing biogas production. The majority of anaerobic digestions occur at either mesophilic (30 - 40 ^{o}C) or

thermophilic (50 - 60 ^{o}C) temperatures (Ahring *et al.*, 1995). It has been shown that an increase in temperature can boost the growth rate and metabolic rate of microbial microorganisms (El-Mashad *et al.*, 2004). Therefore, thermophilic microorganisms digest food more rapidly than mesophilic microorganisms. However, thermophilic digestion tends to be less advantageous because of the high operating costs associated with heating as well as the greater susceptibility of microorganisms to toxic substances, leading to increased free ammonia nitrogen concentrations, resulting in operational instability and, at worst, triggering system failure (Gerardi, 2003). A higher concentration of ammonia will increase ammonia toxicity, inhibiting digestion and leading to a lower methane yield from biogas. A decrease in temperature, on the other hand, will alleviate ammonia inhibition but may have adverse effects on the microbial community. Thus, the mesophilic temperature is the most preferable and was employed in the present study.

2.2.3 The ratio of carbon to nitrogen in the feedstock

A suitable carbon to nitrogen ratio is crucial to the anaerobic digestion process, in which microorganisms need a sufficient ratio of carbon to nitrogen to carry out their metabolic functions. There are two main benefits associated with the presence of nitrogen in the feedstock. Firstly, it provides a crucial element for synthesizing amino acids, nucleic acids, and proteins. Secondly, it increases buffer capacity due to its conversion into ammonia. In addition, ammonia is necessary to neutralize the volatile acids generated by fermentative bacteria, thereby maintaining a neutral pH level essential for the growth of cells (Procházka *et al.*, 2012). However, an excessive amount of nitrogen in a substrate can cause excessive ammonia production, resulting in toxicity.

On the other hand, a low ammonia concentration may have a negative effect on methane yields and acetoclastic methanogen activity. Carbon to nitrogen ratios are usually high in crop residues, and pH and buffering capacities are low, resulting in the accumulation of volatile fatty acids (Wang *et al.*, 2012). The lack of nitrogen also resulted in an insufficient utilization of carbon sources (Resch *et al.*, 2011). Consequently, less biogas will be produced since methanogenic archaea will rapidly consume the nitrogen (Kayhanian, 1999). It is caused by a lack of buffer capacity and an inadequate supply of nutrients from nitrogen (Rajagopal *et al.*, 2013). Thus, appropriate amount of nitrogen is required in the feed to prevent toxicity due to

ammonia (excess nitrogen) or nutrient deficiency (insufficient nitrogen). The nitrogen content of the feed has previously been stated as the primary factor in inhibition caused by ammonia (Yao *et al.*, 2017).

In general, anaerobic microbes consume carbon at a rate 20 to 30 times greater than nitrogen. Therefore, to ensure an efficient biogas production process, feedstocks should have a carbon to nitrogen ratio between 20 and 30 (Haque and Haque, 1970). When feedstocks with lower C/N ratios are digested, the concentration of ammonia produced will be higher, resulting in greater ammonia inhibition. Specifically, the present study explored the effects of CO_2 sparging and simultaneous microbubble batch stripping on an anaerobic digestion system for food wastes with a low C/N value.

2.2.4 Mixing

Proper mixing optimises anaerobic digestion since mixing ensures chemical, biological, and physical uniformity within the digester (Appels et al., 2008). There is a tendency for solids to accumulate at the bottom of the digester when there is insufficient mixing, leading to an inefficient digestion process. Mixing also provides contact between active biomass and organic substrate (Appels et al., 2008). Furthermore, the digestion process can also be accelerated by efficient mixing. The mode and intensity of mixing directly affect the methane yield of anaerobic digestions (Karim, Klasson, et al., 2005; Vavilin and Angelidaki, 2005; Ahmadi-Pirlou et al., 2017). There are three common ways to introduce mixing in the anaerobic digesters. These include gas-mixing systems where biogas and other gases are recirculated, mechanical mixing systems in which turbine impellers working at low speeds are installed through the digester cover or wall of the digesters, and lastly, using mechanical pumping systems, achieved by circulation of working liquid using pumps installed either internally or externally (Karim, Hoffmann, et al., 2005; Deublein and Steinhauser, 2008). It has been noted that mechanical mixing is the most effective method for mixing input power per unit volume. However, this method is subject to certain limitations such as wear and high-cost maintenance associated to the presence of mobile features such as ball bearings, impellers, and shafts in the digester. Liquid recirculation is considered to be a simple and energy-efficient process. It is commonly

employed in conjunction with mechanical mixing or gas injection, but may also be applied as a standalone technique (Dabiri et al., 2021).

The operation of mixing affects the efficiency of the digester at higher solid contents (more than 4%). However, mixing is unnecessary at lower solid contents (below 4%) as the results were the same in mixed and unmixed digesters (Singh et al., 2020). The maintenance and operational costs of the mixing system are often high-priced. Despite the great importance of mixing in anaerobic digesters, it was reported that mixing faults are responsible for approximately 44% of the failures of biogas plants (Hopfner-sixt and Amon, 2007). Therefore, it is vital to obtain efficient mixing to increase productivity and reduce the energy requirements of the anaerobic digestion systems. Simulation results from the previous study on the application of microbubbles in anaerobic digestion observed that the use of microbubbles enhanced efficiency of mixing by increasing the circulation liquid velocity (Al-Mashhadani, 2013).

2.3 Carbon dioxide enrichment to anaerobic digester

Multiple research groups have examined the benefits of CO_2 seeding in biogas production for a variety of anaerobic processes. The reduction of carbon dioxide to methane during anaerobic digestion has been associated with hydrogenotrophic methanogens (Demirel and Scherer, 2008). A number of early studies utilized exogenous hydrogen to facilitate biological feasibility of CO_2 to promote hydrogenotrophic methanogenesis, thereby increasing methane production (Alimahmoodi and Mulligan, 2008; Götz et al., 2016; Yan et al., 2016). However, the high-cost production and low water solubility of hydrogen posed a barrier to wide-scale implementation. The problem was then overcome by injecting carbon dioxide directly into the digesters without adding exogenous hydrogen. The effectiveness of this procedure has been evaluated in a number of studies. An increase of 20% in the production of methane was observed following the flushing of AD headspace with CO_2 (Koch et al., 2015). Increasing the proportion of CO_2 in the flush gas increases methane yield, as demonstrated in previous research in which a significant increase in methane yield of up to 30% was achieved at a ratio of 100% CO_2 compared to 100% N_2 gas (Koch et al., 2016). In a study of batch anaerobic digestions used to

treat food waste, methane production increased by 11 - 16% within the first 24 hours following seeding with CO_2 (Bajón Fernández *et al.*, 2014). Another study observed a significant increase (about 100-110%) in the production of methane in an anaerobic digestion food waste sparged with microbubbles of pure carbon dioxide gas. (Al-Mashhadani *et al.*, 2016). Further, it has been reported that continuous sewage sludge digestion seeded with CO_2 increased the production of methane by 12 percent (Alibardi et al., 2017). The results of this study indicate that it is possible to convert exogenous carbon dioxide into methane biochemically without adding exogenous hydrogen to the process. Furthermore, these previous studies also achieved significant improvements in methane yields. Consequently, this study aims to investigate the feasibility of removing ammonia from digestate during anaerobic digestion sparged with carbon dioxide microbubbles to maximize methane yield.

There have been several hypotheses proposed regarding the process by which exogenous CO_2 can significantly increase methane production including the *in situ* stripping of inhibitor ammonia by CO_2 microbubbles within the digester increases the degradation rates/efficiency of the substrates (Al-Mashhadani, 2013). Chapter 5 of the present study investigated the validity of this hypothesis. Also, it evaluated whether CO_2 gas would be able to remove ammonia from the system and if it could be utilized as stripping gas in the batch stripping rig.

2.4 Ammonia in anaerobic digestion

2.4.1 Introduction

Anaerobic digestion systems produce ammonia (NH_3) and ammonium ions (NH_4^+) as by-products of protein digestion and organic nitrogen reduction. Anaerobic microorganisms require these nutrients to grow, but when the concentration of free ammonia reaches a high level, the anaerobic digestion system is significantly inhibited. Therefore, biogas plants experience low biogas production rates due to the toxicity effect of high ammonia levels in anaerobic digestion. In addition, Methanogenesis is said to be hindered by ammonia. There is substantial evidence that methanogens are sensitive to ammonia (Borowski *et al.*, 2014).The theoretical amount of ammonia produced from a substrate can be calculated by using stoichiometric Equation 2.1 (Kayhanian, 1999; Chen *et al.*, 2008):

$$C_aH_bO_cN_d + \frac{4a - b - 2c + 3d}{4} H_2O \rightarrow \frac{4a + b - 2c - 3d}{8} CH_4 + \frac{4a - b + 2c + 3d}{8} CO_2 + dNH_3$$

Equation 2.1

Previous studies have found that the level of ammonia inhibition varies according to operational conditions, such as temperature and pH. The equilibrium in an aqueous system is established by the formation of ammonia and ammonium ions, as expressed in equation 2.2:

$$NH_3\ (g) + H^+ \rightleftharpoons NH_4^+\ (aq)$$

Equation 2.2

Total ammonia-nitrogen, also known as TAN, is composed of free ammonia nitrogen, NH_3 (FAN), and ammonium ions, NH_4^+. Temperature and pH are commonly attributed to the composition of these two components. Most previous studies have indicated that the free ammonia in total ammonia-nitrogen is more toxic to the AD process than ammonium ions (Chen *et al.*, 2008). The free ammonia concentration, FAN, can be calculated using equations 2.3 and 2.4 (Angelidaki and Ahring, 1993; Hansen *et al.*, 1998; Calli *et al.*, 2015):

$$FAN\left(\frac{mg}{L}\right) = \frac{TAN\left(\frac{mg}{L}\right)}{1 + 10^{(pKa - pH)}}$$

Equation 2.3

$$pKa = 0.09018 + \frac{2729.92}{T + 273.15}$$

Equation 2.4

In this case, pK_a and T stand for the dissociation constant of the ammonium ion, NH_4^+, and the temperature (^oC), respectively. Based on the equations above, it can be concluded that an increase in temperature will result in a reduction of the pK_a value, which in turn will result in an increase in the concentration of FAN. Based on Le Chatelier's principle, an increase in pH initiates a similar trend in FAN concentration. Figure 2.2 shows the FAN concentrations for digesters treating food waste and cattle manure at different TAN concentrations, temperatures and pH for mesophilic and thermophilic systems (Borja *et al.*, 1996; Banks *et al.*, 2012). In Figure 2.2, it can be seen that an increase in pH from 7.6 to 8.1 results in a two-fold

increase in FAN concentration. In addition, the red lines in Figure 2.2 illustrate the effect of temperature on the concentration of FAN. At pH 8, 700 mg/L of FAN can be obtained in mesophilic and thermophilic systems with TAN concentrations of 5500 mg/L and 2500 mg/L, respectively. A high FAN concentration in TAN can be toxic to AD systems, so it can concluded that mesophilic digesters are able to tolerate a higher TAN concentration than thermophilic digesters (Serna-Maza, 2014).

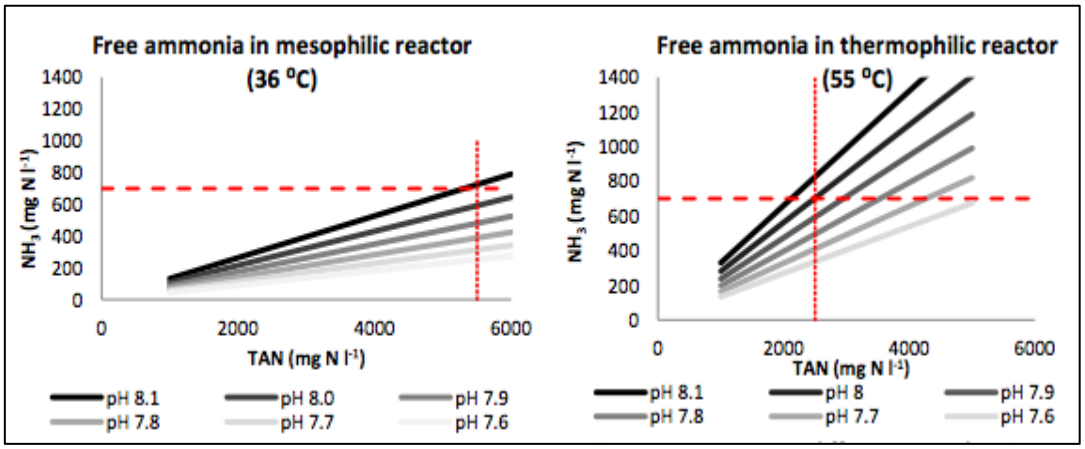

Figure 2.2: Concentrations of FAN at different TAN concentrations, temperatures, and pH (Serna-Maza, 2014)

The rise in biogas production can also be attributed to the relief from ammonia inhibition caused by FAN as the operating temperature and pH were reduced. There is also the possibility, however, that different microorganisms may dominate the process based on the operating temperature (Akindele, 2016).

Previous studies have shown that the toxic effects of ammonia on anaerobic digestion systems are affected by pH. An increased amount of free ammonia, considered more toxic than ammonium ions, was found at a higher pH. Free ammonia diffuses into the cells of microorganisms, obstructing their metabolic enzymes (Gallert *et al.*, 1998). Studies have shown that adjusting the pH of anaerobic digestion may alleviate the toxic effects of ammonia. For instance, according to a study on the anaerobic digestion of piggery manure, ammonia inhibition is relieved by decreasing the pH level from 8 to 7.4 (Braun, 1981). As a result of the reduced pH level in the anaerobic bioreactor, the FAN concentration is lower. An additional study revealed that an optimal pH level is required for the growth of microorganisms. An

inappropriate pH level may also lead to anaerobic digestion system failure, even if the ammonia concentration is not very high (Kroeker *et al.*, 1979).

Fig. 2.3 illustrates the effects of pH and temperature on the percentage of FAN concentration in TAN. At higher temperatures and pH levels, the percentage of FAN increased significantly.

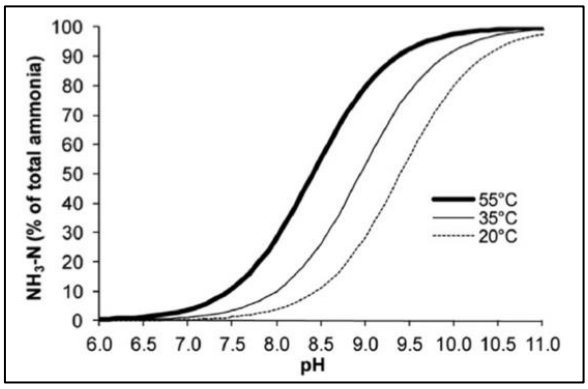

Figure 2.3: The percentage of FAN in solution at different temperatures and pH levels (Fernandes *et al.*, 2012)

The equilibrium between NH_3 and NH_4^+ also affects CO_2 and volatile fatty acids, VFA production in anaerobic digestion. Ammonia (NH_3) is a weak base and can contribute to the alkalinity of the system. Adequate alkalinity is important for maintaining a stable pH within the optimal range for microbial activity during anaerobic digestion (Procházka *et al.*, 2012). The stability of pH conditions contributes to maintaining the activity of acidogenic bacteria, which are responsible for breaking down complex organic matter (Li *et al.*, 2020). In this way, ammonia can indirectly support CO_2 production by promoting acidogenic bacteria activity.

VFAs are intermediate compounds formed during the breakdown of organic matter and are typically converted to methane by methanogenic microorganisms. Elevated ammonia concentrations can increase VFA production. As ammonia accumulates in bioreactors, it consumes alkalinity (buffering capacity) by reacting with free protons, H^+, and carbonate ions, CO_3^{2-}. Excessive ammonia concentrations can deplete the alkalinity in the system, resulting in a reduction in buffering capability. Consequently, reducing the ability of the system to neutralize acids produced during digestion. This then leads to the accumulation of VFAs due to

methanogenic inhibition caused by ammonia toxicity. The accumulation of VFAs lowers the system's pH, resulting in acidification, which may adversely affect the activity of methanogens and further exacerbate the inhibition caused by ammonia (Braguglia *et al.*, 2018).

On the other hand, low ammonia concentrations can also adversely affect anaerobic digestion. The growth and function of methanogens are dependent upon a certain level of ammonia. An inadequate level of ammonia can restrict microbial growth and activity, resulting in a reduction in biogas production (Braguglia *et al.*, 2018).

The balance between ammonia, CO_2, VFAs, and alkalinity is crucial to anaerobic digestion. This can be achieved by controlling feedstock composition, maintaining appropriate pH levels, and monitoring ammonia concentrations. Additionally, it is essential to monitor and adjust operating parameters regularly to avoid the accumulation of excess ammonia, which could lead to acidification, the accumulation of VFAs, and the inhibition of methanogens. Moreover, it is possible to maintain adequate alkalinity levels by selecting appropriate substrates and supplementing them to prevent pH fluctuations and maintain process stability. Anaerobic digestion systems can be maximized by understanding the relationship between ammonia, CO_2, VFAs, and alkalinity and carefully managing these parameters.

A number of critical concentration ranges have been reported in the literature studies that trigger ammonia inhibition. It is mainly due to differences in the operational conditions or substrates applied. Studies have indicated that a concentration of TAN of between 1700 and 14000 mg/L inhibits methane production (Chen *et al.*, 2008). An experimental study revealed that TAN concentrations must be less than 2500 mg/L to prevent ammonia inhibition during anaerobic digestion of food waste using a side-stream stripping method (Serna-Maza *et al.*, 2015). A separate study found that the anaerobic digestion of dairy manure with simultaneous ammonia stripping was inhibited when the nitrogen concentration was above 1800 - 2400 mg/L (Yao *et al.*, 2017). According to another study examining the effect of ammonia concentration on anaerobic digestion performance, ammonia inhibition occurred at concentrations above 3000 mg/L TAN. Additionally, the findings of this study indicate that ammonia is toxic regardless of its pH value (Calli *et al.*, 2015).

According to previous research, plants at full scale would be too expensive or time-consuming to remediate the ammonia toxicity effect (Wang, 2016). For example, the dilution method developed to reduce ammonia concentrations has weakened the economic justification of AD of piggery wastewaters. As a result of decreased mass retention time and efficiency, as well as rising dewatering costs, biogas production has decreased (Nielsen and Angelidaki, 2008). Accordingly, this study aims to evaluate a feasible and sustainable solution for mitigating the effects of ammonia toxicity in anaerobic digesters seeded with CO_2 microbubbles. Notably, fluidic oscillators constitute the cheapest and most cost-effective method for producing microbubbles, as they have no moving parts and require little maintenance (Zimmerman *et al.*, 2008). Section 2.5 provides a detailed description of this technology.

2.4.2 Previous work in removing ammonia from digestate

There are several different methods through which ammonia can be removed from digestate, including chemical, biological, or physical methods (Magrí *et al.*, 2013). As part of the biological process of anaerobic ammonia oxidation (Anammox) or nitrification/denitrification, soluble nitrogen is released into the atmosphere as nitrogen gas (Jördening and Winter, 2005). An example of physical treatment is thermal-drying, whereby some of the liquid is removed from raw digestate to recover nutrients (Rehl and Müller, 2011). Through this process, ammoniacal nitrogen can be liberated and recovered in the gas phase. However, a high energy requirement is associated with this technique (European Biogas Association, 2013).

Different chemical methods have different levels of effectiveness based on the amount and type of chemicals used. For example, treatment using struvite precipitation achieved a 95% removal efficiency of ammonia from digestate (Escudero *et al.*, 2015). While this technique has some advantages, there are also some limitations, including the need to use expensive reagents and to maintain a precise pH level (Pastor *et al.*, 2010).

In addition, stripping is an alternative method that has proven to be effective in removing and recovering ammonia from digestate, slurries, and waste. In this method, air is passed through the liquid, allowing the ammonia to vaporise into the gas phase, where it can be absorbed and recovered. A number of characteristics of the digestate, such as its high pH and ammonia

content, make it a more suitable candidate for stripping than other methods of removal (Saracco and Genon, 1994; Bonmatí and Flotats, 2003; Lei *et al.*, 2007).

Stripping can be applied in various configurations to decrease the concentration of TAN within a bioreactor. Therefore, this study is using this technique to reduce ammonia in digestate. Section 2.5 will provide a more detailed explanation of the stripping technology and its application to AD.

2.5 Stripping

2.5.1 Introduction

It has been demonstrated that stripping ammonia from liquid wastes such as digestate or urea fertilizer plant wastes and leachate (Cheung et al., 1997) can be a valuable technique to recover ammonia (Minocha and Prabhakar Rao, 1998). A stripping method involves transferring dissolved components from a liquid to a gas by the principle of mass transfer (Kinidi et al., 2018). Various stripping reactors have been implemented, including bubble columns, packed columns, spray towers, and trayed towers. Due to the possibility of plugging in packing or trays, handling slurries or digestate can be challenging (Minocha and Prabhakar Rao, 1998). It is therefore recommended that spray contactors and bubble columns be used to handle slurries in order to eliminate any potential problems associated with them. Figure 2.4 shows the basic operation of ammonia stripping using a bubble column, in which gas is introduced into the bottom of the rig to create bubbles inside the rig. The stripping gas absorbs ammonia from the liquid and releases it into the headspace. The ability to strip ammonia from the liquid highly depends on the ammonia dissociation equilibrium (Equation 2.2) and the amount of ammonia present in gaseous form. By selecting suitable operational conditions, this amount can be increased. High temperatures and high pH levels mainly facilitate the removal of ammonia. By increasing the contact area between the gas and the liquid, the mass transfer could be maximized during the stripping process. The gas can be dispersed into a continuous liquid phase using a technique such as dispersion. By employing this technique, operational problems associated with slurries or digestates can be avoided (Rousseau, 1987).

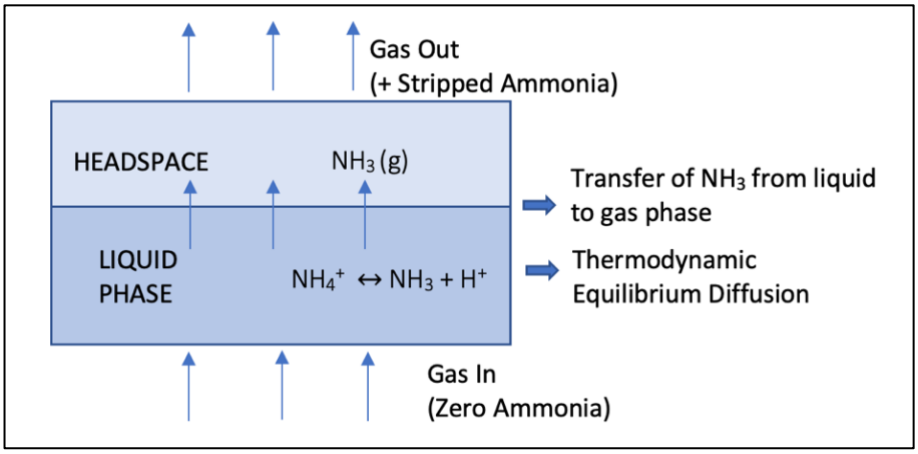

Figure 2.4: An illustration of the ammonia stripping

The process of stripping ammonia is simple and does not produce any additional sludge. Ammonia stripping can generate highly concentrated ammonia, which has a higher value as a fertilizer. This technique also offers the benefits of a relatively simple process and a high transfer rate (Rousseau, 1987). The present study involved the use of a simple rig filled with digestate through which a gas is bubbled. Previous research had investigated the use of microbubbles as a new method of removing ammonia from gas (Desai *et al.*, 2021). Microbubbles were generated by the fluidic oscillator to increase the area of contact in this research. Section 2.6 describes this technology in more detail.

2.5.2 pH and Temperature

In an aqueous solution, temperature and pH greatly influence the concentration of FAN (ammonia dissociation equilibrium). The efficiency of ammonia removal is primarily determined by two thermodynamic equilibrium states, namely the ammonia dissociation equilibrium ($NH_4^+ \leftrightarrow NH_3 + H^+$) and Henry's law equilibrium. A relationship between the concentration of ammonia in a liquid [$NH_{3(L)}$] and that in a gas [$NH_{3(g)}$] can be determined using Henry's law (Yoon *et al.*, 2008):

$$H = \frac{[NH_{3(g)}]}{[NH_{3(L)}] \cdot \alpha_{NH_3}} \qquad \text{Equation 2.5}$$

where H and α_{NH3} represent dimensionless Henry's law constant and the fraction of ammonia in the liquid phase, respectively. With a larger H value, the equilibrium becomes more favourable. Substances with larger Henry's law constants tend to volatilize more readily. Perry's Chemical Engineers' Handbook states that H values increase as temperature increases. At higher temperatures, the equilibrium is much more favourable. This equilibrium is altered by an increase in temperature, where a more substantial percentage of FAN is present. By increasing the driving force, the free ammonia will be able to volatilize into a gaseous form as the saturated vapour of free ammonia increases with heat (Kinidi *et al.*, 2018). At higher pH and temperature, free ammonia content is greater. Conventionally, ammonia stripping can be achieved at moderate temperatures (ranging from room temperature to 50 ^{o}C), provided the pH is between 10 and 12. pH adjustment requires a large quantity of reagent. Alternatively, a higher temperature can be applied to reduce the operating pH and reagent use.

The effect of pH on the removal of ammonia from piggery wastewater at 37 ^{o}C was investigated by Zhang *et al.* (2011). Figure 2.5 illustrates how the removal rate of ammonia increases significantly with an increase in pH after 48 hours of stripping.

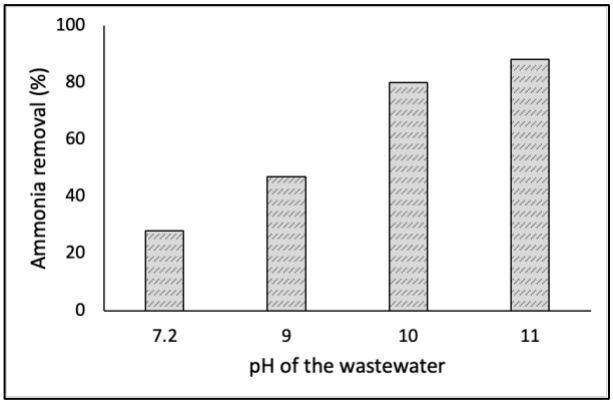

Figure 2.5: Ammonia removal after 48 H of stripping at different pH (Zhang *et al.*, 2011)

A pH increase may be achieved by adding alkaline agents such as calcium hydroxide ($Ca(OH)_2$), calcium oxide (CaO) or sodium hydroxide (NaOH). A study of air stripping on pig manure revealed that sodium hydroxide is the simplest and can increase the pH rapidly, however AD inhibition was observed by sodium ions as a result of air stripping (Zhang and Jahng, 2010; Zhang *et al.*, 2011). It has also been reported that sodium hydroxide requires the addition of

an antifoaming agent since problems related to foaming may occur during the stripping process. Under the same operating conditions and dose, calcium oxide and calcium hydroxide were able to achieve the required pH. There is, however, a 1.5-times higher dosage required for these two alkaline agents compared to sodium hydroxide (Serna-Maza *et al.*, 2015). Calcium hydroxide may cause a solid blockage if it reacts with carbon dioxide in the biogas. Moreover, the addition of chemicals to control pH increases operating costs. This study had a major concern concerning the accumulation of additional ions since the digestate was returned to the digester after being stripped. Microbubbles have been reported to remove ammonia even at pH levels below 8 (Desai, 2017). Therefore, microbubbles were utilized in the present study to remove ammonia simultaneously from AD.

As part of this research, microbubble stripping experiments were carried out at different temperatures. (Chapter 4). In accordance with expectations, the efficiency of ammonia removal increased with temperature. The stripping temperature in the present paper was carried out at no higher than 70 ^{o}C to avoid disruption to the microorganism in the digestate. There was no pH adjustment in the present study, so the effect of pH was not studied. The digestate from the bioreactor was stripped at its original pH.

2.5.3 Stripping gas and its flow rate

A suitable stripping medium is essential because it influences both the efficiency of the removal process and the operating cost. Gases such as steam, air, inert gases and hydrocarbons are the most common stripping gases (Seader *et al.*, 2011). Anaerobic digestion of food waste with a working volume of 35 L was previously studied with the simultaneous removal of ammonia by stripping using biogas as the stripping medium. Based on the results, the amount of ammonia-nitrogen in the system was reduced to levels below toxic levels compared to control digesters without stripping (Serna-Maza, 2014). In another study, ammonia stripping using nitrogen gas was combined with AD systems for treating dairy manure. The nitrogen gas was introduced to the liquid phase of the digester through an aquatic air stone. Ammonia is captured by passing the off gases of the stripping through sulphuric acid and sodium hydroxide. A comparison is made between the results obtained in this experiment and the results obtained in a control AD system without stripping. It was observed that the efficiency of the AD system had improved

significantly. Moreover, the level of TAN was maintained below the inhibitory threshold (Yao et al., 2017).

In the stripping process, the flow rate of gas does not affect chemical reactions. However, it does affect the area of contact between liquids and vapours. It has been reported that increasing the gas flow rate reduces the resistance in mass transfer, thereby increasing the ammonia removal rate to some extent (Quan *et al.*, 2009). De la Rubia *et al.* (2010) observed the same effect when biogas was used in the ammonia stripping from food waste digestate. When the gas flow rate was increased from 0.125 to 0.375 $L_{biogas}\ L_{digestate}^{-1}\ min^{-1}$, an increase in ammonia removal rate of 4.5 times was observed. It is important to note, however, that high gas flow rates may cause issues associated with water evaporation, foaming, and cooling of wastewater (Liao *et al.*, 1995; De la Rubia *et al.*, 2010). Moreover, Serna-Maza *et al.* (2015) found there was no increase in ammonia removal when the gas flow rate was doubled. The present study also found a higher flow rate for greater ammonia removal (Chapter 4). Even so, high flow rates are not recommended due to the possibility of water evaporation, foaming, and substrate cooling caused by high flow rates. In addition, the low methane production is further attributed to the loss of organic materials due to a high stripping rate.

2.5.4 Duration of the stripping

Ammonia removal efficiency is also heavily influenced by the duration of stripping. The effect of stripping time on the efficiency of ammonia removal from the concentrated liquid from reverse osmosis systems has been investigated by Youcai (2018). The experiment was conducted at a mass flow rate of 6 L min^{-1} L^{-1}, with NH_3-N concentration at an initial level of 2121 mg L^{-1}. The operating temperature was 30°C with a pH of 11. Figure 2.6 presents the results.

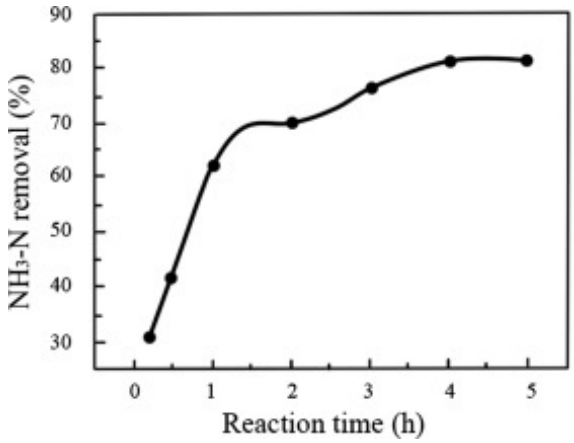

Figure 2.6: Reaction time versus percent ammonia nitrogen removed (Youcai, 2018)

The removal of ammonia nitrogen was observed to increase with the stripping time. An increase in ammonia nitrogen removal can be observed during the first half hour of the experiment, followed by a slowdown in the increasing trend. After four hours of running the experiment, equilibrium was reached in the air stripping process with little change in the efficiency of ammonia nitrogen removal (Youcai, 2018).

A sufficient air stripping time is essential for increasing ammonia-nitrogen removal rates. A recent study has employed microbubble generation induced by fluidic oscillations to achieve 100% separation efficiency in only 30 minutes as opposed to the 95% efficiency achieved by the industrial benchmark over a period of 30 hours (Desai *et al.*, 2021). The present study used a similar reactor to Desai et al. (2021) in order to conduct stripping in a short period of time since this is an exponentially decaying concentration profile, for which short running times offer the greatest return on investment.

2.5.5 Stripping Configuration in Anaerobic Digestions

In previous studies, it has been demonstrated that the stripping process can be used to remove ammonia liberated during anaerobic digestion (De la Rubia *et al.*, 2010; Serna-Maza *et al.*, 2015; Yao *et al.*, 2017). Stripping can be applied in different techniques to reduce the TAN of ADs (Figure 2.7). These include gas stripping as part of the feedstock preparation process, gas stripping following hydrolysis, *in situ* gas stripping from the primary digester simultaneously with biogas production, side-arm stripping to the anaerobic digester, and finally, post anaerobic digestion stripping (Walker *et al.*, 2011).

Pre-digestion stripping involves the removal of ammonia from the feedstock before feeding it to the anaerobic digester. It has been shown that this technique can be used to tackle the issue of ammonia inhibition by recovering ammonia before anaerobic digestion, thus preventing ammonia accumulation. This approach has been demonstrated in previous studies using nitrogen-rich substrates such as piggery wastewater and poultry manure (Angelidaki and Ahring, 1993; Zhang *et al.*, 2011; Niu *et al.*, 2013). However, pre-digestion stripping does not permit the maximum recovery of ammonia since it is impossible to recover the ammonia produced during anaerobic digestion itself.

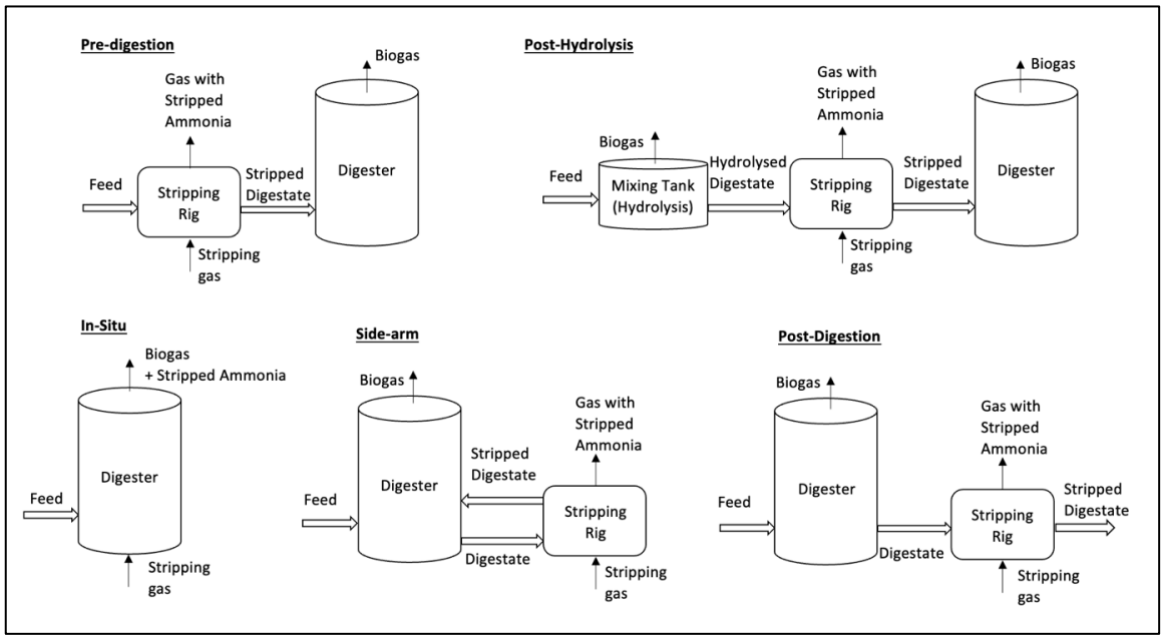

Figure 2.7: Different configurations of ammonia stripping in anaerobic digestion (Walker *et al.*, 2011)

Alternatively, the stripping of ammonia may also be accomplished after the hydrolysis step. The feedstock is initially fed into the first tank for hydrolysis to occur. The effluent from this tank is directed to a stripping column, which allows pH and temperature to be adjusted. It is possible to maximize hydrolysis and methane production in different reactors using this technique, thereby minimizing the impact of toxic ammonia on the methanogens (Serna-Maza, 2014). However, the selection of the volume of the hydrolysis tank and its residence time is a highly crucial aspect of this process. There are also significant uncertainties associated with this technique. The reason for this is the insufficient amount of experimental data available to

determine whether ammonia can be released at full capacity during the hydrolysis process. As a result, it may be necessary to use large quantities of chemicals to increase the rate of hydrolysis. Additionally, the effluent of the hydrolysis reactor may contain a high level of VFA, which could affect the stripping process (Walker *et al.*, 2011).

The *in situ* ammonia stripping procedure is the most straightforward and most economical technique because there is no additional equipment required (Yao *et al.*, 2017). As ammonia is released during the degradation process, it also offers the possibility of eliminating it directly from the primary digester. However, significant changes in the digester's pH and temperature cannot be accommodated to facilitate the stripping process because this may adversely impact production of methane. Accordingly, the concept is based on modifying the flow rate of gas and the gas transfer system to improve stripping efficiency (Serna-Maza, 2014). Previously, a study of *in situ* ammonia removal from a digester using biogas as a stripping gas found that there was insufficient reduction of TAN concentration to prevent the complete inhibition of methanogenesis in thermophilic digestion of food wastes (Serna-Maza *et al.*, 2017). The high carbon dioxide content of biogas may be responsible for this phenomenon, resulting in a pH decrease and ultimately restricting the removal of free ammonia nitrogen. In contrast, a study on *in situ* ammonia stripping from the thermophilic anaerobic digestion of dairy manure was able to overcome ammonia inhibition. Stripping was carried out for 2 hours every two days. The stripping gas used was nitrogen gas, and an optimal stripping rate was determined to be 1 LPM. It was observed that the maximum cumulative production of methane in this study was 192.3 L/ kg VS (Yao *et al.*, 2017).

In the side-arm ammonia stripping process, a portion of digestate is transferred from the digester to the stripping rig, and following the stripping, the digestate is returned to the digester. In this technique, stripping is performed in a separate reactor attached to the side of the digester. This allows the pH and temperature of the stripping process to be independently altered. Several studies have shown that side-arm stripping of the digester was effective for reducing ammonia concentrations. Source-segregated domestic food waste was previously studied in laboratory digesters coupled with side stream biogas stripping in which 3.5% of the digester volume was stripped with the biogas, and TAN levels were reduced below thermophilic toxic levels (between 2500 and 3500 ppm). However, this process required a high

pH (above 10) and a high temperature > 70 ^{o}C. This study observed no significant change in specific biogas production with 0.83 ± 0.03 L/g VS and 0.84 ± 0.05 L/g VS from control and test reactors, respectively (Serna-Maza, 2014). It has been demonstrated that the air side-stream ammonia stripping in a thin-film evaporator could remove TAN with efficiencies of 17.1–33.3%, sufficient to avoid inhibition in the process of high-solid anaerobic digestion of sewage sludge. No adverse effects were observed due to ammonia stripping, but methane increase was not observed (Di Capua *et al.*, 2021).

As opposed to observations made during the pre-AD and *in situ* stripping processes, the side-stream stripping method did not significantly alter methane yield, despite a reduction in ammonia concentration. This could be due to the high temperatures and pH levels used in the side-arm stripping reactors.

A post-digester stripping technique is used to remove ammonia from digester effluent. It is possible to optimize the stripping conditions regardless of the anaerobic digestion process conditions (Walker *et al.*, 2011). This technique, however, is primarily used to recover ammonia from digester effluent and to meet discharge consent requirements. Consequently, this does not impact the digester's performance since it cannot reduce ammonia inhibition in the digester (Serna-Maza, 2014).

The initial plan of the present work was to utilize continuous side-arm stripping but due to technical problems and time constraints, a batch stripping process was exploited. Batch operation is typically considered a steppingstone to continuous operation. In the present work, batch stripping was used as a starting point to demonstrate the feasibility of microbubbles engendered by fluidic oscillators in reducing TAN. During this process, 2 L of digestate was removed daily from the digester, the digestate was stripped in a batch operation, and the stripped digestate was then reintroduced to the digester.

2.6 Application of microbubbles engendered by fluidic oscillator

2.6.1 Fluidic Oscillator

The size of microbubbles ranges between 1 μm and 1000 μm. A wide range of applications have been developed using them. The technology is used in industrial applications to transfer a specific gas component into a bulk liquid, as well as in medical diagnosis for imaging combined with ultrasound (Kiessling *et al.*, 2012). The use of microbubbles increases mixing efficiency and the interfacial area. There are three general techniques that can be used to produce microbubbles. Most commonly, gas is compressed through a nozzle into a liquid and subsequently forms tiny bubbles that will grow into larger ones. Ultrasound is another method for generating microbubbles, however it is an energy-intensive process. In the third method, a gas stream is distributed under low offset pressure and bubbles are produced by fluid oscillation. This method is characterized by the lowest power consumption. A fluidic oscillator, mechanical vibrator, or flow focusing device can be used to accomplish this. A new microbubble generator has been developed by Zimmerman *et al*., 2008, using a fluidic oscillator (Tesař-Zimmerman Fluidic Oscillator, TZFO) that produces gas bubbles that are micron in size (Zimmerman *et al.*, 2009, 2011). In particular, this fluidic oscillator is the cheapest method for producing microbubbles with a low maintenance requirement due to the lack of moving parts within the oscillators (Zimmerman *et al.*, 2008). Figure 2.8 illustrates the structure of a fluidic oscillator, TZFO with a non-moving component amplifier (Zimmerman *et al.*, 2008).

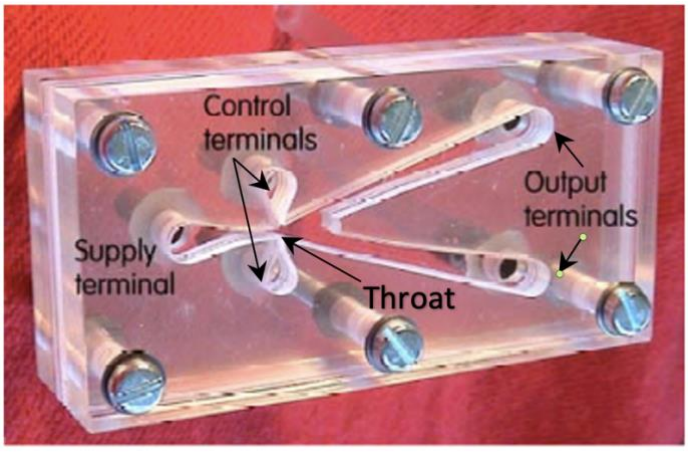

Figure 2.8: Photograph of fluidic oscillator, TZFO (Zimmerman *et al.*, 2008)

In Tesař-Zimmerman fluidic oscillators, microbubbles are produced by pulsating flows caused by oscillations of the flow between two outlets. Fluid flowing from the main supply terminal to the oscillator randomly attaches to one of the two outlets due to the Coanda effect, which is the tendency of a fluid to follow and adhere to a curve or plate adjacent to it (Tesař, 2004). In fluid dynamics, the Coanda effect is a phenomenon in which a fluid jet following a curved surface tends to follow the contours of the surface rather than following straight lines. Accordingly, as illustrated in Figure 2.9, fluid flows from the port on the non-flowing side (higher pressure) back to the lower pressure port with the current flow due to a pressure difference in the feedback loop. Consequently, the gas pushed out of the low-pressure port encounters the main passing flow and switches directions. The cycle is repeated periodically, leading to pulsation flow between the two outlets. This oscillation disrupts the flow, which results in a delay in the growth of bubbles (Zimmerman *et al.*, 2008).

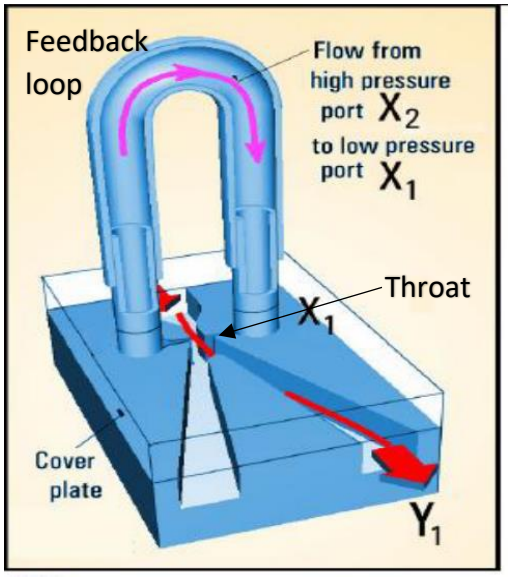

Figure 2.9: An illustration TZFO with the feedback loop connecting the two control terminals, alternating gas pulses are generated from each output (Zimmerman *et al.*, 2008).

The use of fluidic oscillators, TZFO for the production of microbubbles has many advantages, including low cost, reliability, and robustness. Furthermore, the energy requirements of this method are less than those of other methods of generating microbubbles. The novel technique uses oscillatory flow to disrupt airflow and limit the time available for bubbles to grow.

Microbubbles generated by the fluidic oscillator rise uniformly and without coalescence as shown in Figure 2.10.

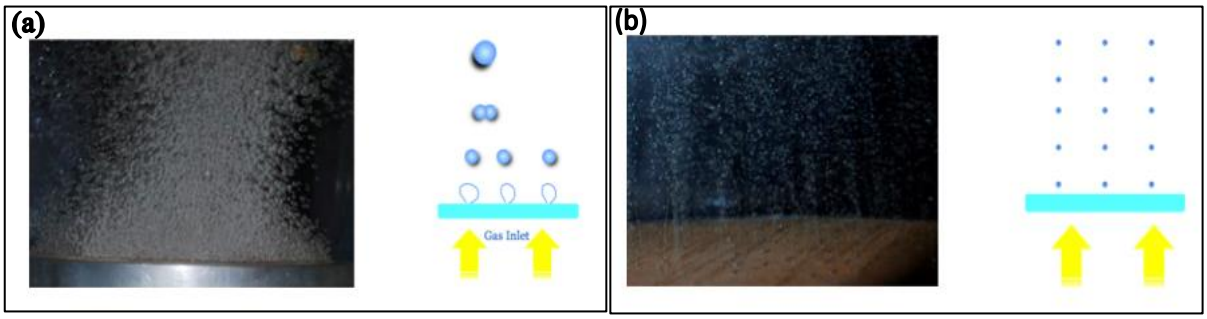

Figure 2.10: Microbubbles produced without (a) and with (b) fluidic oscillator

In the absence of an oscillator, conventional continuous flow can be observed when microbubbles are generated. Typically, bubbles are relatively large and rapidly rising (2.10a). When microbubbles are produced using the fluidic oscillator, oscillatory flow can be observed. Monodisperse, uniformly spaced, and non-coalescent bubbles are observed (2.10b).

TZFO needs to achieve selective flow across the throat to achieve flow switches and bistability, and for this reason, the control nozzles must be smaller than the supply nozzles. As a result, friction loss occurs in the throat, resulting in wasted energy due to fluid meeting resistance (Desai, 2017). Desai et al. (2017) improved upon this fluidic oscillator with a new mode of oscillation, naming it the Desai-Zimmerman fluidic oscillator, DZFO (Zimmerman and Desai, 2020). The new DZFO incorporates new features while retaining all the advantages of the previous fluidic oscillator. It has higher pulse amplitude, lower frictional losses, and a new switching mechanism. Due to these properties, the DZFO produces smaller bubbles as compared to other oscillators and is therefore better at generating microbubbles (Desai, 2017). In this study, DZFO was utilized in the batch microbubble stripping to generate microbubbles. The patent (Patent No. WO2020208250, 2020) outlines the detailed description of DZFO (Zimmerman and Desai, 2020).

2.6.2 Stripping using microbubbles engendered by fluidic oscillator

In microbubble stripping, the ammonia is stripped out from a high concentration liquid into microbubbles containing no ammonia. Hot microbubble stripping is characterized by air and

liquid initially having different temperatures and maintaining a substantial temperature difference. The removal of volatile components was achieved by heating the gaseous phase instead of the liquid phase. Consequently, the evaporation rate is accelerated due to the non-equilibrium thermal driving force between the hot microbubble and colder liquid. A previous study showed that the efficiency of stripping could be improved by increasing the temperature of the air injected into the stripping and the temperature of the liquid mixture being increased very modestly (Al-Yaqoobi and Zimmerman, 2014). Contrary to traditional distillation, which involves a large amount of energy to raise the temperature of the liquid to its boiling point, microbubble distillation allows separation to occur at a temperature lower than the boiling point of the mixture (Al-Yaqoobi *et al.*, 2016). A fluidic oscillator produces microbubbles which have a smaller coefficient of heat transfer than larger bubbles because they follow a laminar path throughout the liquid as they detached themselves from the pores of the diffuser (Zimmerman *et al.*, 2013). Moreover, it has been demonstrated that microbubble clouds possess a high surface-to-volume ratio, which results in a large interfacial area, leading to increased mass transfer rates (Zimmerman *et al.*, 2008). Microbubble distillation is able to achieve significant increases in separation efficiency while reducing energy consumption due to the method for producing microbubbles and the concept behind heating the air stream.

Furthermore, it has been observed that the liquid layer height has the most significant effect on the separation performance and that the separation efficiency increases with decreasing liquid levels (Al-Yaqoobi and Zimmerman, 2014; Al-Yaqoobi *et al.*, 2016). The rate of transfer is generally determined by the contact time between the liquid and microbubbles, which is determined by the height of the liquid within the rig. The volume of liquid determines the liquid level in the rig poured into, and the approximate volume can be defined as follows:

$$\text{Volume of liquid} = \text{Base area of the rig} \times \text{Liquid height} \qquad \text{Equation 2.6}$$

The previous work demonstrated that, with microbubble-mediated batch distillation, it was possible to separate the azeotropic mixture of water and ethanol with 98.2% purity at a liquid level of as low as 3 mm (Abdulrazzaq et al., 2015). The research conducted by Al-Yaqoobi et al. (2016) also examined the composition of the vapour and liquid during microbubble distillation at a liquid level of 3.5 mm. Vapour phase sensors were employed in both studies. Desai et al.

(2021) demonstrated that the highest removal rates of ammonia about 99% were achieved after 30 minutes of processing time and air flow rate of 2 LPM with a liquid layer height of 5 mm. This study reports a higher liquid level than the others because the ammonium probe required for this experiment must be submerged in the liquid. This study also demonstrated that hot microbubble stripping could be used to remove ammonia at pH levels lower than nine without adding a pH modifying agent (Desai *et al.*, 2021). In the present study, ammonia stripping was conducted at the original pH of the leachate and digestate. No chemicals were added to adjust the pH since this would interfere with the anaerobic digestion process and increase operating costs.

2.7 Summary of literature review

Growing concern over the global problem of waste generation, energy consumption, and global warming has led to increased research on enhancing the anaerobic digestion (AD) process. This chapter discusses AD as a promising process that can significantly reduce greenhouse gas emissions and can be used to generate renewable energy from food waste. Recent studies have shown that CO_2 sparging can significantly improve the methane production from AD. In the current study, the focus is on anaerobic digestion with microbubbles of CO_2. In one hypothesis, the ammonia may be stripped from the digester by the CO_2 injected into the digester. Among the objectives of this study is to investigate this hypothesis and determine whether CO_2 can remove ammonia from digestate.

The inhibition of ammonia is one of the challenges associated with anaerobic digestion, which reduces the amount of biogas produced and ultimately results in system failure. The presence of high concentrations of ammonia in low C/N substrates impedes the degradation process, which results in a lesser quantity of methane being produced. There is still a need for efficiency improvement by reducing TAN in AD, particularly with feedstocks with a low C/N ratio. Ammonia stripping has been demonstrated to be an effective method of removing ammonia. Despite relatively easy to operate, generating no extra sludge, and having comparatively low energy requirements and capital costs, one of its disadvantages is the long operational period. The various configurations of stripping were discussed, and it was decided to couple batch

stripping with anaerobic digestion in the present study. In most studies on ammonia stripping, conventional stripping was used with chemical additives to adjust pH, which could interfere with the process of AD. An earlier study demonstrated that microbubbles generated by a fluidic oscillator (Desai-Zimmerman Fluidic Oscillator, DZFO) could be used to strip ammonia efficiently and economically. Moreover, hot microbubble stripping was previously observed to be able to remove ammonia at pH values less than 9 without the addition of alkaline pH modifiers. Therefore, this research aims to integrate microbubble stripping engendered by DZ fluidic oscillator in the anaerobic digestion of food waste, sparged with CO_2 microbubbles.

Chapter 3 : Research Methodology

This chapter provides an overview of the research methodology and approach employed to obtain and analyse data in the following three experimental chapters. Additionally, this chapter provides information regarding the design and construction of the stripping rigs and anaerobic digesters utilised in the present study.

3.1 Analytical Methods

3.1.1 Total Solids and Total Volatile Solids

Percentage of the total solids (%TS) and total volatile solids (%TVS) were calculated as per the standard methods (APHA, 2017) and using the following Equation 3.1 and 3.2:

$$\%\mathrm{TS} = \frac{\text{Weight of dry sample}}{\text{Weight of wet sample}} \times 100\% \qquad \text{Equation 3.1}$$

$$\%VS = \frac{Weight\ of\ vaporized\ solid}{Weight\ of\ dry\ sample} \times 100\% \qquad \text{Equation 3.2}$$

The weight of total solids in the homogenised wet samples was determined by oven-drying them at 105°C for 24 hours (Genlab, UK). Weights of the wet (initial) and dry (final) samples were measured. The samples were further heated in a furnace (Carbolite, CSF 1100) operating at 570 ^{o}C and incinerated for 2 hours to determine the weight and percentage of solids vaporized. Analytical balance scales with an accuracy of 0.0001g (Fisher Brand, PS-202) were used to weigh all samples.

3.1.2 COD, DOC and pH

For the analysis of chemical oxygen demand, a COD cuvette test kit (HACH LCK014) was used. The soluble chemical oxygen demand, sCOD levels were determined after samples had been filtered through a 0.45 m syringe filter. Samples were pipetted into the cuvette test before being heated in a thermostat for two hours at 148°C. Cuvettes that had been heated were then removed from the thermostat, inverted twice, and allowed to cool to room temperature. COD

readings were taken using a HACH DR3900 Laboratory Spectrometer, ensuring that the sediment was settled entirely before the evaluation.

An analysis of dissolved organic carbon, DOC, was conducted using the GE Instruments Sievers 5310C Portable Total Organic Carbon Analyzer. About one ml of each raw sample was placed into a 1.5 ml Eppendorf tube and centrifuged for five minutes at relative centrifugal force of 16,110 x g. A volume of 0.05 ml of supernatant sample was pipetted and diluted into a 25ml volumetric flask. The flask was filled up to a total volume of 25mL using ultrapure deionised water, mixed thoroughly, and transferred to a vial for DOC analysis.

The pH substrates and digestate samples were immediately determined after sampling using a benchtop pH meter (Mettler-Toledo^{TM} FE20 FiveEasy, Switzerland) with accuracy of ±0.01. Calibration of the pH meter was performed weekly using technical buffer solutions of pH 4, 7, and 10 (Mettler Toledo, InLab Solutions).

3.1.3 Elemental Composition

Elemental composition of carbon, nitrogen, hydrogen, and sulphur (CHNS) were determined using Flash 2000 CHNS Elemental Analyzer. The feedstock sample was homogenized using a food mixer before being dried in an oven at 105°C for 24 hours. Following this, a pestle and mortar was used to grind the sample, which was then dried at 105°C for another 24 hours. The sample and standards were prepared for analysis by adding a combustion catalyst (vanadium pentoxide) and sealed in tin foil capsules. The capsules were placed in the instrument autosampler, which dropped them, one by one, into the furnace. A measure of the CHNS content of the samples was obtained following combustion in the furnace. A subsequent calculation of the oxygen content was then performed (Sosnowski *et al.*, 2003).

3.1.4 Volatile fatty acids

A gas chromatograph, GC was used to measure volatile fatty acids (VFA) in accordance with APHA standard method (APHA, 2017) . Formic acid (Sigma-Aldrich, UK) was used to acidify a liquid sample of 2 mL to pH 4 after being diluted to 10 mL with deionized water. In the present study, VFA measurements were taken only for acetic, propionic, isobutyric, butyric, isovaleric,

valeric, isocaproic, hexanoic and n-heptanoic acids. Therefore, adding formic acid to the sample will not affect the VFA analysis. The sample was centrifuged, and the supernatant was subsequently filtered through a sterile, 0.22 µm syringe filter (Millex, Merck Millipore Ltd). A GC vial was filled with 1.5 ml of the filtered sample. A standard solution mixture consisting of formic, acetic, propionic, iso-butyric, n-butyric, isovaleric, valeric, hexanoic and heptanoic acids was also prepared at concentrations of 0.1, 1.0, 5.0 and 10.0 mM. Gas Chromatography is equipped with a flame ionization detector, FID (TRACE 1310, Thermofischer Scientific) and a capillary column Thermo TR-FFAP. Helium gas was used as the carrier. It took 20.6 minutes to analyse each sample.

3.1.5 Biogas composition and volume

Biogas composition (%) was analysed using a Gas Data GFM-406 gas analyser (Gas Data, UK), which utilizes proprietary infra-red methane and carbon dioxide sensors. Service and calibration of this analyser were performed by Gas Data to ensure that it is reliable and operating at the highest level of efficiency possible.

An electric vacuum pump (DC 12V, 3A) was used to release gas from the gas bag in the fume cupboard to measure its volume at room temperature. The flowrate of gas released was measured using a flowmeter and time taken to release all the gas was noted (Figure 3.1). The total volume of the gas was obtained by multiplying the time and the flow rate of the gas released. The gas volumes were corrected to standard conditions of 273.15K and 1 atm.

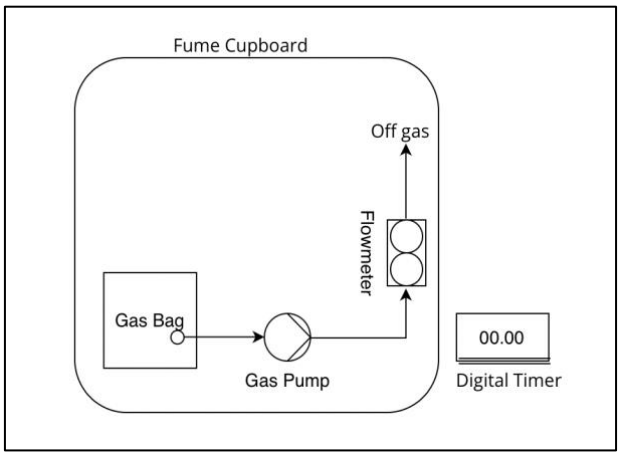

Figure 3.1: The volume of the biogas measurement

3.1.6 Total ammonia nitrogen

Total ammonia nitrogen, NH_3-N consists of the sum of ammonium ion. NH_4^+ and free ammonia, NH_3. As a result of the following equilibrium, the ratio of NH_4^+ to NH_3-N is dependent on the pH of the solution.

$$\mathrm{NH_4^+ + OH^- \rightleftharpoons NH_3 + H^+} \qquad \text{Equation 3.3}$$

The concentration of ammonium in the liquid was measured by using an ammonium ion selective electrode (ISENH4181, Hach) in accordance with the American Public Health Association (APHA, 2017). This probe is capable of measuring up to 9,000 ppm of NH_4^+. Total ammonia nitrogen was then evaluated using Equation 3.4 (Bonmatí and Flotats, 2003):

$$\frac{[\mathrm{NH_4^+}]}{[\mathrm{NH_3 + NH_4^+}]} = 1 - \frac{1}{1+10^{\mathrm{pK}a-\mathrm{pH}}} \qquad \text{Equation 3.4}$$

where $[NH_4^+]$ is the concentration of ammonium ions obtained from the ammonium ion-selective electrode, $[NH_3 + NH_4^+]$ represents the concentration of total ammonia nitrogen (TAN). pK_a is a measure of acid dissociation constant that is affected by temperature (in degree Kelvin) and can be expressed using Equation 3.5 (Emerson et al., 1975):

$$\mathrm{pK_a} = 0.09018 + 2729.92/\mathrm{T} \qquad \text{Equation 3.5}$$

The percentage of total ammonia present as unionised ammonia, NH_3, is affected by pH and temperature. This is consistent with a previous study that evaluated the literature data on ammonia-water equilibrium, which demonstrated the need to calculate pK_a values at different temperatures and pH levels. This previous work compared several equations. A mean square residual (MSR) was calculated from the errors quoted by Bates and Pinching 1999 and compared to MSR in the fit of each equation. Experimental MSR is calculated assuming the errors represent a 50% confidence interval, which is common in scientific writing. It was concluded that equation 3.5 has a MSR similar to experimental points. The data presented

provide a better and more accurate representation of the dependence of the pK_a for NH_3 over the study interval (Emerson *et al.*, 1975).

3.2 Design and Construction

3.2.1 Anaerobic Digesters

Anaerobic digestion bioreactors used in this study are cylindrical stainless-steel tanks with inner diameter of 29.5 cm and heights of 48 cm (Figure 3.2a). The working volume of the bioreactor is approximately 66% of its total volume. Toggle latches were used to tighten the lid to maintain anaerobic conditions and prevent leakage. All reactors were tested for leakage before running an experiment. Each reactor was fitted with a submersible heater, and all bioreactors were stored in an incubator, where the temperature was maintained at 35 ± 2 °C. The lid for each bioreactor is fitted with ports for liquid sample collection, gas inlet, and gas outlet (Figure 3.2b).

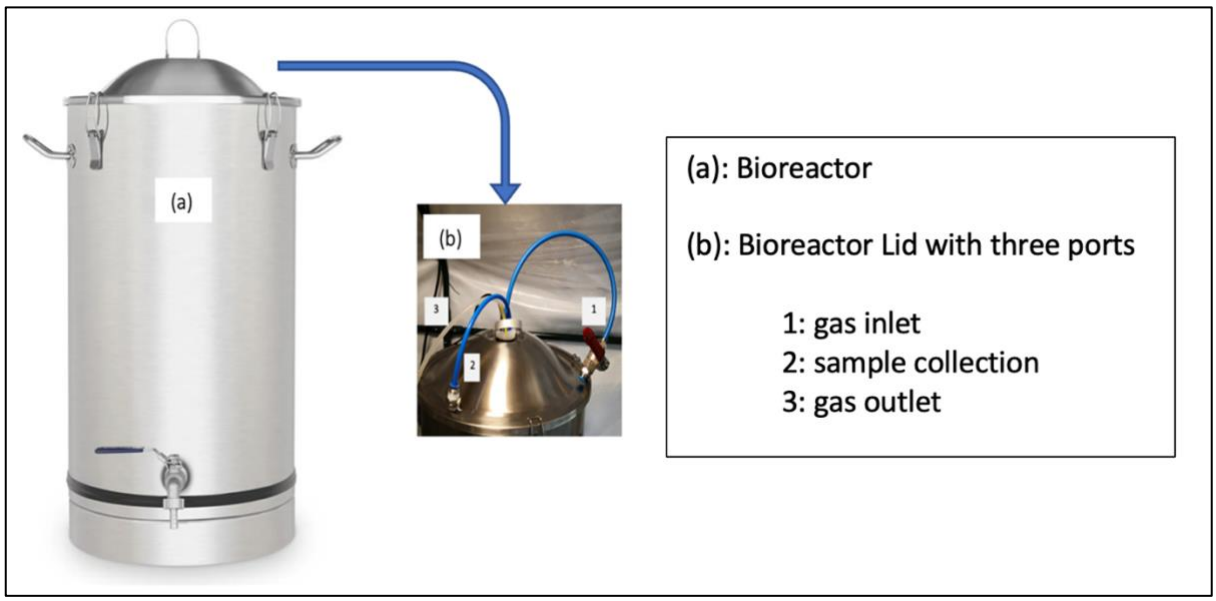

Figure 3.2: Reactor used for anaerobic digestion in the present study

3.2.2 Stripping Rigs

The present study involved the use of DZ Stripping rigs which utilize the Desai-Zimmerman fluidic oscillator to generate microbubbles. Three designs of stripping rigs were constructed for this study, including the following:

1. Lab scale DZ stripping rig
2. DZ stripping rig with recirculation
3. Pilot continuous DZ stripping rig

3.2.2.1 Lab scale DZ stripping rig

Lab scale DZ stripping rig is made of stainless-steel with the inner dimensions of 15.8 cm x 5.0 cm x 5.0 cm and a sparger is fitted at the bottom (Figure 3.3). This sparger consists of a sintered steel membrane with 100 um pore size that covers an area of 149 x 40 mm^2. A similar rig was used in the paper by Desai et al., 2021, however the rig used in the present work had a larger surface area. Accordingly, the height of the liquid above the membrane varies in relation to the amount of liquid poured into the rig.

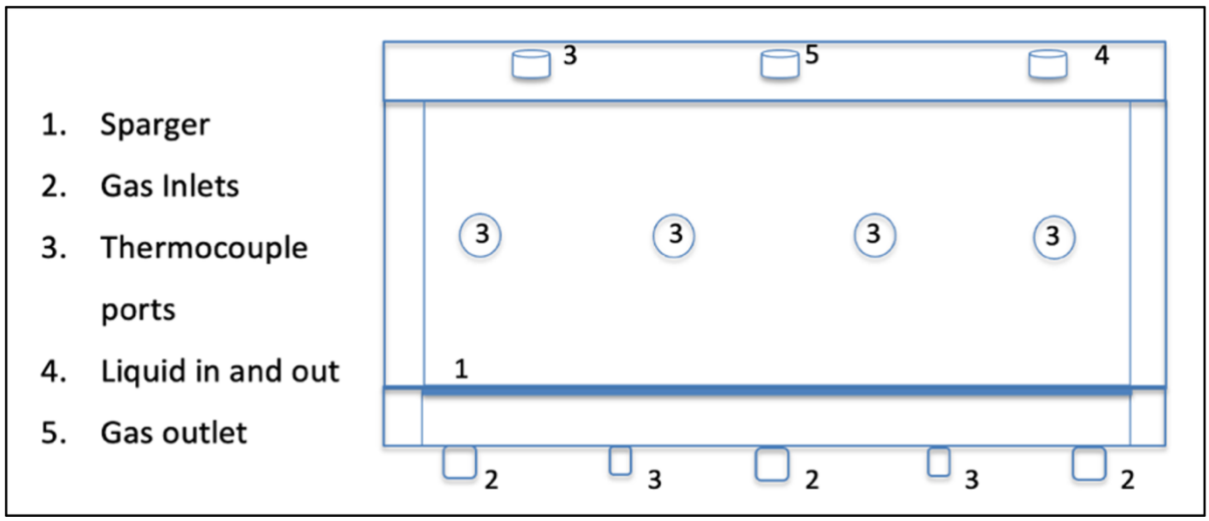

Figure 3.3: Schematic representation of DZ Lab scale stripping.

3.2.2.2 DZ stripping rig with Liquid Recirculation

DZ stripping rig (Figure 3.4)with liquid recirculation is also made of stainless steel with an internal diameter of 20 cm. This design utilizes a recirculated liquid system that circulates liquid between the bottom cell (rig cell 1, the sump) and the top cell (rig cell 2), which contains six spargers. The height of rig cell 2 is 250 mm with an active height of 10 mm. The liquid was first poured into the sump and pumped into the top cell. The liquid was bubbling on the spargers and flowing back into the sump. As the foam produced in the top cell flows into the bottom cell, a defoaming module has been installed between the two rig cells. This is to prevent the accumulation of bubbles/foam in the top cell, which could damage the pump. 4L of liquid was poured in each run.

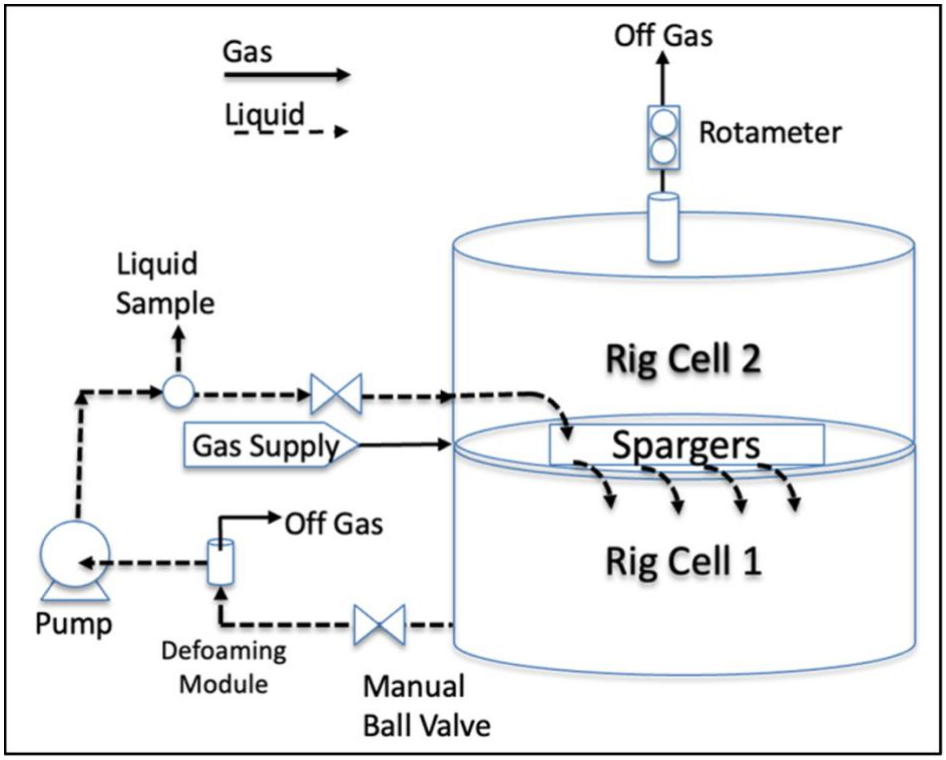

Figure 3.4: Schematic diagram of DZ stripping unit with recirculation

3.2.2.3 Pilot Continuous DZ stripping unit

DZ stripping unit is the pilot continuous stripping unit can utilize up to 20 L of liquid in each run (Figure 3.5). The stripping time for each run is approximately five minutes. Sixteen microporous diffusers were installed in this rig, HP Technical Ceramics, with 50 um-sized pores. As the gas exits the oscillator, it is directed to the gas inlets of the continuous rig. Subsequent gas distribution occurred between the 16 spargers, generating microbubbles. The liquid is then pumped to the inlets and flows across the rig, passing over the microporous diffusers, then leaves at the end of the rig and is collected in the drum.

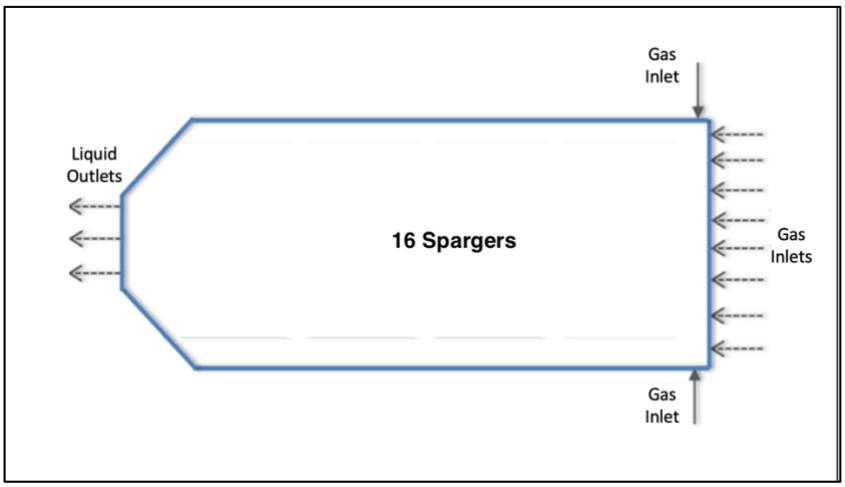

Figure 3.5: DZ Continuous stripping unit

3.3 Data Analysis

3.3.1 Determination of mass transfer coefficient

Several studies have demonstrated that the removal of ammonia from liquids by gas stripping follows a model that is governed by the first-order kinetics (Quan *et al.*, 2009; Zhang *et al.*, 2011; Zhu *et al.*, 2017). Total ammonia nitrogen concentrations in liquid phases decrease over time as described by Equation 3.6.

$$\frac{dC}{dt} = -K_L aC \qquad \text{Equation 3.6}$$

Integrating Equation 3.6 leads to Equation 3.7:

$$-\ln\frac{C_t}{C_0} = K_L a t \qquad \text{Equation 3.7}$$

where C_0 is the initial concentration and C_t is the concentration of ammonia in the liquid phase at any given time, t. K_La is defined as the volumetric mass transfer coefficient of ammonia from the liquid to gas, min^{-1}. The K_La value can be determined by plotting $-\ln(C_t/C_0)$ versus stripping time graph and performing a linear regression.

3.3.2 Kinematic Model

The experimental data obtained were fit to the kinematic model to compare the efficiency of anaerobic digesters in this study. The modified Gompertz model (Zwietering *et al.*, 1990) has been proposed to predict degradation of the substrates and production of biogas and is one of the most widely used semi-empirical methane production models. Through the use of this model, it is possible to calculate parameters such as the potential for methane production, the rate at which methane is produced at its maximum, and the lag phase time. The modified Gompertz equation is expressed in Equation 3.8 below:

$$G_t = G_0 . \exp\left\{-\exp\left[\frac{R_{max}.e}{G_0}(\lambda - t) + 1\right]\right\} \qquad \text{Equation 3.8}$$

Where G_t is the cumulative production of methane (L), G_0 is the potential production of methane (L), R_{max} and λ represent the maximum specific production rates of methane (L/day) and the lag phase period, respectively. The lag phase period (days) is the minimum time required to produce biogas. Lastly, e represents the mathematical constant which is 2.7182.

3.3.3 Statistical Data Analysis

The kinetic constants were calculated using nonlinear regression analysis using SPSS software. Based on the experimental results, one-way ANOVA and t-tests were used to determine whether the observed differences between different bioreactors were significant (Microsoft Excel 2021). Statistical difference was significant when $p < 0.05$.

3.3.4 Theoretical Methane Yield

The theoretical amount of methane provides an indication of the maximum amount of methane that may be expected from a specific waste stream (Angelidaki et al., 2011) and it can be estimated from the amount of food waste fed into the anaerobic bioreactor. The theoretical biogas and methane production was calculated using Boyle's formula (Boyle, 1977), which is based on a modified chemical reaction of Buswell and Mueller (Buswell and Mueller, 1952). For this chemical equation, nitrogen and sulphur are included in order to determine the concentration of ammonia and hydrogen sulphide in the produced gas. On the basis of its elemental composition, the chemical formula of the food waste was determined.

$$\mathrm{C_aH_bO_cN_dS_e} + \left(\mathrm{a} - \frac{\mathrm{b}}{4} - \frac{\mathrm{c}}{2} + \frac{3\mathrm{d}}{4} + \frac{\mathrm{e}}{2}\right)\mathrm{H_2O} \rightarrow \left(\frac{\mathrm{a}}{2} + \frac{\mathrm{b}}{8} - \frac{\mathrm{c}}{4} - \frac{3\mathrm{d}}{8} - \frac{\mathrm{e}}{4}\right)\mathrm{CH_4} + \left(\frac{\mathrm{a}}{2} - \frac{\mathrm{b}}{8} + \frac{\mathrm{c}}{4} + \frac{3\mathrm{d}}{8} + \frac{\mathrm{e}}{4}\right)\mathrm{CO_2} + \mathrm{dNH_3} + \mathrm{eH_2S}$$

Equation 3.9

The theoretical biochemical methane potential (TBMP) is calculated using the following equation (Feng *et al.*, 2013):

$$\mathrm{TBMP\ (L\,CHC_4\ /g\,VS)} = \frac{22.4 \times \left(\frac{\mathrm{a}}{2} + \frac{\mathrm{b}}{8} - \frac{\mathrm{c}}{4} - \frac{3\mathrm{d}}{8} - \frac{\mathrm{e}}{4}\right)}{12.017\mathrm{a} + 1.0079\mathrm{b} + 15.999\mathrm{c} + 14.0067\mathrm{d} + 32.065\mathrm{e}}$$

Equation 3.10

Chapter 4 : Microbubble Stripping of Ammonia Engendered by Fluidic Oscillator

4.1 Abstract

This chapter aims to examine three different designs of DZ rigs that incorporate a Desai-Zimmerman fluidic oscillator (DZFO) to generate microbubbles for the stripping of ammonia. The designs include a DZ Lab-Scale, a recirculating DZ rig, and a continuous DZ rig. The primary objective of this chapter is to investigate the performance of these three rigs in ammonia stripping to test the hypothesis that microbubble stripping designed with DZ fluidic oscillator can improve ammonia removal from highly concentrated ammonia solutions, in this instance leachate and synthetic wastewater. In general, the three rigs differ in terms of their number of spargers, liquid capacity, and operating procedures. Efficiencies in removing ammonia and volumetric mass transfer coefficients, K_La, were assessed for each design in order to evaluate their effectiveness. The effects of gas flow rate, liquid volume, and operating temperature on the removal efficiencies were studied. The results of the studies demonstrate that microbubble stripping using these rigs, notably the DZ lab-scaled rig and continuous rig, yields greater mass transfer coefficients and higher removal efficiencies than other methods using conventional fine bubbles. The findings presented in this chapter will provide valuable insight into the effectiveness of these rigs and their feasibility to be coupled with anaerobic bioreactors in the subsequent chapters.

4.2 Introduction

Landfill sites generate greenhouse gases and leachate from the disposal of solid waste. Landfill leachates and digestates typically contain high concentrations of ammonia, exceeding 1000 parts per million, which can cause severe burns and scarring to sensitive skin (Oregon Department of Human Services, 2000). The leachate must be treated chemically and physically prior to being biologically treated, particularly to reduce the ammoniacal nitrogen concentration, as the biodegradation of carbonaceous materials is challenging at high levels of ammoniacal nitrogen (Leite *et al.*, 2013). Ammonia inhibits microorganism activity, especially

in anaerobic digestion. Therefore, remedial action is necessary as digestate, and leachate do not have a degradation pathway for ammonia.

Industry has extensively utilized air stripping, which is a low-energy method of recovering ammonia. Due to its simplicity, efficiency, and cost-effectiveness, it may also be used to treat wastewater. However, the downside of the stripping process is that it has a long processing time. Therefore, it is crucial to improve the process design to enhance separation efficiency. Various applications of microbubbles have been explored since they provide better mixing efficiency and greater interfacial area. Microbubble stripping has the significant advantage of achieving a higher separation efficiency than traditional methods (Al-Yaqoobi et al., 2016). The Desai-Zimmerman Fluid Oscillator is a novel device for treatment of ammonia from high concentrated liquid that promises to be more economical and efficient than conventional treatment methods (Desai, 2017). In recent studies on hot microbubble stripping for ammonia separation in thin liquid films, it has been shown that hot microbubbles generated by fluidic oscillations can enhance separation efficiency by up to 100% in 30 minutes (Desai *et al.*, 2021).

An energy-efficient fluidic oscillator is used in the DZ stripping unit to generate microbubbles through a built-in sparger (Zimmerman *et al.*, 2008; Desai, 2017). In comparison to conventional stripping columns, DZ stripping unit offers a simpler design and lower maintenance costs. This experiment aims to investigate the removal of ammonia from high ammonia concentration liquid using microbubble engendered by fluidic oscillator in three different designs of DZ stripping unit described in Section 3.2.2. Furthermore, this also seeks to identify the feasibility of coupling each of these designs with anaerobic digesters for reducing ammonia inhibition and improving biogas production. In the present study, leachate was primarily used because it contains high levels of ammonia, between 1700 and 2000 ppm. The effects of gas flow rate, liquid volume and operating temperature were studied.

4.3 Materials and Methods

4.3.1 Characterization of leachate, digestate and samples

Leachate obtained from the Viridor wastewater treatment plant was used in the experiments using lab-scale and recirculating DZ units, while synthetically prepared wastewater with ammonia concentration of 2000 ppm was used in the continuous large rig. This is due to the limited amount of leachate available in the lab and the lack of ventilation if continuous stripping of leachate was to be run. A landfill produce leachate when water infiltrates and leaches components from the waste. The leachate may contain organics, inorganics, or heavy metals, which pose a serious threat to the environment and human health (Bakhshoodeh *et al.*, 2016; Farishi and Setiawan, 2019). As a result, it is necessary to provide better ventilation when running experiments using leachate rather than synthetically prepared wastewater. Work was carried out using leachate and synthetic wastewater in the DZ stripping unit with recirculation, it was observed that the removal percentage were almost the same (Appendix A).

A detailed characterization of the leachate was conducted, including the determination of pH, COD, total ammonia nitrogen (TAN), total solids (TS), and total volatile solids (TVS). The characteristics of the leachate are reported in Table 4.1. The leachate used in the present work represents a typical example where ammonia removal is necessary because of its high concentration.

Table 4.1: Leachate characteristics used in this study.

Parameters	Unit	Value
pH		8.08 ± 0.01
Total Solid	g/L	10.320 ± 0.13
TDS	g/L	6.388 ± 0.24
TSS	g/L	3.932 ± 0.71
TVS	g/L	3.426 ± 0.14
TCOD	g/L	5.163 ± 0.25
sCOD	g/L	4.758 ± 0.19
TAN	mg/L	1851 ± 71.3
TVFA	mg/L	375.3 ± 15.2

The experiments conducted on the continuous rig were conducted with a solution of ammonia (2000 ppm) made by diluting standard solutions of ammonium hydroxide. From a previous study, the efficiency of ammonia removal is not affected by the initial ammonia concentration (Desai *et al.*, 2021). Thus, the continuous rig used the same initial ammonia concentration for each run.

Total ammonia nitrogen concentration, TAN in the liquid samples was measured using a probe according the American Public Health Association (APHA, 2017) and described in Section 3.1.6. TAN, pH, temperature, and total ammonia concentration can be used to calculate the free ammonia concentration, FAN. Equations 3.4 and 3.5 indicated earlier were used to calculate FAN.

Equation 4.1 below can be used to calculate the efficiency of ammonia removal (De la Rubia *et al.*, 2010):

$$ARE(\%) = \frac{[ammonia]_i - [ammonia]_f}{[ammonia]_i} \times 100 \qquad \text{Equation 4.1}$$

where $[ammonia]_i$ and $[ammonia]_f$ represent the initial and the final concentrations of ammonia, respectively.

4.3.2 Lab Scale DZ Stripping Rig

The batch microbubble-stripping of ammonia from the digestate was performed with the stainless-steel rig mentioned in Section 3.2.2.1. Figure 4.1 illustrates the experimental set-up for this batch stripping. A hot water bath was used to maintain the operating temperature during each run. Stripping gas from the supply passed through the fluidic oscillator and was oscillated by virtue of aerodynamic principles alone (i.e., Coanda Effect as discussed in Section 2.6.1). A stainless-steel sparger was used to introduce stripping gas into the rig and the flow rate was controlled by the two valves on the fluidic oscillator. The temperature of the stripping gas increased as it introduced into the rig. The temperatures of the stripping gas in the rig and that of the digestate were monitored using the K-type thermocouples. Stripping was

conducted in the fume cupboard, which allowed gases to be vented from the top port so as to minimize pressure build-up.

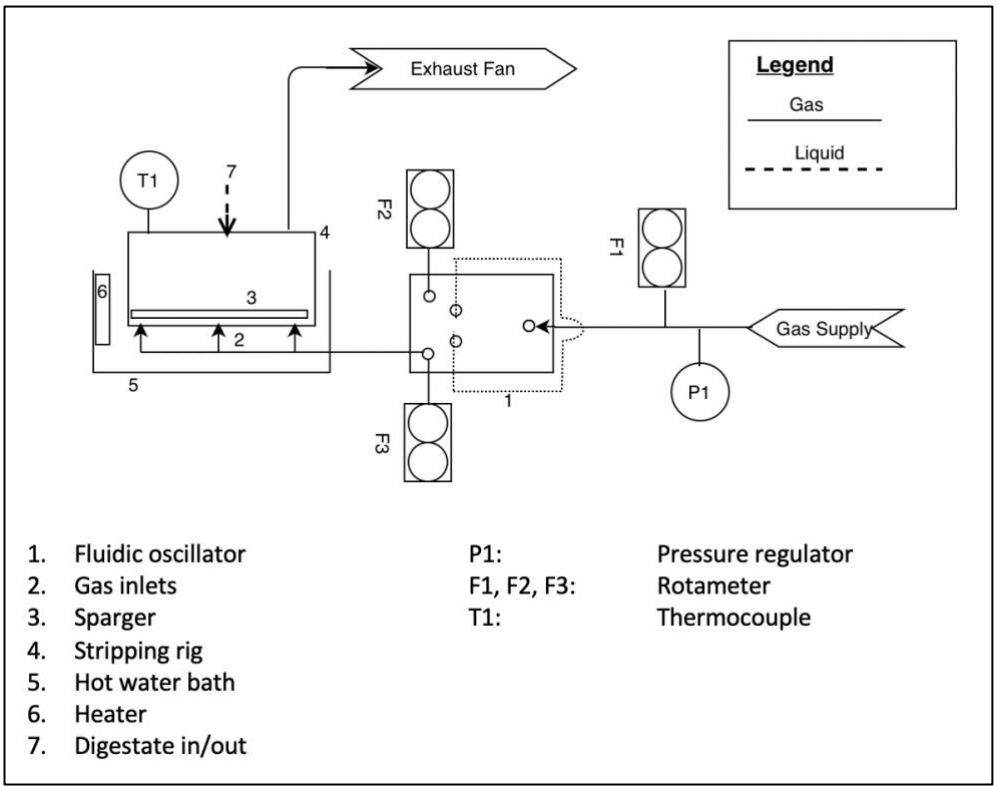

Figure 4.1: Schematic representation of the experiment system for lab-scale DZ stripping unit

TAN removal efficiency was examined based on the volume of the liquid, gas flow rate, and operating temperature of the system. While one factor was studied, other factors remained unchanged. The temperature of the stripping gas in the rig was controlled by varying the temperature of the water bath. pH was not modified in all experiments. A sample was collected every five minutes during each experiment, which lasted 30 minutes. Analyses were conducted including pH, temperature, and TAN concentrations.

Table 4.2: Operating conditions in ammonia stripping using lab-scale DZ rig

Process Parameter Studied	Liquid Volume (mL)	Gas Flow rate (LPM)	Temperature (°C)
Liquid Volume	38.5, 25	0.5	35
Gas flow rate	25	0.5, 1.0, 2.0	35
Temperature	25	1.0	20, 35, 45, 55, 70

A description of the parameters examined during the ammonia stripping process is presented in Table 4.2. Based on the method described in section 3.3.1, volumetric mass transfer coefficients were calculated. The experiment was repeated three times under the same conditions to assess the reliability of the results and the extent of repeatability. The mean and standard deviation of the measurements taken from the three repeated experiments were calculated. The coefficient of variation which a relative measure of variability and expressed as a percentage was then calculated using the Equation 4.2 below:

$$CV\ (\%) = \frac{standard\ deviation}{mean} \times 100 \qquad \text{Equation 4.2}$$

A low CV indicates that the standard deviation (i.e., variability) is small compared to the mean value, thus indicating that the measurements are highly repeatable and consistent (Abdi, 2010).

4.3.3 Recirculating DZ Stripping Rig

The purpose of running experiments on this rig is to investigate the feasibility of liquid recirculation during microbubble stripping of ammonia. A larger volume of liquid was used in comparison to the previous DZ lab-scale rig, thereby allowing recirculation of the liquid. This experiment was conducted in Viridor Waste Management Service in Parkwood, Sheffield where ventilation is sufficient, and leachate may be run in large quantities.

In Figure 4.2, a schematic representation of the experiment design is shown. The design consists of two cells for stripping, with the top cell containing six spargers (Figure 3.4). The liquid was recirculated between the bottom cell (the sump) and the top cell that contained the spargers during ammonia stripping. The air supply was regulated by a pressure regulator and an emergency shut-off valve. In this experiment, air was introduced into the supply nozzle of the fluidic oscillator. The air passed through the oscillator and achieved oscillation solely through aerodynamic principles (i.e., Coanda Effect as discussed in Section 2.6.1). Following the fluidic oscillator, air was directed towards the inlet of the process air heaters (AHP-7562 Omega, 750 watts), which heated the air to the specified temperature. The process heater was

controlled by a PID controller, with the controller thermocouple mounted on the gas inlet of the rig. As hot air was passed through the DZ stripping unit, microporous diffusers (spargers) were utilised to generate microbubbles. Heat loss from the hot air reaching the diffuser was minimised by providing adequate insulation to all tubes, connectors, and valves.

A specific volume of leachate was poured into the sump of the DZ stripping unit, which was then pumped into the top cell, where the spargers are located. Stripping took place as the microbubbles diffused through the leachate. The leachate then flowed back into the sump and was continuously recirculated between the sump and the top cell. As the foam produced in the top cell may overflow into the bottom cell, a defoaming module is installed between the two rig cells to prevent the accumulation of bubbles or foam produced in the top cell, which could damage the pumps. Finally, the off gas from the DZ stripping unit was vented into the exhaust fan.

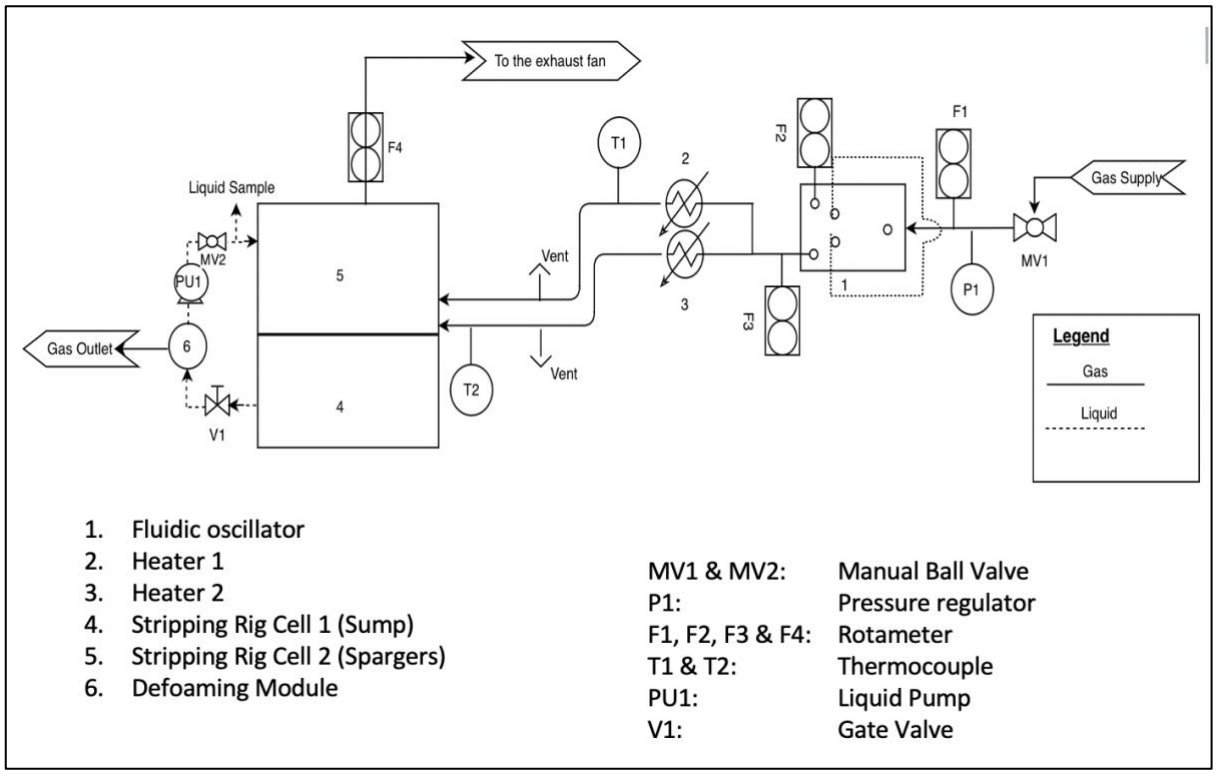

Figure 4.2: Illustration of the experimental system for recirculating DZ stripping unit

Prior to entering the rig, gas was heated to a temperature of 100 ^{o}C. The leachate volume and gas flow rate varied in this work. Each experiment was conducted over a period of 120 minutes.

Samples of liquid were taken at intervals of five minutes from the port between the recirculation between the sump and the top cell. The spargers and DZ stripping unit were rinsed with water between each run. This location provides holistic measurements of fluid concentration, pH, and properties and is easily accessible. Samples taken from the sump, or the recycled stream should not differ due to the well-mixed system within the sump. Furthermore, the sample from above the diffusers will be a dynamic system, and the amount of fluid being mixed over the diffusers cannot be controlled. Hence the location between the sump and top cell was chosen for collecting the samples.

Table 4.3: Operating conditions in ammonia stripping using Recirculating DZ rig

Process Parameter Studied	Liquid Volume (mL)	Total Gas Flow rate (LPM)	Gas Flow rate/Sparger (LPM)	Liquid Pump Rate (LPM)	Gas Temperature (°C)
Liquid Volume	3L, 4L, 5L	20	3.33	1.56	100
Gas flow rate	4L	16, 18, 20	2.67, 3, 3.33	1.56	100

Table 4.3 provides details regarding the parameters examined during the ammonia stripping process. Based on the equations described in section 3.3.1, volumetric mass transfer coefficients were calculated. Three replicates of the experiment were conducted under the same conditions.

4.3.4 Pilot Continuous DZ Stripping Rig

This experiment utilised a DZ continuous rig to examine ammonia removal from a high concentration solution. The experimental setup is illustrated in Figure 4.3. Pressurized air flows through tubing into the supply nozzle of the fluidic oscillator and subsequently passes through the specially shaped cavities. Oscillations were achieved by applying aerodynamic principles alone (i.e., Coanda Effect as discussed in Section 2.6.1). in the fluidic oscillator. Air flowed out from the oscillator and directed towards the gas inlets of the continuous rig, where microporous diffusers were utilized to generate microbubbles.

The ammonia solution was pumped across the rig, passing over microporous diffusers at constant flow rates and collected in the drum at the end of the rig. The duration of each run

was 8 minutes. Just prior to the start of the experiment, liquid samples were collected at the inlet to record the initial ammonia concentration. Liquid samples were collected from the outlet and drum at 1-minute intervals throughout each run. pH and ammonia nitrogen (NH_4^+-N) were measured immediately using ammonia probes following the procedures described in Section 3.1. These concentrations were applied to Equation 4.1 to calculate the amount of ammonia that was removed for a specific period.

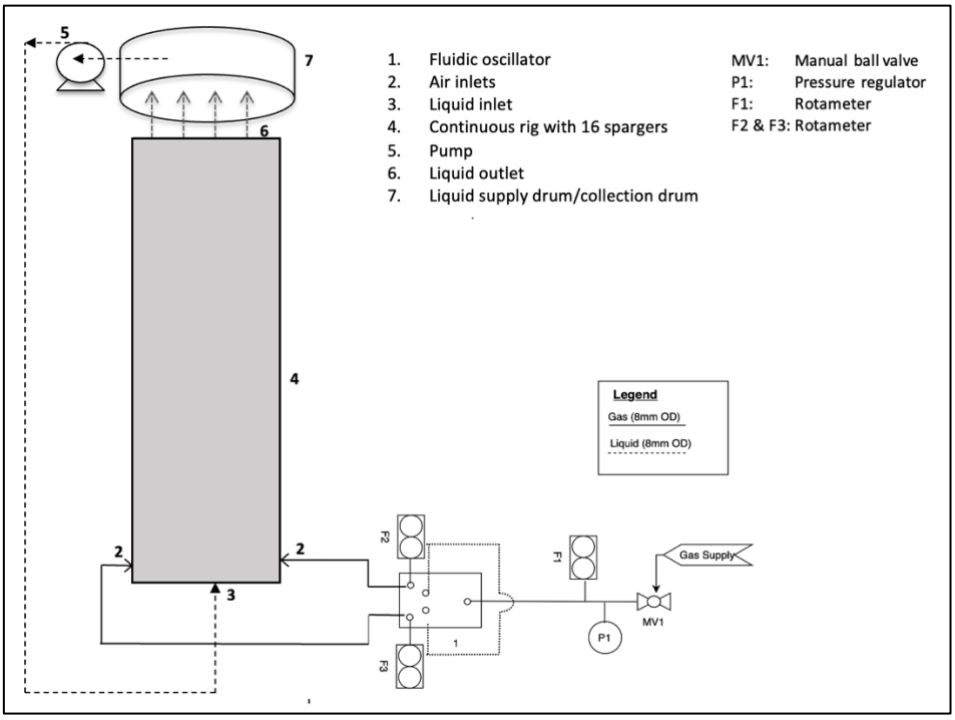

Figure 4.3: Schematic representation of the experiment system for pilot scale continuous DZ stripping unit

All experiments were conducted at a room temperature of 19 ^oC using a total volume of 19L of liquid. This study investigated gas flow rates of 20, 30, 40, and 45 LPM. Each run was performed in triplicate. Water was used for rinsing the diffuser and rig between each run.

4.4 Results and Discussion

The volumetric mass transfer coefficient, K_La is a parameter that determines the rate at which gaseous compound can transfer between gas phase and the liquid phase. The 'K_L' represents the rate of molecular diffusion through the gas-liquid interface and the 'a' represents the area of this interface per liquid volume (Quan *et al.*, 2009). To evaluate the stripping performance of the three rigs used in this chapter, TAN removal efficiencies and volumetric mass transfer coefficients K_La were determined for each experiment. The mass transfer coefficients can be compared in constant conditions such as gas flow rate, liquid volume, or temperature. Thus, the K_La values obtained from the three rigs were compared since their contact times differed. This way, the scale-up issues could be better understood and would not become a time-dependent process. The K_La for the first two rigs was calculated using the equations described in Section 3.3.1. In contrast, the K_La for the continuous rig was calculated based on the equation derived in Section 4.3.3. All experiments were conducted in triplicate and each data point presented is the mean value derived from the three runs. There was minimal deviation among three repetitions of the average values of the measured TAN for all experiments. The coefficient variations, CV were less than 5%, indicating a high level of repeatability.

4.4.1 Lab Scale DZ Stripping Rig

Several factors contribute to the removal of ammonia, including the contact area between liquid and bubbles, the air flow rate, and the temperature. An initial task in the present section involved stripping ammonia from two liquid levels. Figure 4.4 shows the results of stripping ammonia from different liquid volumes and, therefore, different liquid levels at an operating temperature of 35 ^{o}C and a gas flow rate of 0.5 LPM. It was observed that after 30 minutes of stripping, removal efficiency increased from 32.7% to 38.9% when the liquid volume was reduced from 38.5 mL to 25 ml. The equivalent liquid level was 5 mm to 3 mm. Additionally, the K_La value increased from 0.014 to 0.018 min^{-1}. According to these results, the efficiency of TAN removal appeared to be indirectly proportional to the liquid level, which corresponds to the contact area between the liquid and microbubbles. A liquid level of 3 mm was used in the next experiments using this rig.

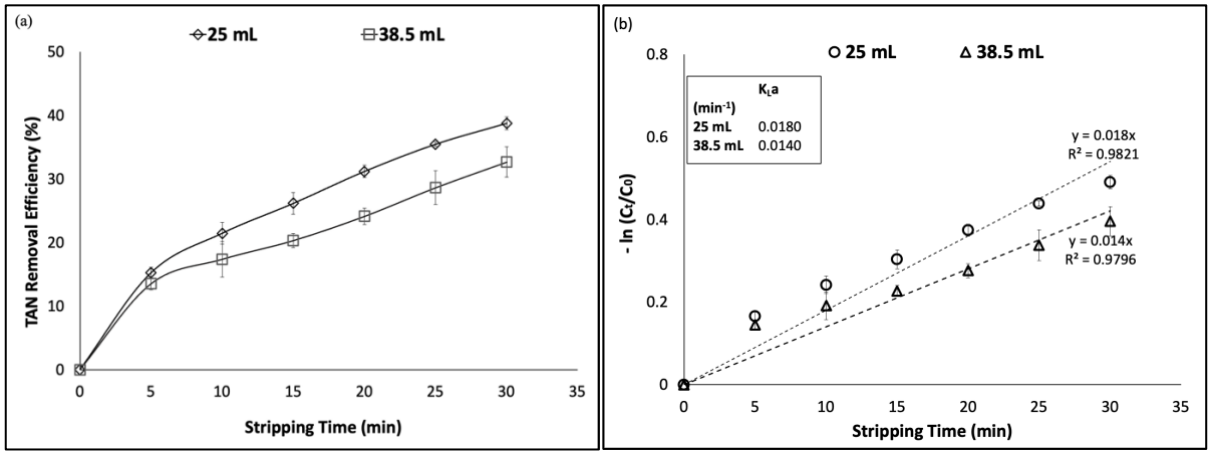

Figure 4.4: The effect of ammonia stripping from different liquid volumes (different liquid levels) at the same gas flow rate of 0.5 LPM and temperature of 35 ^{o}C. (a) TAN removal efficiencies (b) logarithm of the ammonia concentration ratio, giving the K_La values

The next set of experiments included running three different gas flow rates of ammonia stripping with 25 mL of liquid at an operating temperature of 35 ^{o}C. The TAN removal efficiencies and K_La from these experiments are presented in Figure 4.5. After 30 minutes, the average TAN removal efficiencies reached 38.9%, 45.5% and 69.9% at gas flow rates of 0.5, 1.0 and 2.0 LPM, respectively. The removal efficiency increases as gas flow rates increase because the contact area between gas and liquid increases, thus increasing the amount of ammonia diffused into the atmosphere (Srinath and Loehr, 1974). A similar trend was observed in a study evaluating ammonia stripping for the pre-treating of anaerobic digestion effluents (Lei *et al.*, 2007). A microbubble system is shown to be highly effective at removing significant amounts of ammonia within a short period at a moderate temperature of 35 ^{o}C. The ammonia removal efficiency would be expected to increase significantly at higher temperatures and for more extended periods. Figure 4.5b provides the natural logarithm associated with the variation in ammonia concentration ratio. The R^2 values obtained from linear regression analysis against time ranged between 0.979 and 0.999. Accordingly, a high flow rate results in a greater mass transfer coefficient, K_La. A significant increase in TAN removal was observed after 10 minutes when the gas flow rate was 2.0 LPM, resulting in a double K_La value compared with 1.0 LPM. This may be caused by the loss of organic substrate.

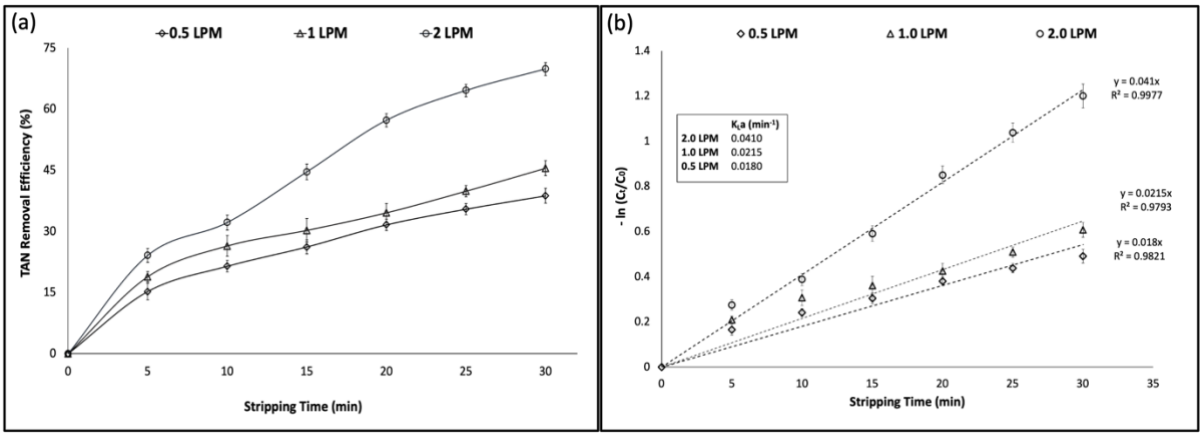

Figure 4.5: The effect of ammonia stripping under different gas flow rates using the same liquid volume and at the same temperature. (a) TAN removal efficiencies (b) logarithm of the ammonia concentration ratio, giving the K_La values

The chemical oxygen demand (COD) is a vital parameter in assessing organic content and the overall efficiency of anaerobic digestion processes. For these set of experiments, the reduction of total COD for different gas flow rates were also measured and the results are presented in Figure 4.6 below. COD reductions have been observed during the microbubble stripping of ammonia, and these reductions increase with the rate of gas flow. The average COD reductions were 19.9%, 26.2%, and 49.6% following 30 minutes at gas flow rates of 0.5, 1.0, and 2.0 LPM, respectively. Anaerobic digestion coupled with ammonia stripping requires a balance between ammonia stripping efficiency and organic compound preservation. Consequently, it is not appropriate to select a gas flow rate of 2.0 LPM when coupled with anaerobic digestion, despite the fact that the K_La value for stripping was the highest at this flow rate. This is because the loss of organic compounds was too high and may negatively impact methane production in the anaerobic digestion process. Furthermore, a high flow rate may also cause the digestate to overflow from the rig. Consequently, removing ammonia from anaerobic digesters at 1 LPM was determined to be the most effective to minimize ammonia inhibition.

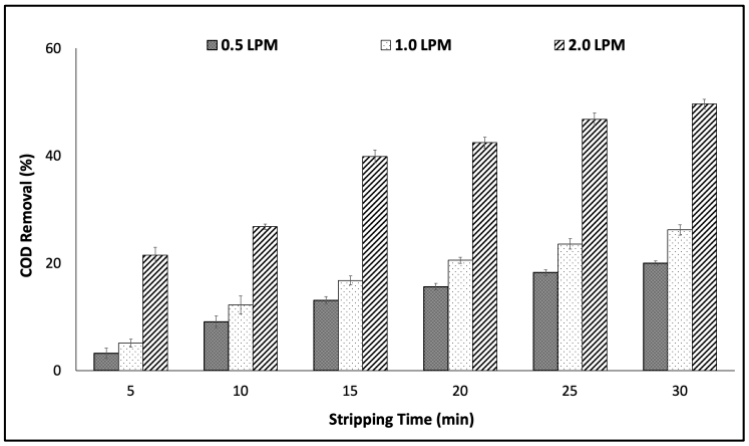

Figure 4.6: COD reduction during the ammonia stripping at different gas flow rates

The last set of experiments conducted using this rig examined the effect of operating temperature on the removal efficiency of ammonia and volumetric mass transfer coefficients when using a 25 mL volume of liquid at a gas flow rate of 1 LPM. Figure 4.7 illustrates the results of these experiments at various temperatures.

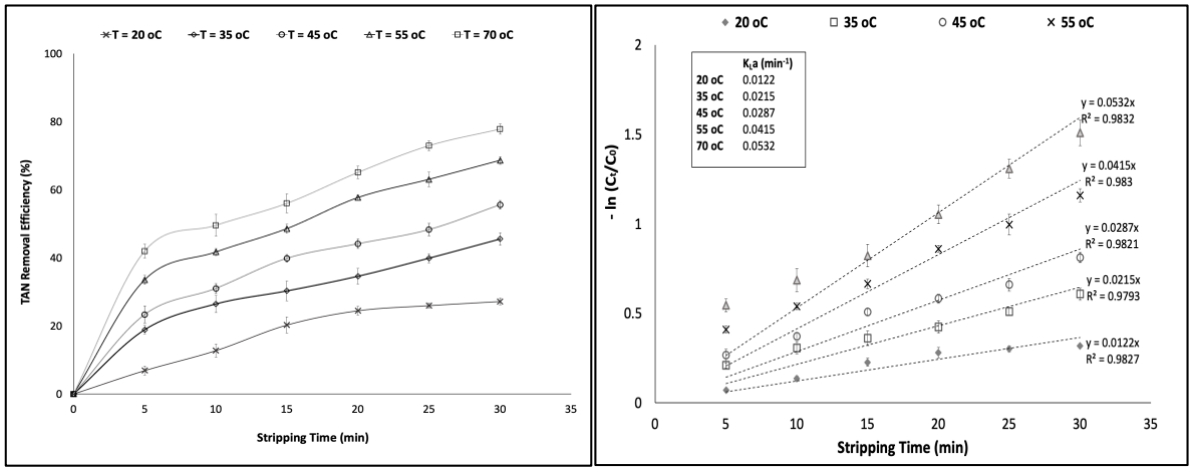

Figure 4.7: Ammonia stripping performance at different temperatures using the same liquid volume and at gas flow rate of 1 LPM (4.7a) TAN removal efficiencies (4.7b) Logarithm of the ammonia concentration ratio, giving the K_La values for stripping at 1LPM at different temperatures.

The removal rate has increased over time, as seen in Figure 4.7a. The TAN removal efficiencies were observed to be 27.2%, 45.5%, 55.6%, 68.6% and 77.8% for 20, 35, 45, 55 and 70 ^oC, respectively, after 30 minutes of stripping. As shown in Figure 4.7b, the accuracy of calculated K_La varies between R^2 values of 0.979 and 0.983 for all temperatures. This indicates that the

results are fitted well with first-order kinetics. The K_La values increased with temperature, indicating that the ammonia removal rate was directly correlated with temperature.

The efficiency of ammonia stripping has also been observed to increase with increasing temperature in previous studies (Liao et al., 1995; Collivignarelli et al., 1998; Zhu et al., 2017). The ammonia stripping process involves volatilizing ammonia from a liquid phase into a gas phase. This increase in efficiency can be attributed to the principle of thermodynamics, ammonia in the liquid phase shifts towards favouring the gas phase as the temperature increases. As a result, more ammonia molecules will transition from liquid to gas phase, increasing stripping efficiency. Moreover, higher temperatures also cause an increase in the kinetic energy of the ammonia molecules, resulting in an acceleration of the rate at which the ammonia molecules move and interact with the stripping agent. Consequently, ammonia is removed from the liquid phase more quickly and effectively. Despite this, there is an optimum temperature range for ammonia stripping, which should not be exceeded. An extremely high temperature can disrupt the microbial community balance in the digester, resulting in process instability and potential system failure (Yenigün and Demirel, 2013). As such, the optimal temperature must be determined according to the circumstances and limitations of the ammonia stripping process.

At an operating temperature of 70 ^{o}C, the K_La value was 0.0532 min^{-1}, and the average ammonia removal reached 77.8% in just 30 minutes of stripping. This K_La value was 2.3 times greater than that observed in the previous study involving conventional heating at 60 ^{o}C and gas flow rate of 7.5 LPM to remove ammonia at pH 11 for 240 minutes (Ata *et al.*, 2016). Another study using a stripping column at a flow rate of 72.8 LPM and an operating temperature of 70 ^{o}C showed an average K_La value of 0.0037 min^{-1} over a period of 6 hours; the maximum ammonia removal rate was 63.0% (Kim *et al.*, 2021). This demonstrated that microbubble stripping resulting from fluidic oscillations resulted in a higher removal efficiency in a short period of time and at moderate temperatures.

4.4.2 Recirculating DZ stripping Rig

The recirculating DZ stripping rig can accommodate a greater volume than the previous lab scale rig. The rig consists of two cells with the top cell containing six spargers (Figure 3.4). The

experiments were conducted at Viridor Waste Management Services in Parkwood, Sheffield. The initial ammonia stripping experiments used three different volumes of leachate, 3L, 4L, and 5L. The initial average TAN concentration in the leachate was around 1900 - 2100 mg/L. The gas was heated up to 100 °C before entering the rig and flowed at a rate of 20 LPM, equivalent to 3.33 LPM per sparger. Figures 4.8a and 4.8b illustrate how ammonia stripping from different liquid volumes affects the removal efficiency of TAN and K_La, respectively. Following the stripping of 3L, 4L and 5L of liquid for 120 minutes, the TAN removal efficiencies were 51.2%, 49.5% and 46.1%, respectively. The K_La values were also significantly lower than those of the previous rig. As shown in these figures, the liquid volume does not significantly impact the removal efficiency of TAN and the K_La values. By using one-way ANOVA and t-test statistical programs (Microsoft Excel 2021) to test for statistical significance, it was found that there is no significant difference in TAN removal efficiency between these three different volumes ($P > 0.05$). As the liquid in this rig was continuously recirculating between the bottom cell and the top cell with the spargers, the volume of liquid does not correspond to the liquid level on the spargers. Therefore, despite differences in the volume of the liquid, the liquid level remained constant. Thus, based on the data presented here, the volume of liquid had no significant impact on the removal rate of ammonia.

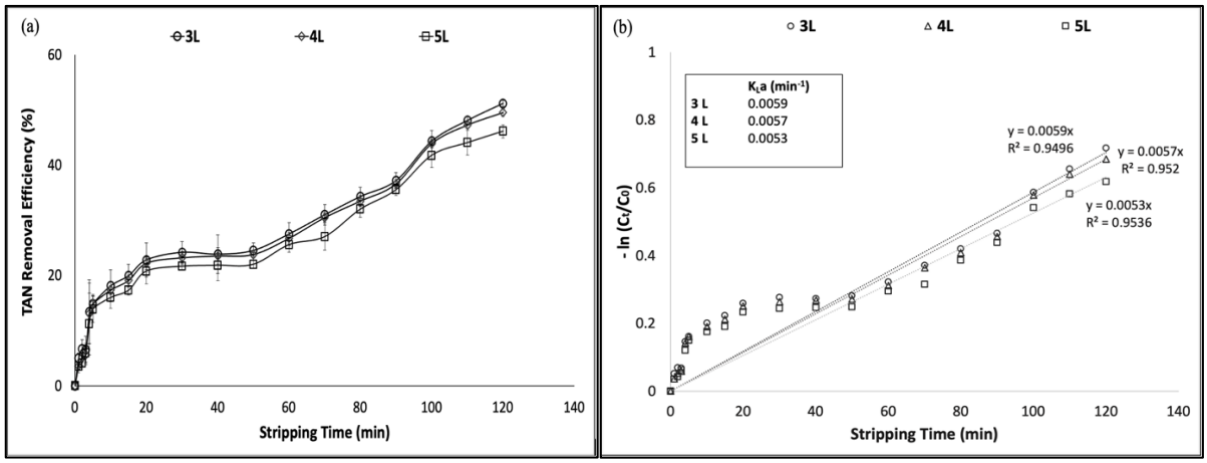

Figure 4.8: The effect of ammonia stripping from different liquid volumes on (a) TAN removal efficiencies (b) logarithm of the ammonia concentration ratio, giving the K_La values

Following this, experiments were conducted with a liquid volume of 4L, the same operating temperature, but with varying gas flow rates. Based on Figure 4.9a, the TAN removal efficiencies reached 30.9%, 38.5%, and 49.5% after 120 minutes of stripping at gas flow rates

of 16, 18 and 20 LPM, respectively. In general, the removal rate increases with the increase in flow rate. This illustrates the importance of the gas flow rates in the removal process in comparison to the liquid volume in this rig. A greater flow rate of the stripping gas would result in more bubbles entering the liquid, which would be beneficial for mixing the liquid and removing the ammonia in the liquid phase.

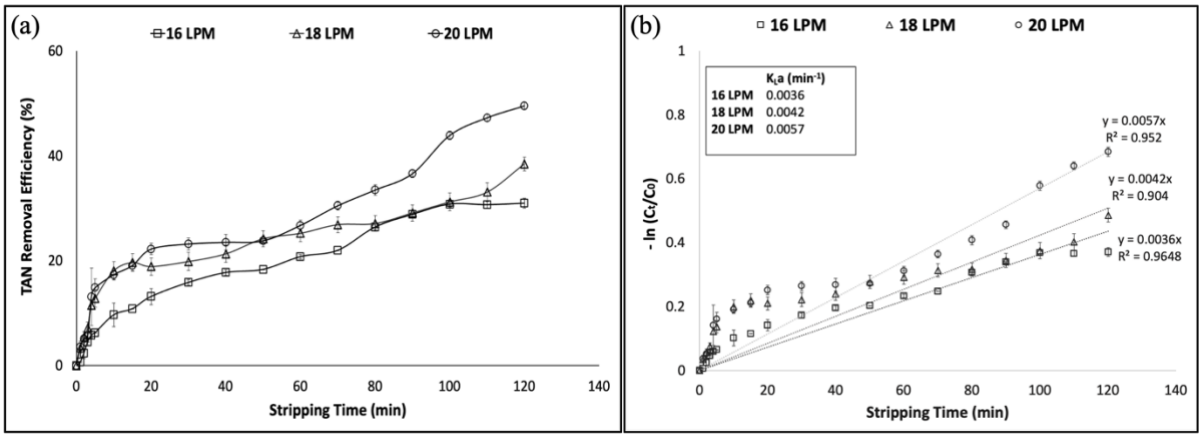

Figure 4.9: The effect of ammonia stripping under different gas flow rates using the same liquid volume and at the same temperature. (a) TAN removal efficiencies (b) logarithm of the ammonia concentration ratio, giving the K_La values

A linear regression of -ln C_t/C_0 with stripping time led to K_La values of 0.0036, 0.0042 and 0.0057 min^{-1} for 16, 18 and 20 LPM, respectively. There were R^2 values ranging from 0.904 to 0.965, which were relatively low. However, the results are still considered reliable (Kim *et al.*, 2021). Similarly, to the TAN removal efficiency, K_La values increased with increasing flow rate, however they were significantly lower compared to those of the lab-scale rig.

It is typical for TAN removal curves to follow an exponential decay pattern, with the concentration of TAN decreasing rapidly at first, and then gradually slows down. Figures 4.8 and 4.9 demonstrate similar shapes and trendlines, with a plateau in TAN removal occurring between 20 and 45 minutes. The removal efficiency increases at first, and then remains constant between minutes 20 and 40. In spite of this, after minute 40, the rate has continued to increase gradually. A number of factors influence the shape of the curve, including the type and design of reactor, the concentration of TAN in the wastewater, and the operating conditions. TAN removal may reach a plateau due to the limitations of the equipment and the

design constraints of the rig since the plateau appears to be independent of both liquid volumes and air flow rates. It is unlikely that this design will provide improvement on the removal of ammonia during AD and reduce the inhibition of ammonia by AD. It was found that the recirculation of the liquid in this design was ineffective. The effect of the pump rate on liquid recirculation would also be a factor to be considered. The pump rate is a significant part of the liquid recirculation process, as it affects the contact time between the liquid and microbubbles over the spargers, which is crucial for effective mass transfer and microbubble-liquid interactions. The increase in pump rate leads to increased circulation velocity, resulting in shorter contact times over the diffuser. Nevertheless, higher velocities can also increase the contact time since liquid circulation increases. Furthermore, higher pump rates can create more turbulent flow patterns, increasing the contact area between the microbubbles and possibly promoting better gas-liquid contact and more effective volatile compound removal. In addition, the pump rate affects the degree of mixing and homogeneity within the stripping rig. Turbulent flow conditions resulting from a higher pump rate led to better liquid mixing and improved homogeneity. This way, concentration gradients can be prevented, and uniform conditions can be maintained throughout the rig. Unfortunately, due to limited time and resources, the effect of pump rate was not included in the study.

4.4.3 Pilot Continuous DZ Stripping Rig

Unlike the previous two rigs, the time duration for the pilot continuous rig does not matter as much as the batch rig and recirculating rig because it should continuously provide the same concentration at the outlet over the course of the experiment. The evaluation of the volumetric transfer coefficient of ammonia from liquid to gas in this continuous rig differs from that in the previous two rigs because the liquid is continuously running in this rig. The plug flow reactor model is an idealised model commonly used in the design of reactors; therefore, this model can be employed to describe the separation taking place in the stripping process with continuous rigs. In the present work, the rate of stripping was used instead of the rate of reaction. Following is the derivation of this equation.

The equation used to model PFR:

$$\frac{dC}{dV} = \frac{-r}{F_L}$$

Equation 4.3

Where C is the concentration of the species, V is the volume contact area of the bubbles times liquid level from the top of diffuser, r is rate of reaction and F_L is flow rate through the rig.

Additionally, the rate of stripping can be expressed as follows:

$$r = k_L a(C - C_{eq})$$

Equation 4.4

Where C_{eq} is the concentration of the species in the liquid phase at the equilibrium.

Substituting Equation 4.4 into Equation 4.3 gives:

$$\frac{dC}{dV} = \frac{-k_L a(C - C_{eq})}{F_L}$$

Equation 4.5

Rearranging and integrating the above equation:

$$-F_L \int_{C_{in}}^{C_{out}} \frac{dC}{k_L a(C - C_{eq})} = V$$

Equation 4.6

$$k_L a = \frac{-F_L}{V} \left[ln(C - C_{eq})\right]_{C_{in}}^{C_{out}}$$

Equation 4.7

$$k_L a = \frac{-F_L}{V} ln \frac{(C_{out} - C_{eq})}{(C_{in} - C_{eq})}$$

Equation 4.8

C_{eq} is assumed to be zero and the Equation 4.8 can be simplified to the following equation:

$$k_L a = \frac{F_L}{V} ln \frac{C_{in}}{C_{out}}$$

Equation 4.9

Equation 4.9 was then used to calculate the $K_L a$ for each experiment using continuous rig.

Ammonia stripping was performed using continuous rig at different gas flow rates including 20 LPM, 30 LPM, 40 LPM and 45 LPM. This is equivalent to 1.25, 1.875, 2.50 and 2.81 LPM per sparger, respectively. Figure 4.10 shows the total ammonia nitrogen removal efficiencies from stripping experiments at various gas flowrates. Samples were taken at the liquid and gas outlets at intervals of one minute. All gas flow rates initially showed a rapid increase in TAN removal efficiency, which subsequently remained constant over time. Consequently, this is in accordance with the characteristics of continuous processes in which raw materials flow in and out at a constant rate, resulting in constant ammonia removal rates over time. The removal efficiency of TAN was calculated by averaging the values between 5 and 8 minutes for each gas flow rate. This led to TAN removal efficiencies of approximately 21.8%, 33.4%, 44.3%, and 48.9% for 20, 30, 40 and 45 LPM, respectively. This same trend was also observed for the other two rigs. As previously mentioned, the removal efficiency increases with increasing gas flow rates because the increasing gas flow rate increases the contact surface area between gas and liquid, thereby increasing ammonia diffusion.

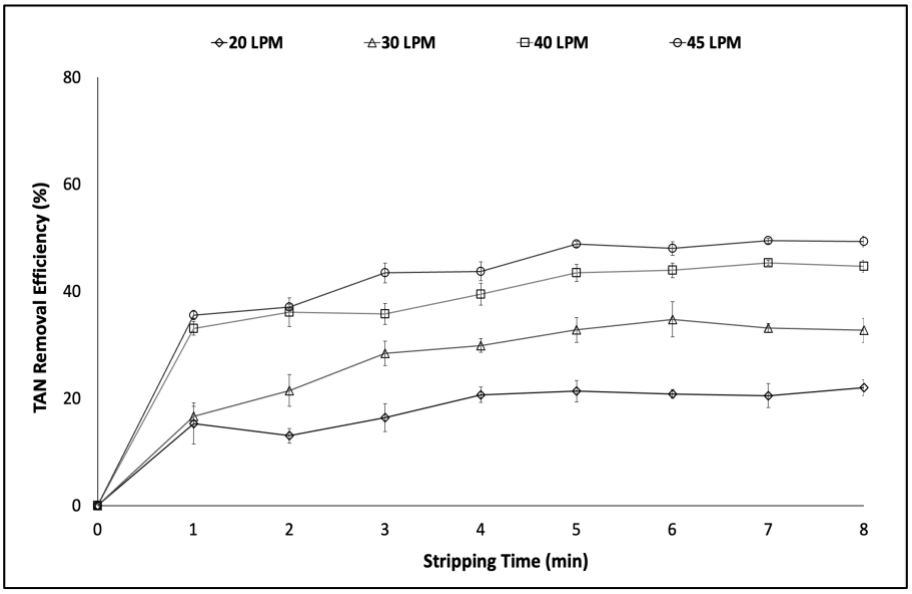

Figure 4.10: Total ammonia nitrogen (TAN) removal efficiencies at various gas flow rates versus stripping time

The K_La was calculated for each sample. K_La for stripping at each gas flow rate was determined based on an average of K_La data obtained between 5 and 8 minutes. In Table 4.4, K_La stripping at different flow rates are summarized. Similar to the removal efficiency of TAN, K_La increased

with gas flow rate. Similar results were reported in a previous study by Zhu et al. (2017), where K_La increased with increasing gas flow rate.

Table 4.4: Volumetric mass transfer coefficient of ammonia stripping using continuous rig at different gas flow rates.

Flowrate (LPM)	K_La (min^{-1})
20	0.132 ± 0.004
30	0.224 ± 0.008
40	0.324 ± 0.009
45	0.371 ± 0.007

Even though there is no heating involved, the K_La values obtained using these continuous rigs were significantly higher. This can possibly be explained by the use 16 spargers in this rig and microbubbles generated by the fluidic oscillator. Moreover, the pH of the synthetic ammonia solution is slightly higher than that of the leachate used in the other two rigs.

4.4.4 Summary of Ammonia Stripping Experimental Results

Table 4.5 summarizes the ammonia stripping experiments conducted using three stripping rigs. Experimental results for each rig are analysed, providing insight into their effectiveness and efficiency in stripping ammonia under different operating conditions and rig designs. It was found that all rigs performed satisfactorily even without adjusting the pH and at relatively low temperatures and short times. All rigs exhibit increased ammonia removal efficiencies with increasing flow rates and temperatures.

In light of these findings, the use of the DZ fluidic oscillator to generate microbubbles in the stripping rig has shown that relatively high ammonia removal efficiency can be achieved within a short period of time, under moderate temperature conditions, and without the need to adjust pH levels. These characteristics make it an efficient and cost-effective method of removing ammonia.

The lab-scale DZ stripping rig demonstrated promising performance in the removal of ammonia in a small volume and batch process. It can be seen that DZ lab-scale is capable of being

combined with AD in the current study. Pilot continuous DZ stripping rig is suitable for large-scale ADs where there is adequate ventilation and continuous stripping is possible. However, further research and optimization are required to improve the performance of the DZ recirculating rig.

Table 4.5: Summary of experimental results from the ammonia stripping

Stripping Rig	Run	Duration (h)	Liquid Volume (L)	Total Gas Flow Rate (LPM)	Gas Flow Rate/Sparger (LPM)	pH	Temperature (°C)	TAN Removal Efficiencies (%)	K_La (min^{-1})
Lab Scale DZ Stripping Rig (1 Sparger)	1	0.50	0.025	1.0	1.0	7.99	20	27.2	0.012
	2	0.50	0.0385	0.5	0.5	7.96	35	32.7	0.014
	3	0.50	0.025	0.5	0.5	8.00	35	38.9	0.018
	4	0.50	0.025	1.0	1.0	8.03	35	45.5	0.022
	5	0.50	0.025	1.0	1.0	8.04	45	55.6	0.029
	6	0.50	0.025	1.0	1.0	7.98	55	68.9	0.042
	7	0.50	0.025	2.0	2.0	7.97	35	69.9	0.041
	8	0.50	0.025	1.0	1.0	7.86	70	77.8	0.053
Recirculating DZ Stripping Rig (6 Spargers)	9	2.00	4.00	16.0	2.7	8.64	100	30.9	0.004
	10	2.00	4.00	18.0	3.0	8.89	100	38.5	0.004
	11	2.00	5.00	20.0	3.3	8.82	100	46.1	0.005
	12	2.00	4.00	20.0	3.3	8.92	100	49.5	0.006
	13	2.00	3.00	20.0	3.3	8.98	100	51.2	0.006
Pilot Continuous DZ Stripping Rig (16 Spargers)	14	0.13	19.00	20.0	1.3	9.00	19	21.8	0.132
	15	0.13	19.00	30.0	1.9	9.00	19	33.4	0.224
	16	0.13	19.00	40.0	2.5	9.00	19	44.3	0.324
	17	0.13	19.00	45.0	2.8	9.00	19	48.9	0.371

The K_La values obtained using the continuous rigs were significantly higher than those obtained using the lab scale. The scale of a continuous unit and a lab unit should be taken into consideration when comparing their performance. The continuous units are usually larger, designed for industrial-scale operations, whereas the lab units are smaller and used for research. The exact K_La value of a continuous unit might be challenging to achieve in a laboratory-scale unit. Scaling up a lab unit to a continuous unit requires a significant system expansion. The available surface area for mass transfer increases with increasing system size. The increased surface area facilitates better contact between the liquid and gas phases, facilitating more efficient mass transfer. Compared to a continuous unit, the available surface area in a lab unit with smaller dimensions makes it difficult to achieve the same K_La value. In

addition, laboratory-scale equipment may be limited in terms of agitation intensity, surface area, and control mechanisms compared with continuous industrial units. These limitations can affect the efficiency of mass transfer and, consequently, the K_La value.

While it may be challenging to replicate the exact K_La value of a continuous unit in a lab-scale unit, lab experiments are still valuable for studying the underlying mass transfer mechanisms, studying the effects of various factors, and developing empirical correlations. The results of laboratory experiments can be used to gain insight into the system behaviour, identify possible improvements, and refine process parameters to improve mass transfer efficiency in larger continuous production units.

4.5 Comparison of the NH_4-N removal efficiencies and K_La with Literature

Performance of each stripping rig was evaluated based on K_La values, volumetric transfer coefficients for ammonia from liquid to gas. Generally, higher K_La values indicate a more efficient transfer of ammonia between liquid and gas phases. Industrial processes can benefit from improved mass transfer efficiency, improved performance, and reduced environmental impact by aiming for high K_La values. The values of these parameters play an important role in the design, optimization, and operation of systems that involve the transfer of ammonia between liquid and gas phases.

Table 4.6 compares results from the present work with those published in the literature. Ammonia stripping and mass transfer rates were observed to be improved by increasing pH levels. In all previous studies in Table 4.6 below, NaOH was used to adjust the pH. A significant difference between the present study and the studies described in the table below is that all experiments in the present study were conducted without the use of any additional chemicals to adjust the pH. In this case, the original pH of the liquid was used. The microbubble stripping produced by fluidic oscillators using lab-scale and continuous DZ rigs achieved a significantly higher K_La value than other studies at comparable operating conditions. All experiments were conducted using thin layers of liquid, leading to a high separation efficiency for both rigs within a short period of time.

Further removal of ammonia from the liquid could be achieved by extending the stripping time. Therefore, treatment by both rigs is viable and more likely to result in a positive outcome when combined with AD to reduce the inhibition of ammonia production. However, the K_La value for the recirculating DZ rig was smaller than that of these two, but higher than that of the previous study on packed towers with circulation (Kim *et al.*, 2021). As compared with the other two methods in this study, liquid circulation did not significantly improve ammonia removal. It is necessary to perform further research, such as varying the flow rate of the liquid pump.

Microbubble stripping engendered by a fluidic oscillator performed better than most other techniques described in Table 4.6 based on K_La values and stripping period. This may be due to the fact that the present study used microbubbles generated by the fluidic oscillator, while the other studies used conventional fine bubbles of millimetre size (typically 1 – 4 mm). This size of microbubble provides a substantially larger surface area per unit volume, resulting in a large interfacial area, in turn, an enhanced mass transfer rate and separation (Zimmerman et al., 2008). Traditionally, a stripping unit requires a substantial amount of energy to increase the temperature of the mixture, making it an energy-intensive process. However, the microbubble stripping engendered by the fluidic oscillator has the advantage of achieving separation at a moderate temperature within a shorter period of time with less energy consumption.

The ability to strip ammonia without pH modification would significantly reduce operating costs. In addition, the method would be well integrated with wastewater treatment or any liquid with a high concentration of ammonia. The absence of chemicals for pH adjustment and minimal energy consumption for creating microbubbles by fluidic oscillators would certainly reduce operating costs.

Table 4.6: Comparison of ammonia removal efficiencies and the K_La with the previous work

Stripping Technique	T (°C)	pH	Time (h)	Gas Flow Rate (LPM)	Liquid Volume (L)	Air Supplied (L-Air/L-Liquid)	Removal Efficiency (%)	K_La (min^{-1})	Liquid	Reference	Note
Stripping Column	20	8.9	2.5	15	1	2250	13.9	0.00365	Artificial ammonium hydroxide wastewater	(Kim *et al.*, 2021)	NaOH was utilised to adjust the pH
	20	9.4	2.5	15	1	2250	38	0.0057			
	20	10.8	2.5	15	1	2250	72.6	0.00957			
	40	12	5	3.33	0.4	2500	91	0.0084	Acetylene Purification Wastewater	(Zhu *et al.*, 2017)	
	60	12	2	3.33	0.4	1000	91	0.0146			
Packed Tower with circulation	70	8.5	6	437	100	1572	57.1	0.00323	Artificial ammonium hydroxide wastewater	(Kim *et al.*, 2021)	
	70	8.5	12	36.4	100	262	77.3	0.00290			
	70	8.5	24	18.2	100	262	81.5	0.00165			
Lab Scale Air Stripping Tower	50	10	24	1	0.25	4	98.7	0.00613	Urine Sample	(Liu *et al.*, 2015)	
Stripping Rig using Conventional Heating	60	11	7.5	4	0.5	3600	100	0.0228	Synthetic Ammonia solution	(Ata *et al.*, 2016)	
Jet Loop Reactor	20	11	13.33	50	9	5.56	100	0.0105	Synthetic Ammonia solution	(Deĝermenci *et al.*, 2012)	
Lab-scale DZ Unit	70	7.97	0.5	1	0.025	1200	77.8	0.0532	Leachate	Present work	No pH adjustment
Recirculating DZ Unit	100	8.92	2	20	4	600	49.5	0.0057	Leachate		
Continuous DZ Unit	19	9	0.133	40	19	16.8	48.9	0.371	Synthetic Ammonia solution		

4.6 Conclusion

This study investigated three designs of DZ units to determine whether they are feasible for improving the removal of ammonia from high concentrated ammonia solution. The DZ lab-scale and Continuous DZ stripping rigs showed remarkable improvements in ammonia stripping. However, the recirculating DZ rig required additional work in order to optimize the operating conditions and improve the separation. According to the findings of the present chapter, ammonia stripping using the lab-scale DZ rig was the most feasible method for coupling with AD in the following chapters. This is because in the present study, the AD's working volume was 20L, and only 10% of the working volume was intended to be stripped, which is 2 L. In larger AD plants, continuous DZ rigs can be beneficial if excellent ventilation is provided.

Desai *et al.* (2021) reported on exceptionally fast rates of ammonia stripping, relative to the literature, with hot microbubbles and/or high pH, both of which provide a Gibbs-free energy boost. In this study, although the stripping rates are lower than Desai *et al.* (2021), they are substantially higher than in the literature, but this case aimed at operating conditions practically applicable to simultaneous operation with anaerobic digestion, including the pH range, gas and liquid temperatures and flow rates. Hence, due to tailoring of the conditions, inherently lower Gibbs free energy boosts than Desai *et al.* (2021). In particular, the range of temperatures is compatible with waste heat often used in municipal waste AD plants for mesotrophic thermal control. Moreover, the stripping period was shorter than in other studies. Generally, high operating pHs and temperatures are not economically viable because of the cost and supply of energy; they are better suited to ammonia stripping as a separate single process than to being coupled with anaerobic digestion. Collivignarelli *et al.* (1998) reported that removing 90% of ammonia without adding chemicals to adjust the pH was possible. Still, the initial pH of the leachate must be around 8.0, the temperature must be at least 70 ^{o}C, and the operating time must be at least six hours (Collivignarelli *et al.*, 1998). In the present study, the ammonia removal rate was 77.8% in just half an hour when ammonia was stripped with a DZ lab-scale rig operated at 70 ^{o}C. A temperature of 70°C was chosen because higher operating

temperatures are not cost-effective and may adversely affect microorganisms. Anaerobic digestion usually occurs at temperatures as high as 70 ^{o}C in thermophilic conditions.

As indicated in a previous study, stripping ammonia at 1 LPM using bubbles of normal size results in a K_La of 0.00613 min^{-1} (Liu et al., 2015). In the present study, microbubbles were generated by DZ fluidic oscillators which the size between 70 – 150 μm on average were generated and offered a greater K_La value. Due to concerns over upsetting the anaerobic system, a higher bubbling rate was not selected with respect to AD coupled with ammonia stripping to avoid inhibition. This is because the removal efficiency obtained when using flow rate of 1 LPM seems sufficient and cost-effective. In addition, COD reduction was significant when the flow rate was at 2 LPM. Thus, AD in Chapter 6 of the present work was coupled to a lab-scale DZ rig with an operating temperature of 70 ^{o}C and a gas flow rate of 1 LPM. Air microbubble stripping was successful, but an anoxic gas is required for simultaneous AD operations. As a cheap gas and potential C-source, CO_2 is a good candidate. The next chapter discusses the possibility of using carbon dioxide as a stripping agent.

Chapter 5 : An Investigation into the Possibility of *in situ* Ammonia Stripping from an Anaerobic Digester Sparged with CO_2 Microbubbles

5.1 Abstract

Recent research suggests that seeding anaerobic digestion with microbubble carbon dioxide is an effective method of increasing methane production from waste food. There are several hypotheses pertaining to the mechanism underlying the increase in methane production following the injection of exogenous CO_2 including the *in situ* stripping of inhibitor ammonia by CO_2 microbubbles in the digester. The present study investigates this hypothesis and the ability of carbon dioxide sparging to strip ammonia from the digestate. Two bioreactors treating food waste were operated in a batch anaerobic digestion. One was sparged daily with microbubble CO_2 for 10 minutes at a flow rate of 1LPM while the other acted as control. To further study the ability of the carbon dioxide to remove ammonia from digestate, batch stripping of ammonia using microbubbles of various gases including carbon dioxide was also performed. Based on the findings of this study, carbon dioxide did not strip ammonia from digestate. Rather, it only reduces the fraction of non-ionised free ammonia which is believed to be a powerful inhibitor in anaerobic digesters. Additionally, the batch stripping experiments in this chapter indicate that air or nitrogen can be used to strip ammonia.

5.2 Introduction

Ammonia is also generated during anaerobic digestion as a result of the degradation of organic nitrogen. A substantial amount of ammonia is an essential nutrient for many organisms in the digester. It also functions as a buffer for the digestion process, however, high concentrations of ammonia can inhibit digestion (Procházka *et al.*, 2012; Serna-Maza *et al.*, 2017). A number of studies have found that digestion failures are frequently associated with high levels of total ammonia nitrogen (de Baere *et al.*, 1984). An accumulation of ammonia and volatile fatty acids (VFAs) in the digester will result in a decline in biogas production and the failure of the digester. It is due to the presence of high concentrations of ammonia, which inhibits the methanogen's ability to produce methane and triggers the accumulation of VFA in the digester, resulting in its malfunction (Nielsen and Angelidaki, 2008).

It was hypothesized that the mechanism by which CO_2 microbubbles enhance substrate utilization is by stripping ammonia, an inhibitor of anaerobic digestion (Al-Mashhadani, 2013; Nugroho, 2021). Ammonia inhibits the production of methane from hydrogen and carbon dioxide. The present study is investigating this hypothesis. Two digesters treating food waste were operated at a controlled mesophilic temperature of 35 ± 2 °C. These include a control digester and a test digester with microbubble CO_2 sparging. Both digesters were operated with the same conditions except for microbubble sparging in the test reactor. They also had the same working volume, and they were fed with the same type of food waste and inoculum. Both digesters were operating in a batch mode under mesophilic conditions.

In addition to this, experiments on batch stripping of ammonia from the digestate using the microbubbles was also carried out to investigate the stripping performances using different gas including air, nitrogen, and carbon dioxide. This experiment was carried out to further investigate the ability of CO_2 gas to strip ammonia off from the digestate and identify the suitable gas medium for the ammonia stripping from the anaerobic digesters. The energy efficient fluidic oscillator was used in these experiments to create microbubbles. Microbubbles have been shown to affect both the mechanisms of evaporation and sensible heat transfer, and to achieve maximum evaporation rates in a short time frame (Zimmerman et al., 2013). Recent study on ammmonia stripping was conducted using microbubbles engendered by fluidic oscillator, in which air was used as the stripping gas (Desai et al., 2021). It was observed that 100% separation efficiency could be achieved in 30 minutes at pH less than 9. Moreover, the study also found that cold microbubbles are effective in removing ammonia, albeit at a slower rate.

5.3 Materials and Methods

5.3.1 Characterization of seeding sludge, food waste and samples

Seeding sludge was collected as an inoculum source from a full-scale anaerobic digestion facility in Stockport, England. Seeding sludge was reactivated at 35 ± 2 °C for five days before the commencement of the anaerobic digestion to ensure that no digestible substrate remains in it and that all methane produced in the experiments is from the targeted substrate only. Food waste was prepared in bulk quantities to ensure a homogeneous feedstock supply, and this was frozen at -18 ^{o}C. Prior to use, food waste was thawed and stored at a temperature of 4°C. The characterisation of the substrate and seeding sludge was carried out particularly on the determination of the total solids (TS), total dissolved solids (TDS), total suspended solids (TSS), total volatile solids (TVS), dissolved organic carbon (DOC), ammonium content, and total and soluble chemical oxygen demand (TCOD and sCOD). A food information label on the packaging is used to estimate the nutritional content of food waste. The characteristics of the seeding sludge and food waste are represented in Table 5.1 and Table 5.2, respectively. The percentage of total solids of food waste was also in the optimum concentration for anaerobic digestion with a range of 20 -50% (Kothari et al., 2014).

Table 5.1: The characteristics of the seeding sludge

Parameters	Unit	Value
pH		8.433
Total Solid	g/L	7.100
TDS	g/L	4.950
TSS	g/L	2.149
TVS	g/L	2.587
TCOD	g/L	3.873
sCOD	g/L	2.189
DOC	mg/L	584.0
Ammonium	mg/L	2694.556

Table 5.2: Feedstock proximate analysis
[a] determined per 100 grams of non-dried sample. [b]value from dry weight

Parameters	Unit	Value
Carbohydrate[a]	g	18.46
Fibre[a]	g	3.21
Protein[a]	g	7.92
Fat[a]	g	2.33
Total Solid (TS)	%	23.596
Volatile Solid (VS)	%	22.542
VS/TS (f_{vs})		0.955
C[b]	%	47.29
H[b]	%	6.18
N[b]	%	4.32
S[b]	%	0.25
O[b]	%	41.96
C/N		10.95

5.3.2 Characterization of digestate for stripping experiment

Digestate used in this experiment was collected from the previous mesophilic anaerobic digestion of food waste. In this study, the pH of the digestate was not adjusted because the aim was to investigate the ability of CO_2 to strip ammonia in the digester. Hence, the original pH of the digester was maintained. Moreover, the addition of chemicals to adjust the pH could interfere with anaerobic digestion. Characteristics of the digestate used in the stripping are presented in Table 5.3. The values presented are the mean values from all runs. There were differences in the initial parameters especially on the total ammonia nitrogen, (NH_3-N) of each run, but they were not statistically significant. The possible reason for this dissimilarity is due to the heterogeneity of the digestate (De la Rubia *et al.*, 2010). It was observed that the initial concentration of ammonia was the least sensitive parameter affecting the removal efficiency (Desai *et al.*, 2021). Furthermore, previous study on ammonia stripping confirm that the removal efficiency was constant irrespective of initial ammonia concentration (Deĝermenci *et al.*, 2012; Kim *et al.*, 2021).

Table 5.3: Analyses of the digestate used in the stripping experiments

Parameters	**Unit**	**Value**
pH		8.75 ± 0.08
Total Solid	g/L	10.055 ± 0.2
Total Volatile Solid	g/L	3.360 ± 0.2
NH_3-N	mg/L	3842.22 ± 50.6

5.3.3 Experimental setup and procedure of runs

5.3.3.1 Anaerobic Digestion with CO_2 microbubbles sparging

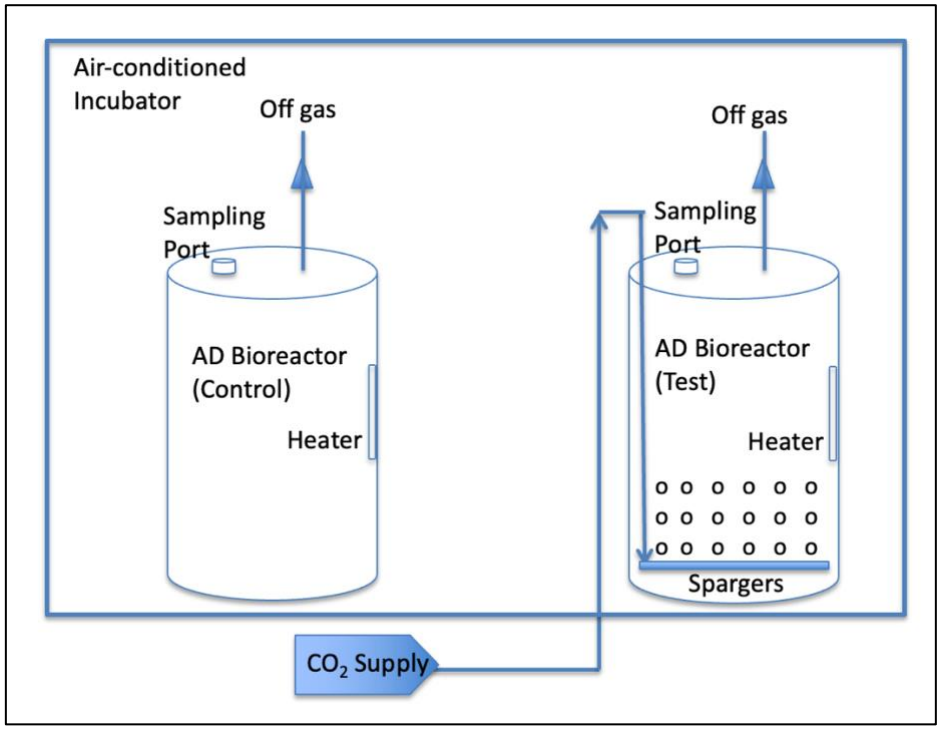

Figure 5.1: Schematic diagram of the two digesters used in this study

Two 30L bioreactors used as a control and test reactors were set up, as shown in Figure 5.1. Three ceramic diffusers (Point Four MBD 75, Sterner) were placed inside the test reactor. The average size of the bubbles generated by these diffusers were in between 100 – 500 µm without fluidic oscillator. Carbon dioxide was sparged in the test reactor for 10 minutes daily and at a flow rate of 1 LPM.

Each 30L bioreactor was fed with 2kg food waste and inoculated with 20L seeding sludge. The headspace was flushed with nitrogen gas to remove air from the system and introduce an anaerobic condition. These bioreactors were placed in an incubator, in which the air-conditioner was used to maintain the mesophilic operating temperature (35 ± 2 ^{o}C). In addition to this, a 50 W submersible heater (HT-6050 Uniclife) is also attached to the wall inside of each reactor. An automatic temperature controller (InkBird, ITC-308) was connected to each heater to avoid over-heating.

Biogas (off gas) was collected in a gas-impermeable bag. The volume and composition of the gas produced were monitored daily. Liquid samples were collected every two days from each reactor for the analysis of TAN. The pH and temperature of the working liquid were monitored daily. Total solids and volatile solids were analysed at the start and end of the experiment. The experiment was running until no significant amount of biogas was produced. The experiment was conducted in three continuous cycles, each taking approximately 30 to 35 days. After the completion of each cycle, degassing was performed, and the food waste was fed again into the reactors to begin the next cycle.

5.3.3.2 Ammonia stripping using microbubbles engendered by fluidic oscillator

Stripping experiments were performed to assess the ability of carbon dioxide gas to remove ammonia from the digestate compared with other gases. An evaluation of the effectiveness of the stripping process was conducted in terms of the removal rates of TAN. This batch ammonia stripping was operating at the temperature of 35 ^{o}C, the same temperature as mesophilic anaerobic digestion. Stripping gases used include carbon dioxide (BOC, UK), air and nitrogen (BOC, UK).

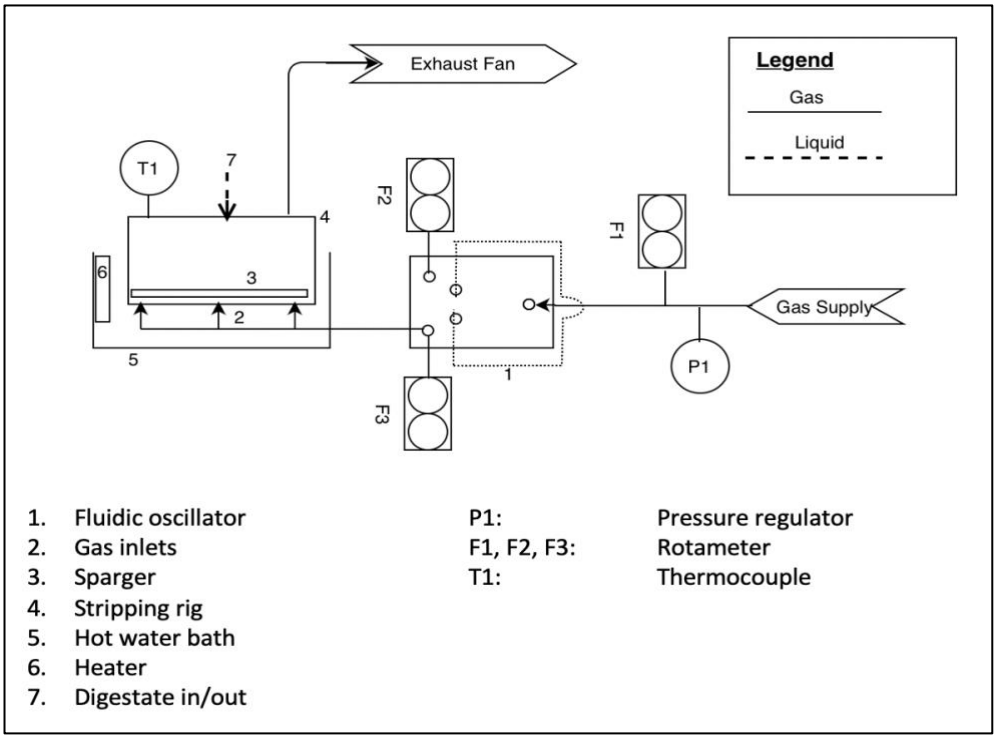

Figure 5.2: Schematic representation of the experiment system for hot stripping

The experiment setup is the same as that described in Section 4.3.2 and is shown in Figure 5.2. Stripping took place in the fume cupboard to minimize pressure build-up in the rig by venting gases from the top port. Lab-scale rig made of stainless-steel was designed for the microbubble stripping. Gas from the supply passed through the fluidic oscillator and it was allowed to oscillate solely by virtue of aerodynamic principles (i.e., Coanda Effect as discussed in Section 2.6.1). The two valves on the fluidic oscillator were used to control the gas flow rate introduced into the rig through stainless-steel spargers. Generally, the rate of transfer depends on the contact time between the bubble and the liquid, or the height of the liquid in the rig, which varies with the volume of liquid poured into the active area. Digestate of 38.5ml was fed into the rig, this gave maximum liquid level of 5mm. Previous study concluded that the optimum performance can be achieved with the lower liquid level of 5 mm (Desai *et al.*, 2021). Gas flow rates were set at 1.0 LPM into the rig, which corresponds to the flow rates of CO_2 gas injected into digesters in the previous section of this chapter. Stripping gas was liberated and stripped free ammonia from the digestate. Duration for each run was 30 minutes and digestate was sampled at 5 minutes interval from the sample port. TAN and pH were monitored. 3 runs were carried out with three replications of each. Table 5.4 summarizes the operational conditions the experiments conducted.

Table 5.4: Experimental conditions of ammonia stripping

Run	Temperature (^{O}C)	Stripping Gas	Gas Flow rate (LPM)
1	35	Air	1.0
2	35	Nitrogen	1.0
3	35	Carbon Dioxide	1.0

5.4 Results and Discussion

5.4.1 Methane Production and Yield from Anaerobic Digestion

The cumulative production of methane from both reactors in three cycles are shown in Figure 5.3. Each cycle took about 30 – 35 days to complete. All the gas produced is considered the product from the targeted substrate only since degassing of the inoculum was carried out prior to the experiment. There was a significant difference in the amount of methane produced from both reactors in all cycles. In the test reactors, the amount of methane produced exceeded

92.9% on average compared to the amount of methane produced in the control reactors. A similar observation was made in a previous study by Al Mashhadani et al. (2016), in which anaerobic digestion of food waste was sparged with CO_2 microbubbles. The methane production rate in this study was approximately double that in the control reactor without carbon dioxide sparging.

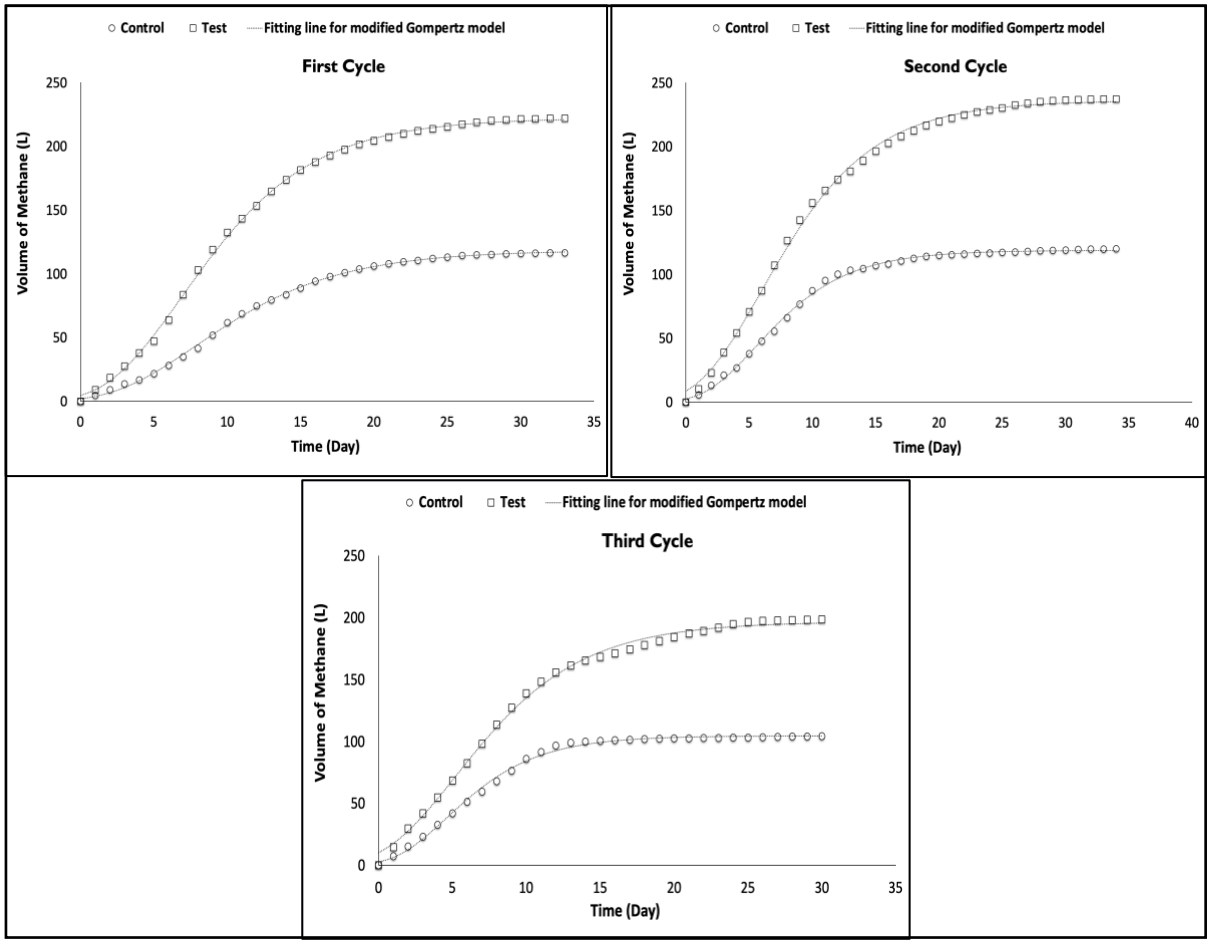

Figure 5.3: Cumulative methane production from the control and test reactors

Table 5.5: Fitting results of modified Gompertz model for cumulative methane production curves

Cycle	Digesters	Modified Gompertz model			
		G_0 (L)	R_{max} (L/day)	ʎ (days)	R^2
First	Control	118.3 ± 0.5	7.8 ± 0.1	2.3 ± 0.1	0.999
	Test	222.2 ± 0.7	16.1 ± 0.2	1.8 ± 0.1	0.999
Second	Control	118.9 ± 0.5	10.7 ± 0.2	1.5 ± 0.1	0.998
	Test	235.8 ± 1.0	17.4 ± 0.3	1.0 ± 0.1	0.998
Third	Control	104.4 ± 0.5	10.9 ± 0.3	1.1 ± 0.9	0.997
	Test	196.5 ± 1.3	15.0 ± 0.4	0.4 ± 0.1	0.997

Methane production potential, G_0, the maximum rate of methane production R_{max}, and lag phase time, ʎ calculated using this model are shown in Table 5.5. Based on the observation from Figure 5.3 and Table 5.5, the experimental data fitted well with this model with high R^2 values. The correlation coefficients (R^2) for all digesters in each cycle provide an excellent fit between experimental data and those predicted, with a convinced correlation coefficient R^2 ranging from 0.997 – 0.999. The G_0 and R_{max} of the test reactor were almost double those of the control reactor during the three cycles. These findings are in accordance with previous studies which suggest that microbubbles sparging carbon dioxide in an anaerobic digester enhances methane production (Bajón Fernández *et al.*, 2015; Al-Mashhadani *et al.*, 2016; Alibardi *et al.*, 2017). Biogas data are presented to demonstrate that all digesters are functioning effectively.

The theoretical yield of methane was determined by using the methods described in Section 3.3.4. The elemental composition of the food waste was used to determine its chemical formula. Biogas produced from one mole of food waste has the following molar composition:

$$C_{12.77}H_{19.88}O_{8.50}NS_{0.03} + 4.31H_2O \rightarrow 6.36CH_4 + 6.41CO_2 + NH_3 + 0.03H_2S$$

Equation 5.1

Figure 5.4 illustrates the theoretical and experimental yields of methane. The experimental yields are the mean values from the three cycles. The yield of control digester was lower than

the theoretical yield by 38.7%. The theoretical gas yield depends on the assumption that the substrate has ideal composition and characteristics. However, actual substrates used for anaerobic digestion in practice may differ in design, nutrient content, and biodegradability. In reality, methane production is usually lower than theoretically predicted (Angelidaki *et al.*, 2011). There are several reasons for this due to various factors that can limit the efficiency of the process, such as the practical losses during the experiment caused by pouring, side reactions, impurities, the efficiency of the process, variations in substrate quality, and the fact that approximately 10% of organic matter will be consumed for cellular synthesis, which will adversely affect microbial decomposition (Cudjoe *et al.*, 2021). Anaerobic digestion requires specific process conditions, such as temperature and pH, to optimize microbial activity and gas production. Consequently, digestion may be negatively impacted, resulting in lower gas yields if these conditions are not adequately controlled and maintained. A lower actual yield may also be caused by the presence of other compounds that inhibit the reaction. Certain substances present in the substrate can inhibit the activity of anaerobic microorganisms responsible for gas production. In particular, high levels of ammonia, sulphides, and heavy metals may have toxic effects on microbial communities, resulting in reduced gas production. Additionally, the microbial community involved in anaerobic digestion is complex and is susceptible to environmental changes. As a result of external factors, such as substrate changes, pH shifts, or the presence of inhibitory substances, the microbial population may change, resulting in decreased gas production (Angelidaki *et al.*, 2011).

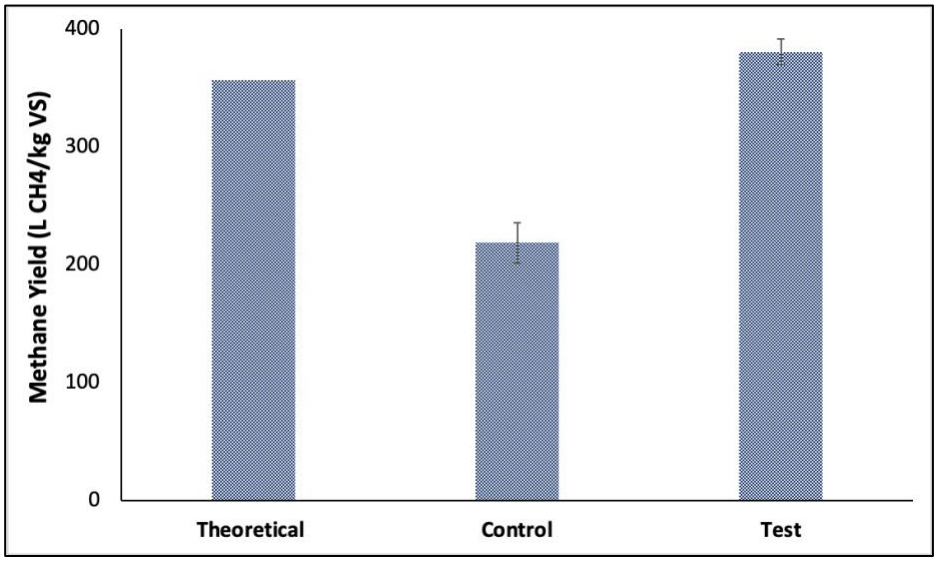

Figure 5.4: Theoretical and experimental yields of methane production.

The methane yield from the test bioreactor with CO_2 sparging is, on the other hand, remarkably higher than the theoretical value. The yield of the test reactor was approximately 107% of the theoretical value. The same observation was made in previous studies on CO_2 microbubbles sparging in anaerobic bioreactors, in which methane production exceeded the theoretical value and control reactor (Al-Mashhadani, 2013; Nugroho, 2021). The sparging system may help in stripping methane in the digestate that is produced during digestion. A difference in concentration between the two phases causes biogas dissolved in the digestate to be transferred to the headspace upon removal from the headspace. However, this significant increase in methane yield is not expected solely from the stripping mechanism. Another possible explanation would be exogenous CO_2 provides additional carbon to the AD, leading to the higher production of methane. According to Equations 5.2 and 5.3, methane is produced by anaerobic digestion through two reactions: the fermentation of acetate (Equation 5.2) and the reaction between carbon dioxide and hydrogen (Equation 5.3).

$$CH_3COOH + H_2O \leftrightarrow CH_4 + CO_2 \qquad \text{Equation 5.2}$$

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \qquad \text{Equation 5.3}$$

Sparging with microbubble CO_2 will likely increase methane production from the second reaction (Equation 5.3) by providing exogenous carbon dioxide. Figure 5.5 shows the daily carbon dioxide volume in the control and test bioreactors for each of the three cycles. For the test bioreactor, the daily volume of CO_2 that was sparged into the reactor had been subtracted. The graphs indicate that CO_2 volume increased in the control bioreactor on the first day, and then declined continuously as methane was produced. With the microbubble CO_2 sparged in the test bioreactor, it can be seen that the volume of CO_2 in the test bioreactor was significantly higher than the volume of CO_2 in the control, even after excluding the sparged volume. Microbubbles of CO_2 sparged in the test reactor may have improved the feedstocks' biodegradability and improved the feedstocks' conversion efficiency into biogas. As the biodegradability of the feedstocks increases, the biogas production and, consequently, CO_2 production in the bioreactors will increase.

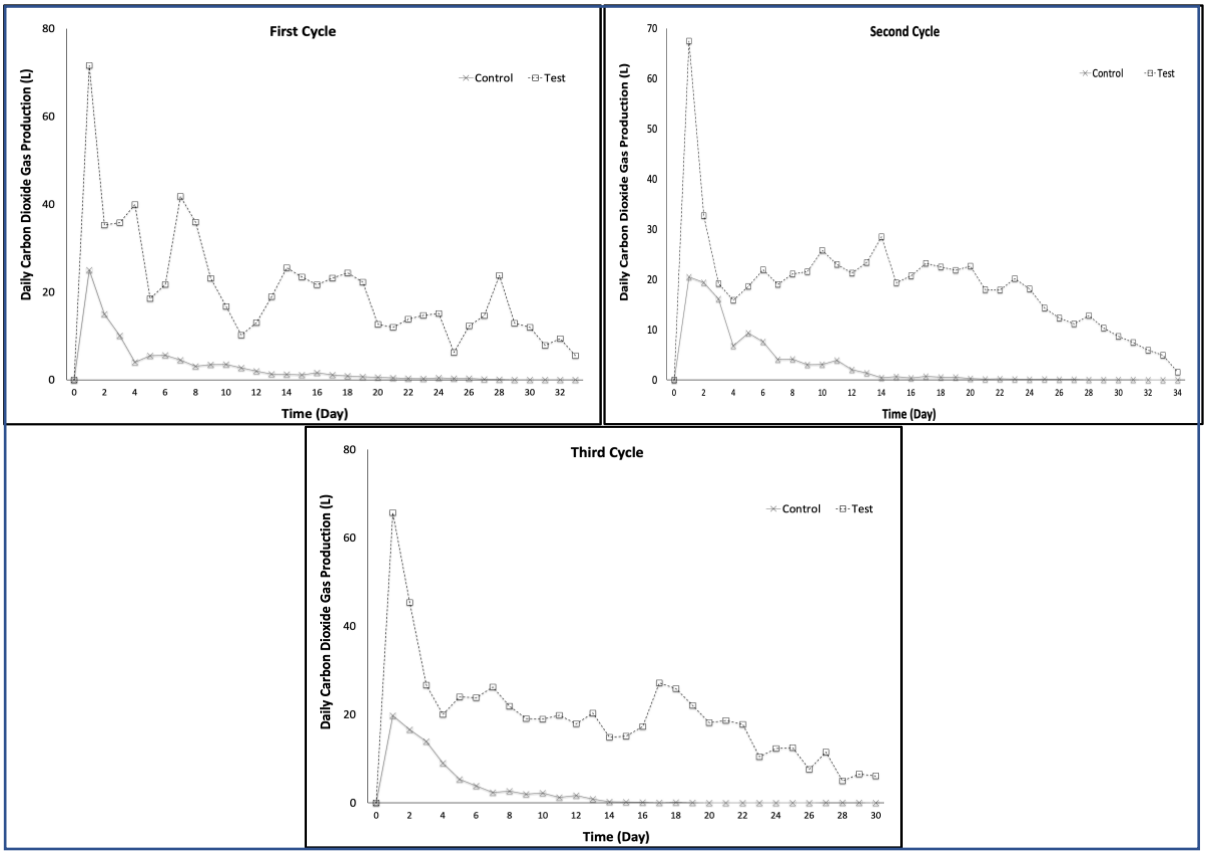

Figure 5.5: Daily volumes of CO_2 in the control and test bioreactors

However, based on Equation 5.3, methane production in this reaction also requires more hydrogen to reduce carbon dioxide. Consequently, the question arises, where did the additional hydrogen gas originate? Microbubble CO_2 sparging may have increased the biodegradability of the feedstock, which may have led to increased hydrogen production during acidogenesis, acetogenesis, or even during the oxidation of acetate. Further research is needed to determine the mechanisms by which CO_2 microbubble sparging produces the observed effects and the mechanisms by which it achieves them.

5.4.2 pH and Total Ammonia Nitrogen in the digesters

There is a significant impact of pH on the AD system as it influences the growth of the microbe population and the accumulation of inhibitory substances such as TAN and volatile fatty acids, VFAs. Studies show mesophilic anaerobic digestion has an optimum pH range between 6.5 - 8.5 for AD (Cioabla *et al.*, 2012; Singh *et al.*, 2020; Xiao *et al.*, 2021). The effect of pH on biogas production from anaerobic digestion of food waste was previously studied. Various pH values

were investigated, and observations indicate that pH 7 was the optimal pH for degradation efficiency and biogas yield (Jayaraj et al., 2014). However, the pH observed for all digesters in this study was between 7.9 – 9 (Figure 5.6).

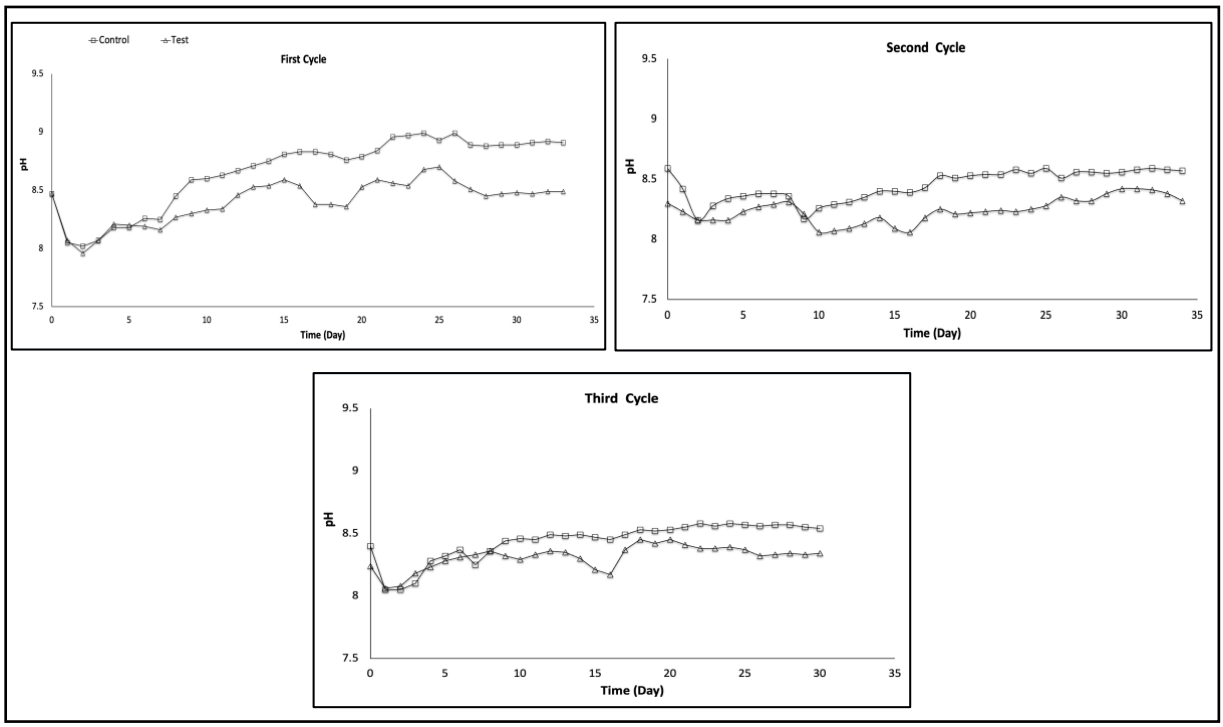

Figure 5.6: pH of the control and test reactors in three cycles of anaerobic digestion

It was also observed that the pH dropped during the first two days of the cycle for all reactors and then started to increase gradually with almost the same trend. The pH drop during the first few days might be due to the rapid acidification phenomena of food waste in AD. Significant pH difference between the control and test reactors can be observed after day 7. The pH of control reactor gradually increased up to 8.55 – 8.99, while the test reactor had a lower pH ranged between 8.01 and 8.70. This could be attributed to an increase in the amount of dissolved carbon dioxide in the test reactors. It is because of the polarity of the carbon dioxide molecule (which has a slight negative charge near carbon and a slight positive charge near carbon), that CO_2 has the ability to dissolve in water (Yang *et al.*, 2022). Injecting CO_2 directly into the sludge, reduces the pH in the system.

Total ammonia nitrogen concentration in each reactor was monitored to investigate whether ammonia removal had occurred during the CO_2 sparging in the AD bioreactors. The TAN concentrations obtained for both reactors are shown in Figure 5.7. The concentration of total ammonia nitrogen in all reactors fluctuated between the range of 3000 – 4000 mg/L. ANOVA and t-test statistical programs (Microsoft Excel 2021) were used to test the statistical significance (P = 0.05) of the experimental data. It was found there is no statistical difference in the TAN concentrations for both control and test reactors. Previously, it was hypothesized that microbubble CO_2 sparging could strip the inhibitor ammonia from the system; hence, the rate of degradation and biogas production increased (Al-Mashhadani, 2013; Nugroho, 2021). However, the observation of daily TAN from this experiment appears otherwise. The decrease of TAN was not observed in the reactors with CO_2 sparging. From this observation, it appears that the CO_2 sparging did not remove ammonia from the digestate.

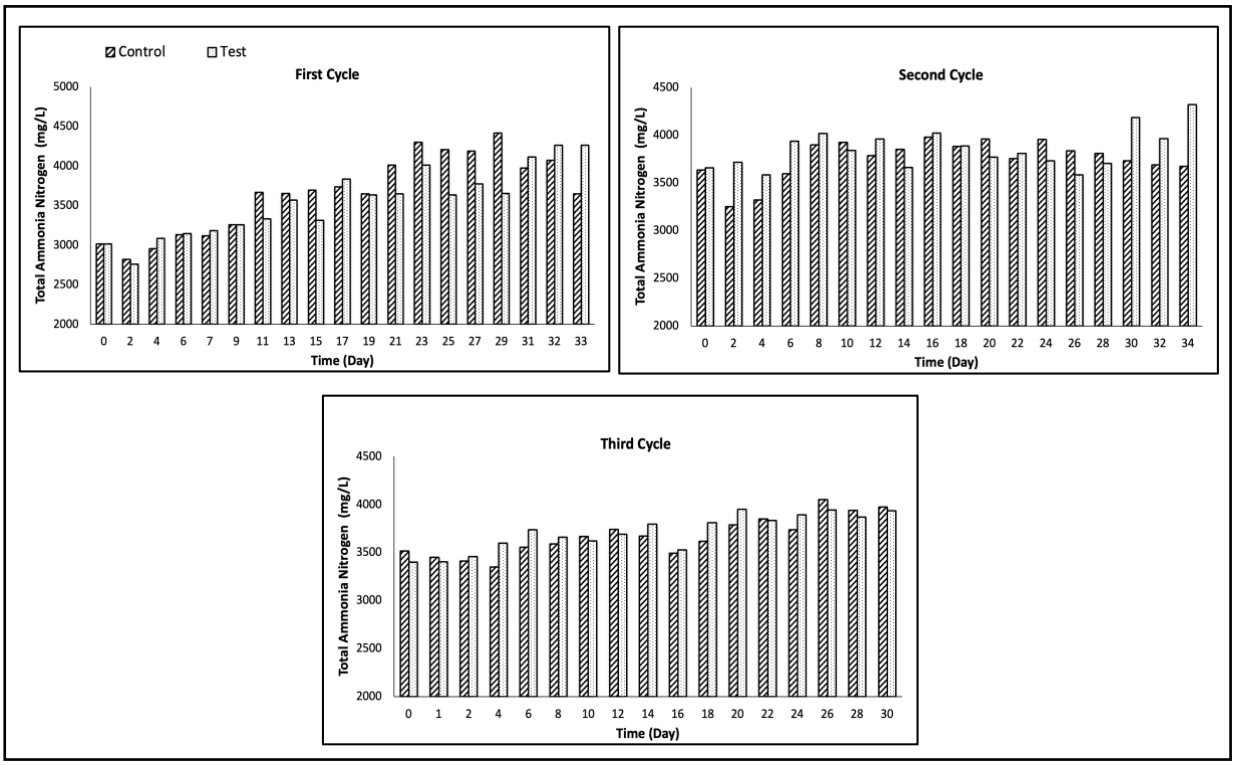

Figure 5.7: Total ammoniacal nitrogen (the sum of ionized NH_4^+ and unionized NH_3)

The pH of the bioreactor plays a crucial role in the composition of free ammonia and ammonium ion. It has been observed that the concentration of free ammonia is correlated with inhibition of total ammonia-N (Hashimoto, 1983). The concentration of the free ammonia

is dependent on pH, as described in Equation 3.4 $\left(\frac{[NH_4^+]}{[NH_3+NH_4^+]} = 1 - \frac{1}{1+10^{pK_a-pH}}\right)$. As mentioned previously (in Figure 5.6), there were substantial differences between the pH of the control and test reactors. A lower pH range was observed in the test reactors. Figure 5.8 illustrates the free ammonia concentration in both reactors for each cycle based on Equation 3.4 and pH values of the respective reactors. As can be seen, the concentration of free ammonia in the test reactor was substantially lower than in the control reactor. The concentration of free ammonia in the test reactor is reduced when the pH is lowered. According to Le Chatelier's principle, at a lower pH (higher H^+ ions), the equilibrium in Equation 3.3 ($NH_4^+ + OH^- \rightleftharpoons NH_3 + H^+$) would shift to the left producing more ammonium ion, resulting in a decrease in the free ammonia in the digestate. According to previous discussions, there was no significant difference between the control and test bioreactors regarding total ammonia nitrogen. Consequently, most of the ammonia nitrogen in the test bioreactor was present as ionic salts, NH_4^+, less readily available for stripping. Therefore, it is unlikely that carbon dioxide sparging will result in the stripping of ammonia from the test bioreactor.

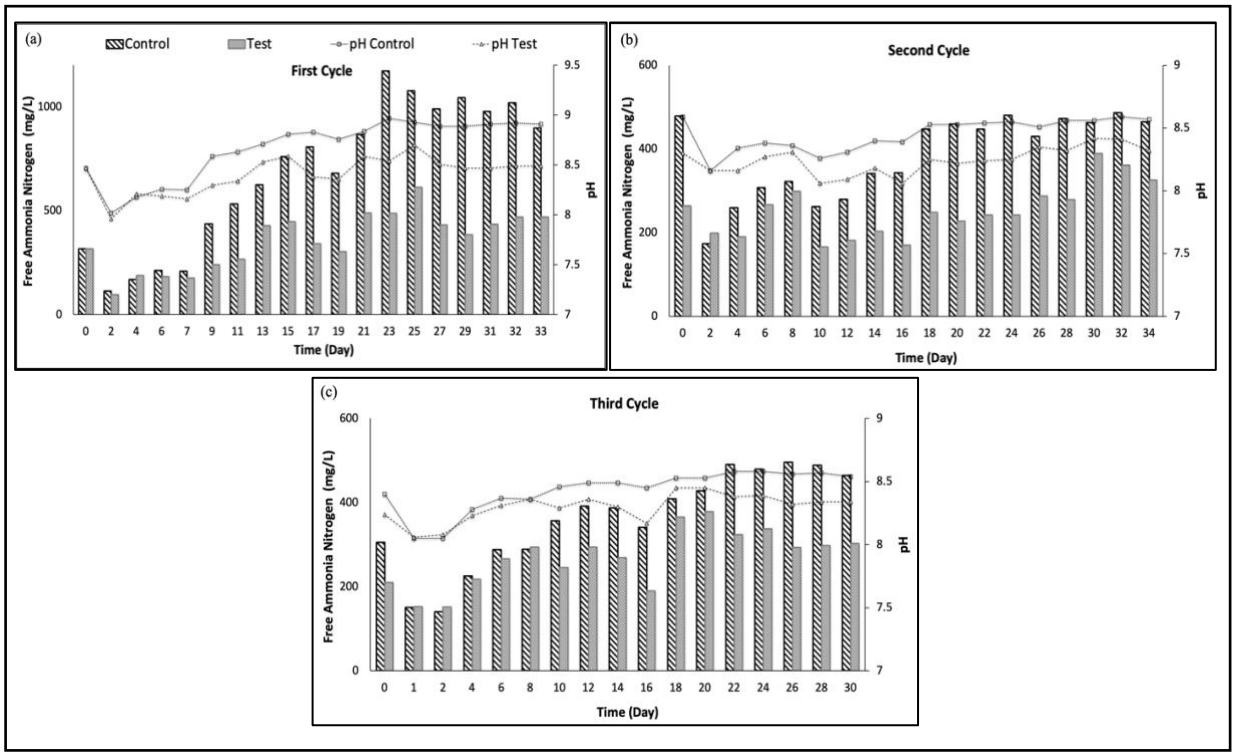

Figure 5.8: Free ammonia levels (unionized NH_3) and pH values for each cycle from both the control and test digesters.

In the control reactor, the pH was generally higher than in the test reactor, which resulted in excessive free ammonia, which may have been the primary cause of inhibition (Angelidaki and Ahring, 1993; Chen *et al.*, 2008). A high concentration of free ammonia in the system can negatively impact the microbial community and the overall performance of the process. (Chen et al., 2008). Free ammonia can penetrate microbial cell membranes and may cause toxicity as it alters the intracellular pH and inhibits certain enzyme reactions (Wittmann et al., 1995). An excessive amount of free ammonia can inhibit methanogenesis, the process responsible for biogas production, resulting in lower methane yields. Furthermore, high free ammonia levels may disrupt the digester's microbial community, decreasing the process's overall stability and efficiency (Capson-Tojo *et al.*, 2020).

There was a decrease in free ammonia fraction with pH in the test bioreactor, which had a pH range lower than the control bioreactor. A decrease in the pH of the bioreactor caused by CO_2 microbubbles resulted in a reduction in free ammonia in the test bioreactor. Hence the effect of the ammonia inhibition in the test reactor is less than in the control reactor, resulting in increased methane production.

In the next section, microbubble stripping of ammonia was carried out using three different gases, including carbon dioxide, nitrogen, and air, to examine the ability of CO_2 to strip ammonia further. This is also to identify the appropriate stripping gas for the final experiment in the current study.

5.4.3 Ammonia removal from microbubbles stripping

The percentage efficiency of total ammonia nitrogen removal, η is defined according to the measured results, as in Equation 5.4 (De la Rubia *et al.*, 2010):

$$\eta = \frac{[NH_3+NH_4^+]_i - [NH_3+NH_4^+]_f}{[NH_3+NH_4^+]_i} \qquad \text{Equation 5.4}$$

where $[NH_3 + NH_4^+]_i$ and $[NH_3 + NH_4^+]_f$ are concentrations of total ammonia nitrogen at the beginning and at any time, t respectively.

This study chose a default flow rate of 1.0 LPM, the same flow rate of CO_2 gas injected in the anaerobic digester. The efficiencies of TAN removal are shown in Figure 5.9a. It is evident that there was no removal of TAN when using carbon dioxide as stripping gas. By using air or nitrogen as stripping gases, a continuous removal rate of ammonia could be achieved, although at a low level. As expected, the ammonia removal at 35 ^{o}C was lower than in other studies with higher temperatures. Despite the low ammonia removal rates, it should be noted that the pH of the digestate was not adjusted, the flow rate was moderate, and the contact time was much shorter than in other studies. Figure 5.9b illustrates the natural logarithm of the relative change in total ammonia concentration over time. Using a linear regression against time, the slope represents the overall volumetric mass transfer. The K_La of the experiment using CO_2 as a stripping gas was very small, indicating that almost no mass transfer occurred. When nitrogen is used as a stripping gas, the TAN and K_La removal efficiency increases slightly compared to when air is used.

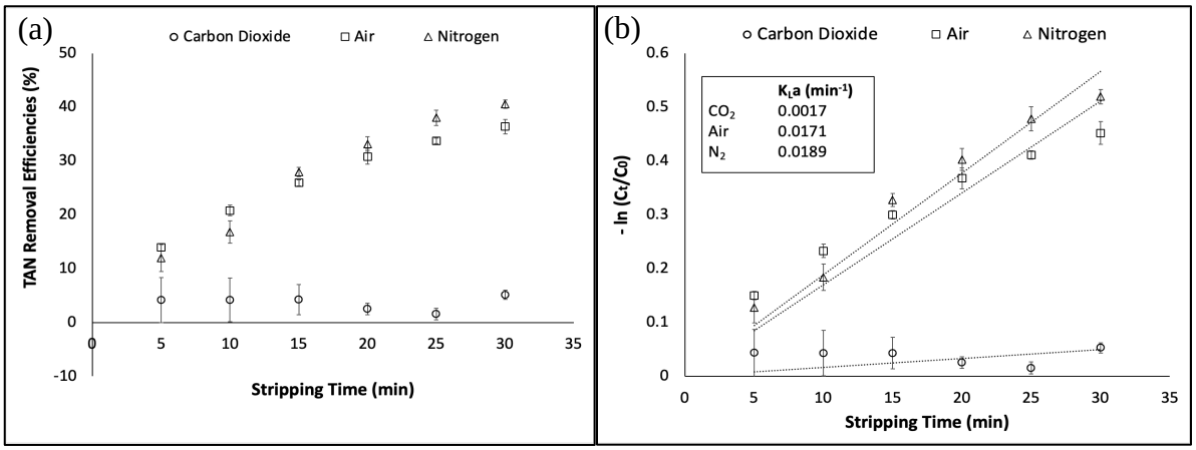

Figure 5.9: The effect of ammonia stripping using three different gases on (a) TAN removal efficiencies (b) logarithm of the ammonia concentration ratio, giving the K_La values

As with the previous anaerobic digestion experiment, a similar observation was made in this stripping experiment, which indicated that the pH of the digestate slightly decreased as carbon dioxide was sparged into the digestate (Figure 5.10). This effect is caused by the dissolution of carbon dioxide in water, which produces carbonic acid (H_2CO_3). The reaction between carbon dioxide and water can be represented as follows:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO^{3-} \qquad \text{Equation 5.5}$$

Carbonic acid formation increases the concentration of hydrogen ions in the solution, resulting in an acidification of the solution and a decrease in pH (Mitchell *et al.*, 2010).

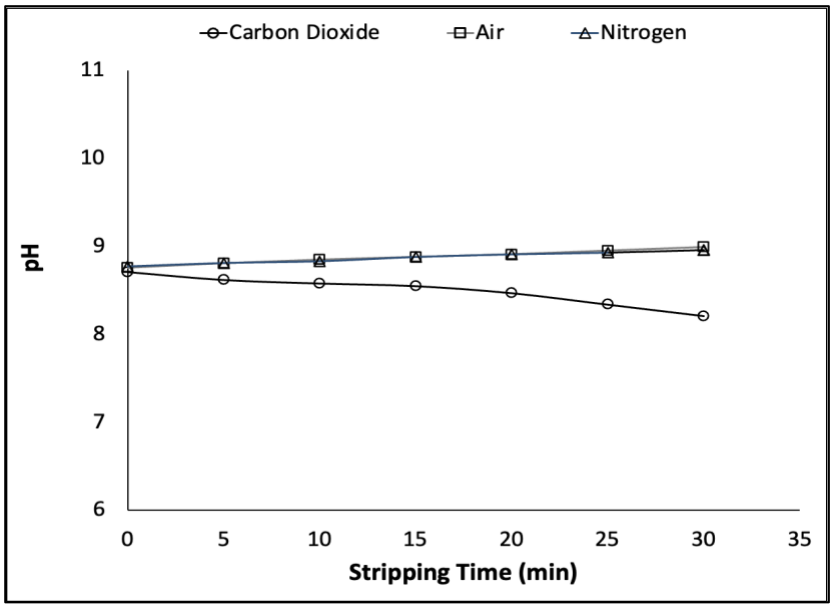

Figure 5.10: Evolutions of pH during ammonia stripping using different gases

The mechanism of ammonia stripping by bubbles is illustrated in Figure 5.11. Initially, ionized ammonium and dissolved free ammonia reached dynamic equilibrium in the bioreactor. As bubbles sparge into the bioreactor, the flow of bubbles removes a portion of the dissolved free ammonia and disrupts the dynamic equilibrium between ionized and free ammonia. A portion of the ionized ammonium is converted to dissolved ammonia in order to reach a new dynamic equilibrium. Consequently, the concentration of total ammonia nitrogen, TAN is reduced (Li *et al.*, 2019).

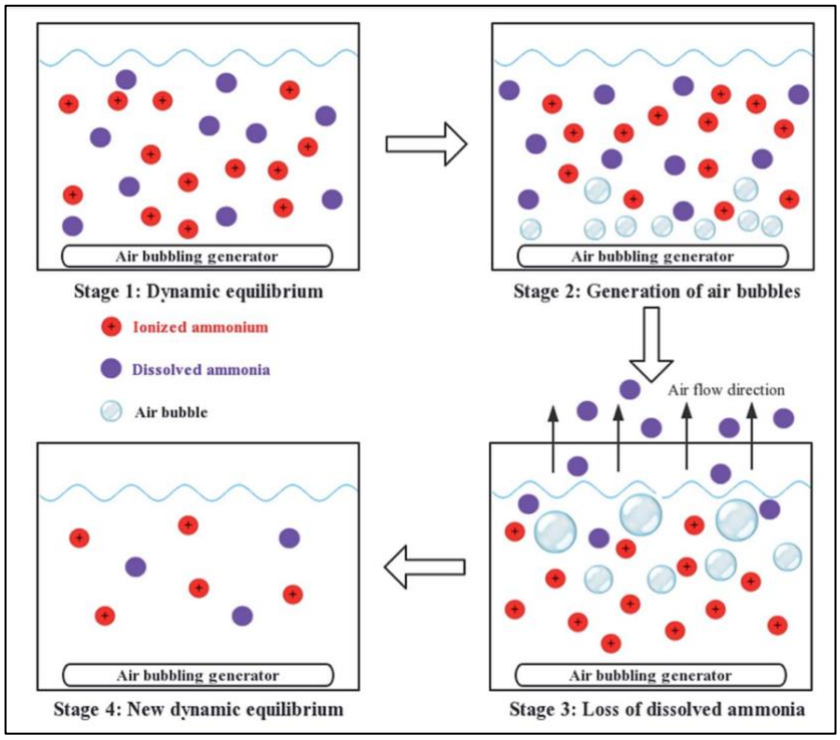

Figure 5.11: Mechanisms for stripping ammonia with the aid of air bubbles (Li *et al.*, 2019)

The carbon dioxide microbubbles, however, create a region around themselves with a high concentration of CO_2 and a low pH value. This region has a low pH, acts as a barrier, and prevents free ammonia from diffusing and evaporating into the bubble. Ammonia molecules remain trapped within the CO_2-rich region of the liquid as microbubbles of CO_2 rise through it. This prevents ammonia molecules from escaping and being effectively removed from the anaerobic sludge. Figure 5.12 shows that the free ammonia concentration slightly decreased when CO_2 was used as a stripping agent, but the ammonium ion concentration increased or remained constant. As a result, there was no stripping of ammonia when CO_2 was sparged into the bioreactor.

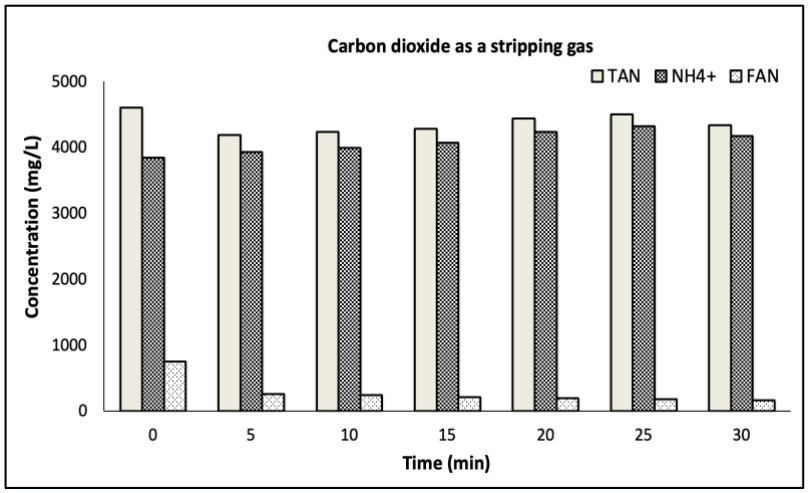

Figure 5.12: Concentrations of TAN, ionized ammonium ion and free ammonia concentrations during ammonia stripping using CO_2 microbubbles

In contrast, the pH increased slightly when nitrogen gas and air were used in the experiments (Figure 5.10). In a higher pH environment, non-volatile ammonium ions were converted into volatile ammonia molecules, which were then stripped from the liquid phase into the gas phase when gas was injected into the digestate. It can be observed that the ammonium ions decreased when using either N_2 or air as a stripping gas (Figure 5.13).

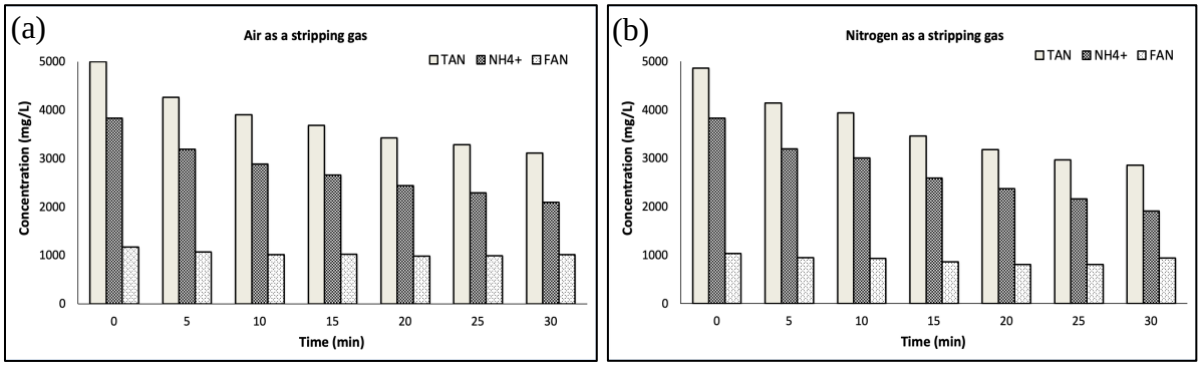

Figure 5.13: Changes of TAN, ionized ammonium ion and free ammonia concentrations during ammonia stripping using (a) air and (b) nitrogen

5.5 Conclusions

It has been demonstrated that methane production increases after sparging with microbubble CO_2 and is thought that this occurs as a result of the CO_2 removing the ammonia inhibitors. In this chapter, an analysis of this has been presented in an attempt to investigate whether *in situ* ammonia stripping occurs during the CO_2 microbubble sparging into the AD reactor and to identify the most suitable gas medium for the batch ammonia stripping process. Regression of the experimental data to the Gompertz model proves that the carbon dioxide injection significantly enhanced the methane production rate. Throughout each cycle, there was no difference in the total concentration of ammonia-nitrogen in both the control and test digesters. This suggests that carbon dioxide sparging does not lead to the removal of total ammonia nitrogen from the digestate, as there was no significant difference in the concentration of total ammonia nitrogen between the test and control bioreactors. It was concluded that carbon dioxide sparging is unlikely to induce the stripping of total ammonia nitrogen from the digestate as there was no significant difference in TAN concentration between the test and control bioreactors. Thus, the increase in methane production and possibly the improvement in substrate utilization in the test bioreactor is not the result of *in situ* stripping of inhibitor ammonia by microbubbles of CO_2. However, it was observed that the test bioreactor had a lower pH compared to the control bioreactor. As carbon dioxide dissolves in water, carbonic acid (H_2CO_3) is produced, and hydrogen ions increase in concentration, causing acidification and pH decrease. At lower pH, the excess of H^+ ions drives the equilibrium ($\mathrm{NH_4^+ + OH^- \rightleftharpoons NH_3 + H^+}$) toward the formation of the ammonium ion (NH_4^+), leading to a decrease in concentration free ammonia (NH_3). The seeding of microbubbles of CO_2 resulted in a decrease in the amount of free ammonia in the system, which decreased inhibition in the test digesters. It is believed that free ammonia is the most potent AD inhibitor compared to ammonium ions. The reduction in free ammonia nitrogen (FAN) caused by the seeding of microbubble CO_2 may have contributed to the increase in methane yield by reducing ammonia inhibition in the test bioreactor.

Additionally, microbubble stripping of ammonia was carried out using three different gases. This is to investigate further the ability of CO_2 to strip ammonia from the digestate and to

investigate the suitable stripping gas for *in situ* ammonia stripping from the anaerobic bioreactors. The amount of ammonia removed during the stripping process was negligible when CO_2 was used as the medium gas. This further indicates that carbon dioxide is unlikely to strip ammonia from the digestate. Using dissolved gases in an aqueous solution that does not dissociate or ionize would be more suitable for removing ammonia. The use of noble gases would be sufficient, but they are expensive. On the other hand, methane, nitrogen, and hydrogen costs are relatively low and relatively inert. Hence, nitrogen was tested in this study, and it was observed that there was a slightly higher ammonia removal rate with nitrogen than with air as the stripping gas. Hence, nitrogen has been selected as the medium gas for the stripping of the ammonia in the next chapter. Additionally, this decision is based on microbial communities being negatively affected by air, thus potentially deactivating methanogens (Pedizzi *et al.*, 2017).

Chapter 6 : Anaerobic Digestion of Food Waste Sparged with CO_2 Microbubbles coupled with Simultaneous Batch Microbubbles Stripping

6.1 Abstract

A significant increase in methane yield has been observed following the direct injection of carbon dioxide into the anaerobic digesters. Food waste with low C/N values exhibits high concentrations of ammonia which inhibits anaerobic digestion. The present study involved the anaerobic digestion of food waste with low C/N values seeded with microbubbles CO_2, which was combined with batch microbubble stripping using a DZ Lab-Scale rig to strip the ammonia from the digestate. Nitrogen gas was used as a stripping gas. There was no pH adjustment made to the digestate prior to stripping. A 51.4% reduction in TAN was observed in the test digester in comparison to the control digester. Moreover, the average methane yield in the test digester increased by 45.9%. This indicates that batch microbubble stripping engendered by DZ fluidic oscillators could overcome ammonia inhibition on AD of food waste with a low C/N value.

6.2 Introduction

In the process of anaerobic digestion of organic nitrogen, ammonia is produced. It is beneficial to have ammonia in an anaerobic digester since it acts as a buffer. At higher concentrations, however, it can hinder the process by inhibiting methanogenic activities and causing VFA accumulation, which eventually leads to the failure of the digester (Nielsen and Angelidaki, 2008). Generally, TAN concentrations greater than 3000 mgL^{-1} can be toxic to methanogens, inhibit anaerobic digestion and therefore lower the yield of methane from a reactor (Gallert and Winter, 1997; Appels *et al.*, 2008). It is crucial to control the ammonia concentration in the AD to prevent ammonia build-up, thereby eliminating the accumulation of VFA. There are no degradation pathways for ammonia in anaerobic systems, so it tends to accumulate in this system (Burton and Watson, 1998; Berge et al., 2005).

Selecting the suitable stripping medium is vital, as it affects both the overall removal efficiency and the operational cost. Previously, microbubbles stripping of ammonia using three different

stripping gases in Chapter 5 observed that air and nitrogen gas were the most effective ways to remove ammonia. Air was the least expensive method, but the use of air as a stripping gas inhibits the activity of fermentative and methanogenic microorganisms, resulting in a reduction in methane production (Di Capua et al., 2021). Therefore, nitrogen gas was selected for the batch microbubble stripping in this chapter.

To date, microbubble technology has not yet been applied in ammonia stripping from anaerobic digesters utilizing nitrogen as the stripping gas. This work was primarily focused on evaluating the technological feasibility of utilizing batch microbubble ammonia stripping from anaerobic digester, which was sparged with CO_2 microbubbles. For this purpose, a number of sub-objectives were identified, including:

- An experiment is being conducted using two bioreactors sparged with microbubble CO_2. While the first bioreactor is the control bioreactor, the second is the test bioreactor coupled with batch stripping. The digester performance was examined by treating 10% of the test reactor volume five times per week and there was no pH adjustment made to the working liquid.
- To assess the effect of batch stripping by comparing the daily TAN content between the control and test bioreactors.
- Comparing the production and digestion of methane between the control and test bioreactors

Following are some of the benefits of stripping ammonia from the anaerobic digester with the application of microbubbles engendered by fluidic oscillator:

- It is possible to overcome ammonia inhibition without incurring significant costs. It is primarily due to the simplicity of microbubbles that are engendered by fluidic oscillators.
- Chemical additions have a detrimental effect on microbial activity, so no chemicals have been used to adjust pH, so the feedstock remains unchanged, thereby reducing operational cost of running an anaerobic digestion.

6.3 Materials and Methods

6.3.1 Characterization of seeding sludge, food waste and samples

A detailed characterization of the leachate was conducted, including the determination of pH, COD, total ammonia nitrogen (TAN), total solids (TS), and total volatile solids (TVS). These were determined based on the standard procedures (APHA, 2017). A pH meter and temperature probe were used to determine the pH and temperature of the digestate. Samples were analysed using the methods described in Chapter 3.

The characteristics of the seeding sludge and food waste are represented in Table 6.1 and Table 6.2, respectively. The percentage of total solids of food waste was also in the optimum concentration for anaerobic digestion with a range of 20 -50% (Kothari et al., 2014).

Table 6.1: The characteristics of the seeding sludge

Parameters	Unit	Value
pH		8.695 ± 0.05
Total Solid	g/L	10.43 ± 1.07
TDS	g/L	7.064 ± 0.61
TSS	g/L	3.348 ± 0.22
TVS	g/L	3.710 ± 0.95
TVFA	g/L	12.70 ± 1.05
TCOD	g/L	3.343 ± 0.15
sCOD	g/L	2.273 ± 0.24
DOC	mg/L	724.5 ± 11.2
Ammonium	mg/L	3995 ± 282

Table 6.2: Feedstock proximate analysis
[a] based on 100 grams of non-dried sample. [b]calculated from dry weight

Parameters	Unit	Value
Carbohydrate[a]	g	25.65
Fibre[a]	g	4.84
Protein[a]	g	10.73
Fat[a]	g	1.36
Total Solid (TS)	%	25.398
Volatile Solid (VS)	%	24.189
VS/TS (f_{vs})		0.952
C[b]	%	44.59
H[b]	%	7.11
N[b]	%	5.21
S[b]	%	0.26
O[b]	%	42.83
C/N		8.559

6.3.2 Experimental setup and procedure of runs for anaerobic digestion

The setup of the anaerobic digestion for control and test bioreactors is shown in Figure 6.1. The control bioreactor was used for establishing the performance baselines of digestion at high concentrations of ammonia without batch stripping. Anaerobic digestion was carried out in batch mode using 30 L bioreactors with a working volume of 20 L. Each bioreactor was fed with 2 kg of food waste and inoculated with 20L seeding sludge, taken from the previous anaerobic digestion of food waste. The headspace was flushed with nitrogen gas to remove air from the system and introduce an anaerobic condition. The lid of the bioreactor was fitted with ports for liquid sampling (outlet and inlet for test digester), gas inlet, and gas outlet. These bioreactors were placed in an incubator, in which the air-conditioner was used to maintain the mesophilic operating temperature (35 ± 1 ^{o}C). In addition to this, a 50 W submersible heater (HT-6050 Uniclife) is also attached to the wall inside of each reactor. An automatic temperature controller (InkBird, ITC-308) was connected to each heater to avoid over-heating.

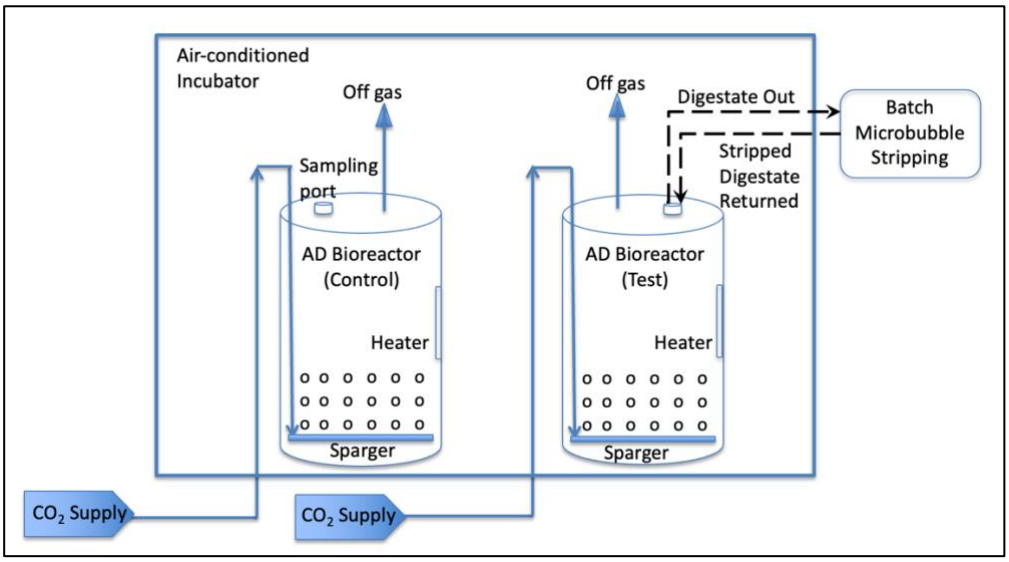

Figure 6.1: Experimental set-up for anaerobic digestions

Each bioreactor was equipped with three ceramic spargers (Point Four MBD 75, Sterner). The average size of the bubbles generated by these diffusers were in between 100 – 500 μm. Carbon dioxide was sparged into each bioreactor for 10 minutes daily and at a flow rate of 1 LPM.

2 L of digestate was removed from the test bioreactor five days in a week. This was stripped in a batch microbubble stripping unit for ammonia removal using nitrogen gas (details in Section 6.3.3). The stripped digestate was then immediately returned to the bioreactor.

Biogas (off gas) from the digesters was collected in a gas-impermeable bag. The volume and composition of the biogas produced were monitored daily. Liquid samples were collected every two days from each reactor for the analysis of TAN. The pH and temperature of the working liquid were monitored daily. Total solids and volatile solids were analysed at the start and end of the experiment. The experiment was running until no significant amount of biogas was produced. The experiment was initially conducted in two continuous cycles to ensure reproducibility. However, the production of methane in the control reactor in the second cycle declined after a few days (Appendix B). The primary cause of this is ammonia inhibition within the control reactor, as the ammonia concentration was extremely high at the end of the first cycle. Therefore, the experiment was repeated using sludge of almost the same characteristics as the first cycle.

6.3.3 Experimental setup and procedure of runs for microbubble stripping

Batch microbubble-stripping of ammonia from the digestate which was performed in Chapter 4 is coupled to the test bioreactor as a side stripping process. Figure 6.2 shows the experimental set-up for this batch stripping. This batch stripping was conducted at a temperature of 70 ^{o}C. A hot water bath was used to maintain a temperature of 70 ± 2 ^{o}C for the stainless-steel rig. Through the fluidic oscillator, nitrogen gas from the cylinder (supply) oscillated solely because of aerodynamic principles (i.e., Coanda Effect as discussed in Section 2.6.1). Nitrogen gas was introduced into the rig through a stainless-steel sparger and its flow rate was controlled by two valves on the fluidic oscillator. Temperatures of the digestate and the system were monitored using K-type thermocouples.

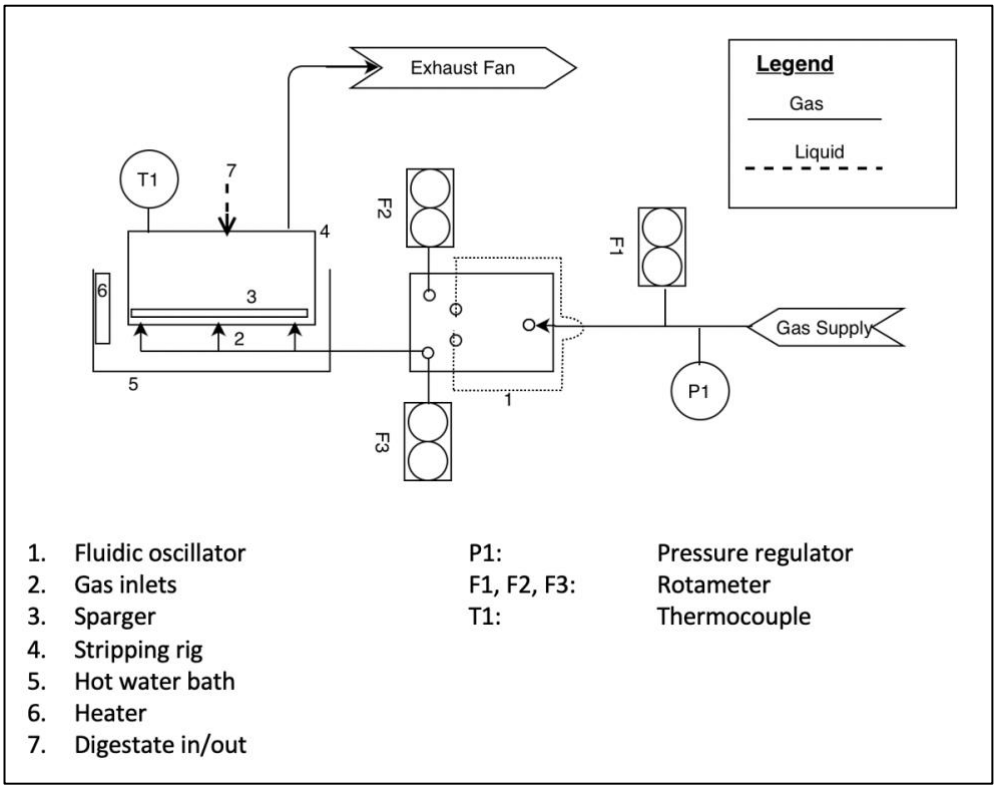

Figure 6.2: Experimental set-up for batch stripping

Batch stripping was performed five days in a week. Each time, 10% of the anaerobic digester's working volume was stripped, and, in total, 50% of the working volume was stripped each week. Digestate taken from the anaerobic digester was placed in another water bath to maintain temperature around 30 ^{o}C. The digestate of 25 mL was fed into the rig in each run, giving a liquid level of approximately 3.1 mm. Recent study concluded that the optimum performance can be obtained by using a liquid level as low as 5 mm (Desai *et al.*, 2021). The approximate level of the liquid was calculated using the following formula:

$$Liquid\ Level\ in\ the\ rig = \frac{Volume\ of\ liquid}{Base\ area\ of\ the\ rig} \qquad \text{Equation 6.1}$$

Stripping gas flow rate into the rig in this work was set at 1.0 LPM. Stripping gas was liberated and stripped free ammonia from the digestate. A total of 2 L digestate taken from the anaerobic digester was stripped in this rig. Each run of stripping 25 ml digestate lasted two minutes, and the stripped digestate was removed from the rig at the end of the run. It was ensured that all digestate was collected after each run of stripping to achieve a minimal volume loss. The initial and final concentrations of TAN, temperature, and pH were determined for the

entire digestate of 2 litres. The stripped digestate was then immediately returned to the anaerobic digester. A volume loss of less than 0.1 L was observed from the two-litre digestate, which was compensated for by the addition of water. Methane production in the bioreactor and TAN reduction were monitored to evaluate the efficiency of ammonia removal and the effectiveness of batch stripping coupled with anaerobic digester.

6.4 Results and Discussion

6.4.1 Methane Production and Yield

Figures 6.3 and 6.4 depict the cumulative methane production from the control and test digesters from the first and second runs, respectively. It took 54 days to complete the first run and 52 days to complete the second run. All the gas produced is considered the product from the targeted substrate only since degassing of the inoculum was carried out prior to the experiment. Despite high initial TAN concentrations, both control and test reactors performed well. There is no doubt that the test digesters produced the higher levels of methane. It was observed that the amount of methane produced from the test digester exceeded the amount of the methane produced from the control digester by 48.5 and 43.3% from the first and second runs, respectively. Further evaluation of the results was carried out using ANOVA, which indicated that production of methane from the test digesters was statistically higher than that from the control digesters ($P < 0.05$).

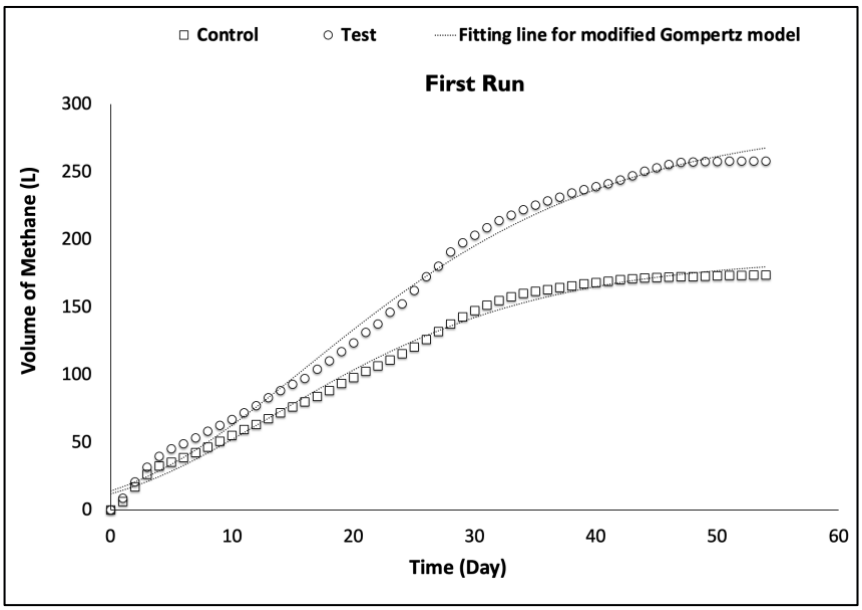

Figure 6.3: Cumulative methane production from the first run of anaerobic digestion

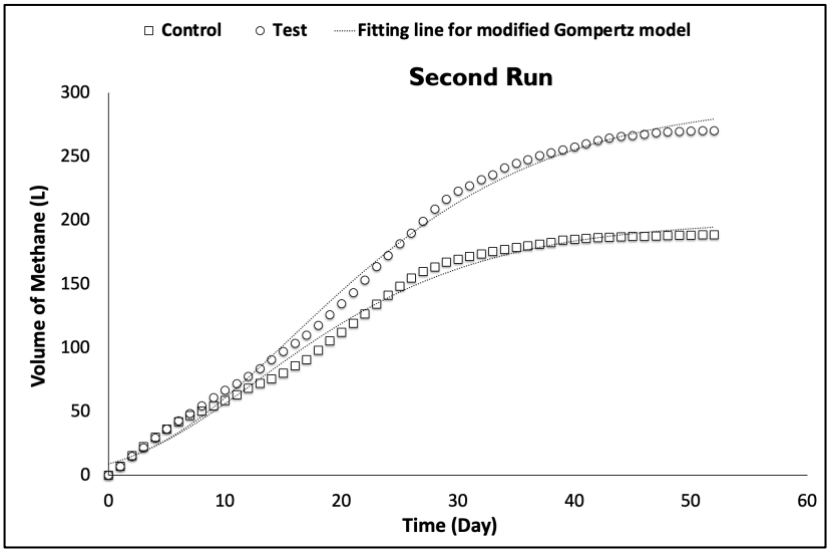

Figure 6.4: Cumulative methane production from the second run of anaerobic digestion

A kinetic model modified Gompertz equation was used to compare this experimental data further. Potential of methane production, G_0, the maximum rate of methane production R_{max}, and lag phase time, ʎ calculated using this model are shown in Table 6.3.

Table 6.3: Fitting results of modified Gompertz model for cumulative methane production curves

Run	Digester	Modified Gompertz model			
		G_0 (L)	R_{max} (L/day)	ʎ (days)	R^2
First	Control	187.9 ± 2.5	5.3 ± 0.1	0.2 ± 0.4	0.992
	Test	289.2 ± 4.5	7.2 ± 0.2	1.5 ± 0.4	0.994
Second	Control	200.5 ± 2.5	6.6 ± 0.2	1.5 ± 0.4	0.991
	Test	295.4 ± 3.6	8.6 ± 0.2	3.2 ± 0.3	0.995

Based on the observation from Figures 6.3 and 6.4, along with Table 6.3, the experimental data fitted well with this model predictions as indicated by the correlation coefficient. The correlation coefficients (R^2) for both control and test digesters in each run provide an excellent fit between experimental data and those predicted, with a convinced correlation coefficient R^2 ranging from 0.991 – 0.995. Moreover, the maximum production potential (G_0) was also consistent with the experimental results.

In terms of maximum specific methane production rate, R_{max}, the improvement made by utilizing microbubble batch stripping is about 34.0 % on average. Higher R_{max} values for test digesters indicate that a more significant portion of the waste is readily converted to methane in the test digester in comparison to the control digester. It is also clear from the data shown that the inhibition of methanogenesis is considerably reduced in the test digester due to the reduction of ammonia caused by batch stripping.

The lag phase for the test digesters was longer than that for the control digesters. The lag phase is an inherent characteristic of microbial kinetics. A delayed response of the microbial population to environmental changes is generally considered to be the cause of this phenomenon (Mao *et al.*, 2017). The removal of 2 litres of digestate daily may influence the hydrolysis and acidification of organic compounds, thereby slowing the buffer capacity of the AD system and increasing the length of lag periods. Despite this, the test digesters still yielded significantly higher specific gas production and the degradation efficiency was improved by the reduction of ammonia in the digester.

Figure 6.5 illustrates the daily methane production between the control and test digesters during the two runs of the experiment. Peaks of methane production can be observed on day 1 for both control and test digesters. The initial daily methane production for both control and test reactors were almost equal, which shows that the batch stripping is not affecting the system yet. The readily biodegradable organic matter in the substrate may have contributed to the initial increase in methane production (Neue, 1993). Following this, methane production declined due to the exhaustion of most of the available substrates. Generally, both experimental runs showed similar trends in daily methane production for the control and test reactors. A major difference between the test reactors and the control digester relates to the peak values, particularly between day 17 and day 28. The peaks in the test reactors were greater than those in the control digester. Additionally, the production of methane in the test reactor was elevated for a longer period than that in the control reactor. A reduction in TAN may have contributed to an increase in methanogenesis in the test digester, resulting in a higher methane production rate. The methane production of both digesters has gradually decreased after day 28, but the production of methane of the test digester remains higher than that of the control digester.

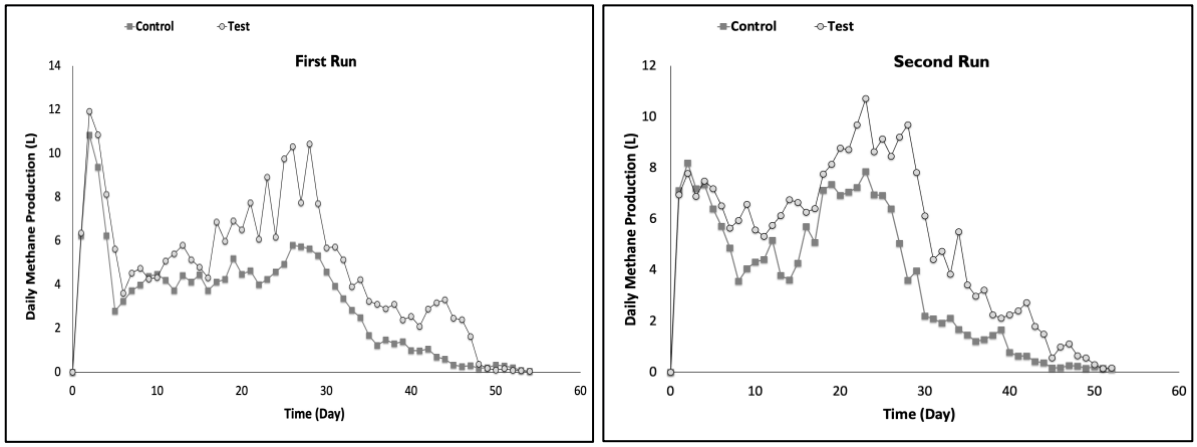

Figure 6.5: Daily methane production from control and test digesters with batch ammonia stripping

The theoretical biochemical methane potential (TBMP) is calculated using the equation mentioned in Section 3.3.4. The elemental composition of the food waste was used to determine its chemical formula. Biogas produced from one mole of food waste in this work has the following molar composition:

$$C_{9.98}H_{18.96}O_{8.50}NS_{0.02} + 2.4H_2O \rightarrow 5.18CH_4 + 4.80CO_2 + NH_3 + 0.02H_2S$$

Equation 6.2

Table 6.4: Theoretical and experimental yields of the methane production

	Theoretical	Experimental	
		Control	Test
Methane Yield (L CH4/kg VS)	431.61	448.41	652.66
Ratio (Theoretical : Experimental)		1 : 1.04	1 : 1.51

The theoretical and experimental yields of methane are presented in Table 6.4. The experimental yields are the mean values from the two runs. The yields of the control and test digesters exceeded the theoretical yields by 4% and 51.2%, respectively. In practice, the amount of methane actually produced is usually less than the theoretical value (Angelidaki et al., 2011). This observation can be seen in the previous chapter's control reactor without the sparging of CO_2 microbubbles. There are a number of reasons for this, such as the practical

losses during the experiment caused by pouring, side reactions, impurities, and the fact that approximately 10% of organic matter will be consumed for cellular synthesis, which will adversely affect microbial decomposition (Cudjoe et al., 2021). The experimental methane yield from both control and test digesters in this chapter are, on the other hand, both higher than the theoretical value. The previous chapter discussed the possibility that exogenous carbon dioxide could provide additional carbon to the AD, increasing methane production. Figure 6.6 illustrates the daily CO_2 volumes in both the control and test bioreactors, both of which were sparged with microbubble CO_2, with the test bioreactor incorporating a batch microbubble stripping. The daily volume of CO_2 that was sparged into the reactor had been subtracted. It was observed that the daily CO_2 in both bioreactors has the same trendline with the test bioreactor in the previous chapter.

In comparison to the control bioreactor, it can be observed that the CO_2 levels in the test bioreactor are relatively lower. The combination of an anaerobic bioreactor and a batch microbubble stripping may have enhanced the conversion of carbon dioxide to methane in the test bioreactor since the amount of free ammonia was reduced. This was demonstrated through the combination of batch ammonia stripping with a test bioreactor, in which methane yields were significantly higher in the test, and daily CO_2 levels were relatively lower.

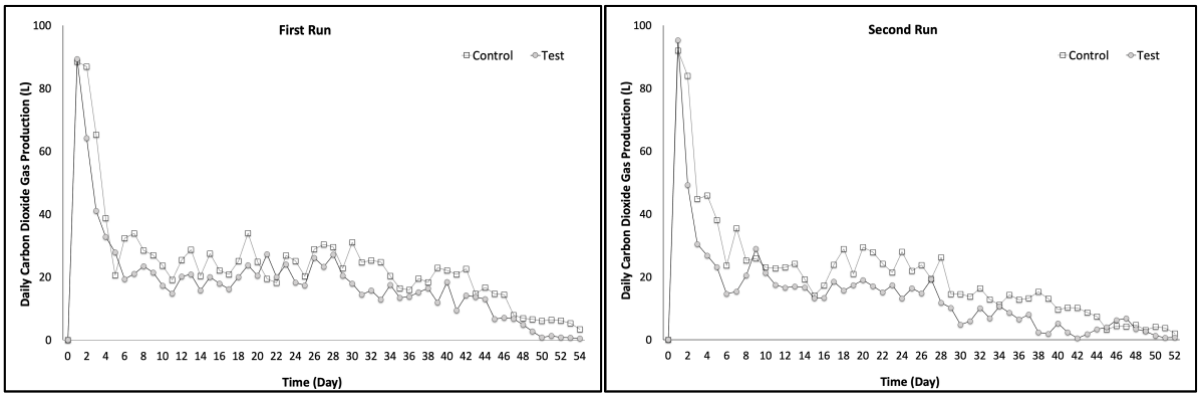

Figure 6.6: Daily volumes of CO_2 in the control and test bioreactors

Based on these results, it was demonstrated that the combination of batch ammonia stripping with anaerobic digestion and the use of an energy-efficient fluidic oscillator to create microbubbles successfully increased methane production.

6.4.2 pH and TAN in bioreactors

In the production of biogas, pH plays a significant role in evaluating the performance of anaerobic microorganisms. As can be seen in Figure 6.7, both control and test reactor pH had similar trends. Batch stripping had no significant effect on the pH of the test reactor, despite a slight difference in pH between control and test reactors. At the 5% level, the ANOVA test did not reveal any significant differences between the pH values of the two digesters ($P > 0.05$).

As previously mentioned, the initial decrease in pH was caused by feedstock hydrolysis, which led to the release of acidic products (VFAs). In both reactors, the pH gradually increased as the microbes consumed the VFAs and remained relatively constant until the digestion was complete. Despite higher TAN concentrations in both the control and test digesters, the pH of both was generally low. It is typical for pH levels to increase throughout anaerobic digestion. However, in this case, the control and test digesters consistently maintained pH levels within a narrow range between 8.01 and 8.24. The reason for this is primarily due to the acidic CO_2 being directly injected into both control and test digesters. Nevertheless, the pH is within the range of pH that the AD process can tolerate, which is between 6.5 - 8.5 (Cioabla *et al.*, 2012; Singh *et al.*, 2020; Xiao *et al.*, 2021).

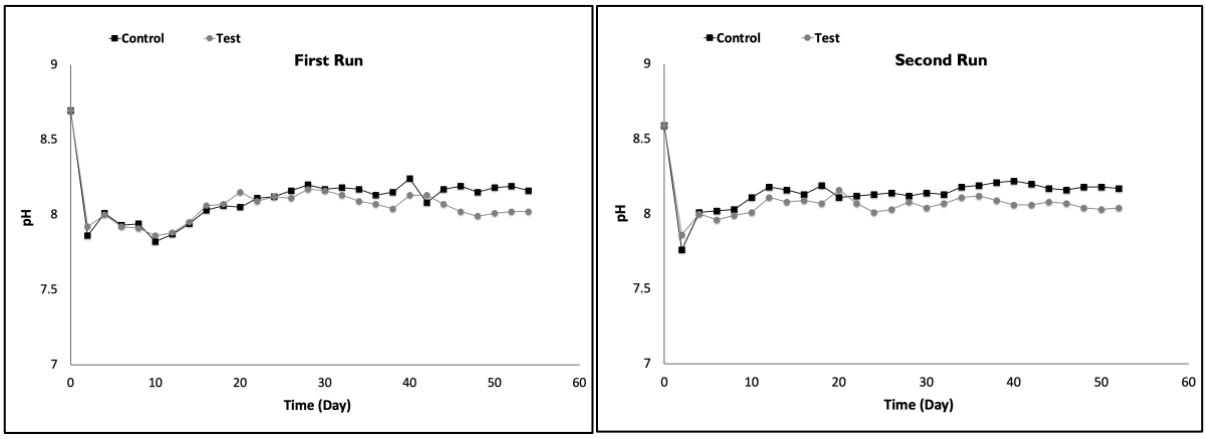

Figure 6.7: pH of the control and test reactors during the experimental periods

Figure 6.8 shows the changes in TAN from two experimental runs in both control and test reactors. The initial increase in TAN in all digesters was primarily due to an initial drop in pH caused by the accumulation of acidic products (VFAs), which decreased the efficiency of ammonia removal (Abouelenien *et al.*, 2010). According to literature studies, there have

previously been several critical concentration ranges for ammonia inhibition due to differences in operating conditions or substrates. Most previous studies observed an inhibition of methane production above 3000 mg/L due to the growth inhibition of methanogenic archaea (Yenigün and Demirel, 2013). While the initial TAN concentration in the present work reached 5000 mg/L for both control and test digesters, no inhibition of methane production was observed in the initial stages. This could be attributed to the injection of the microbubble CO_2. Previous studies have demonstrated that acetoclastic methanogenesis is the main route for degradation of acetate at TAN concentrations of up to 3300 mg/L in mesophilic digestion. In addition, it was observed that when the ammonium-nitrogen concentration exceeded 3000 mg/L, the mechanism switched to syntrophic acetate oxidation, SAO (Schnürer and Nordberg, 2008). This pathway involves acetoclastic methanogens converting acetate to hydrogen and carbon dioxide (acetate oxidation) which is followed by hydrogen utilizing methanogens reducing the carbon dioxide and hydrogen into methane. Microbubble carbon dioxide injected in the test digesters may contribute to an increase in methane production through the SAO pathway in the present study. Thus, despite a high initial TAN, the inhibition of methane production was reduced. Consequently, further work is required including labelling experiments and an analysis by scintillation counting to identify the degradation of acetate (2-^{14}C), formation of methane ($^{14}CH_4$) and carbon dioxide ($^{14}CO_2$) (Schnürer *et al.*, 1994). The degree of acetate oxidation and therefore the main mechanism for methane formation can be confirmed in terms of $^{14}CO_2/^{14}CH_4$.

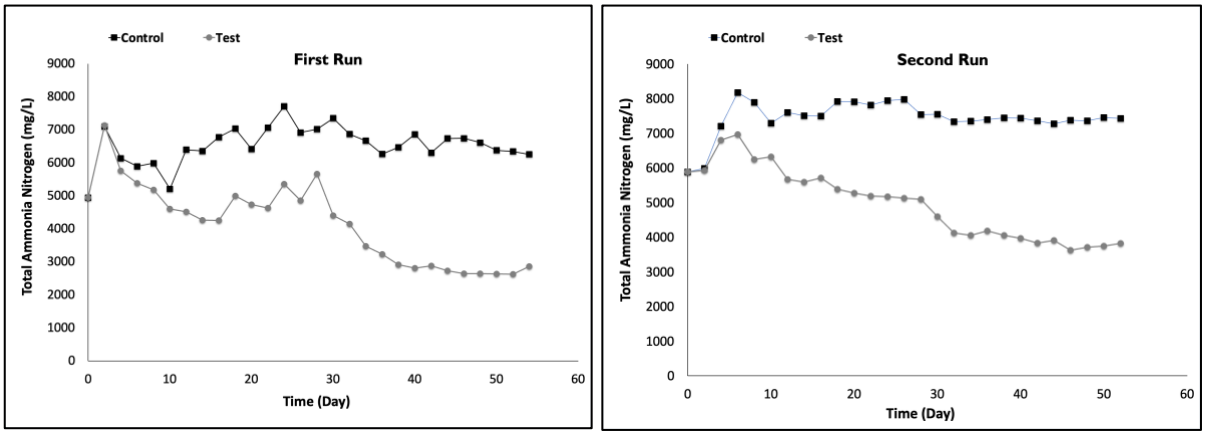

Figure 6.8: Total ammoniacal nitrogen (the sum of ionized NH_4^+ and unionized NH_3) in the control and test reactors

Additionally, Figure 6.8 shows that the TAN levels in control digesters began with an initial increase, followed by a consistent trend around 7000 mg/L throughout the remainder of the experiment. However, the TAN concentration in the test digesters from both experimental runs initially increased and then gradually decreased over time. The results of the test digesters indicate an apparent improvement in the removal of TAN. The overall reduction from the first and second runs was 54.3 and 48.9%, respectively, compared to their respective control values. Generally, these results showed that batch microbubble stripping reduced the TAN in mesophilic food waste digestion containing high ammonia nitrogen content that would have been toxic to methane production.

6.4.3 sCOD, TS and VS in bioreactors

Soluble chemical oxygen demand (sCOD) also plays a significant role in indicating anaerobic digestion progress. It represents the substrate availability for microorganisms in the anaerobic digestion system. The sCOD is hydrolyzed and further oxidised to generate new cellular biomass. Figure 6.9 shows that both the control and test reactors have similar trendlines, although the test reactor had a generally lower sCOD. There was an initial increase in sCOD content in all reactors, followed by a gradual decrease. The availability of sCOD for anaerobic microbes was limited at the beginning. With the acclimation and breeding of hydrolytic bacteria, sCOD increased immediately on day 1, as substrates were increasingly converted into soluble organic substrates. In accordance with the decrease in daily methane production demonstrated previously, sCOD gradually decreased as microbes utilised them.

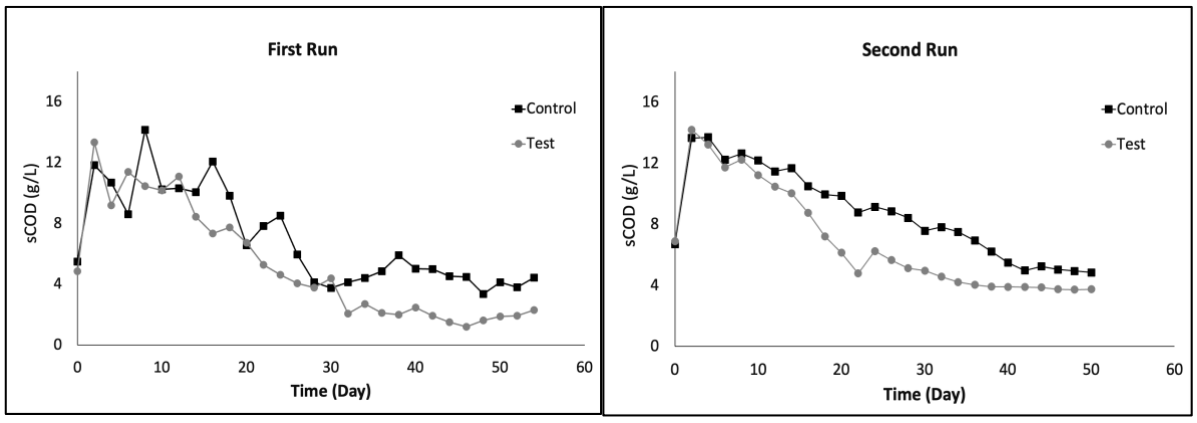

Figure 6.9: Soluble chemical oxygen demand concentrations for two sets of experiment

At the end of the anaerobic digestion period, the average sCOD removal efficiency in the control digesters was 22.6%. However, following the application of batch microbubble stripping, the sCOD removal efficiency increased twofold, resulting in an average reduction of 50.6% for the test digesters. The results indicate that batch microbubble stripping coupled with anaerobic digesters benefits microbial degradation and significantly improves biodegradability.

The production of biogas is the result of the biological conversion of the substrate. Therefore, there will be significant reductions in the dry matter content of the substrates represented by total solids, TS and total volatile solids, TVS. Figure 6.10 represents the reduction of TS and TVS from the two experimental runs. The test reactors showed higher reductions in both TS and TVS than the control reactors. For control digesters, the mean reduction efficiencies for TS and TVS were 43.9% and 64.9%, respectively. As a comparison, the mean TS and TVS reduction efficiencies of test digesters were 64.6% and 78.7%, which were 47.0% and 21.3% higher than those of control digesters, respectively. It was evident from this data that the substrates became more readily available when the microbubble batch stripping of the digestate was coupled with the digesters. Accordingly, the higher TS and TVS reductions in the test reactors may have contributed to the higher methane production. Based on the results of these experiments, it can be concluded that coupling AD reactors to microbubble stripping engendered by fluidic oscillators enhanced the reduction of TS and TVS in anaerobic digestion.

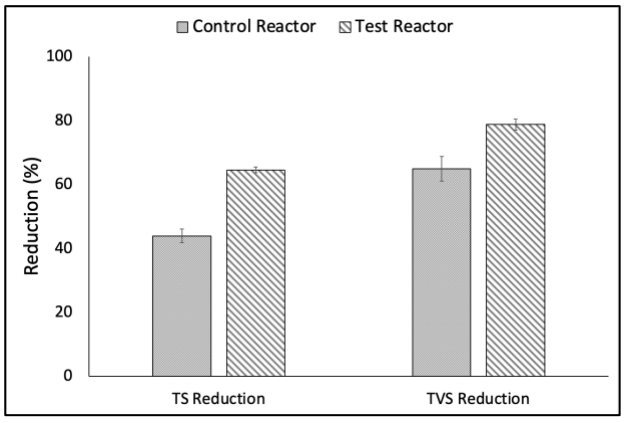

Figure 6.10: Average percentage reduction of TS and TVS from the two experimental runs

6.4.4 VFA

During anaerobic digestion, VFAs are one of the most important intermediates. It was observed that there was no apparent difference in the VFA trends between the control and test reactors. However, VFA concentrations were generally lower in test digesters than in control digesters as can be seen in Figure 6.11.

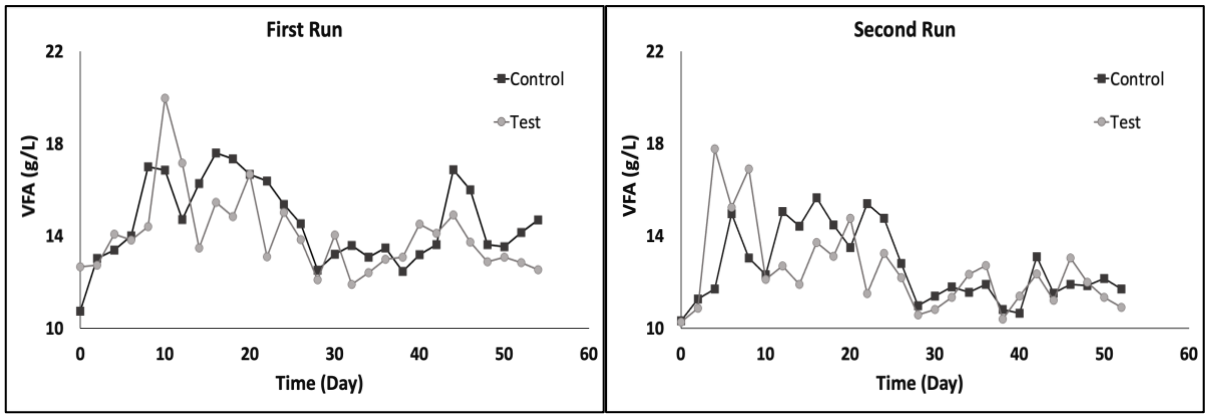

Figure 6.11: Volatile fatty acids progression in anaerobic digestion of control and test experiments

The VFA concentration in both reactors increased in the first few days, indicating rapid acidogenesis and hydrolysis. This is in accordance with the daily methane production, which was high at the beginning. In addition, this provide further explaining on the initial pH drop of both reactors previously presented. VFA is an intermediate product that can both be generated and utilized simultaneously. Food waste is hydrolysed or acidified to generate VFAs. The presence of a lower VFA does not necessarily indicate that the degradation performance is lower but could also suggest that the VFA is utilized more rapidly. VFAs were converted to methane and carbon dioxide during methanogenesis. The level of VFA was relatively high throughout this study. Following the initial significant increase in VFA, the level of VFA decreased and fluctuated over the remainder of the experiment. Despite this, no clear trends were observed in VFA concentrations. Consequently, VFA could not be used to evaluate differences between control and test digesters.

6.4.5 Batch stripping of 2 L digestate

Batch stripping was coupled to the test reactor during each AD experimental run from the first day. A total of two litres of digestate were removed from the test digester five days a week. Each stripping run consisted of 25 mL of digestate fed into the rig, resulting in a liquid level of approximately 3.1 mm. In line with previous studies, the highest removal rates were observed with liquid layers of 5mm (Desai *et al.*, 2021). Stripping 2 L of digestate took approximately three hours, with each run taking only two minutes. The ammonium and TAN concentrations were measured at the start and end of each batch stripping of 2 L digestate removed from the test reactor. Figure 6.12 shows the overall results of batch microbubble stripping of a 2 L digestate, which show the removal percentage of total ammonia nitrogen. Based on this figure, the efficiency of ammonia removal ranged between 33.9% and 46.8% for both experimental runs.

Furthermore, Figure 6.12 also indicated that the TAN removal efficiency was correlated with pH. There is a direct correlation between the removal efficiency and pH, which is consistent with literature. These results are expected, owing to previous studies demonstrating the beneficial effects of higher pH on the removal of ammonia (Zhang *et al.*, 2011). In the present work, pH was not modified so as not to disturb the AD process in the digester. Additionally, pH modification would increase operational costs.

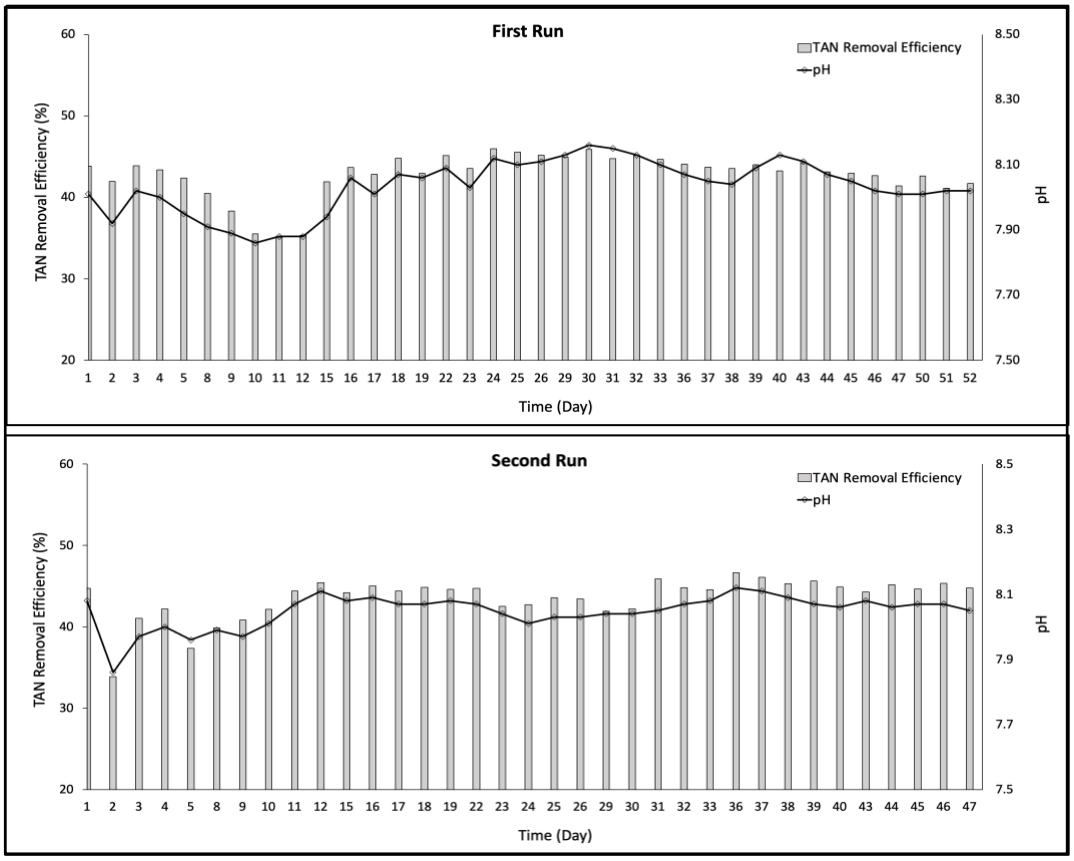

Figure 6.12: Percentage TAN removal efficiencies and pH versus the operating day of anaerobic digestion

Meanwhile, Figure 6.13 illustrates the initial TAN and the relative percentage removal of TAN. On average, TAN removal efficiencies were around 40%, except between days 4 and 7. There was a decrease in the efficiency of TAN removal during these days, which is primarily due to the drop in pH during these days. Despite the continued decrease in TAN concentrations, stripping efficiencies remain at approximately 40%. Therefore, the stripping removal efficiency was not influenced by the initial concentration of TAN. This is in agreement with the previous study, which reported that removal efficiency was independent of the initial concentration of ammonia (Desai *et al.*, 2021). A possible explanation is that temperature, pH, and contact time play a much greater role in driving the transfer of ammonia from the liquid phase to the gas phase than ammonia concentration alone.

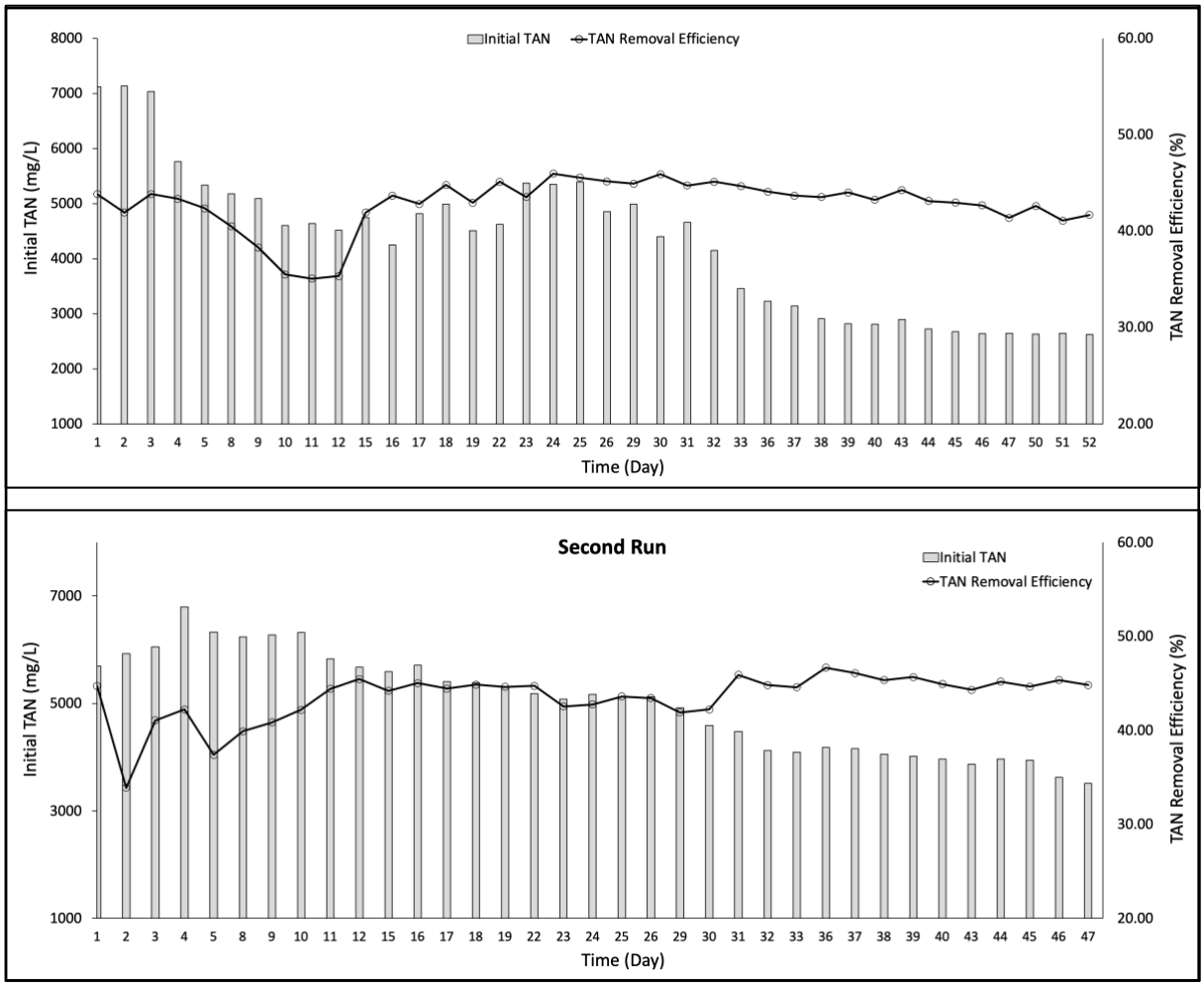

Figure 6.13: Initial TAN of the digestate and percentage TAN removal efficiencies versus the operating day of anaerobic digestion

In comparison with other previous studies, the removal efficiency of 40% was considered low. It should be noted that the contact time was much shorter than in other studies, a moderate flow rate was employed, and pH was not adjusted.

Figure 6.14 illustrates the temperature profiles of the system and the digestate for the three continuous stripping runs in which each run took approximately 120 seconds (2 minutes). A key characteristic of hot microbubble stripping is the difference in initial temperature between gas and liquid and maintaining a substantial temperature difference throughout. In the present work, the stripping gas was heated as soon as it flowed into the rig and the temperature was maintained approximately 70 ^{o}C. Microorganisms in digestate are directly affected by temperature as it directly affects their metabolic rates and activity levels. In general, higher

temperatures increase microbial activity, accelerating organic matter decomposition and biogas production. However, excessively high temperatures can denature enzymes and inhibit the growth of microorganisms. In contrast, a decrease in temperature can result in a slower rate of microbial activity, thus reducing the degradation of organic compounds and methane production (Wang *et al.*, 2019). Consequently, temperature changes may alter the dominant microbial populations and the overall microbiological activity. Variations in temperature outside the preferred range can inhibit their activity and, as a result, decrease the efficiency of biogas production. The digestate in the bottles was placed in a water bath at 30 ± 2 ^{o}C to prevent temperature-related issues and to maintain optimal microbiology. This was also the initial temperature of the liquid when it entered the stripping rig. With the implementation of this strategy, the impact of temperature changes on digestate microbiology can be effectively managed.

Additionally, Figure 6.14 shows that the gas temperature immediately dropped as soon as the liquid was introduced to the rig. Despite this, the gas temperature soon increased and remained around 70 ^{o}C. Although the contact time was extremely short, the temperature difference between the hot microbubble and the digestate fed into the rig accelerated evaporation. Furthermore, previous studies have shown that microbubbles generated by fluidic oscillators have a high surface-to-volume ratio, leading to a high interfacial area and a high mass transfer flux (Zimmerman *et al.*, 2008, 2011). Both of these characteristics contributed to the separation being achieved at a temperature significantly below the boiling point of the mixture (Al-Yaqoobi *et al.*, 2016).

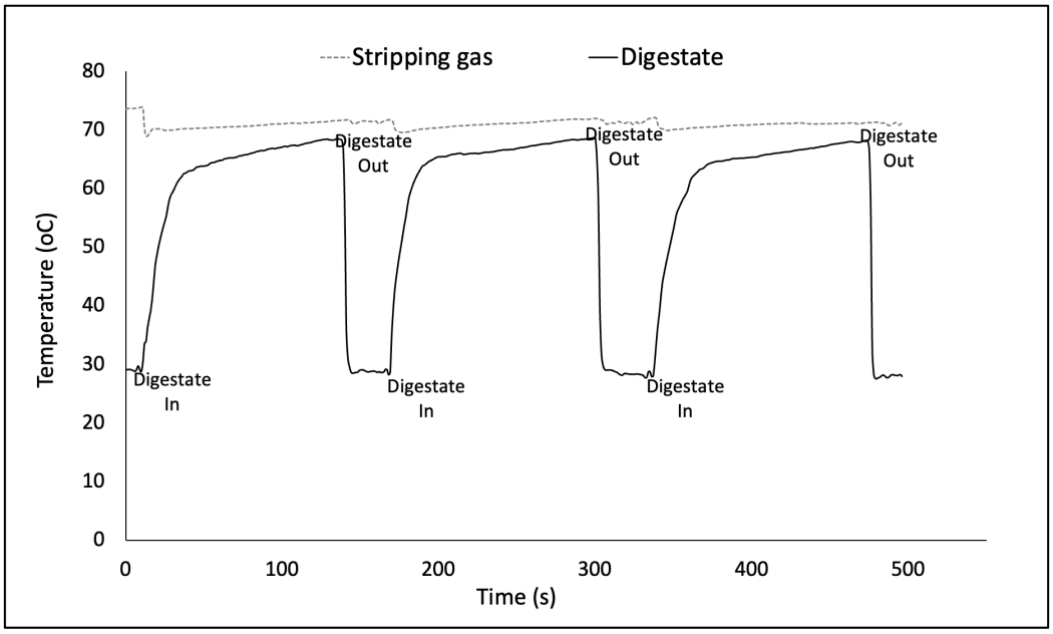

Figure 6.14: A temperature profile of the digestate and system over a period of three continuous stripping runs

The ammonia removal in the present study was lower than the efficiencies from other techniques in previous studies. As TAN concentrations tend to decay exponentially during the stripping process, the shortest runs are likely to achieve the highest returns on investment. Therefore, two minutes of contact time was chosen. The flow rate used in this study was 1LPM, and the operating temperature was approximately 70°C. This is primarily due to the fact that higher velocity and temperature usually result in excessive foaming and evaporation. In addition, high stripping rates adversely affected the AD process, resulting in organic material loss and lower methane yields. Microbubble stripping in this study was conducted at a low gas flow rate, a modest operating temperature, a short contact time, and no pH adjustments were made. Considering both the supply of energy and the cost of energy, the present study's methodology is considered to be advantageous. Furthermore, there has been an increase in methane yield.

Although the stripped ammonia was released into the fume cupboard in this study, it is possible to recover the ammonia stripped by passing the off gas containing ammonia from the stripping rig through sulphuric acid solutions. Sulphuric acid reacts with ammonia to form ammonium sulphate, $(NH_4)_2SO_4$. Because of its nitrogen and sulphur content, ammonium sulphate can be collected, processed, or used directly as a fertilizer.

6.5 Conclusion

An investigation of the feasibility of coupling batch microbubble stripping with anaerobic digestion of food waste with high nitrogen content and low C/N value is presented in this chapter. Energy efficient fluidic oscillator was used to generate microbubbles in the stripping. The effects of utilizing microbubble stripping on anaerobic digester were investigated by stripping 10% of working liquid volume 5 times per week. The batch microbubble stripping was successfully implemented to reduce TAN concentration in test digester on average of 51.4% while boosting methane production by 45.9% on average. It was observed that the removal of 2 L digestate from the test digesters and the subsequent microbubble stripping did not negatively affect the stability of the process or performance on solids destruction. TS and TVS destruction were improved in the test digester by 47.0 and 21.3%, respectively, compared to the control digester. There was a significant improvement in biodegradability as TAN was reduced in the digesters, and this was proven by the twofold increase in sCOD reduction in the test digesters. Moreover, the application of batch microbubble stripping led to a remarkable higher methane yield which exceeded the theoretical value by 51.2%.

Fluidic oscillator-driven microbubble stripping reduces TAN in anaerobic digesters in a feasible and promising way. The separation rate in microbubble stripping was between 33.9 and 46.8%. This was achieved with a much shorter contact time, a moderate flow rate, and no pH adjustment in comparison with the literatures. Therefore, the separation efficiencies are lower than those achieved in previous studies, but sufficient to improve the TAN concentration in the digester as well as the methane yield. Microbubbles in this work were generated by the energy-efficient fluidic oscillator, which is simple in design and inexpensive.

Based on the results obtained, the batch microbubble stripping process is a viable technology for minimizing ammonia emissions during AD of nitrogen-enriched substrates. The approach has the potential to produce methane efficiently from food waste that has a lower C/N value. This technology could significantly reduce the costs associated with the with the anaerobic digestion of food waste with high nitrogen levels by stripping ammonia.

In the present study, however, no studies have been conducted to assess the effects on microbial communities. It is necessary to conduct further research to identify the mechanisms by which the sparged microbubble CO_2 and batch microbubble stripping increased the production of methane in anaerobic digestion.

In the initial plan of this thesis, it was intended to use a side-arm stripping system for anaerobic digestion. Nevertheless, implementing that system proved challenging due to several technical issues, limitations, and the pandemic. Thus, microbubble stripping was performed as a batch operation. This work demonstrated that microbubble technology could reduce TAN (total ammonia nitrogen) in anaerobic digestion. The batch stripping performed in this study can be used to develop mathematical models that describe the system's behaviour. It can then be applied to continuous processes to enhance their efficiency. A continuous process design can be optimized by adjusting the model parameters based on the batch data. In this way, it is possible to optimize the process conditions and predict the likely outcomes on a large scale.

Chapter 7 : Conclusions and Future Work

7.1 Conclusion

The main purpose of this study is to test the hypothesis that there are synergies in operating anaerobic digesters by combining CO_2 microbubble sparging with microbubble stripping of ammonia. This demonstrates the efficacy of microbubble stripping generated by fluidic oscillators in reducing TAN levels, avoiding ammonia inhibition, and improving methane yields, particularly in the anaerobic digestion of food waste with low C/N values sparged with CO_2 microbubbles. To achieve the above objective, three detailed experimental studies have been presented in this thesis as follows:

1. Microbubble stripping using different DZ rigs, and the main feature of this technique is utilizing an energy-efficient DZ fluidic oscillator to create microbubbles.
2. Investigation of *in situ* ammonia stripping by CO_2 microbubbles sparged in the anaerobic digesters and the ability of different gases (CO_2, N_2 and air) to strip ammonia.
3. Investigation on running an anaerobic digestion of food waste with low C/N value, sparged with CO_2 microbubbles and combined with batch microbubble stripping.

Following are the studies and key conclusions obtained from this investigation:

1. Three stripping rigs were designed (DZ lab-scale, DZ Recirculating and DZ Continuous rigs), and their K_La values were higher than stripping using conventional-sized bubbles. Specifically, DZ lab-scale stripping rig resulted in a K_La value of 0.0532 min^{-1}, which is 2.3 times greater than that obtained in a previous study. Additionally, this stripping rig was chosen to couple with AD in the present study.
2. Investigation of batch anaerobic digestion of food waste sparged with CO_2 microbubbles revealed that rather than removing ammonia, CO_2 microbubbles lowered the system's pH. In turn, the fraction of free ammonia in the digestate was reduced. Thus, most of the ammonia nitrogen in the system was present in the form of ionic salts, NH_4^+; as a result, they are less readily available for stripping. Also, CO_2 sparging is unlikely to result in ammonia stripping. Nevertheless, less free ammonia in the system might have contributed to the increase in methane yield as the ammonia inhibition was alleviated. The ability of different gases (carbon dioxide, nitrogen, and

air) to strip ammonia was also studied. A reduction in TAN was not observed when CO_2 was used as a stripping gas; however, air and nitrogen gases can contribute significantly to TAN removal, even at 35°C. Nitrogen was selected as the stripping gas in the final experiment.

3. Batch microbubble stripping using DZ lab-scale rig has shown to be effective in increasing methane production by 45.9% in the anaerobic digestion of food waste sparged with CO_2 microbubbles in comparison with control reactor (without the stripping). This remarkably high methane yield in the test digester exceeded the theoretical value by 51.2%.
4. The reduction of TAN contributed to improving biodegradability, which is beneficial to microbial degradation. It was observed that the sCOD removal efficiency increased two-fold, resulting in an average reduction of 50.6% following batch microbubble stripping. Furthermore, the TAN removal rates were achieved in a short time and no major costs for chemical additions as there was no pH adjustment.

Table 7.1 summarises the hypotheses tested in the present study. Through this study, microbubble stripping generated by fluidic oscillators has been successfully demonstrated to reduce the digester's TAN level, avoid ammonia inhibition, and increase methane production in anaerobic digestion. Considering that fluidic oscillators do not have moving parts and require minimal maintenance, they are the most cost-effective and cheapest method of producing microbubbles. To the best of the author's knowledge, this is the first study to investigate the removal of ammonia from anaerobic digestion systems sparged with carbon dioxide microbubbles. Microbubble batch stripping using fluidic oscillator can provide a feasible and promising means to control ammonia concentrations in the mesophilic digesters sparged with CO_2 microbubbles. Therefore, it is possible to design pilot plants for continuous microbubble stripping as well as larger volumes of digestate. These investigations are anticipated to provide crucial information regarding the applicability of side-arm stripping to the AD of food waste with low C/N ratios.

Table 7.1: Summary of the hypotheses tested and key findings

	Hypothesis Tested	Key Findings	Hypothesis Supported (Y/N)	New Understanding
1	Microbubble stripping designed with DZ fluidic oscillator in this report can improve the ammonia removal from highly concentrated liquid.	Their K_La values were higher than stripping using conventional-sized bubbles.	Y	Microbubble stripping using air was successful, but an anoxic gas is required for simultaneous AD operation. CO_2 as a cheap gas and potential C-source might be a good candidate.
2	*In situ* ammonia stripping due to CO_2 seeding into anaerobic digestion	CO_2 sparging is unlikely to result in ammonia stripping.	N	Less free ammonia nitrogen (FAN) in the system due to CO_2 seeding in the anaerobic digestion might have contributed to the increase in methane yield as the ammonia inhibition was alleviated.
				A reduction in TAN was not observed when CO_2 was used as a stripping gas.
				Dissolved gases that do not dissociate or ionize in an aqueous solution would be better suited to stripping ammonia. Noble gases would suffice but are expensive. Methane, nitrogen, or hydrogen are cheaper and relatively inert. So N_2 was chosen for simultaneous ammonia removal from AD.
3	There are synergies in operating anaerobic digesters by combining CO_2 microbubble sparging with microbubble stripping of ammonia.	Remarkably high methane yield in the test digester as TAN was reduced by ammonia stripping. The reduction of TAN contributed to improving biodegradability, which is beneficial to microbial degradation.	Y	Microbubble batch stripping using fluidic oscillator can provide a feasible and promising means to control ammonia concentrations in the mesophilic digesters sparged with CO_2 microbubbles.

7.2 Future work

During this study, due to the COVID pandemic, the laboratory experiments were limited by technical problems and time constraints. Thus, it was impossible to investigate the feasibility of continuous stripping as a side-arm to AD. However, the findings from this study have demonstrated excellent potential for microbubble stripping generated by a fluidic oscillator in batch microbubble stripping coupled with AD. Thus, in future studies, it would be useful to test microbubble stripping as a side-arm to AD, and it would be necessary to optimise the process to ensure continuous operation.

Another potential area is developing user-customised programming in Aspen Plus specifically for CO_2 dosing in AD (with a microbubbles system) and simultaneous ammonia removal. This goal may be achieved by modifying ADM1, a mathematical model representing anaerobic digesters. The primary reason is to develop a model that can predict the biochemical transformation and pathways of anaerobic digestion of food waste sparged with CO_2 microbubbles and coupled with ammonia removal using microbubble stripping. It would also facilitate the provision of further information regarding mass and energy balances. This can be incorporated into techno-economic analyses, allowing AD with NH_3 stripping to be evaluated as part of the bioprocessing operation. Furthermore, modeling approaches can be utilized to determine the range of productive parameters for this anaerobic digestion system. Using these models, it is possible to simulate the complex interactions between ammonia, VFAs, alkalinity, pH, and temperature to determine optimal operating conditions. A model can be used to predict the effects of varying ammonia concentrations, pH levels, and temperatures on biogas production and system stability by entering varying parameters into it. Therefore, these predictions can assist in determining the best operational parameters that will optimize the efficiency and performance of anaerobic digestion systems, such as adjusting feedstock composition, optimizing temperature control, or removing ammonia.

Additionally, future studies could focus on the effects of sparged CO_2 microbubbles and batch microbubble stripping on microbial communities. This will enable us to determine how the sparged microbubbles increase methane production in anaerobic digestion.

Bibliography

Abdi, H. (University of T. at D. (2010) *Encyclopedia of Research Design*, *SAGE Publications, Inc.* Edited by N. J. Salkind.

Abdulrazzaq, N., Al Sabbagh, B., Rees, J. M., and Zimmerman, W. B. (2015) 'Separation of Azeotropic Mixtures Using Air Microbubbles Generated by Fluidic Oscillation', *AIChE Journal*.

Abouelenien, F., Fujiwara, W., Namba, Y., Kosseva, M., Nishio, N., and Nakashimada, Y. (2010) 'Improved methane fermentation of chicken manure via ammonia removal by biogas recycle', *Bioresource Technology*, 101, pp. 6368–6373.

ADBA (2022) 'Food Waste Recycling: Anaerobic digestion, the net zero level for local authorities', in *ADBA's Policy Briefing*. London, United Kingdom: ADBA.

Ahmadi-Pirlou, M., Ebrahimi-Nik, M., Khojastehpour, M., and Ebrahimi, S. H. (2017) 'Mesophilic co-digestion of municipal solid waste and sewage sludge: Effect of mixing ratio, total solids, and alkaline pretreatment', *International Biodeterioration and Biodegradation*, 125, pp. 97–104.

Ahring, B. K., Sandberg, M., and Angelidaki, I. (1995) 'Volatile fatty acids as indicators of process imbalance in anaerobic digestors', *Appl Microbiol Biotechnol*, 43, pp. 559–565.

Akindele, A. A. (2016) *The Effects of Ammonia on Anaerobic Digestion of the Organic Fraction of Municipal Solid Wastes*. University of Ottawa.

Al-Mashhadani, M. K. H. (2013) *Application of Microbubbles Generated by Fluidic Oscillation in the Anaerobic Digestion Process*. The University of Sheffield.

Al-Mashhadani, M. K. H., Wilkinson, S. J., and Zimmerman, W. B. (2016) 'Carbon dioxide rich microbubble acceleration of biogas production in anaerobic digestion', *Chemical Engineering Science*, 156, pp. 24–35.

Al-Yaqoobi, A., Hogg, D., and Zimmerman, W. B. (2016) 'Microbubble distillation for ethanol-water separation', *International Journal of Chemical Engineering*, 2016.

Al-Yaqoobi, A., and Zimmerman, W. B. (2014) 'Microbubble Distillation Studies of a Binary Mixture', in *Proceedings of the University of Sheffield Engineering Symposium Conference (USES '14)*, pp. 9–10.

Alibardi, L., Green, K., Favaro, L., Vale, P., Soares, A., Cartmell, E., and Bajón Fernández, Y. (2017) 'Performance and stability of sewage sludge digestion under CO 2 enrichment: A pilot study'.

Alimahmoodi, M., and Mulligan, C. N. (2008) 'Anaerobic bioconversion of carbon dioxide to biogas in an upflow anaerobic sludge blanket reactor', *Journal of the Air and Waste Management Association*, 58(1), pp. 95–103.

Angelidaki, I., Karakashev, D., Batstone, D. J., Plugge, C. M., and Stams, A. J. M. (2011) *Biomethanation and its potential*. 1st edn, *Methods in Enzymology*. 1st edn. Elsevier Inc.

Angelidaki, I., and Ahring, B. K. (1993) 'Applied Microbiology Biotechnology Thermophilic anaerobic digestion of livestock waste: the effect of ammonia', *Appl Microbiol Biotechnol*, 38, pp. 560–564.

APHA (2017) *Standard methods for the examination of water and wastewater*. 23rd edn. Washington, DC, New York: American Public Health Association.

Appels, L., Baeyens, J., Degrève, J., and Dewil, R. (2008) 'Principles and potential of the anaerobic digestion of waste-activated sludge', *Progress in Energy and Combustion Science*, 34(6), pp. 755–781.

Ata, O. N., Aygun, K., Okur, H., and Kanca, A. (2016) 'Determination of ammonia removal from aqueous solution and volumetric mass transfer coefficient by microwave-assisted air stripping', *International Journal of Environmental Science and Technology*, 13(10), pp. 2459–2466.

de Baere, L. A., Devocht, M., Van Assche, P., and Verstraete, W. (1984) 'Influence of high NaCl and NH4Cl salt levels on methanogenic associations', *Water Research*, 18(5), pp. 543–548.

Bajón Fernández, Y., Soares, A., Villa, R., Vale, P., and Cartmell, E. (2014) 'Carbon capture and biogas enhancement by carbon dioxide enrichment of anaerobic digesters treating sewage sludge or food waste'.

Bajón Fernández, Y., Green, K., Schuler, K., Soares, A., Vale, P., Alibardi, L., and Cartmell, E. (2015) 'Biological carbon dioxide utilisation in food waste anaerobic digesters', *Water Research*, 87, pp. 467–475.

Bakhshoodeh, R., Alavi, N., Soltani Mohammadi, A., and Ghanavati, H. (2016) 'Removing heavy metals from Isfahan composting leachate by horizontal subsurface flow constructed wetland', *Environmental Science and Pollution Research*, 23(12), pp. 12384–12391.

Banks, C. J., Zhang, Y., Jiang, Y., and Heaven, S. (2012) 'Trace element requirements for stable food waste digestion at elevated ammonia concentrations', *Bioresource Technology*, 104, pp. 127–135.

Berge, N. D., Reinhart, D. R., and Townsend, T. G. (2005) 'Critical Reviews in Environmental Science and Technology The Fate of Nitrogen in Bioreactor Landfills The Fate of Nitrogen in Bioreactor Landfills', *Critical Reviews in Environmental Science and Technology*, 35, pp. 365–399.

Bonmatí, A., and Flotats, X. (2003) 'Air stripping of ammonia from pig slurry: characterisation and feasibility as a pre-or post-treatment to mesophilic anaerobic digestion', *Waste Management*, 23, pp. 261–272.

Borja, R., Sánchez, E., and Weiland, P. (1996) 'Influence of ammonia concentration on thermophilic anaerobic digestion of cattle manure in upflow anaerobic sludge blanket (UASB) reactors', *Process Biochemistry*, 31(5), pp. 477–483.

Borowski, S., Domański, J., and Weatherley, L. (2014) 'Anaerobic co-digestion of swine and poultry manure with municipal sewage sludge', *Waste Management*, 34(2), pp. 513–521.

Boyle, W. C. (1977) 'Energy recovery from sanitary landfills - A review', *Microbial Energy Conversion*. Edited by H. G. Schlegel and J. Barnea, pp. 119–138.

Braguglia, C. M., Gallipoli, A., Gianico, A., and Pagliaccia, P. (2018) 'Anaerobic bioconversion of food waste into energy: A critical review', *Bioresource Technology*, 248, pp. 37–56.

Braun, R. (1981) 'Ammonia toxicity in liquid piggery manure digestion', *Biotechnology Letters*, 3, pp. 159–164.

Burton, S. A. ., and Watson, I. A. (1998) 'Ammonia and nitrogen fluxes in landfill sites: applicability to sustainable landfilling European legislation imposes tough restrictions on the quality of landfill leachate discharges, of which a major component', *Waste Management*, 16(1), pp. 41–53.

Buswell, A. M., and Mueller, H. F. (1952) 'Mechanism of Methane Fermentation', *Industrial & Engineering Chemistry*, 44(3), pp. 550–552.

Calli, B., Mertoglu, B., Inanc, B., and Yenigun, O. (2015) 'Effects of high free ammonia concentrations on the performances of anaerobic bioreactors', *Process Biochemistry*, 40(3–4), pp. 1285–1292.

Capson-Tojo, G., Moscoviz, R., Astals, S., Robles, and Steyer, J. P. (2020) 'Unraveling the literature chaos around free ammonia inhibition in anaerobic digestion', *Renewable and Sustainable Energy Reviews*, 117(September 2019), p. 109487.

Di Capua, F., Adani, F., Pirozzi, F., Esposito, G., and Giordano, A. (2021) 'Air side-stream ammonia stripping in a thin film evaporator coupled to high-solid anaerobic digestion of sewage sludge: Process performance and interactions', *Journal of Environmental Management*, 295(June), p. 113075.

Chen, Y., Cheng, J. J., and Creamer, K. S. (2008) 'Inhibition of anaerobic digestion process: A review', *Bioresource Technology*, 99(10), pp. 4044–4064.

Cheung, L. K. C., Chu, L. M., and Wong, M. H. (1997) 'Ammonia stripping as a pretreatment for landfill leachate', *Water, Air, and Soil Pollution*, 94, pp. 209–221.

Cioabla, A. E., Ionel, I., Dumitrel, G. A., and Popescu, F. (2012) 'Comparative study on factors affecting anaerobic digestion of agricultural vegetal residues', *Biotechnology for Biofuels*, 5(1), p. 1.

Collivignarelli, C., Bertanza, G., Baldi, M., and Avezzù, F. (1998) *Ammonia stripping from MSW landfill leachate in bubble reactors: Process modeling and optimization*, *Waste Management and Research*.

Cudjoe, D., Nketiah, E., Obuobi, B., Adu-Gyamfi, G., Adjei, M., and Zhu, B. (2021) 'Forecasting the potential and economic feasibility of power generation using biogas from food waste in Ghana: Evidence from Accra and Kumasi', *Energy*, 226.

Dabiri, S., Sappl, J., Kumar, P., Meister, M., and Rauch, W. (2021) 'On the effect of the inlet configuration for anaerobic digester mixing', *Bioprocess and Biosystems Engineering*, 44(12), pp. 2455–2468.

Dague, R. R., Mckinney, R. E., and Pfeffer, J. T. (1970) 'Solids retention in anaerobic waste treatment systems', *Journal (Water Pollution Control Federation)*, 42(2), pp. 29–46.

Deĝermenci, N., Ata, O. N., and Yildiz, E. (2012) 'Ammonia removal by air stripping in a semi-batch jet loop reactor', *Journal of Industrial and Engineering Chemistry*, 18(1), pp. 399–404.

Demirel, B., and Scherer, P. (2008) 'The roles of acetotrophic and hydrogenotrophic methanogens during anaerobic conversion of biomass to methane: A review', *Reviews in Environmental Science and Biotechnology*, 7(2), pp. 173–190.

Desai, P. (2017) *A Fluidic Oscillator Based on a New Mechanism : for Microbubble Generation and Developing Microbubble Stripping for Separation Phenomena*. The University of Sheffield.

Desai, P., Turley, M., Robinson, R., and Zimmerman, W. B. (2021) 'Hot Microbubble Injection in Thin Liquid Film Layers for Ammonia Separation from Ammonia Rich-Wastewater', *Chemical Engineering and Processing - Process Intensification*, (October), p. 108693.

Deublein, D., and Steinhauser, A. (2008) *Biogas from Waste and Renewable Resources*. Weinheim, Germany: Wiley-VCH Verlag GmbH& Co. KGaA.

Ebrahimi-Nik, M., Heidari, A., Ramezani Azghandi, S., Asadi Mohammadi, F., and Younesi, H. (2018) 'Drinking water treatment sludge as an effective additive for biogas production from food waste; kinetic evaluation and biomethane potential test', *Bioresource Technology*, 260(January), pp. 421–426.

El-Mashad, H. M., Zeeman, G., Van Loon, W. K. P., Bot, G. P. A., and Lettinga, G. (2004) 'Effect of temperature and temperature fluctuation on thermophilic anaerobic digestion of cattle manure', *Bioresource Technology*, 95(2), pp. 191–201

Emerson, K., Russo, R. C., Lund, R. E., and Thurston, R. V. (1975) 'Aqueous Ammonia Equilibrium Calculations: Effect of pH and Temperature', *Journal of the Fisheries Research Board of Canada*, 32(12), pp. 2379–2383.

EPA (2009) *Technical Support Document for Manure Management Systems: Proposed Rule for Mandatory Reporting of Greenhouse Gases 2009*. Washington, DC, USA.

Escudero, A., Blanco, F., Lacalle, A., and Pinto, M. (2015) 'Struvite precipitation for ammonium removal from anaerobically treated effluents', *Journal of Environmental Chemical Engineering*, 3(1), pp. 413–419.

European Biogas Association (2013) 'EBA opinion on the digestate drying at biogas plants', pp. 22–25.

Farishi, B. Al, and Setiawan, M. R. (2019) 'The Mapping of Contamination Potential Surrounding Bakung Landfill Based on Geological Studies', *IOP Conference Series: Earth and Environmental Science*, 258(1).

Feng, L. *et al.* (2013) 'Biochemical methane potential (BMP) of vinegar residue and the influence of feed to inoculum ratios on biogas production', *BioResources*, 8(2), pp. 2487–2498.

Fernandes, T. V., Keesman, K. J., Zeeman, G., and van Lier, J. B. (2012) 'Effect of ammonia on the anaerobic hydrolysis of cellulose and tributyrin', *Biomass and Bioenergy*, 47, pp. 316–323.

Gallert, C., Bauer, S., and Winter, J. (1998) 'Effect of ammonia on the anaerobic degradation of protein by a mesophilic and thermophilic biowaste population', *Applied Microbiology and Biotechnology*, 50(4), pp. 495–501.

Gallert, C., and Winter, J. (1997) 'Mesophilic and thermophilic anaerobic digestion of source-sorted organic wastes: effect of ammonia on glucose degradation and methane production', *Appl Microbiol Biotechnol*, 48, pp. 405–410.

Gerardi, M. H. (2003) *The Microbiology of Anaerobic Digesters*. Hoboken, New Jersey: John Wiley & Sons, Inc.

Götz, M. *et al.* (2016) 'Renewable Power-to-Gas: A technological and economic review', *Renewable Energy*, 85, pp. 1371–1390.

Gujer, W., and Zehnder, A. J. B. (1983) *Conversion processes in anaerobic digestion*, *Wat.Sci.Tech*.

Hansen, K. H., Angelidaki, I., and Ahring, B. K. (1998) 'Anaerobic digestion of swine manure: Inhibition by ammonia', *Water Research*.

Haque, M. S., and Haque, N. N. (1970) 'Studies on the Effect of Urine on Biogas Production', *Bangladesh Journal of Scientific and Industrial Research*, 41(1), pp. 23–32.

Hashimoto, A. G. (1983) 'Conversion of straw–manure mixtures to methane at mesophilic and thermophilic temperatures', *Biotechnology and Bioengineering*, 25(1), pp. 185–200.

Hopfner-sixt, K., and Amon, T. (2007) 'Monitoring of agricultural biogas plants in Austria – mixing technology and specific values of essential process parameters', *Proceedings of the 15th European Biomass Conference and Exhibition*, pp. 1718–1728.

Jayaraj, S., Velmurugan, S., and Deepanraj, B. (2014) 'Study on the effect of pH on biogas production from food waste by anaerobic digestion', in *The 9th international green energy conference*. Tianjin, China, pp. 799–805.

Jördening, H.-J., and Winter, J. (2005) *Environmental biotechnology: concepts and applications*. Wiley-VCH, Germany.

Jouhara, H. *et al.* (2017) 'Municipal waste management systems for domestic use', 139, pp. 485–506.

Karim, K., Klasson, K. T., Hoffmann, R., Drescher, S. R., DePaoli, D. W., and Al-Dahhan, M. H. (2005) 'Anaerobic digestion of animal waste: Effect of mixing', *Bioresource Technology*, 96(14), pp. 1607–1612.

Karim, K., Hoffmann, R., Klasson, K. T., and Al-Dahhan, M. H. (2005) 'Anaerobic digestion of animal waste: Effect of mode of mixing', *Water Research*, 39(15), pp. 3597–3606.

Kayhanian, M. (1999) 'Ammonia Inhibition in High-Solids Biogasification: An Overview and Practical Solutions', *Environmental Technology*, 20(4), pp. 355–365.

Kiessling, F., Fokong, S., Koczera, P., Lederle, W., and Lammers, T. (2012) 'Ultrasound Microbubbles for Molecular Diagnosis, Therapy, and Theranostics', *Journal of Nuclear Medicine*, 53(3), pp. 345–348.

Kim, E. J., Kim, H., and Lee, E. (2021) 'Influence of ammonia stripping parameters on the efficiency and mass transfer rate of ammonia removal', *Applied Sciences (Switzerland)*, 11(1), pp. 1–13.

Kinidi, L., Tan, I. A. W., Abdul Wahab, N. B., Tamrin, K. F. Bin, Hipolito, C. N., and Salleh, S. F. (2018) 'Recent Development in Ammonia Stripping Process for Industrial Wastewater Treatment', *International Journal of Chemical Engineering*, 2018, pp. 1–14.

Koch, K., Huber, B., Bajón Fernández, Y., and Drewes, J. E. (2016) 'Methane from CO2: Influence of different CO2 concentrations in the flush gas on the methane production in BMP tests', *Waste Management*, 49, pp. 36–39.

Koch, K., Bajón Fernández, Y., and Drewes, J. E. (2015) 'Influence of headspace flushing on methane production in Biochemical Methane Potential (BMP) tests', *Bioresource Technology*, 186(February), pp. 173–178.

Koster, I. W., and Lettinga, G. (1988) 'Anaerobic digestion at extreme ammonia concentrations', *Biological Wastes*, 25(1), pp. 51–59.

Kothari, R., Pandey, A. K., Kumar, S., Tyagi, V. V., and Tyagi, S. K. (2014) 'Different aspects of dry anaerobic digestion for bio-energy: An overview', *Renewable and Sustainable Energy Reviews*, 39, pp. 174–195.

Kroeker, E. J., Schulte, D. D., Sparling, A. B., and Lapp, H. M. (1979) 'Anaerobic treatment process stability', *Journal (Water Pollution Control Federation)*, p. 718.

De la Rubia, M. Á., Walker, M., Heaven, S., Banks, C. J., and Borja, R. (2010) 'Preliminary trials of in situ ammonia stripping from source segregated domestic food waste digestate using biogas: Effect of temperature and flow rate', *Bioresource Technology*, 101(24), pp. 9486–9492.

Lei, X., Sugiura, N., Feng, C., and Maekawa, T. (2007) 'Pretreatment of anaerobic digestion effluent with ammonia stripping and biogas purification', *Journal of Hazardous Materials*, 145, pp. 391–397.

Leite, V. D., Prasad, S., Lopes, W. S., de Sousa, J. T., and Barros, A. J. M. (2013) 'Study on ammonia stripping process of leachate from the packed towers', *Journal of Urban and Environmental Engineering*, 7(2), pp. 215–222.

Lettinga, G. (1995) 'Anaerobic digestion and wastewater treatment systems', *Antonie van Leeuwenhoek*, 67(3), pp. 3–28.

Li, J., Wang, L., Lu, Q., and Zhou, W. (2019) 'Toxicity alleviation for microalgae cultivation by cationic starch addition and ammonia stripping and study on the cost assessment', *RSC Advances*, 9(65), pp. 38235–38245.

Li, Z., Lou, Y., Ding, J., Liu, B. F., Xie, G. J., Ren, N. Q., and Xing, D. (2020) 'Metabolic regulation of ethanol-type fermentation of anaerobic acidogenesis at different pH based on transcriptome analysis of Ethanoligenens harbinense', *Biotechnology for Biofuels*, 13(1), pp. 1–15.

Liao, P. H., Chen, A., and Lo, K. V. (1995) 'Removal of nitrogen from swine manure wastewaters by ammonia stripping', *Bioresource Technology*, 54, pp. 17–20.

Lin, Y., Wang, X., Wang, L., Yang, D., and Lan, H. (2022) 'Effect of pH Shock on the Treatment of High Concentration Organic Wastewater via a Fe0/GO- Anaerobic System', *BioResources*, 17(1), pp. 1591–1605.

Liu, B., Giannis, A., Zhang, J., Chang, V. W. C., and Wang, J. Y. (2015) 'Air stripping process for ammonia recovery from source-separated urine: Modeling and optimization', *Journal of Chemical Technology and Biotechnology*, 90(12), pp. 2208–2217.

Magrí, A., Béline, F., and Dabert, P. (2013) 'Feasibility and interest of the anammox process as treatment alternative for anaerobic digester supernatants in manure processing – An overview', *Journal of Environmental Management*, 131, pp. 170–184.

Mao, C.-L., Wang, X.-J., and Feng, Y.-Z. (2017) 'Process Performance and Kinetic Characteristic of Anaerobic Digestion Focusing on Swine Manure Content', 94(ICSD 2016), pp. 81–84.

El Mashad, H. M., Barzee, T. J., Franco, R. B., Zhang, R., Kaffka, S., and Mitloehner, F. (2023) 'Anaerobic Digestion and Alternative Manure Management Technologies for Methane Emissions Mitigation on Californian Dairies', *Atmosphere*, 14(1).

Midgley, W. J. B., Henshaw, M. J. d. C., and Alshuhri, S. (2021) 'A systems-engineering approach to nation-scale problems: Municipal solid waste management in Saudi Arabia', *Systems Engineering*, 24(6), pp. 480–496.

Minocha, V. K., and Prabhakar Rao, A. (1998) 'Ammonia removal and recovery from urea fertilizer plant waste', *Environmental Technology Letters*, 9(7), pp. 655–664.

Mitchell, M. J., Jensen, O. E., Cliffe, K. A., and Maroto-Valer, M. M. (2010) 'A model of carbon dioxide dissolution and mineral carbonation kinetics', *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences*, 466(2117), pp. 1265–1290.

Neue, H.-U. (1993) 'Methane emission from rice fields', *BioScience*, 43, pp. 466–474.

Nielsen, H. B., and Angelidaki, I. (2008) 'Strategies for optimizing recovery of the biogas process following ammonia inhibition', *Bioresource Technology*.

Niu, Q., Qiao, W., Qiang, H., Hojo, T., and Li, Y. Y. (2013) 'Mesophilic methane fermentation of chicken manure at a wide range of ammonia concentration: Stability, inhibition and recovery', *Bioresource Technology*, 137, pp. 358–367.

Nugroho, W. A. (2021) *Application of CO2 Microbubble to Enhance Methane Production in Anaerobic Digestion of Food Waste*. University of Sheffield.

Oregon Department of Human Services (2000) 'Technical Bulletin: Health Effects Information (Ammonia)', 2162(503).

Pastor, L., Mangin, D., Ferrer, J., and Seco, A. (2010) 'Struvite formation from the supernatants of an anaerobic digestion pilot plant', *Bioresource Technology*, 101(1), pp. 118–125.

Pedizzi, C., Lema, J. M., and Carballa, M. (2017) 'Enhancing thermophilic co-digestion of nitrogen-rich substrates by air side-stream stripping', *Bioresource Technology*, 241, pp. 397–405.

Procházka, J., Dolejš, P., Máca, J., and Dohányos, M. (2012) 'Stability and inhibition of anaerobic processes caused by insufficiency or excess of ammonia nitrogen', *Appl Microbiol Biotechnol*, 93, pp. 439–447.

Quan, X., Wang, F., Zhao, Q., Zhao, T., and Xiang, J. (2009) 'Air stripping of ammonia in a water-sparged aerocyclone reactor', *Journal of Hazardous Materials*, 170(2–3), pp. 983–988.

Rajagopal, R., Massé, D. I., and Singh, G. (2013) 'A critical review on inhibition of anaerobic digestion process by excess ammonia', *Bioresource Technology*, 143, pp. 632–641.

Rehl, T., and Müller, J. (2011) 'Life cycle assessment of biogas digestate processing technologies', *Resources, Conservation and Recycling*, 56(1), pp. 92–104.

Resch, C., Wörl, A., Waltenberger, R., Braun, R., and Kirchmayr, R. (2011) 'Enhancement options for the utilisation of nitrogen rich animal by-products in anaerobic digestion', *Bioresource Technology*, 102, pp. 2503–2510.

Robbins, J. E., Gerhardt, S. A., and Kappel, T. J. (1989) 'Effects of total ammonia on anaerobic digestion and an example of digestor performance from cattle manure-protein mixtures', *Biological Wastes*, 27(1), pp. 1–14.

Rousseau, R. W. (1987) *Handbook of separation process technology*. J. Wiley.

Saady, N. M. C. (2013) 'Homoacetogenesis during hydrogen production by mixed cultures dark fermentation: Unresolved challenge', *International Journal of Hydrogen Energy*, 38(30), pp. 13172–13191.

Saracco, G., and Genon, G. (1994) 'High temperature ammonia stripping and recovery from process liquid wastes', *Journal of Hazardous Materials*, 37(1), pp. 191–206.

Schnürer, A., Houwen, F. P., and Svensson, B. H. (1994) 'Mesophilic syntrophic acetate oxidation during methane formation by a triculture at high ammonium concentration', *Archives of Microbiology*, 162(1–2), pp. 70–74.

Schnürer, A., and Nordberg, Å. (2008) 'Ammonia, a selective agent for methane production by syntrophic acetate oxidation at mesophilic temperature', *Water Science and Technology*, 57(5), pp. 735–740.

Seader, J. D., Henley, E. J., and Roper, D. K. (2011) *Separation Process Principles*. 3rd Edition. Hoboken, New Jersey: Wiley.

Serna-Maza, A. (2014) *Nitrogen Control in Source Segregated Domestic Food Waste Anaerobic Digestion Using Stripping Technologies*. University of Southampton.

Serna-Maza, A., Heaven, S., and Banks, C. J. (2015) 'Biogas stripping of ammonia from fresh digestate from a food waste digester', *Bioresource Technology*, 190, pp. 66–75.

Serna-Maza, A., Heaven, S., and Banks, C. J. (2017) 'In situ biogas stripping of ammonia from a digester using a gas mixing system', *Environmental Technology*, 38(24), pp. 3216–3224.

Singh, B., Szamosi, Z., and Siménfalvi, Z. (2020) 'Impact of mixing intensity and duration on biogas production in an anaerobic digester: a review', *Critical Reviews in Biotechnology*, 40(4), pp. 508–521.

Sosnowski, P., Wieczorek, A., and Ledakowicz, S. (2003) 'Anaerobic co-digestion of sewage sludge and organic fraction of municipal solid wastes', *Advances in Environmental Research*, 7(3), pp. 609–616.

Srinath, E. G., and Loehr, R. C. (1974) 'Ammonia desorption by diffused aeration', *Journal (Water Pollution Control Federation)*, 46(8), pp. 1939–1957.

Staley, B. F., Xu, F., Cowie, S. J., Barlaz, M. A., and Hater, G. R. (2006) 'Release of Trace Organic Compounds during the Decomposition of Municipal Solid Waste Components', *Environmental Science and Technology*, 40, pp. 5984–5991.

Tesař, V. (2004) 'Pressure Driven Microfluidics', in *ESDA04*. Manchester, United Kingdom.

UNEP (2021) *United Nations Environment Programme (2021). Food Waste Index Report 2021.*, *Unep*. Nairobi.

Vargas-García, M. C., Suárez-Estrella, F., López, M. J., and Moreno, J. (2007) 'Effect of inoculation in composting processes: Modifications in lignocellulosic fraction', *Waste Management*, 27(9), pp. 1099–1107.

Vavilin, V. A., and Angelidaki, I. (2005) 'Anaerobic degradation of solid material: Importance of initiation centers for methanogenesis, mixing intensity, and 2D distributed model', *Biotechnology and Bioengineering*, 89(1), pp. 113–122.

Walker, M., Iyer, K., Heaven, S., and Banks, C. J. (2011) 'Ammonia removal in anaerobic digestion by biogas stripping: An evaluation of process alternatives using a first order rate model based on experimental findings', *Chemical Engineering Journal*, 178, pp. 138–145.

Wang, H. (2016) *General rights Optimization of biomethanation focusing on high ammonia loaded processes*. Technical University of Denmark.

Wang, S., Ma, F., Ma, W., Wang, P., Zhao, G., and Lu, X. (2019) 'Influence of temperature on biogas production efficiency and microbial community in a two-phase anaerobic digestion system', *Water (Switzerland)*, 11(1).

Wang, X. M., and Wu, T. (2008) 'Release of Isoprene and Monoterpenes during the Aerobic Decomposition of Orange Wastes from Laboratory Incubation Experiments', *Environmental Science and Technology*, 42, pp. 3265–3270.

Wang, Y., Guo, X., Li, J., Yang, Y., Lei, Z., and Zhang, Z. (2012) 'Efficient Electrochemical Removal of Ammonia with Various Cathodes and Ti/RuO 2-Pt Anode', *Open Journal of Applied Sciences*, 2, pp. 241–247.

Ward, A. J., Hobbs, P. J., Holliman, P. J., and Jones, D. L. (2008) 'Optimisation of the anaerobic digestion of agricultural resources', *Bioresource Technology*.

Wittmann, C., Zeng, A. P., and Deckwer, W. D. (1995) 'Growth inhibition by ammonia and use of a pH-controlled feeding strategy for the effective cultivation of Mycobacterium chlorophenolicum', *Applied Microbiology and Biotechnology*, 44(3–4), pp. 519–525.

Xiao, L., Yang, M., Hu, D., Mei, Y., Zhao, S., and Liang, Y. (2021) 'Comparison of initial ph adjustment prior to thermophilic anaerobic digestion of lime-treated corn stover via liquid digestate or co2', *Applied Sciences (Switzerland)*, 11(22).

Yan, B. H., Selvam, A., and Wong, J. W. C. (2016) 'Innovative method for increased methane recovery from two-phase anaerobic digestion of food waste through reutilization of acidogenic off-gas in methanogenic reactor', *Bioresource Technology*, 217, pp. 3–9.

Yang, D., Chen, Q., Liu, R., Song, L., Zhang, Y., and Dai, X. (2022) 'Ammonia recovery from anaerobic digestate: state of the art, challenges and prospects', *Bioresource Technology*, p. 127957.

Yang, Z., Wang, W., He, Y., Zhang, R., and Liu, G. (2018) 'Effect of ammonia on methane production, methanogenesis pathway, microbial community and reactor performance under mesophilic and thermophilic conditions', *Renewable Energy*, 125, pp. 915–925.

Yao, Y., Yu, L., Ghogare, R., Dunsmoor, A., Davaritouchaee, M., and Chen, S. (2017) 'Simultaneous ammonia stripping and anaerobic digestion for efficient thermophilic conversion of dairy manure at high solids concentration', *Energy*, pp. 179–188.

Yaser, A. Z. *et al.* (2022) 'Composting and Anaerobic Digestion of Food Waste and Sewage Sludge for Campus Sustainability: A Review', *International Journal of Chemical Engineering*, 2022.

Yenigün, O., and Demirel, B. (2013) 'Ammonia inhibition in anaerobic digestion: a review', *Process Biochemistry*, 48(5–6), pp. 901–911.

Yoon, Hyein, Lim, Ji-Hye, Chung, and Hyung-Keun (2008) 'Ammonia Removal Model Based on the Equilibrium and Mass Transfer Principles', *Bull. Korean Chem. Soc.*, 29(3), pp. 555–561.

Youcai, Z. (2018) 'Leachate Treatment Engineering Processes', in *Pollution Control Technology for Leachate from Municipal Solid Waste*, pp. 361–522.

Zhang, L., and Jahng, D. (2010) 'Enhanced anaerobic digestion of piggery wastewater by ammonia stripping: Effects of alkali types', *Journal of Hazardous Materials*, 182(1–3), pp. 536–543.

Zhang, L., Lee, Y. W., and Jahng, D. (2011) 'Ammonia stripping for enhanced biomethanization of piggery wastewater', *Journal of Hazardous Materials*, 199–200, pp. 36–42.

Zhu, L., Dong, D., Hua, X., Xu, Y., Guo, Z., and Liang, D. (2017) 'Ammonia nitrogen removal and recovery from acetylene purification wastewater by air stripping', *Water Science and Technology*, 75(11), pp. 2538–2545.

Zimmerman, W. B., Tesař, V., Butler, S., and Hemaka Bandulasena, H. C. (2008) *Microbubble Generation*, *Recent Patents on Engineering*.

Zimmerman, W. B., Hewakandamby, B. N., Tesař, V., Bandulasena, H. C. H., and Omotowa, O. A. (2009) 'On the design and simulation of an airlift loop bioreactor with microbubble generation by fluidic oscillation', *Food and Bioproducts Processing*.

Zimmerman, W. B., Al-Mashhadani, M. K. H., and Bandulasena, H. C. H. (2013) 'Evaporation dynamics of microbubbles', *Chemical Engineering Science*, 101, pp. 865–877.

Zimmerman, W. B., and Desai, P. D. (2020) 'Fluidic oscilator', Patent Number: WO2020208250.

Zimmerman, W. B., Tesař, V., and Bandulasena, H. C. H. (2011) 'Towards energy efficient nanobubble generation with fluidic oscillation', *Current Opinion in Colloid and Interface Science*.

Zwietering, M. H., Jongenburger, I., Rombouts, F. M., and Van't Riet, K. (1990) 'Modeling of the bacterial growth curve', *Applied and Environmental Microbiology*, 56(6), pp. 1875–1881.

Appendices

Appendix A

Experiments were carried out to strip ammonia from leachate and synthetic ammonia solution using DZ stripping rig. The results are shown in the Figure A1 and A2 below. It was found that there is no significant difference in TAN removal efficiencies ($P > 0.05$).

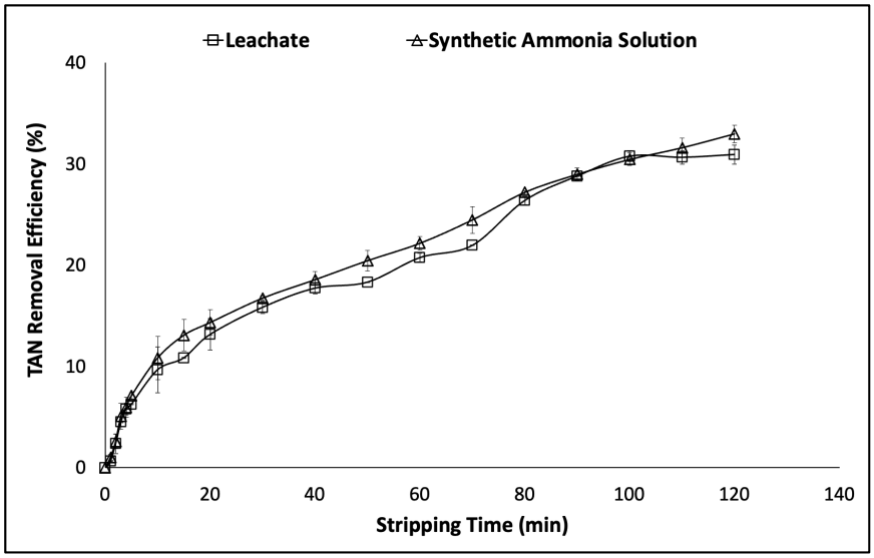

Figure A1: TAN removal efficiencies

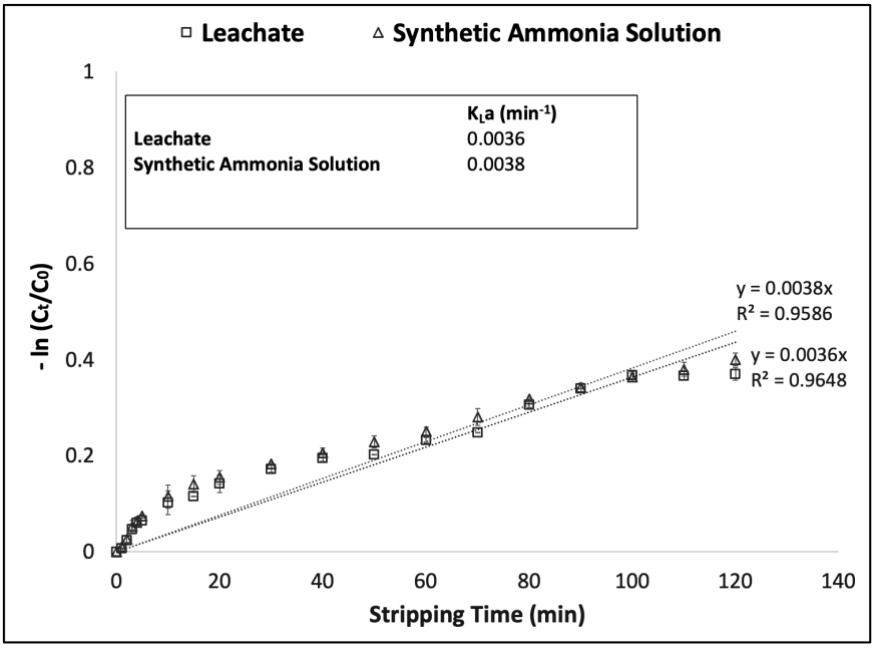

Figure A2: logarithm of the ammonia concentration ratio, giving the K_La values

Appendix B

Running 2nd cycle of anaerobic digestion in Chapter 6. The production of methane in the control reactor in the second cycle declined after a few days (Figure B1). TAN in control digester was extremely high (Figure B2).

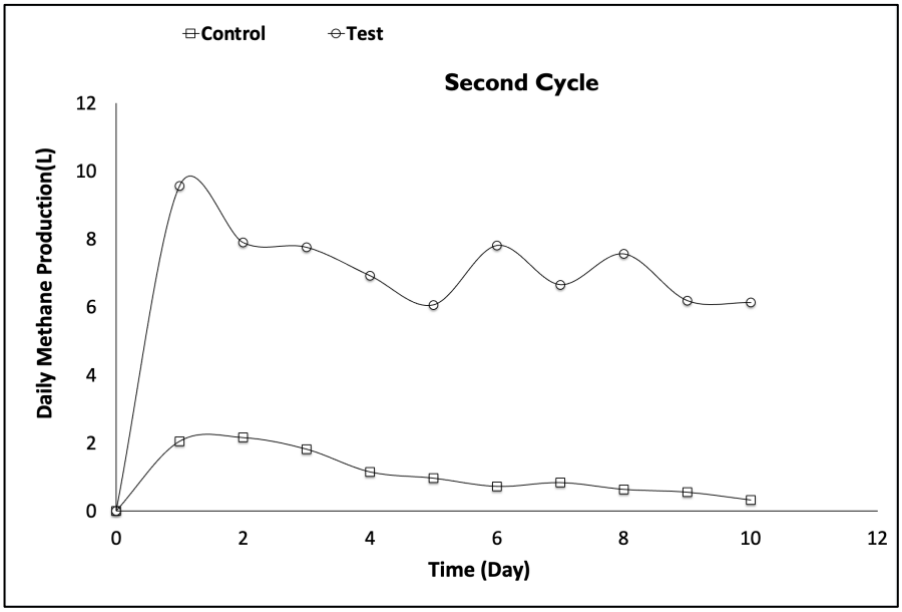

Figure B1: Daily methane production from both control and test digesters.

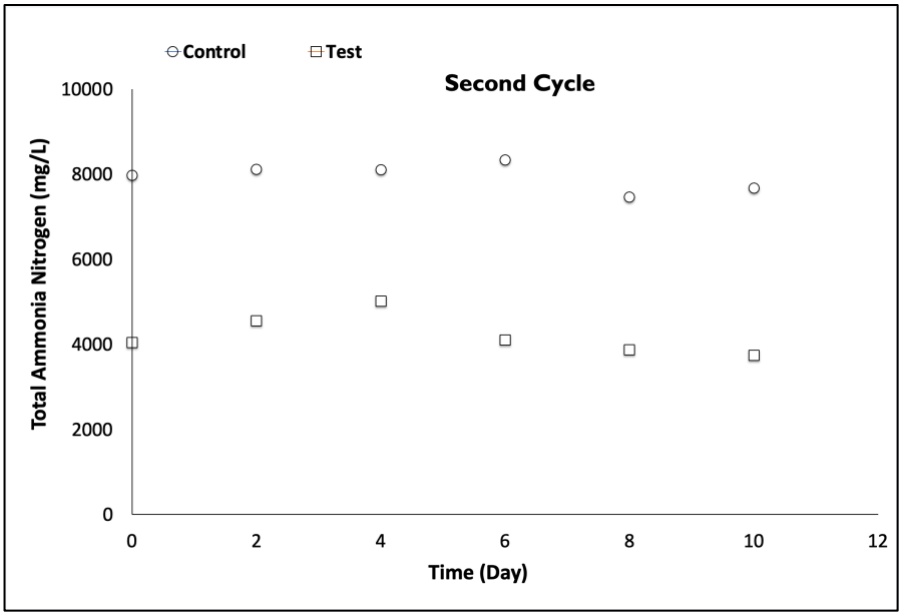

Figure B2: TAN concentration in control and test digesters.

Appendix C1

Batch microbubble stripping engendered by fluidic oscillator coupled with AD, run 1 (Section 6.4.5)

Day	Initial pH	Initial TAN (mg/L)	Final TAN (mg/L)	TAN Removal (%)
1	8.01	7122.76	3999.50	43.85
2	7.92	7135.53	4142.59	41.94
3	8.02	7036.83	3949.92	43.87
4	8.00	5764.62	3264.81	43.36
5	7.95	5337.77	3075.42	42.38
8	7.91	5183.35	3083.77	40.51
9	7.89	5094.58	3142.86	38.31
10	7.86	4606.01	2969.68	35.53
11	7.88	4642.68	3013.61	35.09
12	7.88	4520.30	2922.54	35.35
15	7.94	4752.43	2759.22	41.94
16	8.06	4252.06	2394.28	43.69
17	8.01	4823.80	2758.00	42.83
18	8.07	4995.72	2757.47	44.80
19	8.06	4510.63	2573.31	42.95
22	8.09	4629.59	2540.18	45.13
23	8.03	5377.16	3035.59	43.55
24	8.12	5353.72	2891.62	45.99
25	8.10	5394.10	2936.34	45.56
26	8.11	4859.34	2663.93	45.18
29	8.13	4997.44	2751.58	44.94
30	8.16	4402.17	2380.97	45.91
31	8.15	4664.28	2577.25	44.75
32	8.13	4153.54	2278.99	45.13
33	8.10	3459.01	1913.23	44.69
36	8.07	3228.65	1804.60	44.11
37	8.05	3142.63	1769.33	43.70
38	8.04	2912.34	1643.74	43.56
39	8.09	2819.94	1578.29	44.03
40	8.13	2812.12	1595.17	43.28
43	8.11	2899.61	1615.84	44.27
44	8.07	2730.57	1552.56	43.14
45	8.05	2676.28	1526.18	42.97
46	8.02	2641.27	1513.75	42.69
47	8.01	2646.99	1551.00	41.41
50	8.01	2636.67	1512.76	42.63
51	8.02	2650.97	1561.20	41.11
52	8.02	2624.52	1529.84	41.71

Appendix C2

Batch microbubble stripping engendered by fluidic oscillator coupled with AD, run 2 (Section 6.4.5)

Day	Initial pH	Initial TAN (mg/L)	Final TAN (mg/L)	TAN Removal (%)
1	8.08	5696.79	3149.30	44.72
2	7.86	5924.99	3918.65	33.86
3	7.97	6052.70	3568.55	41.04
4	8.00	6798.52	3929.15	42.21
5	7.96	6329.04	3963.64	37.37
8	7.99	6239.84	3751.74	39.87
9	7.97	6278.07	3714.34	40.84
10	8.01	6316.39	3653.24	42.16
11	8.07	5825.74	3239.62	44.39
12	8.11	5669.08	3092.83	45.44
15	8.08	5590.28	3120.19	44.18
16	8.09	5707.76	3138.07	45.02
17	8.07	5406.39	3005.09	44.42
18	8.07	5381.06	2967.67	44.85
19	8.08	5290.11	2930.74	44.59
22	8.07	5183.88	2865.33	44.73
23	8.04	5076.92	2917.91	42.53
24	8.01	5169.84	2960.45	42.74
25	8.03	5124.61	2890.27	43.60
26	8.03	5124.65	2899.25	43.43
29	8.04	4913.62	2854.95	41.89
30	8.04	5108.09	2861.54	43.98
31	8.05	4893.04	2671.27	45.41
32	8.07	4797.48	2639.03	44.99
33	8.08	4767.78	2605.56	45.35
36	8.12	4738.44	2518.57	46.85
37	8.11	4676.57	2508.74	46.35
38	8.09	4570.42	2500.96	45.28
39	8.07	4536.32	2455.40	45.87
40	8.06	4485.69	2490.80	44.47
43	8.08	4385.54	2429.01	44.61
44	8.06	4350.70	2390.35	45.06
45	8.07	4147.19	2316.62	44.14
46	8.07	3780.75	2060.99	45.49
47	8.05	3787.98	2114.68	44.17