THESIS

NITROGEN RECOVERY FROM ANAEROBIC DIGESTATE VIA AMMONIA STRIPPING AND ABSORBING WITH A NITRIFIED SOLUTION

Submitted by

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ABSTRACT

NITROGEN RECOVERY FROM ANAEROBIC DIGESTATE VIA AMMONIA STRIPPING AND ABSORBING WITH A NITRIFIED SOLUTION

Animal wastes cause environmental pollution, including contamination of air and water, when not managed properly. For example, stored livestock manure releases greenhouse gasses, which contribute to air pollution and global warming. Anaerobic digesters have been used for animal waste treatment in order to reduce the environmental impacts of animal wastes. However, current anaerobic digestion systems have serious economical and operational challenges such as high capital cost, low byproduct price, and ammonia toxicity. Therefore, more research is needed to increase the benefits of anaerobic digestion and reduce its challenges. The goal of this project was to improve the cost and performance of anaerobic digesters by enhancing their byproducts, biogas and fertilizer, while reducing one of their serious operational challenges, ammonia toxicity. To achieve these goals, this project investigated an integrated anaerobic digestion nitrogen recovery process that includes anaerobic digestion, nitrogen recovery and nitrification. The nitrogen produced during anaerobic digestion is volatilized in a stripper, captured in an absorber, and converted to nitrogen certified organic fertilizer in the nitrification process. Recovering the ammonia in anaerobic digesters not only produces organic fertilizer but also reduces ammonia toxicity, enhancing biogas production.

Experiments and modeling were used to identify appropriate operating conditions for the stripper and absorber units of the proposed process. The objective of the nitrogen

recovery system experiments was to find the best operational conditions as well as to evaluate the performance of the nitrification solution as an ammonia absorbent. Stripping and absorption columns were designed to measure the ammoniacal nitrogen recovery. The ammonia stripping and absorption extents were calculated for several operational conditions: stripping and absorption feed pH, stripping temperature and absorbent nitrogen concentration. The experimental results showed that a feed pH of 10 was optimal for ammonia stripping in the pH range 8.5–10.5, providing an ammonia stripping extent of 77%, while the optimal stripping temperature was 50 °C since it provides the highest extent of ammonia stripping in the tested range of 35–65 °C. An Aspen Plus simulation model was also developed for the ammonia stripping process to calculate the effects of the number of equilibrium stages, feed pH, and the amount of CO_2 in the stripping gas. The model showed that the use of three equilibrium stages, a feed pH of 10, and having no CO_2 in the stripping gas provides the most feasible operational conditions considering the stripping performance and economics. Moreover, the data suggested that the stripping units will require pH control for effective ammonia recovery since the pH of the stripper decreases with the ammonia removal. For the ammonia absorption unit, the experimental data showed that ammonia absorption was not greatly impacted by the feed pH nor by the concertation of nitrogen in the liquid feed. With a low concentration of nitrogen in the liquid feed (2 g/L NH_4NO_3 as N), the extents of ammonia absorption for feed pH values of 7 and 2 were 82% and 92, respectively. However, the extents of ammonia absorption using a high concentration nitrogen liquid feed (7 g/L NH_4NO_3) for feed pH values of 7 and 2 decreased to 70% and 85%, respectively. However, a Two-Factor ANOVA test with replication has a p-value >0.05, so there is no statistically

significant difference in the ammonia absorption due to the feed pH nor in the concentration of nitrogen in the absorbent. Consequently, it can be concluded that nitrified solution can be used as an ammonia absorbent because it can affectively absorb ammonia over a wide range of its pH and its nitrogen concentration.

This project demonstrated that it is possible to recover nitrogen in an integrated anaerobic digestion process and determined recommended operational conditions for the nitrogen recovery system. The novel integrated anaerobic digestion system proposed in this work decreases ammonia toxicity for anaerobic digestion, while increasing potential for revenue from increased biogas yield and recovery of ammonia fertilizer. increasing the biogas yield, producing organic fertilizer and decreasing ammonia toxicity.

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1 Background

1.1 Introduction

Animal wastes cause air and water pollution when not managed appropriately. According to the United States Environmental Protection Agency (EPA), agricultural activities including livestock waste storage and runoff are main sources of surface water and groundwater contamination (EPA, 2002a). Moreover, animal wastes such as manure piles release greenhouse gasses such as carbon dioxide, methane, and nitrous oxide that are important contributors to greenhouse gas emissions. The EPA estimates that about 10% of the total greenhouse gas emissions in the United Stat is caused by agriculture activities (EPA, 2015b). In addition to the greenhouse gases, animal waste is the major source of the ammonia pollution in the air. The EPA states that animal waste is responsible for 80% of the ammonia emissions in the United States (Doorn & Natschke, 2002). For those reasons, animal waste is considered a major contributor to air and water pollution.

Anaerobic digesters have been used to reduce the environmental impacts of animal wastes. Anaerobic digestion systems convert organic waste into digested solid and biogas which both are considered more stable and less harmful components to the environment than the original untreated organic waste. According to the United States Department of Agriculture, anaerobic digestion treatment of manure waste has reduced methane and carbon dioxide emissions by 34% (Holly et al., 2017)

However, anaerobic digesters are not currently economically feasible. At the Technology Market Summit 2012, EPA stated that the main two barriers limiting anaerobic digesters are financial barriers which are the high capital cost of the

anaerobic digestion and the low price of its main byproduct, biogas (EPA, 2012a). Therefore, more research is needed to enhance process efficiency and maximize profitable products and resource recovery.

Moreover, anaerobic digestion has operational and technology challenges that need to be overcome. One of the biggest challenges in anaerobic digesters is the toxicity of the ammonia to the microorganisms in the digester. Animal wastes are rich in organic nitrogen components that are converted to ammonia during anaerobic digestion, causing toxicity to methanogenic microorganisms and limiting the biogas yield (Nakakubo et al., 2008). This is particularly a problem in anaerobic digesters where liquid leachate is continuously recycled in the process, which is common for arid region operations (Wilson et al., 2013). Several ways have been used to reduce the ammonia toxicity in anaerobic digestion. One common method to reduce ammonia toxicity is dilution the anaerobic digestion with water which decrease the ammonia concentration and then reduce its toxicity (Kayhanian, 1999). However, this is neither an environmental-friendly method nor a practical way for several anaerobic digestion sites as it requires a large amount of water. Removing ammonia from anaerobic digestion system is another way that has been used to control the toxicity of ammonia. Ozturk et al. (2003) has examined several methods to remove ammonia from anaerobic digestion including membrane technology, precipitation and ammonia stripping. It was found that ammonia stripping has the lowest operation cost between those methods. The traditional way of removing the ammonia is volatilizing it from the anaerobic digesters then capturing it with an acid. However, the need to use acids is financially

burdensome. Therefore, a substitutional method of recovery ammonia with acid is desired to decrease the process cost.

This work proposes an integrated anaerobic digester nitrogen recovery process that reduces those two major issues in anaerobic digestion: (1) high cost of the overall process and (2) ammonia toxicity to methane production in anaerobic digestion, while also providing an opportunity to increase anaerobic digestion system revenue via production of valuable organic fertilizer and biogas. The integrated anaerobic digestion benefits the process cost in two ways: (1) reduction of methane-inhibition due to the ammonia toxicity in anaerobic digestion (2) production of organic fertilizer as the removed nitrogen can be processed and converted to a fertilizer. Simultaneously increasing the biogas production and producing organic fertilizer offer potential to improve the overall economic feasibility of anaerobic digestion.

1.2 Integrated Anaerobic Digestion Nitrogen Recovery System

This project introduced an integrated anaerobic digestion nitrogen recovery process that incudes (1) anaerobic digestion, (2) nitrogen recovery and (3) nitrification (Figure 1). The overall goal of the integrated anaerobic digestion nitrogen recovery process is to improve the cost and performance of the anaerobic digestion system while reducing the ammonia toxicity in anaerobic digesters. In the overall process shown in Figure 1, the anaerobic digestion digestate is sent to a stripping column (through Stream 4, S4) where the ammonia is volatilized with air (S7). The volatilized ammonia then goes through an absorption column (S8) where it is captured with nitrified solution. Depending on the absorption performance, the absorber gas outlet (S9) might still have

a low concentration of ammonia; if so, it would need to undergo through further treatment before it is released to the atmosphere based on the local emission regulation. The nitrified solution leaving the absorber (S11) is richer in ammonia than the nitrified solution entering the absorber (S10). The ammonia-rich nitrified solution leaving the absorber (S11) is then sent to the nitrification unit where the recovered ammonia is converted to nitrate (fertilizer) as describe in Equations (1) and (2) (EPA, 2002b).

$NH_3 + O_2 \rightarrow NO_2^- + 3\ H^+ + 2\ e^-$ (Equation 1)

$NO_2^- + H_2O \rightarrow NO_3^- + 2\ H^+ + 2\ e^-$ (Equation 2)

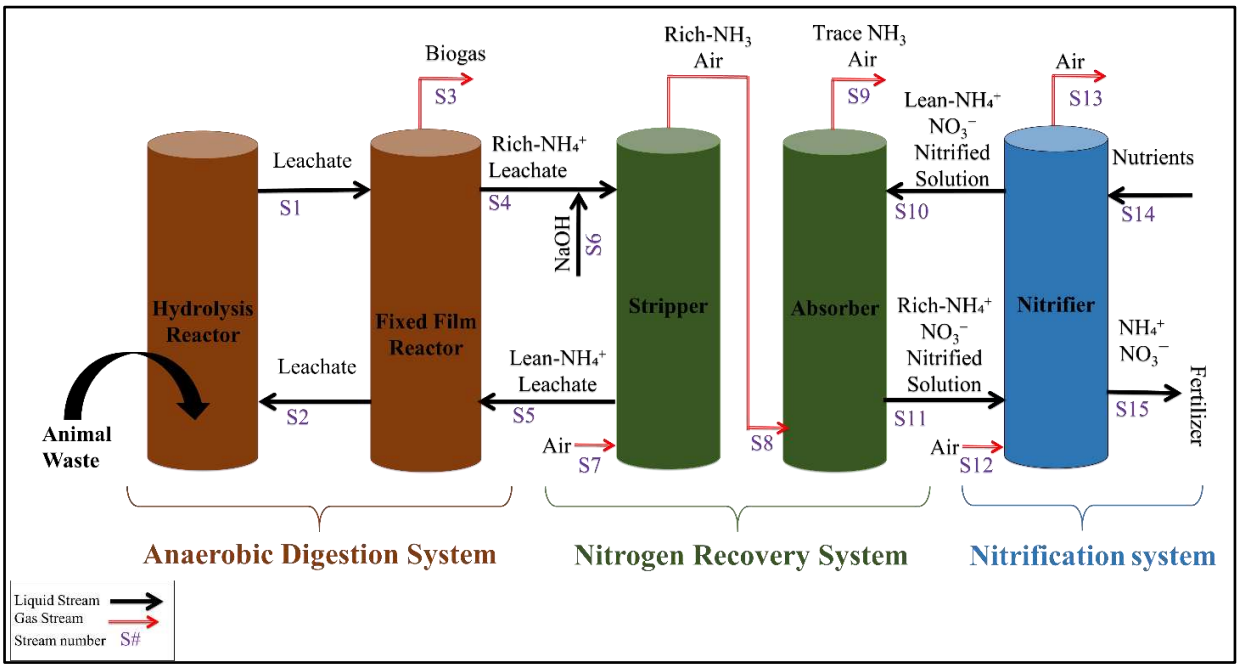

Figure 1: The integrated anaerobic digestion nitrogen recovery system including nitrogen recovery and nitrification where the recovered nitrogen is converted to ammonium nitrate fertilizer through nitrification.

The proposed nitrogen recovery process shown in Figure 1 includes three main systems: (1) anaerobic digestion (2) the nitrogen recovery system (stripper and absorber) and (3) nitrification system. Each system has optimal operational conditions including temperature and pH. When connecting the three systems as proposed in this project, suitable operational conditions for each system is must be identified while also considering whole system impacts. The pH of the system is very critical for the three systems because both anaerobic digestion and nitrification systems have microorganisms which are sensitive to pH. A pH between 6.8 and 8 is suitable for most anaerobic digestion system (Gerardi, 2003) while an optimum pH range for nitrification is 7.5 to 8.0 (EPA, 2002b). One the other hand, the ammonia recovery system has two units (stripper and absorber) and each unit has opposite conventional pH operation. The stripper efficiency is expected to increase as the stripping pH increases, while the absorber efficiency is expected to increase as the absorption pH decreases. Therefore, one of this project main objectives was to assess the performance of the stripper at different pH values considering the anaerobic digestion optimal pH range as well as assessing the performance of the absorber at different pH values considering the nitrification pH range.

Partial nitrification is targeted in the nitrification step to facilitate nitrification pH control. As Equations (1 & 2) show, the nitrification process produces hydronium ions (H^+) decreasing the nitrifier pH below its optimal pH, around pH of 7. On the other hand, ammonia increases the pH as it produces hydroxide ions (OH^-) and ammonium when it reacts with water. Therefore, the recovered ammonia can be used to increase the nitrifier pH as it drops below the desired pH. Thus, both the nitrification rate and the

ammonia supply at the feed need to be controlled to control the pH of nitrification at the optimal pH range. An observation in another project in our laboratory, underway, focused on the nitrification process suggests that a partial nitrification of 1:1 ratio of NH_4-N: NO_3-N keeps the nitrification at the optimal pH range. Therefore, a partial nitrification is considered in this project in order to control the nitrification pH.

1.3 Nitrogen Recovery System (NRS)

This project introduces a novel method to recover ammonia. Whereas the traditional methods to capture ammonia is to use acids such as hydrochloric or sulfuric acid, a nitrified solution is used in this work as substitution for these strong acids to capture the ammonia. Recovery of ammonia with an acid has been studied in previous research including Jiang et al. (2014), Bonmatí and Flotats (2003) and Khakharia et al. (2014) where sulfuric acid is used in all of those three studies. However, the need to use acids is not economically feasible. Moore (2016) states that the main problem in recovery of ammonia with acid is the acid cost, claiming that the cheapest acid cost is higher than the process product cost. Therefore, this project provides an alternate method of ammonia recovery with nitrified solution to decrease the process cost. As it can be seen in the nitrification Equations (1 - 2) that the nitrification process provides acidity through the production of hydronium ions, H^+. The main two benefits of using a nitrified solution instead of strong acids are (1) nitrification process is a biological acid-forming process as Equations (1 - 2) show, so nitrified solution can be used to capture ammonia (2) nitrification process is a biological reaction that converts the removed ammonia to organic fertilizer, nitrate.

This project used a laboratory-scale nitrogen recovery system (NRS) consisting of two units, an ammonia removal unit (stripper) and an ammonia recovery unit (absorber). The performance of the ammonia stripping and absorption were evaluated for several operational conditions: stripping and absorption feed pH, stripping temperature and absorbent nitrogen concertation. The system performance was assessed as a function of those conditions to develop recommendations on appropriate operational ranges.

1.4 The Project Goals and Objective

The overall goal of project is to improve the cost and performance of anaerobic digestion systems while reducing one of the important operational challenges, ammonia toxicity. The achieve the overall goal, this work introduced nitrogen recovery from anaerobic digestate through ammonia stripping and nitrification.

The objective of the nitrogen recovery experiments was to assess the nitrogen recovery system performance under several operational conditions to determine recommended operational conditions that consider the performance and the cost of the overall integrated anaerobic digestion system. This included evaluating the performance of the novel idea of absorbing ammonia with a nitrified solution.

To evaluate the nitrogen recovery system performance, the ammonia stripping extent was determined as a function of stripper feed pH and stripping temperature while the ammonia absorption extent was determined as a function of the absorber liquid feed pH and its nitrogen concentration. Moreover, one major objective within the operation analysis is to assess the stripping unit performance at lower pH than the conventional

ammonia stripping pH in order to reduce the pH disturbance when the stripper influent returns to the anaerobic digester. The performance of the absorption unit at higher pH than the conventional ammonia absorption pH was also assessed to minimize impact to the nitrification process via returning of absorber effluent to the nitrification system.

2 Literature Review

2.1 Environmental Issues of Animal Waste

Animal waste like cattle manure contains contaminants that end up in both water and air. The American Society of Agricultural and Biological Engineers (ASABE) described a typical manure characteristic (D384.2) showing that a typical manure has solids, nitrogen, phosphorous, potassium and calcium (ASABE, 2005). These components can cause environment pollution including water and air contamination.

2.1.1 Surface Water and Groundwater Contaminations

Contaminants in livestock waste can pollute the surface water and groundwater either by animal waste runoff or by leaching through the soil. Livestock waste storage and runoff are major contributors of surface water and groundwater contamination (Copeland, 2010; EPA, 2002a). Livestock waste is rich of solids and nutrients like nitrogen and phosphorous which can contaminate surface water and groundwater. Excessive presence of nitrogen and phosphorous in surface water is harmful to the marine life because it causes eutrophication. Eutrophication is described as an excessive plant and algae growth in water. Eutrophication can happen in a body of water as it receives an excessive nutrient load, mainly phosphorus and nitrogen (USGS, 2020). Eutrophication can cause serious environmental problems such as harmful algal blooms, dead zones, and fish kills (NOAA, 2020). Algal blooms deplete the oxygen from the water as they die and decompose which causes a lack of oxygen in the marine environment causing the death of marine animals such as fish.

2.1.2 Degradation Stages of Anaerobic Digestion

The process of degradation of organic materials by microorganisms in anaerobic digestion involves four stages: 1) Hydrolysis 2) Acidogenesis 3) Acetogenesis 4)

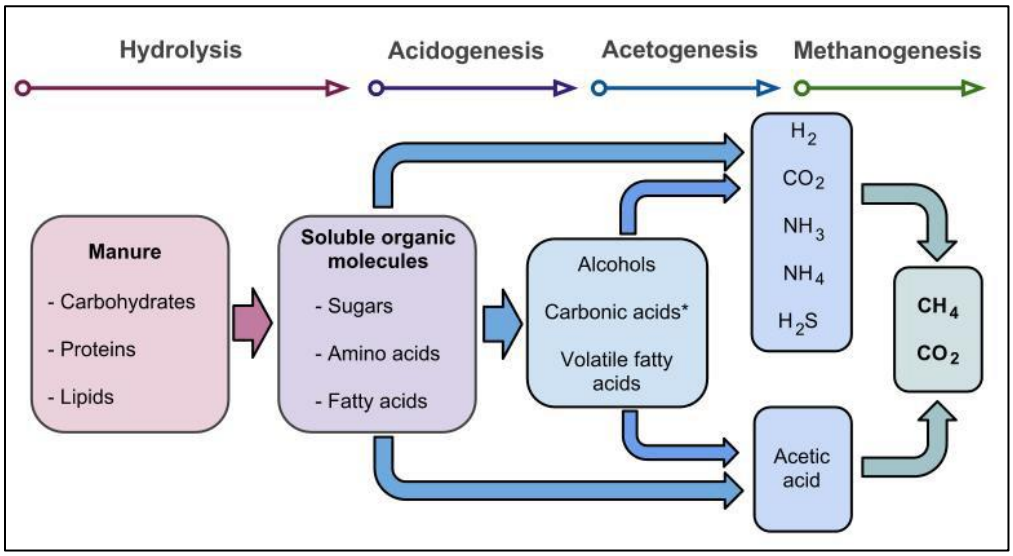

Figure 2: The process of degradation of organic materials in anaerobic digestion (Girard et al., 2013).

Methanogenesis. The result of these four stages is converting the complex organic matter to biogas (methane and carbon dioxide) and the residual of the anaerobic digester feedstock remaining after the digestion, called digestate. Different microorganisms are responsible of each step.

2.1.2.1 Hydrolysis

The first step in the anaerobic digestion is hydrolysis as the complex material in the feedstock such as carbohydrates, lipids and proteins are converted to simpler sugars, fatty acids and amino acids, respectively.

- Conversion of carbohydrates to simpler sugars:

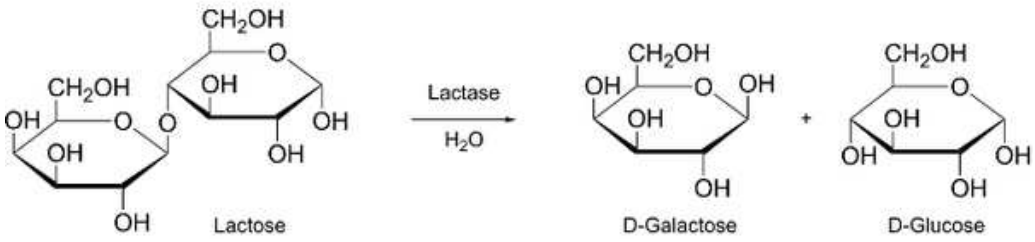

Figure 3: Hydrolysis of lactose into galactose and glucose (PSD, 2019).

- Conversion of lipids to fatty acids:

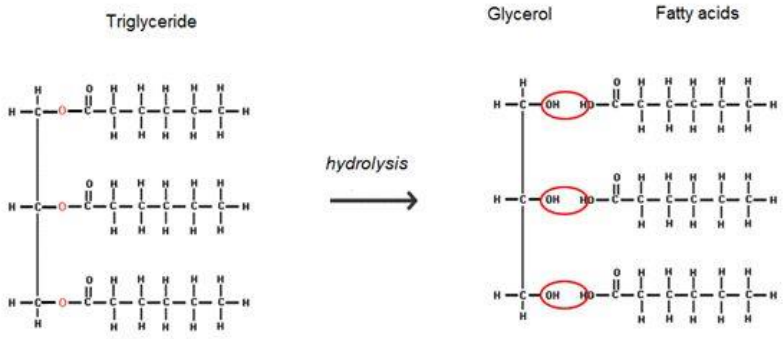

Figure 4: Hydrolysis of a triglyceride into glycerol and fatty acids (Thompson & Thompson, 2018).

- Conversion of proteins to amino acids:

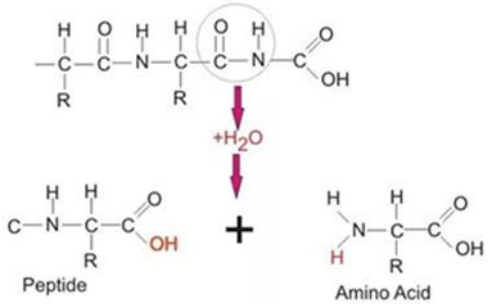

Figure 5: Hydrolysis of proteins into amino acids (Biology Dictionary, 2019).

2.1.2.2 Acidogenesis

In the second step of anaerobic digestion, acidogenesis steps, the products of hydrolysis including simple sugars, fatty acids and amino acids are converted mainly to volatile fatty acids (VFA's) such as acetate by acidogenesis microorganisms. There are also other small compounds that are produce during acidogenesis including hydrogen, carbon dioxide, and ammonia (Rea, 2014).

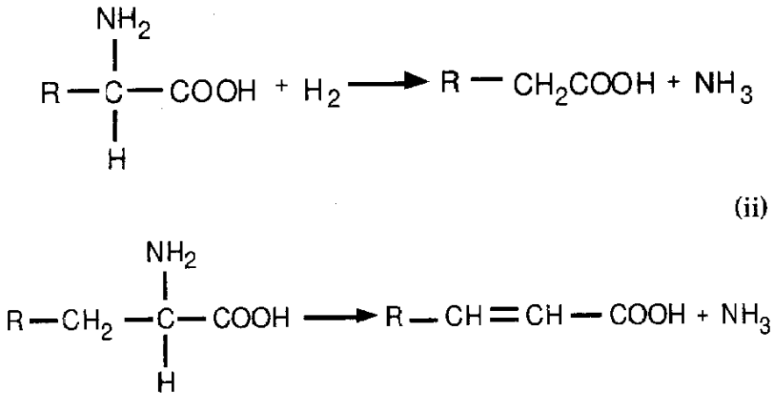

Figure 6: Conversion of amino acid to acetic acid and ammonia (Kayhanian, 1999).

Another reaction from the acid-forming microorganism during the acidogenesis process is the conversion of simple sugar to acid forms. For example, glucose is converted to acetic, butyric or/and propionic as showing in Figure 9 (Mosey, 1983).

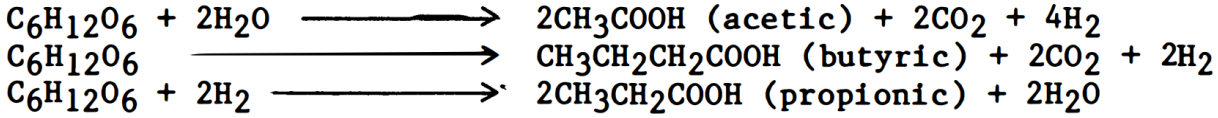

Figure 7: Conversion of glucose into acetic, butyric or/and propionic (Mosey, 1983).

2.1.2.3 Acetogenesis

During Acetogenesis, acetogenic bacteria converts the vitiated fatty such as butyric and propionic acids that are produced during the acidogenesis steps to acetic acid and other byproducts such as hydrogen and carbon dioxide as shown in Figure 10 (Lier et al., 2008; Mosey, 1983)

$$CH_3CH_2COOH\ (propionic) + 2H_2O \longrightarrow CH_3COOH + CO_2 + 3H_3$$
$$CH_3CH_2CH_2COOH\ (butyric) + 2H_2O \longrightarrow 2CH_3COOH + 2H_2$$

Figure 8: Conversion of vitiated fatty to acetic acid and byproducts (Mosey, 1983).

2.1.2.4 Methanogenesis

The final step in anaerobic digestion is methanogenesis where the acetic acids produced during the previous stages of anaerobic digestion are converted into carbon dioxide and methane (biogas) by methanogenic microorganism (Figure 11). This reaction is called acetotrophic methanogens. The second reaction that occurs during this step is the reduction of carbon dioxide by hydrogen to produce methane (Figure 11) which is called hydrogenotrophic methanogens. Considering these two methane-forming reactions, about 70% of the methane comes through acetotrophic methanogens while only 30% resulting from hydrogenotrophic methanogens (Mitchell & Gu, 2010).

Methanogenic
Acetate $CH_3COOH + H_2O \rightarrow CH_4 + CO_2 + H_2O$
$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$

Figure 9: Conversion of acetic acids, carbon dioxide and hydrogen into methane (Mitchell & Gu, 2010).

2.1.3 Air Contamination

Animal manure waste releases greenhouse gasses such as carbon dioxide, methane and nitrous oxide that are important contributors to climate change. Most animal feeding operation air emissions result from the microbial breakdown of manure decomposition by microorganisms (Copeland, 2014). For example, organic nitrogen in manure can convert to ammonia and is then release to the atmosphere. Manure piles also release methane and nitrous oxide which contribute to global warming since they are both considered as greenhouse gases. According to Food and Agriculture Organization of the United Nations, 14.5% of anthropogenic greenhouse gases emissions comes from livestock and most of the livestock emissions are caused by cattle operation including cattle manure (FAO, 2020). Considering only methane, 7% of the global methane emissions are generated from livestock waste (GMI, 2013).

2.2 Anaerobic Digestion and Its Benefits to Reduces Environmental Problems of Animal Waste

Anaerobic digesters have been used to eliminate the environmental impacts of animal wastes by converting the organic waste to more stable and less harmful components to the environment while producing valuable products including methane that can be used as an energy source.

2.2.1 Definition of Anaerobic Digestion

Anaerobic digestion is the decomposition of complex organic materials into simpler forms by microorganisms in the absence of oxygen (Al Seadi et al., 2008). Animal manures, food waste, sewage sludge and industrial organic disposals are common organic material that is degraded by anaerobic digesters (EPA, 2015a). Anaerobic digestion accrues naturally in oxygen-free environment such as in municipal landfills, marshes, sediments of waterbodies and even in stomachs of ruminants (Lier et al., 2008).

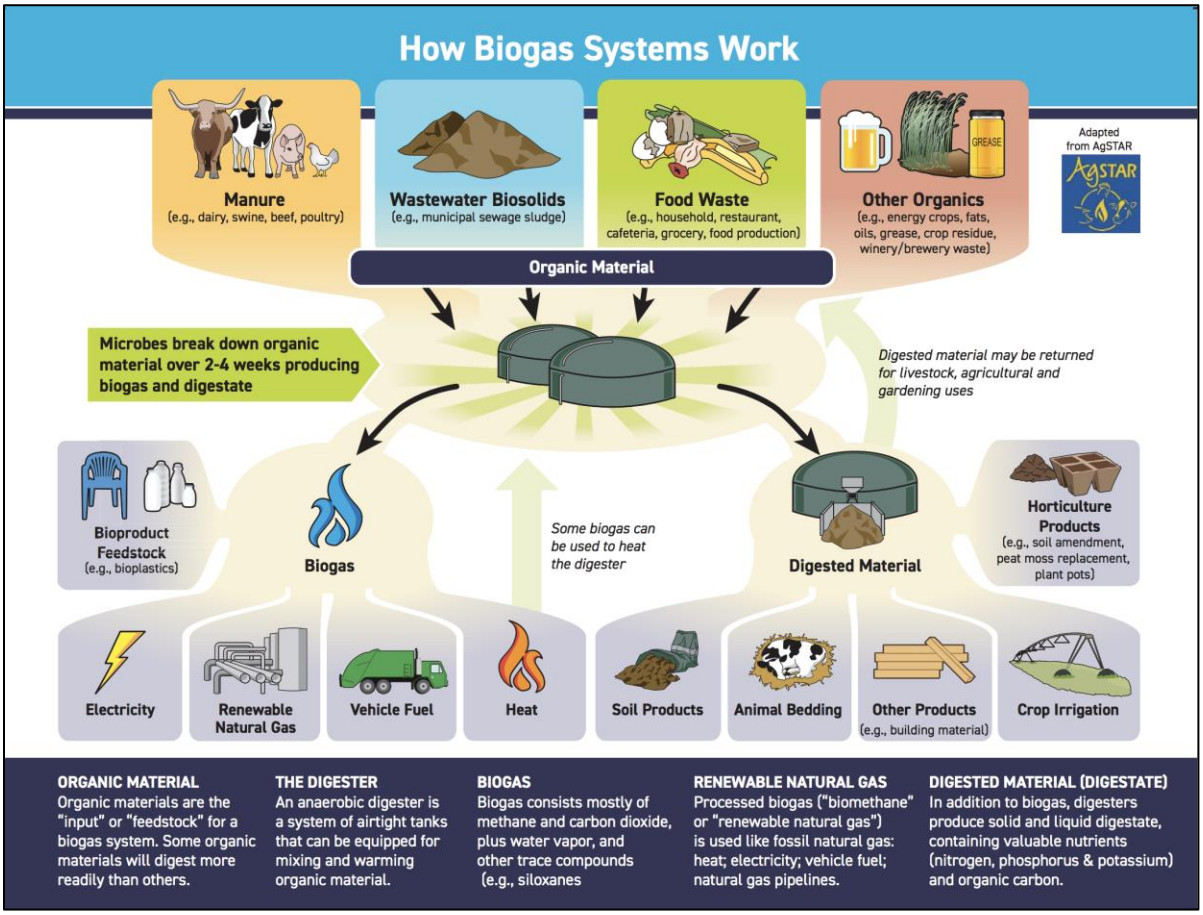

Figure 10: Anaerobic digestion application (American Biogas Council, 2019).

2.2.2 History of Anaerobic Digestion

Anaerobic digestion has been known for centuries but first reported by the Flemish chemist, physiologist and physician Van Helmont in 17th century whereas the first anaerobic digester was built in Bombay, India (Abbasi et al., 2012). By 2017, the International Energy Agency (IEA) has reported more than 14,000 anaerobic digestion plants only for 15 IEA's member countries including Germany with 10,000 anaerobic plants, United Kingdom with 987 and France with 687 anaerobic plants (IEA Bioenergy, 2018). On the other hand, the United States has more than 2,200 anaerobic digestion plants including 250 working on livestock farms, 1,269 at wastewater treatment facilities, 652 on landfill sites and 66 food waste digesters (American Biogas Council, 2019).

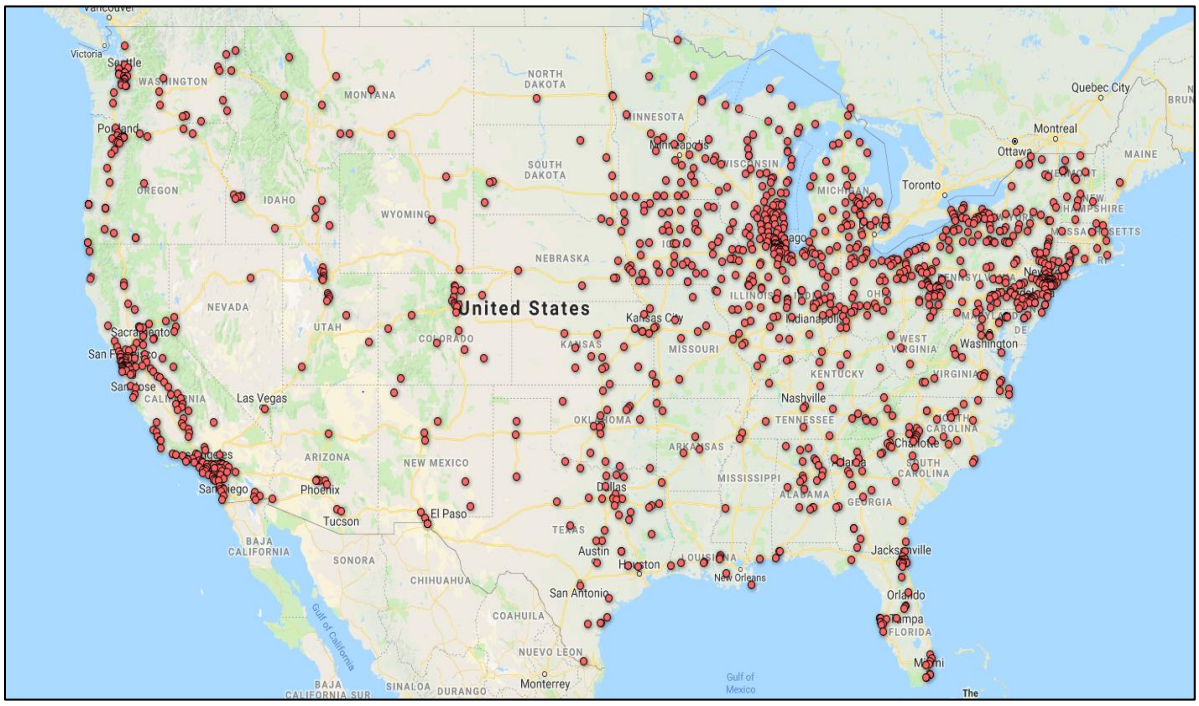

Figure 11: Map of water resource recovery facilities with operating anaerobic digestion (Water Environment Federation, 2015).

2.2.3 Application and Benefits of Anaerobic Digestion

Anaerobic digestion has been used to treat high organic material wastes. The most common anaerobic digestion applications include the treatment of (1) municipal wastewater, (2) industrial wastewater, (3) animal waste (e.g., manure), (4) food scraps (from house holders and businesses) and (5) industrial food processing waste. Based on its application, the benefits of anaerobic digestion can be classified into two types: environmental and financial benefits (EPA, 2006; Wilkie, 2005)

2.2.3.1 Environmental Benefits

Anaerobic digester treats municipal waste, industrial waste, agricultural waste, and animal waste. Anaerobic digestion has mainly five main environmental benefits as a result of the organic waste treatment: (1) reduction of air pollution including reduction of greenhouse gases emission, (2) reduction of pathogens, (3) odor mitigation, (4) improving water quality by water and wastewater treatment and (5) improving nutrients managements by recovering nutrients like nitrogen and phosphorus from organic waste (GMI, 2013; Wilkie, 2005)

Organic material in wastes can be naturally degraded producing greenhouse gases (GHG) including CH_4 and CO_2. Anaerobic digestion reduces GHG emissions by treating organic waste to capture GHG such as methane and nitrous oxide. Anaerobic digestion can also indirectly reduce GHG emissions since anaerobic digestion produces bio-methane reducing the need of fossil fuel which is known with its GHG contributions (Fagerström et al., 2018).

The process of the anaerobic digestion reduces waste pathogens. Anaerobic digestion kills pathogens in organic waste by three methods. The first method is anaerobic digestion system operation temperature because many of pathogens cannot survive the anaerobic digestion system heat. Acids produced during the anaerobic digestion process is the second method that limit pathogens growth. Acids can inhibit pathogens' growth because acids are toxic to many of pathogens. The third method is pathogens starving due to the competition with the anaerobic digestion microorganism. Anaerobic digestion microorganism consume essential growth nutrients such as nitrogen and phosphorus, limiting those nutrients for pathogens (Wilkie, 2005).

Treating organic material existing in wastes such as manure and landfill waste decreases the odor generated from the organic waste. When organic wastes like cattle manure piles are kept untreated, some of the organic components are degraded to volatile acids producing unpleasant odors. However, anaerobic digestion converts the waste mainly to methane and carbon dioxide. Because the gas is captured and used for energy generation, odors are not released. Anaerobic digestion can reduce agricultural waste odors up to 80% (AFBI, 2019). It is claimed that anaerobic digestion has been initially developed in urban area due to its ability to minimize organic waste odors (Wilkie, 2005).

Organic waste treatment by anaerobic digestion can lead to better quality of receiving water. Treatment of waste by anaerobic digestions that include nutrients removal reduces nutrient contamination in waterways. This can decrease eutrophication (algal growth due to excess nutrients availability) in receiving water when treated water is discharged (Fagerström et al., 2018). Moreover, cattle manure and landfill waste

contain nutrients like nitrogen and phosphorus which can leach to the surface water or the ground water causing contamination and eutrophication (EPA, 2004).

Anaerobic digestion improves nutrient management by providing alternative fertilizer. As previously discussed in Section 2.2.3.2, anaerobic digestion converts organic nitrogen to ammonia. The ammonia then can be recovered and used as fertilizer (Costa et al., 2015). Moreover, the digestate of the anaerobic digestion can be used as fertilizer since nutrients are conserved through the process. Digestate is the material remaining after waste degradation. Anaerobic digestion stabilizes the waste by converting organic waste to biogas (methane and carbon dioxide) and digestate. As the biogas can use as an energy source, digestate can be used as a soil amendment containing nutrients. While the original anaerobic digestion feedstock waste contains pathogens, has malodor, and holds volatile acids, anaerobic digestion reduces those issue in the digestate. Moreover, nutrients in digestate can be utilized by plants easier than the nutrients in raw waste, reducing surface and ground water contamination (Fagerström et al., 2018).

2.2.3.2 Financial Benefits

Anaerobic digestion operations have several economic benefits especially for waste treatment facilities that have on-site anaerobic digesters. Anaerobic digestion eliminates cost of transporting organic waste to landfill facilities as well as disposal utility charges once wastes are treated by anaerobic digestion on-site.

Anaerobic digestion is a renewable energy generator producing biogas from organic waste. Biogas is considered one of the most important anaerobic digestion byproducts as it is a sustainable source for electricity and heat. Onsite anaerobic digestion systems can substantially offset operational costs for industries, business and facilities that generate organic waste as recovered energy reduces electricity and heating needs. In industries such as food processing, biogas can be used as heat source for evaporation in distilleries and creameries (Fagerström et al., 2018). In wastewater treatment facilities, biogas can offset part or all of electricity and heat demand. East Bay Municipal Utility District (EBMUD) is an example of water and sewage treatment utility in Oakland, CA, USA that has used anaerobic digestion to produce biogas. In 2012, EBMUD has become the first wastewater treatment facility in North America that produces energy to exceed the demand to operate the treatment process (EPA, 2014). Keske (2009) generated anaerobic digestion enterprise budget models (Table1) to expect annual return for an anaerobic faciality based on proposal submitted to Tri-State Energy, Colorado.

Table 1 Enterprise budget for an anaerobic digestion project in Colorado (Keske, 2009)

	Economic and Production Conditions		
	Poor[a]	Expected[b]	Favorable[c]
Revenue	$1,856,915	$7,851,483	$15,445,432
Costs	-($7,753,023)	-($7,151,278)	-($6,549,533)
Net Income	-($5,896,108)	$700,205	$8,895,899

a: Values expected in Tri-State Digester Proposal

b: Assumes a 20 percent change in the variable, reducing income

d: Assumes a 20 percent change in the variable, increasing income

The models generated by Keske suggests that the expected annual net income for the modeled faciality is 700,205 but could reach to $8,895,899 with assuming 20% increase in the incomes, Table 1. The general outcomes of this model that anaerobic digestion could give a positive net income at its best economic and production conditions.

Anaerobic digestion is a promising sustainable biotechnology to produce fertilizers. Fertilizers are classified into organic and inorganic types based on their production methods and the process feedstock. Organic fertilizers come from organic material sources and are produced biologically whereas inorganic fertilizers come from minerals sources and are produced chemically. Nitrogen, phosphorus, and potassium are the main nutrients that plants need. Although nature is rich with those three elements, plants cannot use nitrogen, phosphorus, and potassium efficiently in the form they exit in nature. For instance, about 78% of the atmospheric air is nitrogen (N_2), yet it needs to be converted to another nitrogen form such as NH_4NO_3 in order to be used by the plants. Ammonia is the original raw material for all ammoniacal fertilizers including ammonium nitrate NH_4NO_3 and ammonium phosphate $(NH_4)_3PO_4$. The most common current technology to produce ammonia is fixation the atmospheric nitrogen by hydrogen as Equations (3 - 4) shows at high temperature (500 °C) and high pressure (200 bar) , known by Haber-Bosch process (Smil, 2001).

$CH_4 + H_2O \rightarrow CO + 3\ H_2$ (Equation 3)

$N_2 + 3\ H_2 \leftrightarrow 2\ NH_3$ (Equation 4)

The Haber-Bosch process requires high energy since the process occurs at 500 °C and 200 bar, and energy requirements create financial burden. Moreover, Haber-Bosch

process cost depends on the natural gas price as it is required in high amount to produce hydrogen (Equations 3 & 4).

Anaerobic digestion eliminates most of the financial limitations of synthetic ammonia productions such as via Haber-Bosch process because it does not require high temperature nor natural gas. Anaerobic digestion can be either operated at mesophilic condition (30 to 35°C) or thermophilic condition (50 to 60°C). Both ranges are significantly lower than what Haber-Bosch process requires, 500°C. Moreover, anaerobic digestion does not require natural gas whereas it produces biogas. In anaerobic digestion, ammonia is naturally produced during the acidogenesis stage as amino acids from raw material protein is converted to acetic acid and ammonia (see Section 2.2.3.2). The produced ammonia can be then captured and converted to more stable fertilizers such as ammonium nitrate as it is one of this project focus study.

Digestate remaining after the organic material has been digested is also a nutrient-rich material that can be used as a fertilizer. Organic waste like animal waste typically contains substantial nutrients including nitrogen, phosphorous and potassium. According to American Society of Agricultural Engineers, typical cattle manure has nitrogen of 25 kg/finished animal, phosphorous 3.3 kg/finished animal and potassium of 17.1 kg/finished animals (ASAE, 2005), meaning the amount of nutrient produced by one animal during finishing period (153 days at the feeding facility). However, those nutrients in anaerobic digestion feedstock are in their organic complex forms, so they do not leach through soils easily and cannot be used by plants root instantly. On the other hand, nutrients in anaerobic digestion digestate are in simple forms such as ammonia which is the preferred form of nitrogen to enhance plant growth. For example, digestate

has nitrogen in the form of ammonia 20% higher than its original feedstock waste (Mitchell & Gu, 2010). Nutrients in anaerobic digestion digestate including nitrogen, phosphorous and potassium has been reported as suitable fertilizers in major agricultural projects such as in wheat production (Sogn et al., 2018) . While valuable products generated during anaerobic digestion can provide financial benefit, there are many challenges to making anaerobic digestion economic (Section 2.3).

2.2.4 Anaerobic Digestion Operational Conditions and Parameters

Anaerobic digestion rate is influenced by its operational conditions and parameters. Gerardi (2003) mentions 9 factors that affect anaerobic digestion system performance: start-up condition, sludge feed, retention times, nutrients, toxicity, mixing, temperature, alkalinity and pH.

Start-up condition includes providing the microorganism (seeding) and substrates to the system. Anaerobic microorganisms are sensitive especially during the start-up and they can die when they expose to air or toxic conditions. Moreover, the start-up conditions are difficult to maintain, so the system should be carefully monitored during start-up to keep the system at the desired operation parameters. As described previously (Section 2.2.3.2), ammonia is produced during acidogenesis. Ammonia production can inhibit the anaerobic digestion process by increasing pH and ammonia toxicity (ammonia toxicity is further explained Section 2.3.2). Therefore, the load of the substrate should be added slowly while maintaining the pH and ammonia concentration in the system to avoid inhibition of the microorganisms via ammonia toxicity.

Mixing in anaerobic digestion improves the system performance since it helps to distribute bacteria, substrate, nutrients and even the temperature. The most common methods used in anaerobic digestion are mixing with gas recirculation and mixing with mechanical mixers.

Toxicity in anaerobic digestion can be caused by waste components or their byproducts generated during anaerobic digestion. An Inhibitory constituent found in waste is iron magnesium, whereas ammonia and hydrogen sulfide are generated during the anaerobic digestion process.

Sludge characteristics and feed rate are other factors that affect the performance of anaerobic digestion. For feed that contains high volatile solids, the methane production can be high, whereas feedstock with high nitrogen or sulfur might cause ammonia or hydrogen sulfide toxicity in the system. Therefore, the suitable feed and feed flow rate should be chosen considering the feed waste characteristics as well.

In anaerobic digesters, retention time can be classified into types: hydraulic retention time (HRT) and solids retention time (SRT). HRT is the average time that organic waste stays in the digester tank which can be calculated by divided the digester tank volume over the flow rate. HRT explains the digestion time of the sludge inside the tank by the microorganisms. It is also an important parameter for the system design including the digester volume. On the other hand, SRT refers to the time that microbes stay in the digester tank. SRT can significantly affect the methanogenesis step and the digester stability. Higher SRT allow more time for the microorganism to digest the solids which can be achieved by increase the digester volume and increase the microorganism concentration.

Temperature of the digester should be maintained at the microorganism optimum temperatures. Most digesters are operated at either mesophilic conditions (30 to 35°C) or thermophilic conditions (50 to 60°C). Methane-forming microorganisms can perform in either ranges, mesophilic condition (30 to 35°C) is preferred by many anaerobic digestion operations because it has lower operational costs, less temperature control issues, and reduced toxicity problems Gerardi (2003).

Like other bacteria, anaerobic digestion microorganisms need substrate or nutrients for growth. Microorganisms obtain the nutrients from the organic feedstock materials. Nitrogen and phosphorus are examples of typical nutrients in anaerobic digesters feedstock. Therefore, the carbon to nitrogen ratio and the carbon to phosphorus ratio in feedstock should not be more than 43 and 187, respectively (Burke P.E, 2001). In addition to nitrogen and phosphorus, microbes need smaller nutrients such as cobalt, iron, nickel, and sulfide as microbes used them during the methanogenesis process.

Alkalinity and pH are important related parameters in anaerobic digestion systems. Alkalinity is the solution buffering capacity that prevents pH change due acid addition. The pH in the system might change during the process due to the biodegradation products and byproducts (see Section 2.2.3). For instance, the production of the carbon dioxide during acidogenesis, acetogenesis and methanogenesis (Section 2.2.3) causes a pH decrease as it reacts with water and produces carbonic acid. On the other hand, ammonia production increases the pH as it is reduced to ammonium as shown in Figure 8. Therefore, it is important to maintain the anaerobic digester at the microorganisms' optimum growth pH. Although different anaerobic microbes have different optimum growth pH, a range of 6.8 to 8 is suitable for most anaerobic digestion microorganisms

(Gerardi, 2003). For example, the optimum growth pH for *Methanosphaera* is 6.8 whereas it is 7.8 for *Methanothrix* (Gerardi, 2003).

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$$

$$NH_3 + H^+ \leftrightarrow NH_4^+$$

Figure 12: The production of carbon dioxide and ammonium during anaerobic digestion degradation that causes pH distribution (Gerardi, 2003).

2.2.5 Most Common Anaerobic Digester Technologies

There are several types of anaerobic digester reach configuration that are used including wastewater treatment facilities, landfill sites, animal feeding operations and food waste treatment. The most common anaerobic digesters types are covered lagoon, completely mixed reactor, plug flow reactor and fixed film reactors.

Covered lagoon digesters are ponds in the ground that are covered to prevent air exposure. Covered lagoons are usually not heated but they depend on the grounds heat. Therefore, they are only suitable in warm places. The overall performance of covered lagoons are low but the operational cost is low as well since they do not required energy for heating (Burke P.E, 2001).

Completely mixed reactors are basically reactor tanks with types of mixing such as stirring impellers. Completely mixed reactors are usually heated systems and commonly operated at mesophilic conditions. This kind of digester is commonly used in wastewater treatment as well as in industrial waste treatment (Burke P.E, 2001).

Plug flow digesters are commonly used in farm feedstock because they are simple and inexpensive (Burke P.E, 2001). A plug flow digester is cylindrical reactor where digestion starts as the feedstock enters from one end of the reactor till it exits from the other side. A plug flow digester is a heated reactor, but its heating system can be as simple as double pipe exchanger where the plug flow digester is jacketed with hot water pipe.

A fixed film anaerobic digester is a continuous reactor tank filled with packing medium. The medium inside the reactor aims to hold the microorganism inside the reactor as they attach on the packing media surface. Consequently, medium enhances the bacterial growth, reduces its washout and increases the retention time (Wilkie, 2000). Since fixed film diesters provide high contact between treated waste and bacteria, it is not only suitable for dairy waste treatment (Wilkie, 2000) but also for airplane deicing fluid, contaminated groundwater and industrial wastewaters (Gerardi, 2003).

2.2.6 Single-stage and Multi-stage Anaerobic Digestion

Anaerobic digestion system can be farther classified into single-stage anaerobic digestion and multi-stage anaerobic digestion. In single-stage units, the four of anaerobic bioreactions (hydrolysis, acidogenesis, acetogenesis and methanogenesis) physically happen in one digester. One the other hand, multi-Stage anaerobic digestion requires two separated reactors and that is why it is also called “two-stage” anaerobic digestion. The first stage is where most of hydrolysis and acidogenesis reactions take place whereas the second stage is primarily for acetogenesis and methanogenesis.

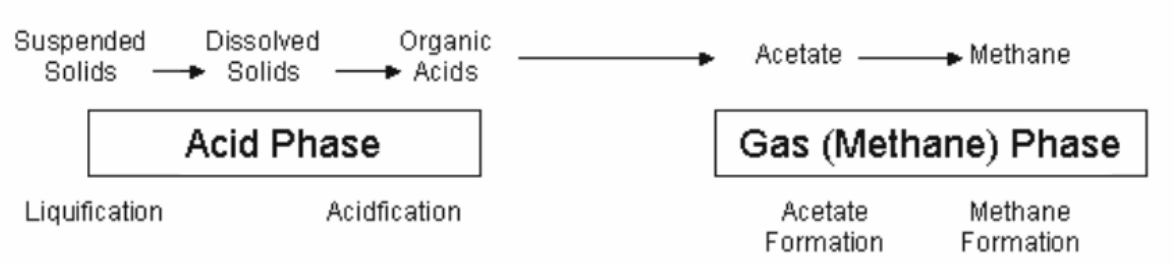

Figure 13: The main two steps of degradation in multi-stage anaerobic digestion (EPA, 2006).

The main goals of the multi-stage anaerobic digestion is to separate the acid-forming digester from the methane-forming digester as this helps stabilizing the methanogenesis step because the first step is disturbed by the process loading, feed heterogeneity and acid toxicity (Mitchell & Gu, 2010). Another advantage that multi-stage anaerobic digestion has is that it allows better process control over each stage, so it can be operated at its optimum operation conditions (EPA, 2006). Therefore, multi-stage anaerobic digestion has better performance than single-stage anaerobic digestion whereas it requires higher installation and maintenance cost (EPA, 2006; Mitchell & Gu, 2010)

2.3 Challenges in Anaerobic Digestion

Despite the benefits that anaerobic digestion provides, it has a couple of severe challenges and barriers. Its main challenges can be classified into financial challenges and operational complexity.

2.3.1 Financial Challenges

As mention previously, the primary use of anaerobic digestion is treatment of waste since the anaerobic digestion process stabilizes organic waste reducing its environmental impacts including the reduction of GHG emissions, malodor and pathogens. Like many other sustainable projects, the economic feasibility of the process is a main challenge. Considering the first financial challenge, the capital cost depends on the capacity and the process design of the anaerobic digestion system. An on-farm anaerobic digestion capital cost can be as low as $500,000 (Butler Farms LLC, NC) or it can be as high as $12 million (Fair Oaks Dairy, Indiana) (EPA, 2012b). On the other hand, a centralized anaerobic digestion facility has higher capital cost than on-farm ones. For example, Eco-park Barcelona Waste Management Facility in Spain has built a anaerobic digestion facility with capital cost of $130.2 million (Arsova, 2010). Cedar Grove Composting in Washington, USA is with capacity of 280,000 tons/year has a capital cost of $87 million (Moriarty, 2013). An anaerobic digestion plant that is designed for biogas generation has a capital costs between $3,700/kWh and $7,000/kWh (Government of Alberta, 2008).

In addition to the capital cost, anaerobic digestion facilities require operation and maintenance costs including labor and maintenance. Anaerobic digestion operates at higher temperature than the room temperature, so it can require energy to heat the system (particularly is colder climate regions) which adds to the operation cost. Although biogas produced form the anaerobic digestion system can be utilized to produce energy, anaerobic digestion electricity production cost is higher than average US electricity retail cost (USDA, 2007).Therefore, several of anaerobic digestion

feasibility study such as Feasibility Study of Anaerobic Digestion of Food Waste in St. Bernard, Louisiana (Moriarty, 2013) concludes infeasibility due to the high capital cost of anaerobic digestion (Moriarty, 2013).

2.3.2 Operation and Technology Challenge (Ammonia Toxicity)

Anaerobic digestion microorganisms are classified into acetate-forming and methane-forming microorganisms. Each group of microorganisms has different favorable growth environmental conditions (such as temperature and pH) and those conditions need to be maintained to sustain microbial growth and maintain a successful anaerobic digestion system (Fagbohungbe et al., 2017). Maintaining ideal anaerobic digestion conditions is a major challenge in anaerobic digestion because the process byproducts and intermediate products distribute the system varying its favorable condition. Considering the system pH as an example, the pH in the system decreases as some organic components are converted to volatile acids during the acidogenesis step.

Another example of an anaerobic digestion byproduct that can cause system instability and even toxicity is ammonia. Ammonia is produced during the acidogenesis step (as explained earlier in anaerobic digestion degradation stages) as amino acid is converted to acetic acid and ammonia. Although nitrogen is an essential nutrient for anaerobic digestion microorganisms (Kayhanian & Rich, 1995), ammoniacal forms of nitrogen can be fatal to the anaerobic digestion microorganisms when it exceed its toxic level (Chen et al., 2008). The ammonia toxicity has been a main challenge in high nitrogenous anaerobic digestion system (Chen et al., 2008; Hansen et al., 1998; Nakakubo et al.,

2008). Ammoniacal nitrogen exists as two forms in anaerobic digestion sludge which are ammonia and ammonium. They exist in equilibrium in an aqueous solution (Equation 5).

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ (Equation 5)

Both forms are harmful to the anaerobic digestion microorganism, but ammonia has been reported as more toxic form than ammonium due to its ability to pass through the cell membrane (Chen et al., 2008).

The issue of ammonia toxicity is more likely to occur in anaerobic digestion systems that allow the liquid digestate to recirculate through the system (Wilson et al., 2013). It is very common that the ammonia concentration reaches the toxicity level when liquid digestate which contain the ammonia is recirculated because it carries more ammonia from the digested organic waste as it recirculates. For example, consider the MSAD system (Figure 15) where the liquid digestate recalculates between the hydrolysis reactor and the methanogenesis reactor. The same liquid digestate stays at the system for a long time where it gets more concentrated with time including the ammonia concentration. Moreover, the increase of the ammonia in the system leads to increase the system pH which convert the ammoniacal nitrogen to its more harmful form, free ammonia.

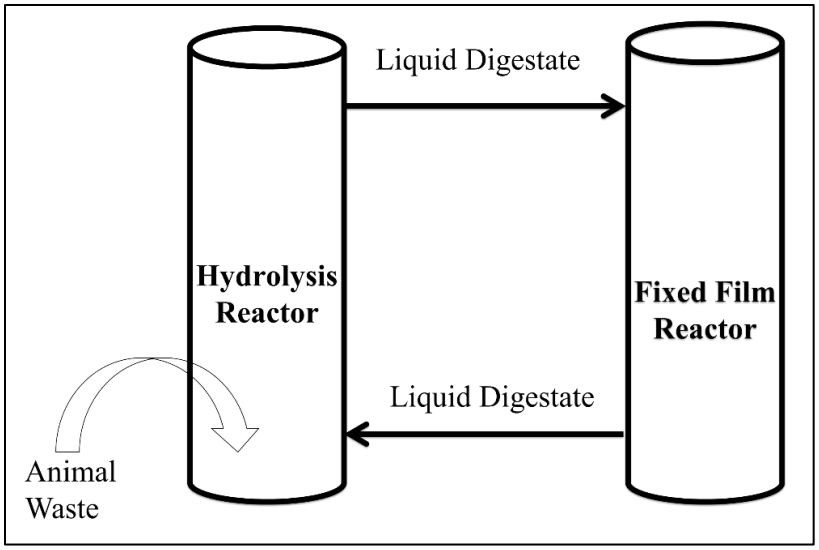

Figure 14: Simplified schematic diagram shows the liquid digestate recirculation in MSAD.

Hansen et al. (1998) have examined the specific growth of the anaerobic digestion microorganisms and found that it decreases as the concentration of free ammonia increase. Moreover, Nakakubo et al (2008) has studied the effect of both ammonium and free ammonia in the methane-forming step and found that both of ammonium and free ammonia decrease the methane generation when they exceed their inhibition limits as shown in Figure 15. Angelidaki and Ahring (1994) found that the free ammonia methane-inhibition in anaerobic digestion starts at 0.7 NH3–N g/L on thermophilic condition. Similarly, Gallert and Winter (Gallert & Winter, 1997) has reported a 50% of methane-inhibition when the free ammonia reaches 0.68-0.69 g-NH_3 /Ll

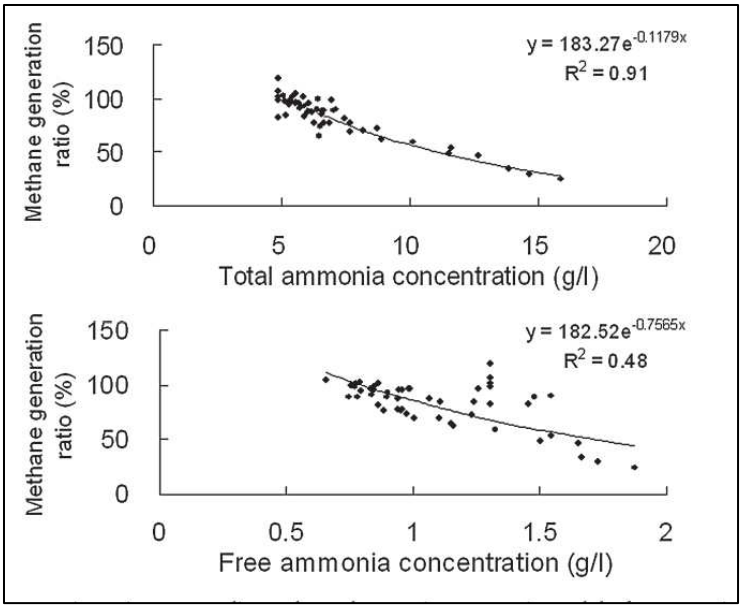

Figure 15: Methane generation inhibition due to total ammonia concentration and free ammonia concentration (Nakakubo et al., 2008).

2.4 Traditional Methods for Ammonia Removal and Recovery in Organic Waste Treatment

Recovering ammonia during organic waste treatments reduces its toxicity to the treatment process and sustainably produces a valuable fertilizer product. Therefore, recovery of ammonia form organic waste has been an important interesting study area. However, finding suitable ammonia recovery methods has been a challenge in process operational and economic feasibility. Several technologies have been used to recover ammonia from organic waste, including membrane technology, chemical precipitation and stripping (Ozturk et al., 2003). Stripping ammonia with air is one of the most common approaches ammonia removal from organic waste slurry and leachates. Ozturk (2003) have studied the performance and economic of those three methods of

ammonia recovery and found that ammonia stripping has the lowest total operational cost with 85% ammonia removal (Table 2).

Table 2: Removal efficiency and operational cost for different methods of ammonia removal, adopted from (Ozturk et al., 2003).

Ammonia removal methods	Removal efficiency %	Total operating cost ($/m^3)
Membrane (UF + RO, SW)	72	0.8
Struvite precipitation	90	4.45
Air stripping	85	0.52

However, ammonia stripping needs an additional process to recover the ammonia from the effluent gas. The traditional methods to recovery the ammonia after ammonia stripping process is to absorb ammonia gas with an acid (Figure 16) such as hydrochloric and sulfuric acid (Bonmatí & Flotats, 2003; Jiang et al., 2014; Khakharia et al., 2014).

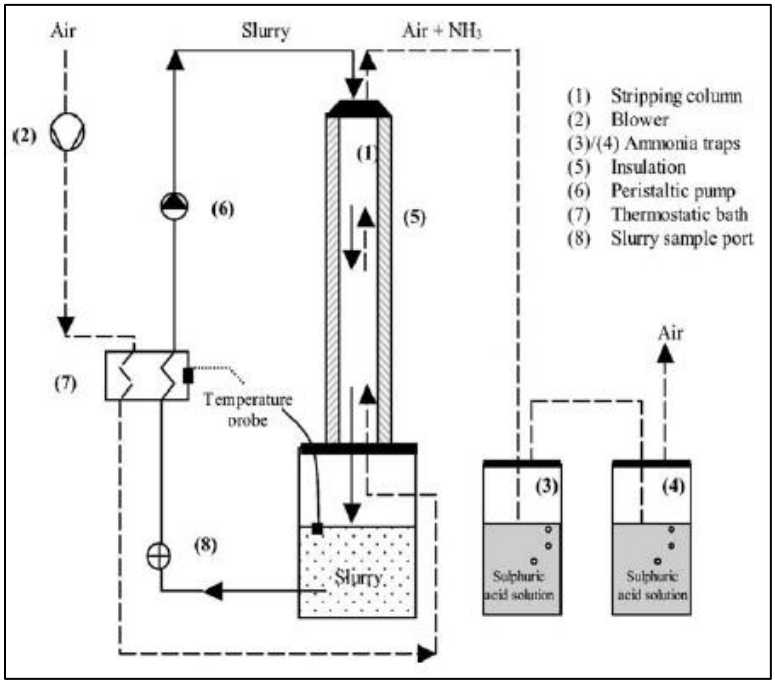

Figure 16 : An example of the traditional method to recovery ammonia through ammonia stripping with air and ammonia absorption with acid (Bonmatí & Flotats, 2003).

However, using acids to absorb ammonia increases the process cost and decreases the process economic feasibility. Considering the process cost, the acids used to absorb ammonia are more expensive than the recovered ammonia (Moore, 2016) which makes absorption of ammonia with acids, economically, infeasible. Therefore, one of the main goals of this project is to evaluate the performance of nitrified solution to substate acid in ammonia absorption in order to eliminate the need of acid which reduces the process cost. More detail about the absorption ammonia through nitrification is provided in the next section.

2.5 Nitrification

Nitrification is the process of ammonia oxidation to nitrite and nitrate by microorganism. The nitrification occurs in two steps:

Ammonia oxidization to nitrite ($NH_3 + O_2 \rightarrow NO_2^- + 3H^+ + 2e^-$).

Nitrite oxidization to nitrate ($NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^-$).

Nitrification occurs naturally in the environment during the nitrogen cycle as shown in Figure 17. Nitrogen cycle is a biological and chemical set of reaction where nitrogen is converted in different form in the environment.

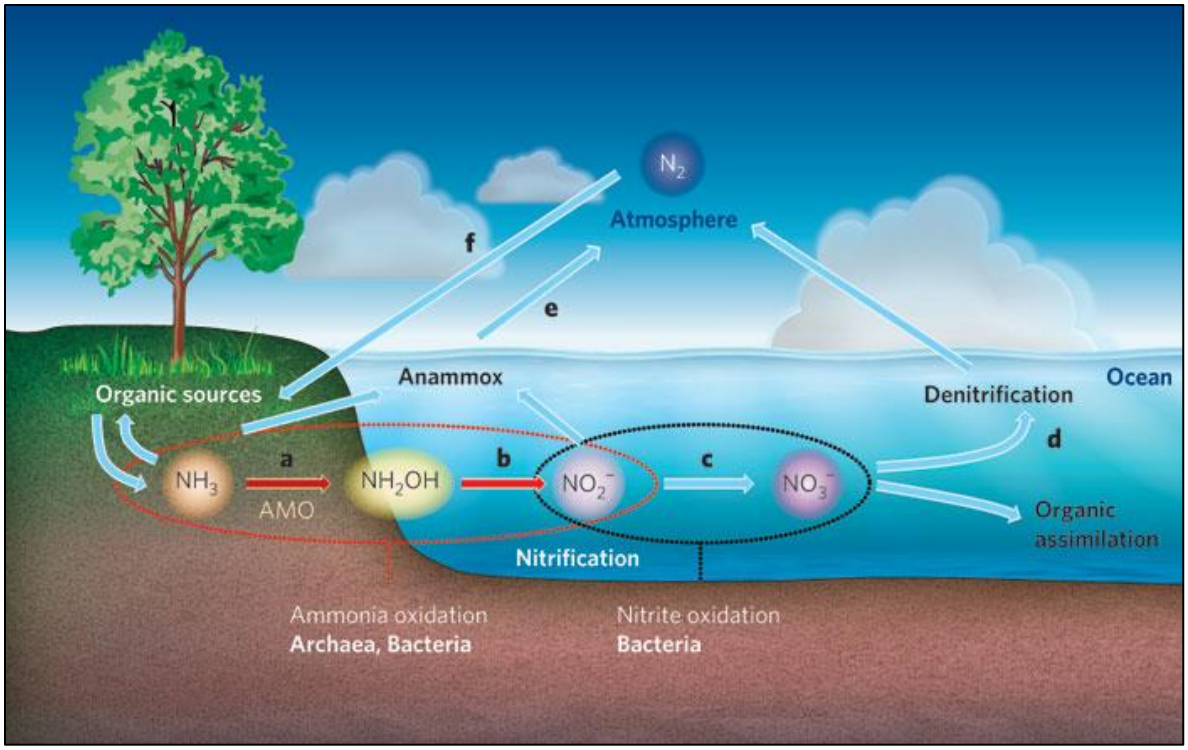

Figure 17: Nitrification during the nitrogen cycle (EBS, 2010).

Also, one of the most common current application of nitrification is the removal of ammonia from maniple wastewater in wastewater treatment facilities. The removal of ammonia in most municipal wastewater treatment plants is a combination of nitrification and denitrification where ammonia is first oxidized to nitrate in a nitrification process which is then reduced to nitrogen gas and realized to atmosphere in denitrification process (Figure 18)

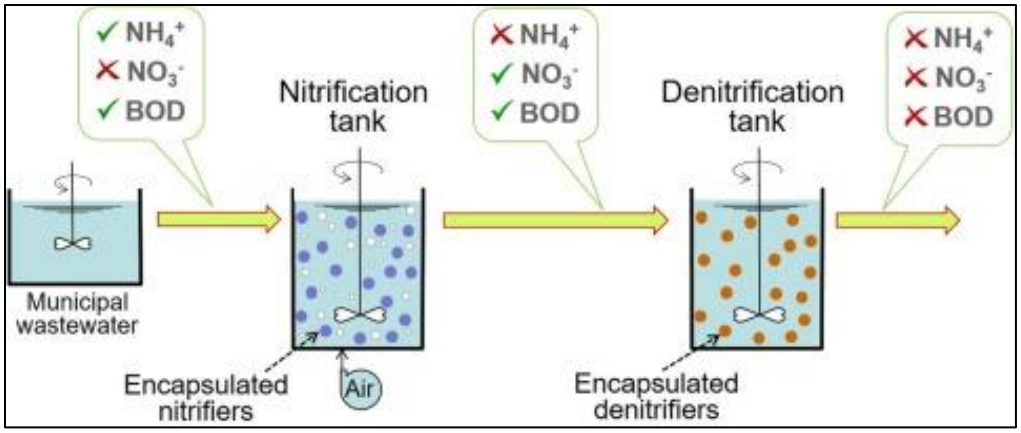

Figure 18: Nitrification and denitrification process in municipal wastewater treatment (Farazaki & Gikas, 2019).

The process of nitrification includes ammonia oxidation to nitrite, and nitrite oxidation to nitrate. Each conversion step requires a separate category of chemoautotrophic microbes, ammonia-oxidizing bacteria (AOB), and nitrite-oxidizing bacteria (NOB). In the first step, ammonia oxidation generates acidity through the production of hydronium ions. This acid is the critical aspect that enables continual ammonia absorption in this proposed nitrogen recovery process. As the final goal of this process is to develop a cost-effective technology to recover and recycle the nitrogen in an anaerobic digester, the cost is a primary driver for process operations. The act of nitrifying each unit of ammonia is costly, both through energy expended to aerate the reactor and capital costs related to tank volume. Therefore, an objective of the nitrification process is to nitrify ammonia the minimum amount needed to neutralize the pH of the ammonia addition and enable continuous process operations. Unpublished observations of this process in our laboratory indicate that a 1:1 ratio of NH_4-N: NO_3-N is achieved in a partially nitrified reactor fed ammonia hydroxide and a pH neutral nutrient feed solution.

This ratio is impacted by pH and buffering capacity of the nutrient solution, as well as the pH setpoint of the nitrification reactor.

Over-oxidation of the added ammonia not only results in generation of a more costly product, but it also results in a reduction of process pH that inhibits the nitrification process performance. As pH levels drop below 6.5, oxidation rates begin to fall for both AOB and NOB organisms (Hellinga et al., 1999). The nitrite oxidation rate though is generally impacted to a greater degree than the ammonia oxidation rate (Hellinga et al., 1999), resulting in an accumulation of nitrite within the reactor. As elevated nitrite concentrations are particularly inhibitory to NOB (Hellinga et al., 1999), this can result in a failure of the two-step nitrification process.

2.6 Summary

The current serious environmental problems such as global warming and water contaminations have been linked to poor animal waste management. Anaerobic digestion is sustainable system that has been used for animal waste treatment to reduce its environmental impact. However, anaerobic digestion has a high capital cost and low byproduct (biogas) price. Moreover, the treatment of animal waste release ammonia in the anaerobic digestion which is toxic to the process. Therefore, this project introduces integrated anerobic digestion system in order to improve the current anaerobic digestion system. The integrated anaerobic digestion process includes a nitrogen recovery system where nitrogen is stripped form the anaerobic digestate and then absorbed with nitrified solution. The traditional method to absorb ammonia is to use acid as an ammonia absorbent (Bonmatí & Flotats, 2003) but this is an expensive

process (Moore, 2016). On the other hand, this project used nitrified solution as ammonia absorption in order to reduce the nitrogen recovery process.

3 Materials and Methods

3.1 Overall Scope

This project has two experimental units: (1) stripping unit and (2) absorption unit. A set of experiments were conducted for each unit separately. Ammonia stripping unit experiments were done first and then the unit setup was modified to be used for the absorption unit. Also, some of the absorption unit operational parameters (such as the ammonia concentration in gas) were chosen based on the stripping unit results since the ultimate goal is to analyze the two units connected as one system. Those two units have the same main constructional items including the jacket column, packings, heat control system (water bath) and pumps (Section 3.2 and 3.3). The material and methods for each unit are presented below separately unless they have the same material and methods.

3.2 Ammonia Stripping Unit Experimental Setup

A laboratory-scale ammonia stripping unit was designed (Figure 19). The stripping unit consisted of a jacketed packed column (stripper; described in Section 3.4) and water bath. The column temperature was controlled with the water jacket. The water bath was used for two purposes. The first one was to control the temperature of the water jacket in the column as the water from the bath was pumped through the water jacket and then recycled back to the water bath. The second purpose of the water bath was to maintain the leachate feed stock at the desired feed temperature as the leachate feed stock was kept into the water bath. A peristaltic pump (Master Flex L/S Cole -Parmer) was used to pump leachate from the leachate feed stock bottle placed in the water bath into the

column. The leachate enters the column from the top and then leaves from the bottom of the column where it passes through a sample port just after leaving the column and before accumulating in a closed tank. One the other hand, the gas enters the column at the bottom, goes through the column and then leaves the column at the top to a fume hood/snorkel. A gas regulator and a rotameter were used to regulate and measure the gas flow entering the column. Air was used as gas supply for all the stripping unit experiments.

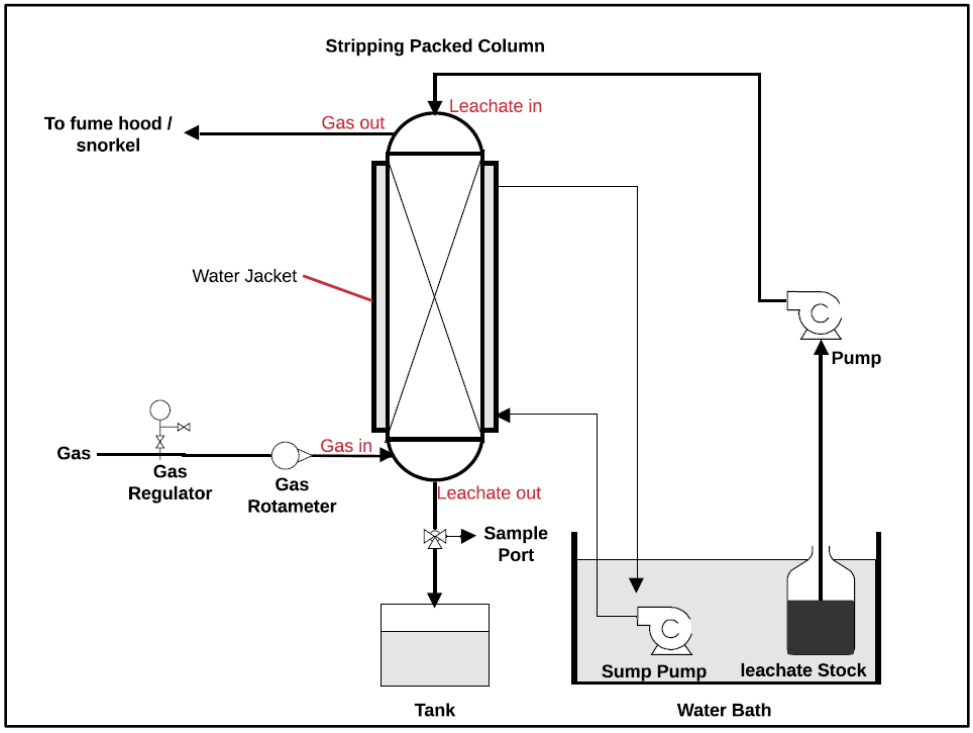

Figure 19: Schematic diagram of the stripping unit experimental setup.

3.3 Ammonia Absorption Unit Experimental Setup

The ammonia stripping unit experimental setup was modified to be used in the ammonia absorption unit (Figure 20). The two experiments had the same main components including the jacket column (described in Section 3.4), the packings, the water bath and

the pumps. The main difference between the two setups was the gas supply. Ammonia gas was used in the ammonia absorption unit experiment whereas it was just air in the stripping unit. More details about the ammonia gas are provided in Section 3.11.

The gas flow initiates from an ammonia gas cylinder and goes through a gas regulator and a gas rotameter in order to adjust to the desired flow rate before entering the absorption column from the bottom and leaving the column from the top to a snorkel fume hood. One the other hand, the liquid starts from the liquid stock bottle which was preadjusted to the desired temperature and placed in a water bath to maintain it at the desired temperature. The liquid is pumped with a peristaltic pump (Master Flex L/S Cole -Parmer) to the top of the column and then leaves from the bottom of the column as it passes through a sampling port. The column temperature was controlled by recycling the water from the water bath through the column jacket.

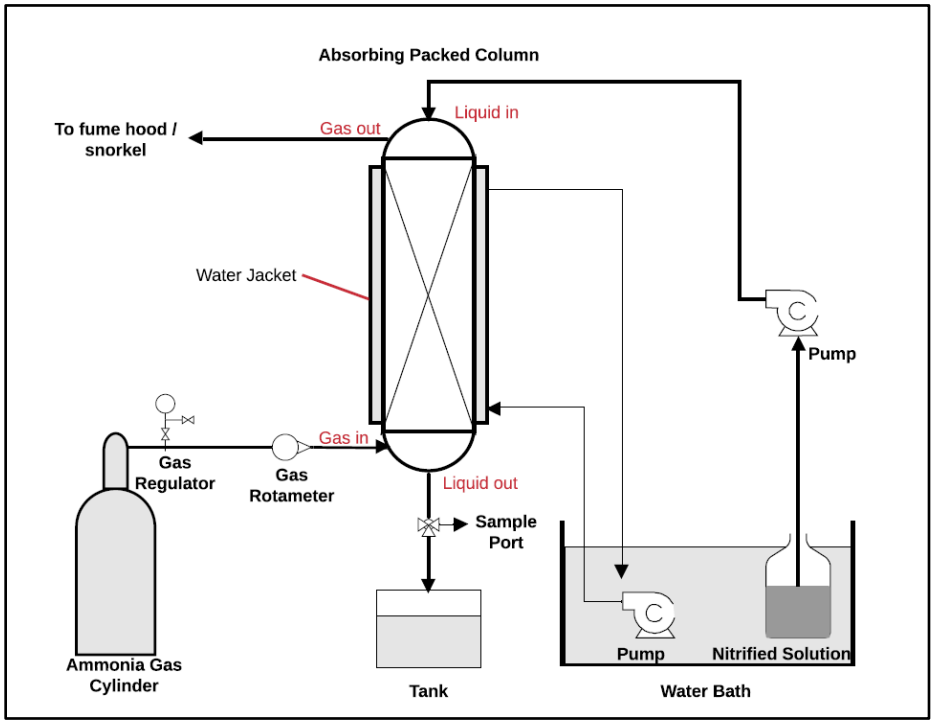

Figure 20: Schematic diagram of the absorbing unit experimental setup.

3.4 The Jacketed Column

The jacketed column was used in both the stripping and the absorption units. The jacket was an annulus pipe surrounding the main column isolating it from the room temperature and keeping it at the desired temperature. The jacket had inlet and exit ports which allowed the heated water from the water bath to be recycled through the jacked. The column was obtained from Ace Glass Inc. (P.O. Box 688 1430 Northwest Blvd. Vineland, NJ 08360 USA; product number 5821-28). and was made of glass with a height of 600mm (2 ft) and internal diameter of 25mm.

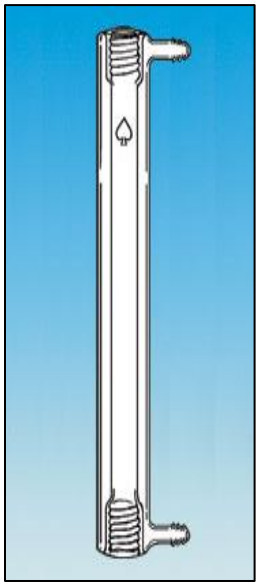

Figure 21: Schematic for the jacketed column (Ace Glass, 2019).

3.5 Packing

The jacketed column was packed with synthetic packing material with the purpose of increasing the gas-liquid interfacial area. Spiral Prismatic packing was used in both of stripping and absorption unit experiments. It was obtained from StillForYou, Wołomin, Poland (Figure 22). It is a laboratory-sized packing (Table 3).

Figure 22: Spiral Prismatic packing (StillForYou, 2019).

Table 3: Characteristics of the Spiral Prismatic packing (StillForYou, 2019).

Material	acid-resistant stainless steel AISI 304
Specific weight	880000 g/m^3
Dimensions	4.4 x 5.5 x 0.24 [mm]
Specific surface area (a)	19000 [m^2/m^3]
Porosity “free volume” (ε)	0.89
Packing factor (F_P= a/ ε^3)	26951.54 [m^2/m^3]
Maximum heat load	115 W/cm^2

To prevent poor liquid distortion and liquid channeling in the liquid, nominal packing size should be less than 1/8 of the column diameter (Seader et al., 2016). The packing diameter of the packing used in this project is 4.4 mm and the inner diameter of the column is 25mm making the ration to the packing diameter to the column diameter about 1/6.

3.6 Sampling

In both the stripping and absorption units, liquid was sampled at two points. The first sample was withdrawn from the liquid stock bottle (Figure 19 & 20) at the beginning of the experiment which represents the column liquid feed stream (influent). The sample was directly withdrawn from liquid stock bottle with a pipette and kept in capped glass vials. The second sample point was taken just after the liquid leaves the column which represented the bottom stream (effluent). The effluent sample was obtained from the sample port at the effluent stream right after the liquid exits the column at the bottom. The sample port was purged by withdrawing some liquid and disposing it before taking the actual sample to ensure obtaining fresh sample. Then, the actual sample was withdrawn into a glass vial. The vials were capped, and analysis of water quality was initiated within two hours.

3.7 Liquid Hold up

Liquid hold up is the amount of the liquid trapped in the column at a specific operational condition. Although packed columns usually run at steady state with constant inlet and outlet liquid flow rate, some of the liquid is trapped in the column due to the gas and packing material resistance. The volume of liquid trapped inside the column is defined as the liquid hold up. It is also commonly reported as the specific liquid hold up (L_H) which is the volume of liquid hold up (V_L) over the volume of column (V_c) and has unit of volume over volume, e.g. m3/m3.

Therefore, the specific liquid hold up can be calculated by

$$L_H = \frac{V_L}{V_C} \quad \text{(Equation 6)}$$

Where: (L_H) is specific liquid hold up, (V_L) liquid volume, (V_C) column volume

Tap water was used as the column liquid feed while air was used as the column gas feed for the liquid hold up experiment. This experiment was done at 50°C because it was the desired stripping temperature. It was done using the same jacketed packed column filled with Spiral Prismatic packing (the column and packing are described Sections 3.4 and 3.5, respectively).

The objective of this experiment was to measure the liquid hold up at several gas and liquid flow rates. Therefore, the gas and liquid flow rates were set at the desired flow rates and then the system was allowed to stabilize for 10 minutes. Then, both the gas and liquid flow rates were rapidly cut. Immediately, the liquid draining from the bottom of the column was collected with graduated cylinder.

3.8 Pressure Drop

A manometer was used to measure the pressure drop in the column. A basic manometer was made with clear polyvinyl chloride (PVC) tube with internal diameter (ID) of 1/4 ″ filled with tap water at room temperature. The manometer was installed at the gas inlet after the gas regulator and the rotameter, just before where the gas enters the column. The gas outlet was at atmospheric pressure, so there was not a need to measure it. Therefore, the pressure drop was just what the manometer read at the gas inlet, Figure 23.

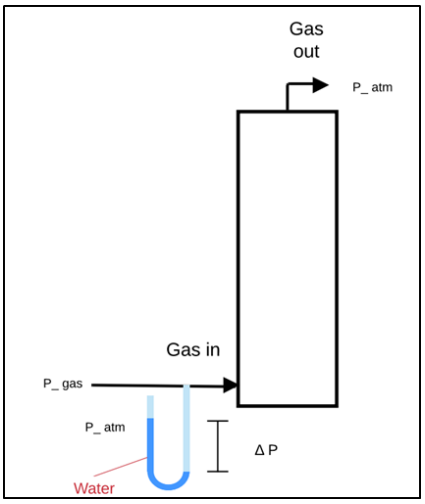

Figure 23: Simplified schematic diagrams of pressure drop experimental set up.

3.9 Stripping Unit Leachate

3.9.1 Anaerobic Digestion Raw Leachate Source, Transportation and Storage

The raw leachate for the stripping unit in this experiment was anaerobically digested cattle manure that was obtained from an anaerobic digestion pilot laboratory at the Foothills Campus, Colorado State University (CSU), Fort Collins, Colorado 80521 USA. The Foothills Campus anaerobic digestion system is a multi-stage anaerobic digestion (MSAD) system where the methanogenesis stage is separated from the other anaerobic digestion stages in a fixed film reactor (FFR; (Loetscher, 2017)). The raw leachate for the stripper was withdrawn directly from the FFR into 5-gallon plastic bottles (Figure 24). The bottles then were immediately transported to the CSU main campus and refrigerated at 4 °C.

Figure 24: Raw anaerobic digestion leachate during transport to the main campus.

3.9.2 Anaerobic Digestion Raw Leachate Characteristic

The main and commonly reported characteristics of the raw leachate which were also believed to influence experiment results were measured and reported in Table 4. Measured parameters include alkalinity, pH, conductivity, chemical oxygen demand (COD), and different forms of nitrogen including total nitrogen, total Kjeldahl nitrogen, ammonia nitrogen and organic nitrogen.

Table 4: Characteristic of raw anaerobic digestion leachate

Constituent	Unit	Value ± SD
Alkalinity	[mg/L as $CaCO_3$]	7380 ± 28
COD	[mg COD/ L]	7415 ± 261
pH	----	7.9
Conductivity	[µS/cm]	21100
NH_3-N	[mg/L]	632 ± 7.7
Total N	[mg/L]	1025 ± 7.1
TKN	[mg/L]	934
ON*	[mg/L]	301 ± 7.7
NO^-_3-N + NO^-_2-N	[mg/L]	91 ± 7.1

* ON: Organic Nitrogen

3.9.3 Anaerobic Digestion Leachate Stock Preparation and Modification

Some of the properties of the leachate stock used in the stripping experiment were modified based on the experiment goals. The ammonia concentration, pH and temperature of the leachate were adjusted before using the leachate in the stripping experiments. The ammonia concentration of the raw leachate was increased with ammonium sulfate to the desired influent ammonia concentration (see Section 4.1). The pH was adjusted using sodium hydroxide. The modified leachate then was heated to the desired temperature (see Section 4.1) with a hot plate. After the leachate met the desired properties of the ammonia concentration, pH and the temperature, it was placed into the water bath at the experiment station to maintain its temperature and used immediately.

3.9.4 Synthetic Leachate Preparation

One of experimental objectives is to compare the ammonia stripping behavior in anaerobic digestion leachate with a prepared simple leachate solution which is called here synthetic leachate. Synthetic leachate was prepared by adding an ammonia source as ammonium sulfate to deionized water. Then the pH of synthetic leachate was adjusted with sodium hydroxide to the desired pH. The temperature of synthetic leachate was increased to the desired temperature with a hot plate and then placed into the water bath at the experiment station before being used.

3.10 Absorption Unit Nitrified Solution

The absorbent used in this unit was a synthetic nitrification nutrient solution. The nitrification nutrient solution was prepared to represent a nitrified industrial wastewater with high ammonia concentration. The synthetic nutrients added for the nitrified solution including the trace solution elements was adapted from Ruiz, Jeison, and Chamy (2003) with some modifications to fit this project process (Table 5). The nutrients were added at concentrations to support nitrification organism growth based on ammonia nitrogen additions.

Table 5: Nitrification nutrient solution used as absorbent in the absorption unit, without the addition of ammonia nitrate, adopted form (Ruiz et al., 2003).

Compound	Concentration (mg/L)
Synthetic wastewater	
$MgSO_4$	140
KH_2PO_4	529
NaCl	90.9
$CaCl_2$	58.6
Trace solution*	(5 mL trace /1 L wastewater)
***Trace solution**	
EDTA$^{\#}H_2Na_2 . 2H_2O$	50000
$ZnSO_4 . 7H_2O$	2200
$CaCl_2$	5540
$MnCl_2 . 4H_2O$	5060
$FeSO_4. 7H_2O$	5000
$(NH_4)_6Mo_7O_{24}. 4H_2O$	1100
$CuSO_4. 5H_2O$	1570
$CoSO_4. 7H_2O$	1900
KOH	to pH 6

#: ethylenediaminetetraacetic acid (EDTA)

Ammonia nitrate was added to the nutrient solution at high and low concentrations (Table 6) representing high and low nitrification nutrient feed. Those two wide nitrogen levels were chosen to examine the effect of the ammonia and nitrate concentrate on the

absorption performance. Ammonia nitrate concentration was added as N to target a representative 50% nitrified solutions.

Table 6: Ammonia nitrate concentration added to the nutrient solution.

Ammonia nitrate level	Concentration (g/L NH4NO3 -N)
Low	2
High	7

3.11 Absorption Unit Ammonia Gas Supply

In the absorption units, the gas stream was supplied from a gas cylinder (gas cylinder was obtained from Airgas, USA) which had an ammonia concentration of 2,000 ppm or 0.2% (mole base) balance with nitrogen gas, N_2. All the parts downstream the gas cylinder including the gas regulator, rotameter and the hoses were constructed of stainless steel because stainless steel is compatible with ammonia gas as it was recommended by the gas manufacturer company, Airgas, USA. The gas regulator, rotameter and the hoses were also obtained from Airgas, USA.

The ammonia concentration in the absorption unit gas feed was 2,000 ppm (mole base) and it was chosen based on the stripping unit results. Although the stripping and absorption units were operated separately for experiments, the ultimate goal is for integrated operation where gas leaving the stripping unit becomes feed gas for the absorption unit. Therefore, the stripping unit was run at different operational conditions to guide recommended stripping conditions. The ammonia concentration of gas leaving the stripping unit at this recommend condition was set as the absorption unit feed gas. An ammonia concentration of 2,000 ppm was chosen by setting the stripping column at the ammonia stripping recommended operational condition.

3.12 Water Quality Measurements

3.12.1 Alkalinity

Alkalinity of the raw anaerobic digestion leachate was measured using burette titration which was adopted from Hach Buret Titration Method 8221 (DOC316.53.01151, 05/2017, Edition 9). In this method, the leachate was diluted to reach the method range. An amount of 2.5 ml of the leachate was diluted with deionized water until the total volume of sample reached 50 ml. The diluted sample then was placed in a 250 ml flask and titrated with a 0.02 N sulfuric acid solution by burette until the pH of the sample reached 4.5. The total volume of the 0.02 N sulfuric acid solution needed to acidify the sample to 4.5 was measured to calculate the total alkalinity. The total alkalinity equation associated with this method is provided by Equation 7.

$$Total\ Alkalinity\ [mg/L\ as\ CaCO_3] = Volume\ of\ Titrant\ [ml] \times Multiplier \quad \text{(Equation 7)}$$

Where the multiplier is a correction that accounts for the dilution and the acid normality given in the method. Considering this experiment dilution explain above, the multiplier was 400. The alkalinity test was duplicated, and the average of the two results was reported.

3.12.2 Chemical Oxygen Demand (COD)

The chemical oxygen demand (COD) of the raw anaerobic digestion leachate was measured using Hach USEPA Reactor Digestion Method, Method 8000 (DOC316.53.01099, 10/2014, Edition 10). High range (HR) ,20 to 1500 mg/L COD, Hach COD vials were used in this method. Before starting the COD test, the leachate was diluted with DI water to meet range appropriate for the method. Two dilutions were

made with 10 and 100 dilution factors. To start the test, an amount of 2.00 mL of diluted sample was added to the HR COD vials and another 2.00 mL of deionized water was added to another HR COD vials to be used as a blank (blank is the vial that has zero COD since it was filled only with DI water). Then, both the sample and the blank vials were heated in a COD reactor at 150 °C for two hours. After the vials were digested for two hours, the vials were allowed to cool down to 120 °C then were inverted to mix. The vials then were allowed to cool to room temperature, before measuring the COD. The COD of the vials were measured using a Hach spectrophotometer (DR3900 Laboratory Spectrophotometer). The spectrophotometer was programed to HR COD code (435 COD). The blank was cleaned with KimWipes and then inserted into the cell holder of the spectrophotometer to zero it. Then, the sample vial was also cleaned and inserted into the cell holder of the spectrophotometer to read the COD. Spectrophotometer gave the COD reading in mg/L COD. The reading was multiplied by the dilution factor to correct for the dilution. The method is duplicated, and the average was reported.

3.12.3 Nitrogen

Measuring the amount of nitrogen in the leachate in its different forms is important for this project since the project focuses on ammonia recovery. Therefore, total nitrogen, total Kjeldahl nitrogen, ammoniacal nitrogen and organic nitrogen in the raw anaerobic digestion leachate were measured.

Moreover, ammoniacal nitrogen measurement was used to calculate the percentage of ammonia stripping as well as the percentage of ammonia absorption in both of ammonia stripping and ammonia absorption systems.

3.12.3.1 Total Nitrogen and Total Kjeldahl Nitrogen

Total nitrogen and total Kjeldahl nitrogen of the raw anaerobic digestion leachate were measured using Hach Simplified TKN (s-TKN™) Method 102421, TNTplus 880 (DOC316.53.01258, 05/2019, Edition 8). The range of this method is from 0 to 16 mg/L TKN, so the leachate was diluted 100 fold to meet the method range. The Hach TKN TNTplus test consists of two test vials (named by Hach by the green vial and the red vial), Solution A, Reagent B, Micro Cap C and Solution D. To start the test, an amount of 1.3 mL of diluted leachate sample and 1.3 mL of Solution A and 1 Reagent B tablet were added to a 20-mm reaction tube then allowed to react in a 100 °C reactor for an hour. After the reaction time was done, the vial was allowed to cool down to the room temperature and then one Micro Cap C was added to the reaction tube. The reaction tube was invert until the Micro Cap C was completely mixed. After that, an amount of 0.5 mL of the digested sample from the 20-mm reaction tube was placed into a red test vial and then 0.2 mL of Solution D was added to the test vial, as well. The vial then was inverted to mix. Immediately, an amount of 1.0 mL of undigested sample was added to the other test vial (green vial) followed by 0.2 mL of Solution D. The vial then was inverted to mix, and both vials were allowed to react for 15 minutes. Both vials were cleaned with KimWipes and the red vial was inserted in the cell holder of the Hach spectrophotometer (DR3900 Laboratory Spectrophotometer). Finally, the green vial was inserted into the spectrophotometer cell holder. The spectrophotometer shows results in mg/L for Total Nitrogen, NO_3–N + NO_2–N and TKN. The reading was multiplied by the dilution factor to correct for the dilution. The method was duplicated, and the average was reported.

3.12.3.2 Ammoniacal Nitrogen

Ammoniacal Nitrogen (NH_3 and NH_4) was measured using Hach TNT 832 Nitrogen, Ammonia, TNTplus®—Method 10205 (DOC312.53.94127, 02/2019, Edition 1). The range of this method is 2 – 47 mg/L NH_3-N, so the samples were first diluted with a dilution factor of 100 or 50 to meet the method range. The Hach TNTplus ammonia test method only consists of a test vial that has a liquid reagent inside the vials and separated sealed solid reagents in the vial cap. To measure the ammoniacal nitrogen in the sample, an amount of 0.2 mL of the sample was added into the test vial after the vial cap was removed. Then, the solid reagent in the vial cap was unsealed and the cap was replaced in a way that the solid reagent was in contact with the liquid inside the vial. The vial was then shaken until the solid and liquid reagent were mixed. The vial was then allowed 15 minutes to react. After that, the vial was cleaned up with a Kimwipe and inserted into in the cell holder of the Hach spectrophotometer (DR3900 Laboratory Spectrophotometer). Spectrophotometer shows the result in mg/L NH3-N. The reading was multiplied by the dilution factor to correct for the dilution. The method was duplicated, and the average was reported.

3.12.3.3 Total Organic Nitrogen

Total organic nitrogen (TON) was then calculated from both Total Kjeldahl Nitrogen (TKN) and ammoniacal ammonia using the following relation:

$$Total\ Kjeldahl\ Nitrogen = Total\ Organic\ Nitrogen + Ammoniacal\ Ammonia$$ (Equation 8)

$$Total\ Organic\ Nitrogen = Total\ Kjeldahl\ Nitrogen - Ammoniacal\ Ammonia$$ (Equation 9)

3.12.4 pH

The pH the samples was measured using a pH meter (OAKTON pH 150). The pH meter measures the pH value and temperature at the same time, and it has automatic temperature compensation (ATC) which allows it automatically to take the temperature in the pH measuring account. The probe was calibrated with Hach pH standards of 4, 6, and 10 standards. Two readings of the sample pH were obtained, and the average of the two readings were reported as well as the associated temperature.

Figure 25: The pH meter used in this project (www.4oakton.co).

3.12.5 Conductivity

The conductivity of the raw anaerobic digestion leachate was measure with a conductivity meter (Thermo Orion, Orion 145A+) which comes with a conductivity probe. Two calibration standards of 12.9 mS/cm and 1413 µS/cm were prepared with 7230 ppm as NaCl and 692 ppm as NaCl, respectively. The NaCl concentration for the standards were obtained from Thermo Orion conductivity standards. The conductivity probe was first calibrated with those two standards and then two reading of the leachate conductivity was taken. The average of the two reading was reported.

3.13 Analytical Methods

3.13.1 Height Equivalent to a Theoretical Plate (HETP)

Height equivalent to a theoretical plate (HETP) is defines as the packed height (H) over the number of equivalent equilibrium (N) (Seader et al., 2016) .

$HETP = \frac{H}{N}$ (Equation 10)

Where HETP: height equivalent to a theoretical plate H: packed height N: number of equivalent equilibrium stages

The packed height (H) was directly found by measuring the packed height in the column. For the experiments conducted here, the column packing height was 2 ft (Section 3.4) and was completely filled with the packing, so H is 2 ft.

Number of equivalent equilibrium stages (N) is calculated using the Kremser Equation. Several forms of the Kremser Equation are available (Wankat, 2017) to calculate N and the form shown in Equation 11 was selected because it is in terms of liquid phase compositions and liquid phase compositions are measured in this experiment.

$$N = \frac{ln\left[\left(1-\frac{L}{mV}\right)\left(\frac{X_0-X_N^*}{X_N-X_N^*}\right)+\frac{L}{mV}\right]}{ln\left[\frac{mV}{L}\right]} \quad \text{(Equation 11)}$$

$$X_N^* = \frac{y_{N+1}-b}{m} \quad \text{(Equation 12)}$$

Where

L: Liquid flow rate in mole per time

V: Vapor flow rate in mole per time

x_0: mole fraction of inlet liquid, liquid influent

x_N: mole fraction of outlet liquid, liquid effluent

y_{N+1}: mole fraction of inlet vapor, vapor influent.

m and b: the slop and constant in the equilibrium equation ($y = mx + b$), respectively.

The compositions and flow rates for the vapor and liquid in Equation 11 are in terms of moles whereas flow rate in the experiment are measured in volume over time (e.g., L/min) and compositions were measured mass per volume (e.g., g/L). Therefore, the volumetric flow rate is converted to molar flow rate by multiplying the volumetric flow rate by the liquid density then diving by the liquid molecular wight. For example, for the liquid flow rate, (1 L/min) (1000g/L)/ (18 g/mol) which gives 1 L/min = 55.5 mol/min. The ammonia compositions are also measured in mass per volume and then converted to molar compositions by dividing by the molecular wight. Mole fractions then was calculated and used with molar flow rate in Equation 11 to find number of equivalent equilibrium stages (N). Finally, HETP was calculated by dividing packed height (H) over the number of equivalent equilibrium stages (N) as shown in Equation 10.

3.13.2 Ammonia Stripping Percentage

The ammonia stripping percentage was calculated from the measured ammonia concentration in the influent and effluent as shown in Equation 13. Ammonia concentration in the influent and effluent were measured using methods described in

Section 3.12.3.2. Hach TNT 832 Nitrogen gives a result of ammonia concentration as mg/L-N which allowed calculation of the ammonia stripping directly using the following equality, Equation 13

$$Ammonia\ Stripping\ \% = \frac{Cl,in\ (mg/l) - Cl,out(mg/l)}{Cl,in(mg/l)} \times 100 \qquad \text{(Equation 13)}$$

Where Cl,in is liquid influent concentration and Cl,out is liquid effluent concentration.

3.13.3 Ammonia Absorption Percentage

The ammonia absorption percentage is calculated by measuring the ammonia concentration in the liquid influent and effluent with the same method mentioned Section 3.12.3.2. Then, a mass balance calculation was done to calculate the ammonia concentration in the gas stream using the following mass balance equation:

$$CG,in\ (known\ \ feed) + Cl,in\ (known\ \ feed) = CG,out\ (unknown) + Cl,out\ (measured\ with\ HACH\ test) \qquad \text{(Equation 14)}$$

Where: Cl, in is liquid influent concentration and Cl, out is liquid effluent concentration

CG, in is gas influent concentration and CG, out is gas effluent concentration

As shown in the equation above, there are four components. The ammonia concentration of CG,in is known (Recall, gas in is the feed gas which is provided from a known ammonia composition gas cylinder, y_{NH3}= 0.2%). The ammonia concentration of liquid in and out liquid streams were measured. The mass concentrations were then converted to molar concentration and mole fraction using ammonia molar mass.

As it can be seen from the above mass balance equation that the only unknown is the ammonia concentration in gas out which can be then calculated using mass balance principle.

After the ammonia concentration in the gas was calculated the ammonia recovery was calculated as shown in Equation 15

$$Ammonia\ Absorption\ \% = \frac{y,in - y,out}{y,in} \times 100 \quad \text{(Equation 15)}$$

Where y,in is gas influent mole fraction and y,out is gas effluent mole fraction

3.13.4 Superficial Velocity (u)

The superficial velocity (u) was calculated by dividing the volumetric flow rate by the column sectional cross area A_s, Equation 16.

$$u = \frac{Q}{A_s} \quad \text{(Equation 16)}$$

Where: u is the superficial velocity, Q is volumetric flow rate (L/min), A_s is the column sectional cross area ($A_s = \pi r^2$) and r is the inner radius of the column.

3.14 Replication of Measurements and Experiments

The leachate quality data (Section 4.1.1, Table 7) was duplicated, the average and the standard deviation of the two measurements were reported. The ammonia measurements at liquid influent and effluent in all stripping and absorption experiments were repeated three times in all experiments where three different samples were taken for each interested measurement, each sample were analyzed separately and the

average of the three samples were reported. In the stripping temperature analysis, the explement was triplicate at 35 °C and 3 samples were analyzed for each experiment making the total of analyzed samples 9 in order to evaluate the method accuracy by calculating the standard deviation for the three experiments. Similarly, the absorption experiments were duplicated for each case in all of the absorption explements, the average and standard deviation were reported.

3.15 Calibration

3.15.1 Pump Calibrations

The peristaltic pump (Master Flex L/S Cole -Parmer) which was used to pump the liquid to the column was calibrated using volumetric flow rate calibration. The pump was set at different flow rates (5, 10, 20, 100 mL/min) and the actual flow rate was measured with a graduated cylinder over time with stopwatch. Then, a calibration curve was made to set the pump at the actual desired flow rate.

3.15.2 Rotameters

All gas rotameters used in this experiment were calibrated using water displacement method. A 500ml flask was submerged in 5-gallon packet that was halfway fill of water. The air coming out of the rotameters was blown into the flask the, and the time to empty the flask was calculated. Figure 26 is a schematic figure illustrates how this calibration was made.

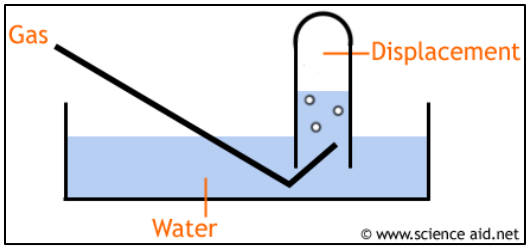

Figure 26: A general schematic diagram for a flow meters calibration by displacement method.

3.15.3 Micropipette Calibration

All micropipette used in this experiment had an accuracy (A) of 99-100%. The accuracy of the micropipette was calculated using weight calibration. A micropipette was set to a desired volume and a tip was pre-rinsed 3 times. A desired amount of deionized water was then placed into a weighing dish what was zeroed before placing the water in. The weight of the water was recorded and the process was repeated 3 times. The average of the wight was calculated then multiplied by the water density at the specific water temperature to get the actual volume. Then the accuracy % of the micropipette (A) was calculated by dividing the actual volume by the theoretical volume (set volume in the pipette) as following:

$$V_{actual} = w\,\rho \qquad \text{(Equation 17)}$$

$$A\,[\%] = \frac{V_{actual}}{V_{theoretical}} \times 100 \qquad \text{(Equation 18)}$$

Where:

w is the weight of the water, ρ is the density of the water, A is the accuracy %, and $V_{theoretical}$ is the set volume of the pipette.

3.16 Simulation Model

Aspen Plus V11 was used to model the Nitrogen Recovery System. The simulations aimed to provide supportive and additional data to the experimental data as the ammonia stripping and ammonia absorption extents were calculated as a function of several operational conditions. Aspen Plus Electrolyte Model was chosen in this simulation which is recommended by Aspen Technology (Aspen Technology, 2013) for electrolyte systems including wastewater solution. An electrolyte system involves species that dissociate in a solvent in equilibrium. The electrolyte model in Aspen Plus provides several thermodynamic models, Electrolyte Non Random Two Liquid- Redlich Kwong (ENRTL-RK) was chosen for this simulation because it is suitable for non-ideal mixture. Non Random Two Liquid (NRTL) is an activity coefficient model that accounts of the non-ideality of the mixture in the equilibrium phase. On the other hand, Redlich Kwong (RK) is an equation of state that is more accurate that the ideal gas equation for non ideal gas systems. Both of NRTL and RK allows this model to provide more accurate thermodynamic properties. For example, the equilibrium data for an ammonia-water system generated by this Model was compared for the experimental data reported in Perry's Chemical Engineers' Handbook (Perry et al., 1997) and was found the same.

ENRTL-RK model allows the users to choose between the two calculation models of equilibrium model or rate-based model. The equilibrium model was selected for this simulation because it allows us to validate the simulation equilibrium calculations with ammonia-water equilibrium published data. RadFrac columns were used for both of the stripper and absorber with no internal specifications of high, diameter or packed/tray column. For the equilibrium stages model, the number of equilibrium stages was varied

to determine a suitable number of equilibrium stages. After that, the number of equilibrium stages was set at 3 with no condenser and no reboiler for all of the models. For feed stages, the liquid enters the columns at the very top stages and leaves below the very low stages whereas the gas is the opposite, it always enters below the last stages and exits above the top stages. The process of the system including all streams and columns was set 1 atm. The temperature of the stripping column was set at 50 °C and the temperature of the absorption column was set at 25 °C. The feed pH of the stripping was set at different values (8, 9, 10, 11 and 12) and the ammonia stripping extents were calculated at each value. The ammonia absorption extents were calculated function of feed pH of 2, 4, 6 and 7.

4 Results and Discussion

4.1 Ammonia Stripping Units

4.1.1 Leachate Quality

Analyzing the leachate quality is important because it describes the raw leachate used in this experiment. Moreover, it shows whether the raw leachate represents an anaerobic digestion leachate. A common way to study the leachate quality is to compare its characteristic to reported characteristics in relevant literatures. Therefore, the characteristics of the anaerobic digestion raw leachate used in this work is compared with the leachate characteristics from previous works at the same anaerobic digestion system (CSU Foothill Campus AD) as well as with characteristics reported in similar works in literature.

Table 7: Comparison of the anaerobic digestion raw leachate used in this work with the standard deviation of duplicate measurements and those used in other studies.

Constituent	This project raw leachate	CSU Foothill Campus Anaerobic Digestion (previous works)	(Zeng et al., 2006)	(Georgiou et al., 2019)
Alkalinity [mg/L as $CaCO_3$]	7380 ± 28	ND*	5493	7900
COD [mg COD/ L]	7415 ± 261	4500	ND*	4576
pH	7.9	8	8.14	8.32
Conductivity [µS/cm]	21100	12000-1600	13610	12900
NH_3-N [mg/L]	632 ± 7.7	1000-2000	956	1652
Total N [mg/L]	1025 ± 7.1	ND*	ND*	ND*
TKN [mg/L]	934	ND*	ND*	ND*
ON# [mg/L]	301 ± 7.7	ND*	ND*	ND*
NO-3 -N + NO-2-N	91 ± 7.1	ND*	ND*	ND*

* ND: No Data

ON: Organic Nitrogen

Chemical oxygen demand (COD), alkalinity, conductivity, pH and the amount of nitrogen in different forms are the main characteristics that are considered because they characterize the leachate quality. Moreover, some of those characteristics are hypothesized to affect the ammonia recovery process. For example, alkalinity measures the buffering capacity of the leachate and it affects the leachate pH change while ammonia is removed. Considering the pH in the stripping column, the pH is expected to drop as the ammonia is removed. The value of the pH drop is dependent in the leachate alkalinity since the alkalinity represents the leachate capacity to the pH resist change. The change in pH affects the ratio of ammonia to ammonium in the leachate which consequently affects the ammonia stripping performance since ammonia is more volatile than ammonium.

The raw leachate used in this work has similar values of alkalinity and pH to the other reported leachates. However, it has higher chemical oxygen demand (COD), higher conductivity and lower ammonia than other reported leachates. Each anaerobic digestion system might have a different leachate base on its operation and design including how long the system has been operated as well as the frequency of providing the process feedstock, the loading rate and the quality of the manure. It is expected that the main reason behind having lower ammonia amount in the leachate used in this work is that this work anaerobic digestion system was not provided with manure feedstock regularly which decrease the system concentration including the amount of ammonia.

In general, the leachate used in this work has similar alkalinity and pH to the compared leachates. However, it has higher COD, higher conductivity and lower ammonia than

those used in previous works at CSU Foothill Campus and to the anaerobic digestion leachates reported in relevant reports (Table 7).

4.1.2 Operational Parameters and Design Model Analysis

Finding suitable operational parameters for the system improves both its performance and economic feasibility. For the ammonia recovery system, it was hypothesized that the most important parameters that affect the ammonia stripping as well as the operational cost are (1) liquid and gas flow rates, (2) the pH of the system (3) temperature of the system. The effects of those three factors on ammonia stripping are examined and appropriate values or ranges of system flow rates, pH and temperature were recommended considering the ammonia stripping performance and its economics.

4.1.2.1 Column Hydraulic (Flow Rate) Analysis

Choosing appropriate flow rates for both liquid and gas is necessary in a stripping process because both too high and low flow rates have negative effects on the stripping system. A low flow rate causes poor distribution of the liquid through the column and between the packings, which decreases the liquid-gas interfacial area leading to poor stripping performance (Seader et al., 2016). On the other hand, a flow rate that is too high increases the pressure drop over the column as the liquid hold up increases, which also causes entrainment and eventually can cause flooding in the column. Those conditions decrease the stripping efficiency and increase HETP (Seader et al., 2016).

Therefore, both the liquid hold up and HETP were calculated over range of a gas and liquid flow rates in order to determine suitable gas and liquid operational flow rates.

4.1.2.1.1 Liquid Hold up

The specific liquid hold up (L_H) was found for several gas and liquid superficial velocities (u). The specific liquid hold up is defined as the volume of liquid trapped in the column over the volume of the column and has a unit of volume over volume (e.g., m3/m3). Superficial velocity is the volumetric flow rate over the inner cross-sectional area of the column and has a unit of length over time (e.g., m/s or m/h). It is very common in literature to represent the superficial gas velocity (u_v) in m/s and the superficial liquid velocity (u_L) in m/h.

The liquid hold up data shown in Table 8 was calculated using the stripping/absorption column described in material and methods part (Sections 3.7).

Table 8: The specific liquid hold up (L_H) as a function of the superficial gas velocity (u_v) and superficial liquid velocity (u_L).

liquid flow rate [mL/min]		5	10	15	20	30	40	50	80	170
Superficial liquid velocity, u_L [m/s]		0.6	1.2	1.7	2.4	3.5	4.7	6	20	41
Gas flow rate [L/min]	Superficial gas velocity, u_v [m/s]	Liquid hold up (L_H) [m^3/m^3]								
6	0.19	0.009	0.013	0.016	0.019	0.026	0.037	0.041	0.051	0.095
10	0.32	0.009	0.012	0.016	0.019	0.026	0.034	0.041	0.051	0.095
20	0.65	0.009	0.013	0.016	0.019	0.026	0.037	0.041	0.057	0.095
30	0.98	0.009	0.013	0.016	0.019	0.026	0.037	0.041	0.057	0.095
40	1.31	0.009	0.014	0.015	0.019	0.026	0.033	0.041	0.054	0.118
50	1.64	0.018	0.02	0.02	0.021	0.037	0.041	0.051	0.071	0.135

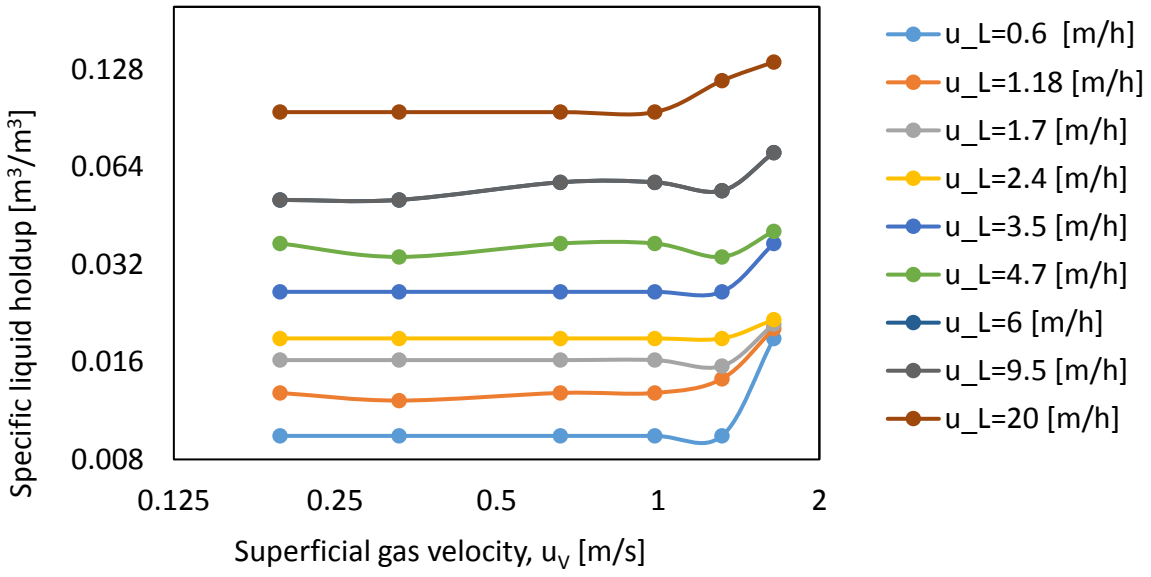

Figure 27: The specific liquid hold up (L_H) as a function of the superficial gas velocity (u_v) and superficial liquid velocity (u_L).

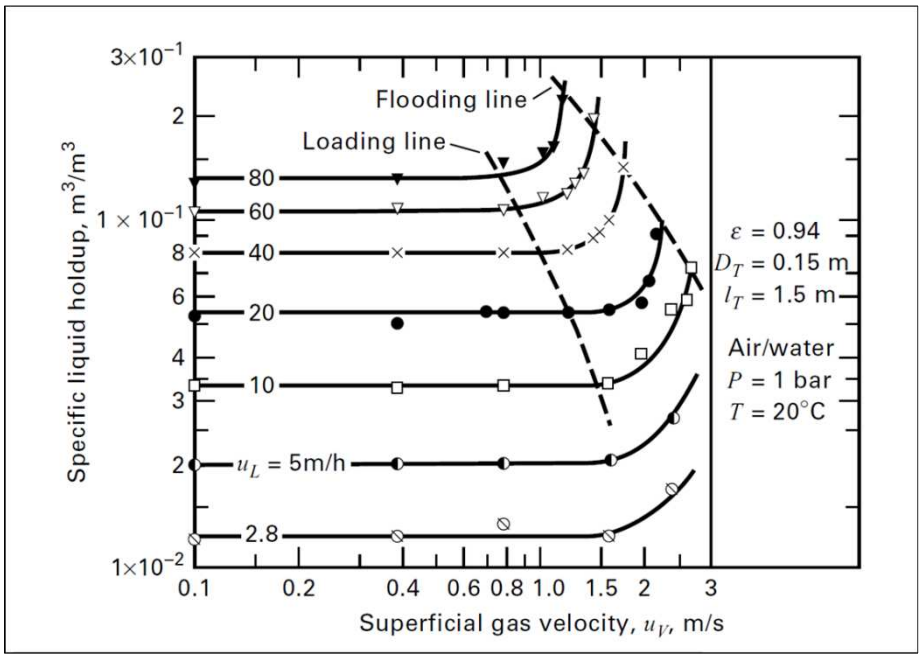

Figure 28: The specific liquid hold up (L_H) function of the superficial gas velocity (u_v) and superficial liquid velocity (u_L) (Seader et al., 2016).

The liquid hold up behavior shown in Figure 27 can be classified into three regions: preloading region, loading region and flooding region (Seader et al., 2016). The preloading regions are the horizontal constant lines where the superficial liquid hold up stays constant as the superficial gas velocity increases for a particular liquid velocity. At loading region, superficial liquid hold up starts to increase as superficial gas velocity increases until it reached the flooding region where a sharp increase of the specific liquid hold up is noticed.

The data in Figure 27 shows that superficial liquid hold up increases as liquid flow rate increase while it stays constant over a wide range of superficial gas velocity. For example, at superficial liquid velocity of 2.4 m/h, the liquid hold up is 0.0189 m^3/m^3 over a wide range of superficial liquid velocity of 0.197 m/s to 1.315 m/s. Among the three regions, the column operates best at the preloading region to avoid flooding (Seader et al., 2016). On the other hand, a very low liquid flow rate leads to poor distribution of the liquid through the column, decreasing the liquid-gas interfacial area and then leading to poor stripping performance. Therefore, the recommended flow rate that maximizes liquid-gas interfacial area while preventing flooding is just before the loading region.

4.1.2.1.2 Height Equivalent to a Theoretical Plate (HETP)

HETP can be used to represent the column efficiency. Low values of HETP indicate to a more efficient system. Therefore, HETP is calculated here over a range of gas and liquid flow rates in order to find a suitable and efficient operational gas and liquid flow rate range.

Like the liquid hold up analysis, HETP results shown in Figure 29 can be classified into three regions: preloading region, loading region and flooding region. Considering the data in Table 9, the superficial gas velocity point that separates the preloading region and the flooding region is at u_v = 0.046 m/s. HETP values before that point are almost constant, indicative of the preloading region. On the other hand, it sharply increases above u_v = 0.046 m/s, where the flooding region starts. Therefore, considering the HETP analysis, the optimal gas flow rate range is between u_v = 0.0093 m/s to u_v = 0.0374 m/s for ammonia stripping at the operation condition of pH 10, T 50 °C and constant (L/V) of 1.9

Table 9: HETP of the ammonia stripper as a function of superficial gas velocity (uv) at pH 10, T 50 °C and constant (L/V) of 1.9 .

u_v [m/s]	HETP [in]	Region
0.0094	28.75	Preloading
0.0187	30.12	
0.0281	33.60	
0.0374	33.60	
0.0469	35.24	loading
0.0562	44.26	Flooding
0.0656	50.77	

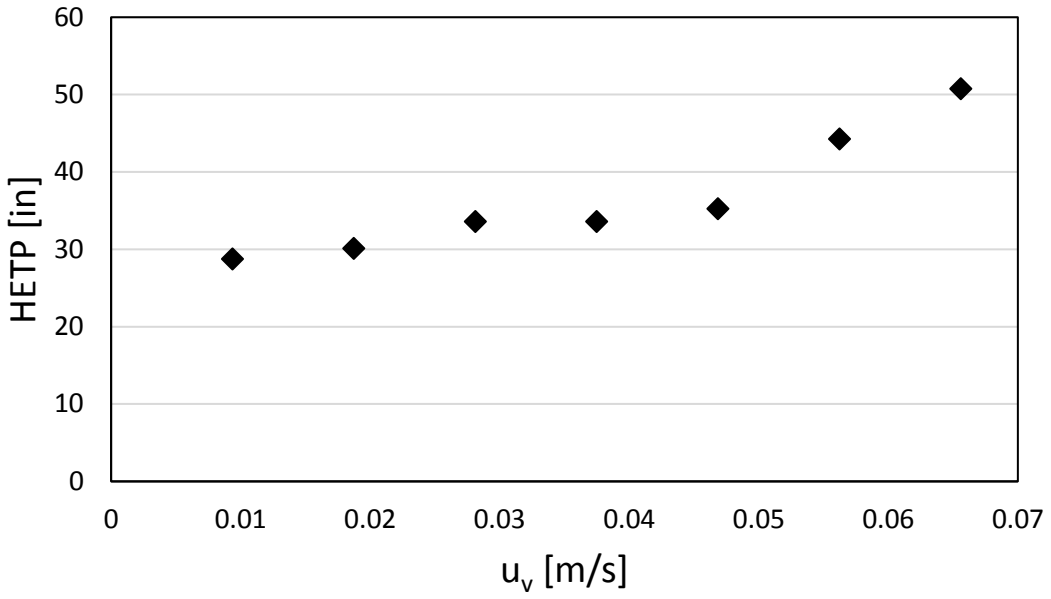

Figure 29: HETP of the ammonia stripper function of superficial gas velocity u_v at pH 10, T 50 °C and constant (L/V) of 1.9 .

4.1.2.1.3 Pressure Drop

The pressure drop in the column is measured at the desired gas and liquid flow rate (V=40 L/min & L=20 mL/min) and it was found to be15 inches of H_2O (0.54 psi). This represents the pressure loss in the gas from the column gas inlet to the gas outlet. The main source of the pressure loss in the column is friction against the gas flow due to the presence of the packing in the column and due to the gas–liquid interface as the liquid goes down through the column and gas goes in the opposite direction. The pressure drop through the column should not exceed 2 inches of water per foot of packed height (Seader et al., 2016). The column in this experiment has packed height of 2 ft, so the pressure drop should not exceed 4 inches of water. However, the pressure drop increases as the packing size decreases (Seader et al., 2016). The packing in this experiment is small laboratory-scale packing, which is substantially smaller than the

packings used in industrial applications such those listed in (Seader et al., 2016). The second reason that causes the pressure drop in the column is the liquid resistance as liquid flows downs against the gas flow. Since liquid and gas flow are in countercurrent configuration, some of the liquid trapped in the column as it faces the air (defined earlier as the liquid hold up) causing higher pressure losses in the column.

4.1.2.2 Analysis of the System pH

The pH analysis in this work shows that the pH of system has a major impact on ammonia stripping. Considering the ammonia stripping extent at different stripping feed pH values shown in Table 10, the data shows that there is almost no ammonia removal at pH 8.5, which is the original pH of the raw leachate. Increasing the pH of the system to 9 did not enhance the ammonia removal by much as it is still below 10%. The ammonia stripping extent is 32% at pH 9.5, which is also low. However, increasing the pH only 0.5 unit more to 10 leads to 78% ammonia stripping. At pH 10.5, the system was able to remove 94% of the ammonia.

Table 10: Ammonia concentration in the stripper influent and effluent as a function of pH.

Feed pH	Influent NH_3-N [mg/L]	Effluent NH_3-N [mg/L]
8.5	2903	2893
9	2876	2670
9.5	2920	1990
10	2796	626
10.5	2700	152

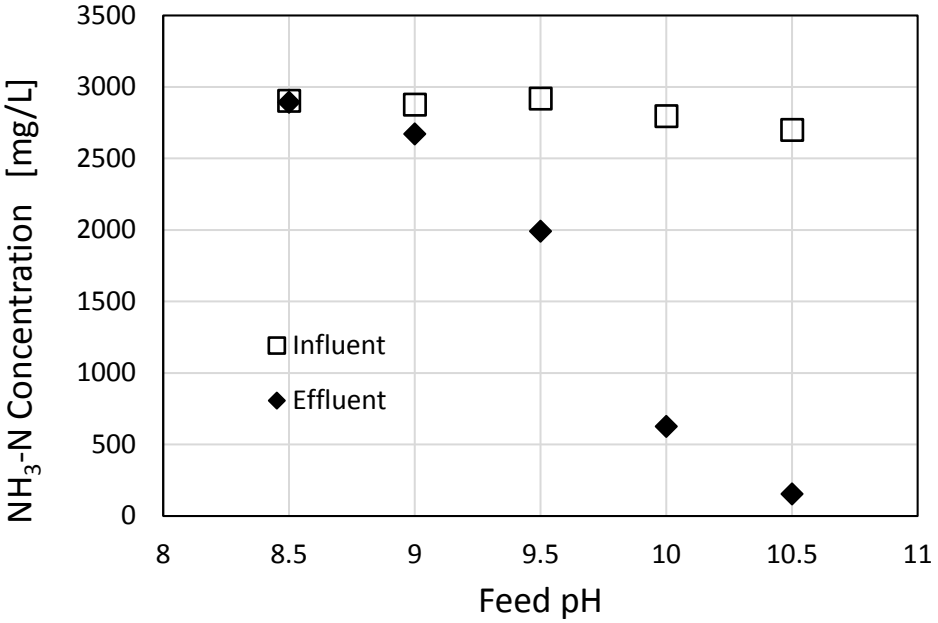

Figure 30: Ammonia concentration in the stripper influent and effluent as a function of pH.

Table 11: Ammonia stripping extent and HETP as a function of the stripping pH.

Feed pH	Ammonia Stripping %	HETP [m]
8.5	0.34	296
9	7.2	14
9.5	32	2.5
10	78	0.57
10.5	94	0.27

Considering HETP at different pH values, it is clear that pH 8.5 is not a practical option at this system condition because it gives a HETP of 296 m. Stripping at pH of 9 and 9.5 gives a HETP of 14 m and 2.5 m, respectively. At pH 10, the HETP value drops below to 0.57 m while it is 0.27 m at pH 10.5. From a design perspective, both pH 10 and 10.5 give a sensible HETP and an influent pH below 10 should be avoided.

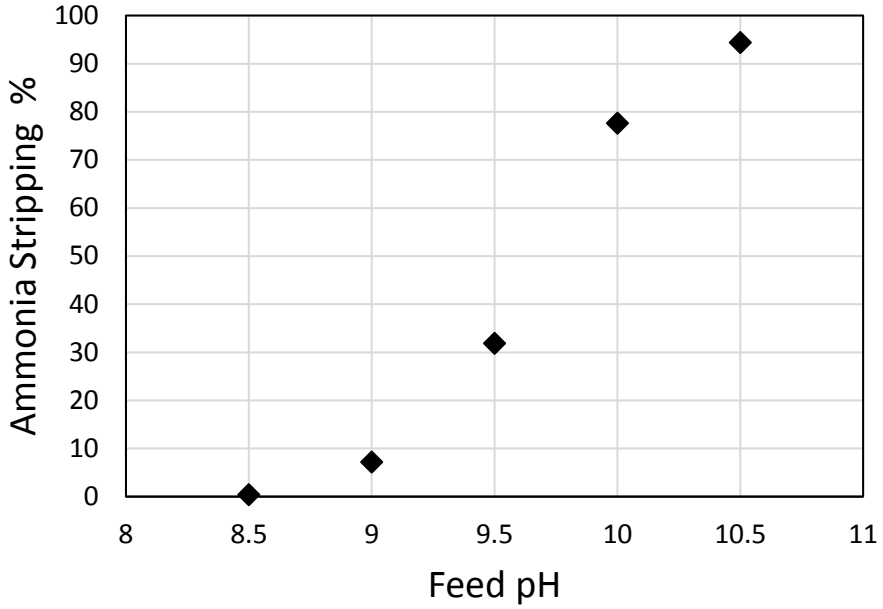

Figure 31: Ammonia stripping extent as a function of the stripping pH.

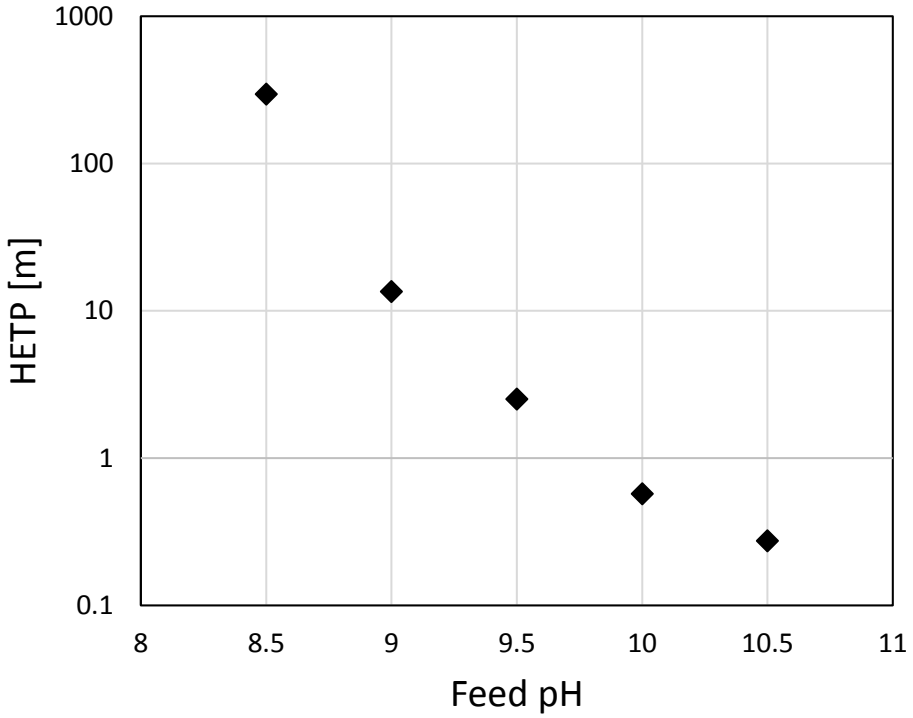

Figure 32: HETP of the stripper as a function of the stripping pH.

The major effect of pH in the ammonia stripping can be theoretically supported. Ammonia and ammonium exist in equilibrium in an aqueous solution ($\mathrm{NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-}$) as pH and temperature increase the reaction shifts to the left converting NH_4^+ to NH_3 which makes the ammonia stripping easier since NH_3 is more volatile than NH_4^+. The fraction of ammonia to total ammoniacal nitrogen (f) as function of temperature and pH can be found using Equation (20 & 21; Florida Department of Environmental Protection 2001):

$$f = \frac{[NH_3]}{[NH_3] + [NH_4^+]} \quad \text{(Equation 19)}$$

$$f = \frac{1}{10^{pKa-pH}+1} \quad \text{(Equation 20)}$$

$$pKa = 0.0901821 + \frac{2729.92}{T(K)} \quad \text{(Equation 21)}$$

where: pKa is the dissociation constant and T(K) is temperature in degrees Kelvin

The pKa of ammonium at 50 °C is 8.54 calculated with Equation 21 which agrees which the empirical value found by Bates and Pinching (1949). Keeping the temperature constant at 50 °C, Equation 20 can be used to find the fraction of ammonia to total ammoniacal nitrogen (f) only as a function of pH as shown in Table 12.

Table 12: The fraction of ammonia to total ammoniacal nitrogen (f) as a function of pH at 50 °C.

pH	f	%
8	0.10	10.10
8.5	0.26	26.22
9	0.53	52.92
9.5	0.78	78.04
10	0.92	91.83
10.5	0.97	97.26

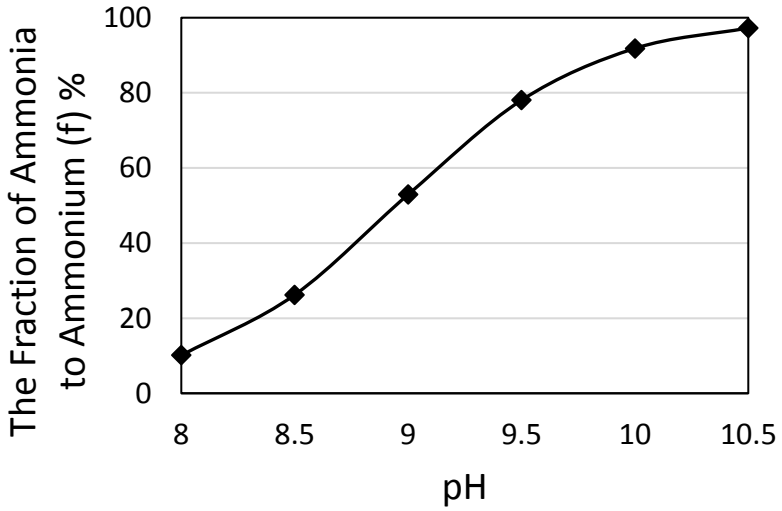

Figure 33: The fraction of ammonia to total ammoniacal nitrogen (f) as a function of pH at 50 °C.

The calculated values of the fraction of ammonia to total ammoniacal nitrogen (f) function of pH shown in Table 12 support the ammonia stripping data function of pH found in this work. As shown in Figure 33, (f) increases as pH increases. For instance, at pH 10.5, 97% of the total ammoniacal nitrogen exists in its more volatile form, NH_3 which enhance the ammonia stripping. On the other hand, there is only 10% NH_3 at pH 8 which makes the ammonia recovery more challenging.

Figure 34 shows the calculated theoretical percentages of ammonia to total ammoniacal nitrogen (f) and ammonia stripping experimental data as a function of pH at 50 °C. The diagram explains that f increases as pH increases enhancing the ammonia stripping and increasing ammonia stripping percentages.

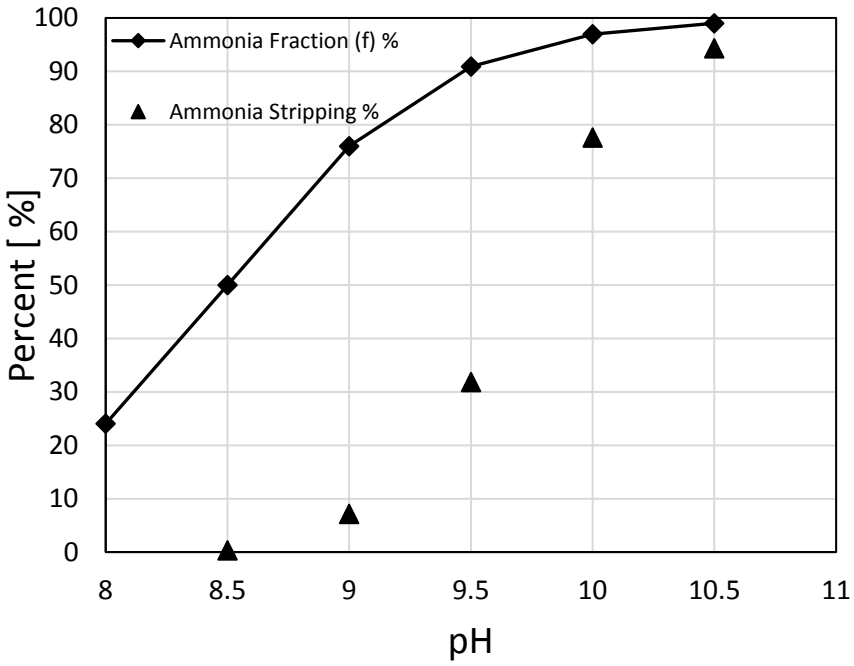

Figure 34: The calculated theoretical values percentage of ammonia to total ammoniacal nitrogen (f) and ammonia stripping experimental data as a function of pH at 50 °C.

4.1.2.3 Analysis of the System Temperature

The results indicate that the temperature has large impacts in the stripping process. The ammonia stripping extents were considerably different for the four tested temperatures, 35, 50, 55 and 65 °C. It was noticed that the stripping process became more efficient (higher ammonia stripping and lower HETP) as the temperature increases until it reaches 50 °C. Then, the system efficiency was found to be lower at 55 and 65 °C. To measure the error of the temperature analysis experiments, the standard deviation of the ammonia stripping extent and HETP at 35 °C was calculated for triplicate runs which was 0.94 for ammonia stripping extent and was 0.083 for HETP. The ammonia stripping extent and HETP values as a function of temperature are listed in Table 13

Table 13: The ammonia stripping extent and HETP as a function of temperature at pH=10.

T [°C]	Ammonia Stripping %	HETP [m]
35	39	1.89
50	78	0.57
55	70	0.72
65	52	1.25

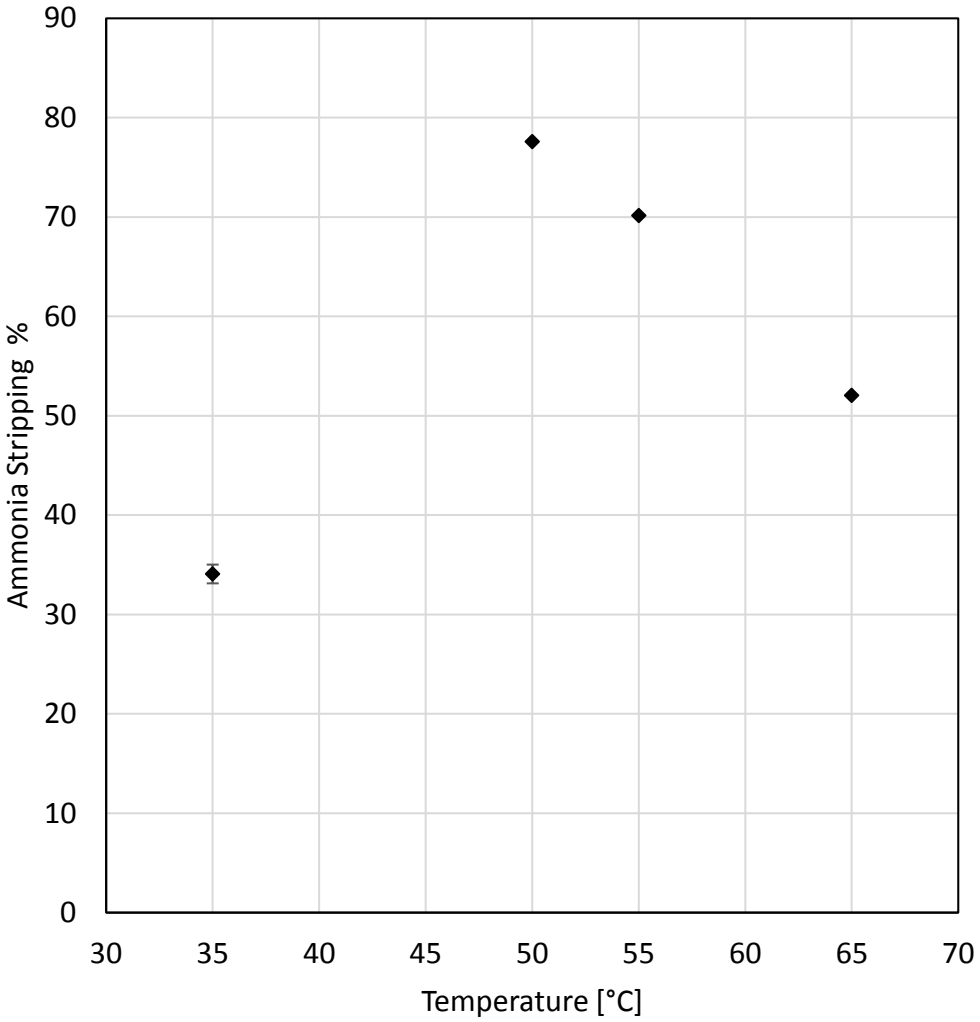

Figure 35: The ammonia stripping extent and HETP function of temperature at pH=10. The error bars shown at 35 °C represent the standard deviation of triplicate experiments

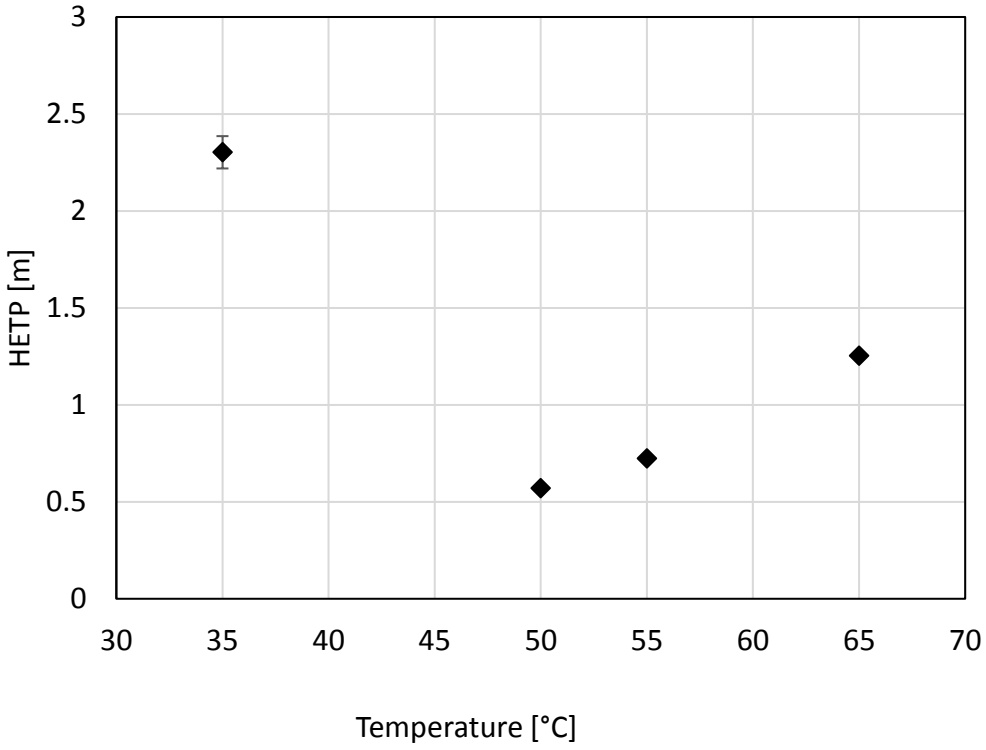

Figure 36: HETP as a function of temperature at pH=10. The error bars shown at 35 °C represent the standard deviation of triplicate experiments.

The increase of the system efficiency due to increasing the temperature in the range of 35 °C to 50 °C can be explained by equilibrium constant between ammonia and ammonium. Higher temperature shifts the equilibrium to form more ammonia which is the more volatile form enhancing the ammonia stripping process. As it can be seen from Table 14 (generated using Equation 21, $\mathrm{pKa} = 0.0901821 + \frac{2729.92}{\mathrm{T(k)}}$) that the pKa decreases as the temperature increases. However, the fraction of ammonia to ammonium (f) is function of both of the temperature and the pH as it can be seen from

Equation 20 ($f = \frac{1}{10^{pKa-pH}+1}$). Although the pH of the influent to the stripper was set at pH 10 at room temperature, the pH of the leachate changes as it enters the column due to the column temperature since pH is function of temperature. The pH decreases as the temperature of the feed increases (Table 15). This does not enhance the stripping process since the fraction of ammonia to ammonium (f) decreases as pH decreases reducing the amount of ammonia.

Table 14: Theoretical pKa ammonium function of temperature

T [°C]	pKa
35	8.95
50	8.54
55	8.41
65	8.16

An empirical equation that describes the relation between the temperature and pH of the anaerobic digestion leachate was obtained from the experimental data shown in Table 15: pH = -0.0215 T(°C) + 10.402 or T(°C) = -46.43pH + 483.08 with the Coefficient of Determination (R^2) of 0.99 for both equations.

Table 15: The effect of temperature on the pH of anaerobic digestion leachate

T [°C]	pH
19	10
35	9.65
50	9.3
55	9.22
60	9.14
65	9

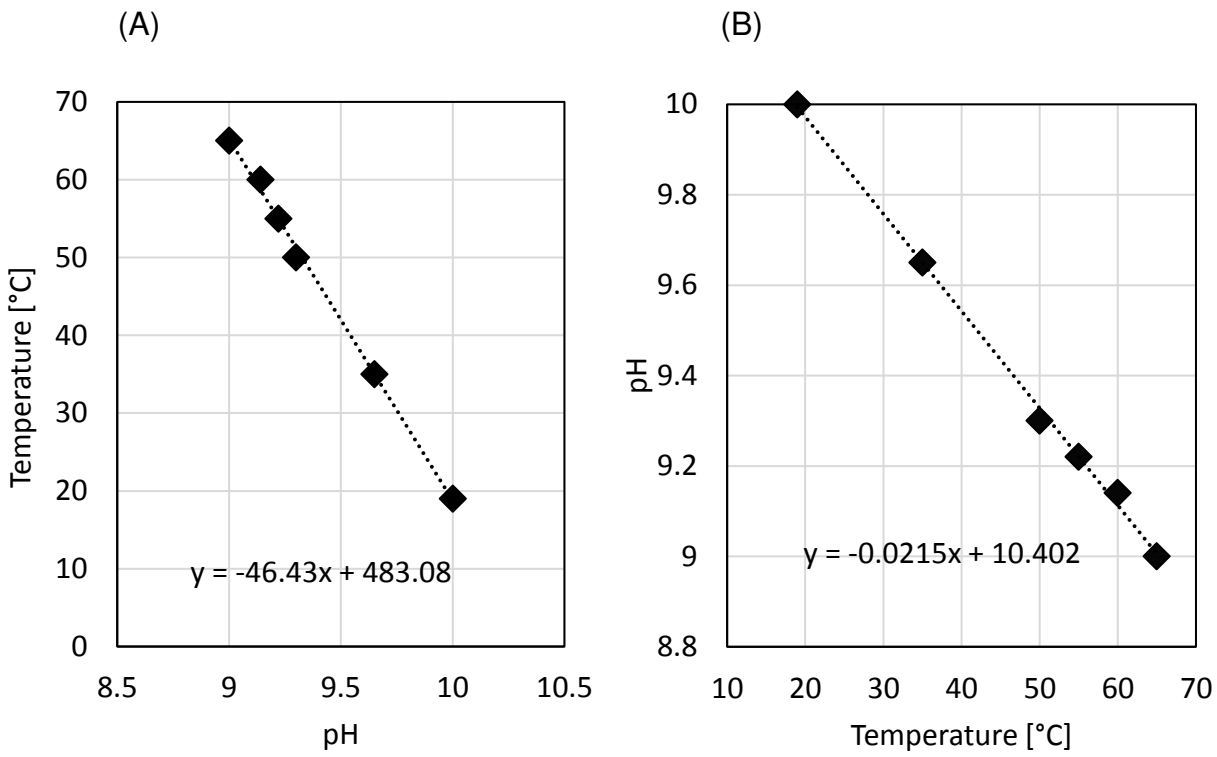

Figure 37: The effect of temperature on the pH of the anaerobic digestion leachate. (A) pH function of T (B) T function of pH.

Since the dissociation constant pKa is function of both the temperature and pH, an optimal temperature is needed to be determined at certain pH. Considering both of stripping extent and HETP values found in this experiment, the optimal temperature is at pH 10 is 50 °C since it provides the highest stripping and lowest HETP.

4.1.2.4 Comparison of Synthetic and Anaerobic Digestion Leachate Analysis

Ammonia stripping is compared in synthetic leachate (deionized water + ammonium sulfate) and anaerobic digestion leachate and it was found that the ammonia stripping has different behavior in the two leachates for the same initial operational conditions (pH, T and flow rates). Considering the ammonia stripping for anaerobic digestion

leachate and synthetic leachate at feed pH of 10, T = 50 °C, gas and liquid flow rates of 40 L/min and 20mL/min, respectively, were used. It was noticed that anaerobic digestion leachate has a higher rate of ammonia stripping than synthetic leachate. The data on ammonia stripping and HETP provided in this comparison is an average of two runs with the standard deviations shown in Table 16.

Table 16: Comparison of ammonia stripping extent and HETP in synthetic and anaerobic digestion leachate.

leachate	Stripping %	Standard deviation	HETP [m]	standard deviation
synthetic	50	1.18	1.3	0.049
AD	75	4.29	0.63	0.087

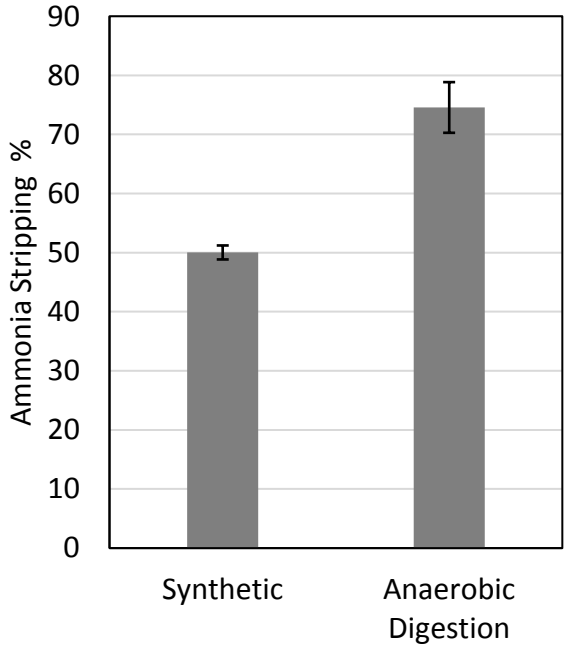

Figure 38: Comparison of ammonia stripping extent in synthetic and anaerobic digestion leachate.

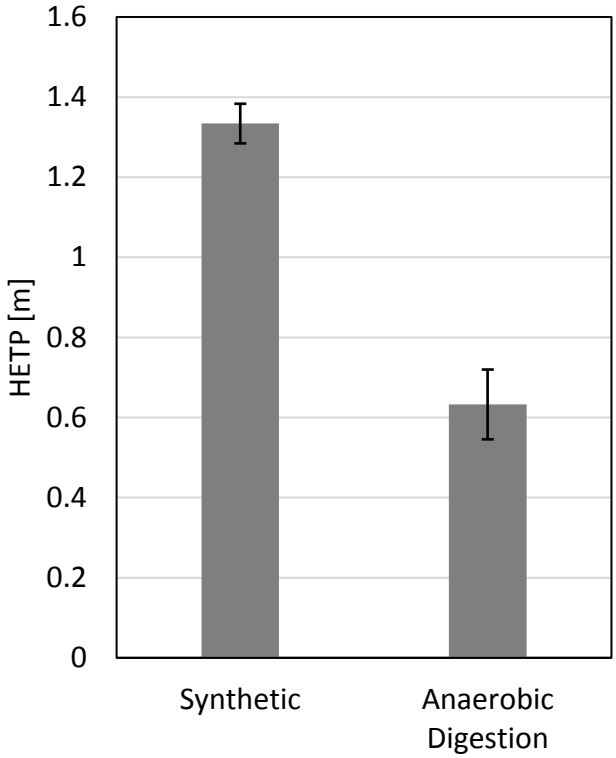

Figure 39: Comparison of HETP of in synthetic and anaerobic digestion leachate.

As shown in Table 16, the ammonia stripping extent in the anaerobic digestion leachate at pH 10 and T = 50 °C is 75% whereas it is only 50% in synthetic leachate for the same conditions. The ammonia stripping in synthetic leachate is lower than what was found in anaerobic digestion leachate because synthetic leachate has a lower buffering lower than anaerobic digestion leachate. The buffering capacity resists the pH change during stripping process due to the ammonia removal. Considering the ammonia and ammonium equilibrium in water ($NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$), it can be seen that removing NH_3 forces the equilibrium to shift to the left side, reducing OH^- and decreasing the pH of the solution. The drop in pH decreases the fraction of ammonia to

ammonium, causing a decrease in the stripping performance since ammonia is more volatile than ammonium. The previous analysis can be supported by comparing the effluents pH of both anaerobic digestion leachate and synthetic leachate. The effluents of anaerobic digestion leachate had a pH of 9.31 whereas the synthetic leachate had a pH of 8.9. Therefore, the synthetic leachate has lower ammonia stripping % due to the pH drop as result of the ammonia removal since it has lower buffering capacity.

4.1.3 Stripping Simulation Models with Aspen Plus

4.1.3.1 Stripping Model Operational Specifications

An Aspen Plus model of the ammonia stripping column was used to calculate the extent of ammonia stripping at different operational parameters and different equilibrium states.

The temperature and pressure in the stripping models set at 50 °C and 1 atm. The air flow rate was set at 40 L/ min whereas the liquid flow rate was at 0.002 L/min making the molar ration (L/V) 0.66. The gas used in this model was air, and the liquid was synthetic leachate. The synthetic leachate is composed of water, $CaCO_3$ and NaCl. $CaCO_3$ was added to represent the anaerobic digestion leachate alkalinity of 7.4 $CaCO_3$ g/L which was the alkalinity measured in the anaerobic digestion leachate used in the stripping experiments. Also, 7.23 g/L NaCl was added to represent the conductivity of the anaerobic digestion leachate of 12,900 µS/cm.

Table 17: Stripping model operational specifications.

Model Operational Condition	
T	50 °C
P	1 atm
Gas flow rate	40 L/min
Liquid flow rate	0.02 L/min
Molar ration (L/V)	0.66
Gas	Air
Liquid	Synthetic Leachate
Synthetic Leachate	
component	Mole fraction
$CaCO_3$	0.0013
NaCl	0.0022
H_2O	0.9964

4.1.3.2 Equilibrium Stages Model in the Stripping Column

The first analysis model is to assess the stripping performance at different equilibrium stages for several values of feed pH. The results show that the number of stages does not have a major impact on the ammonia stripping. For example, the ammonia removal for a feed of pH 8 is 11% for two equilibrium stages whereas it is 15% for 9 equilibrium stages. Considering feed pH of 10, ammonia stripping extent is 93% for 3 equilibrium stages which is significantly higher than at a feed pH of 8. Considering 3 equilibrium stages and 4 equilibrium stages for a feed pH 10, it can be noticed that adding a fourth equilibrium stages only increases the ammonia stripping from 93 to 98%. Moreover, as illustrated in Figure 40 the extent of ammonia stripping is almost constant after the third equilibrium stage. The choice of the number of equilibrium stages should consider both the column performance and the cost. It is important to notice that although the extent of

ammonia stripping is higher at 4 equilibrium stages, this requires a higher column, which increases the column cost. Therefore, it can be concluded that three equilibrium stages stripper is the most feasible considering both the ammonia stripping extent and column design.

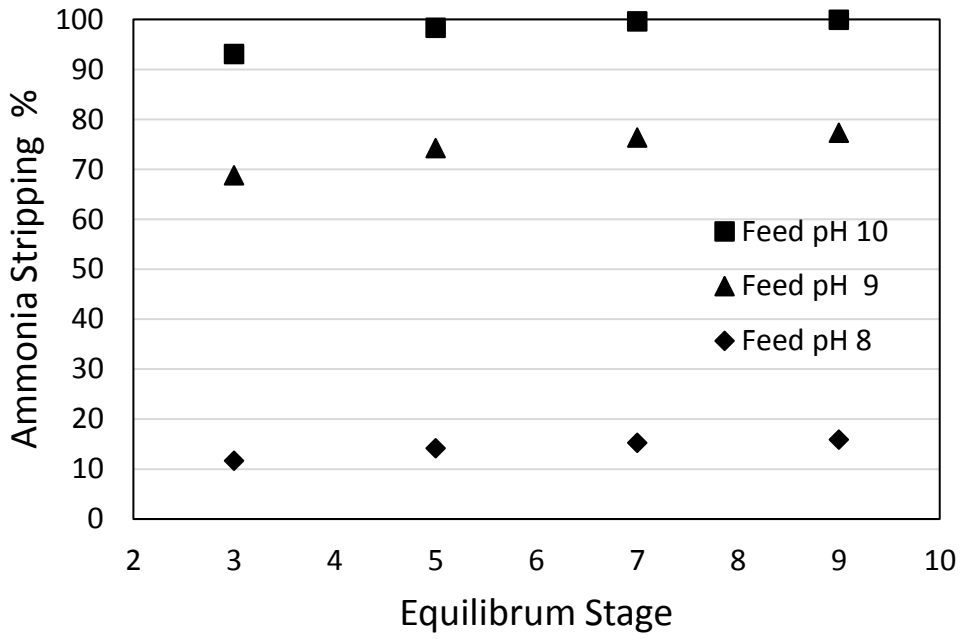

Figure 40: Ammonia stripping extent function of equilibrium stages at different feed pH.

4.1.3.3 pH Model in the Stripping Column.

The second simulation model is to evaluate the ammonia stripping with 3 equilibrium stages at different feed pH. The model shows that the feed pH has an impact on the ammonia stripping. As Figure 41 shows, the result can be divided into two feed pH ranges. The first feed pH range is from 8 to 10, a range in which the feed pH has a major effect on the extent of ammonia stripping. The second pH range is from 10 to 12, in which the ammonia stripping extent is not significantly affected by the feed pH.

Therefore, this model suggests that a feed pH of 10 is the most feasible operational pH for ammonia stripping.

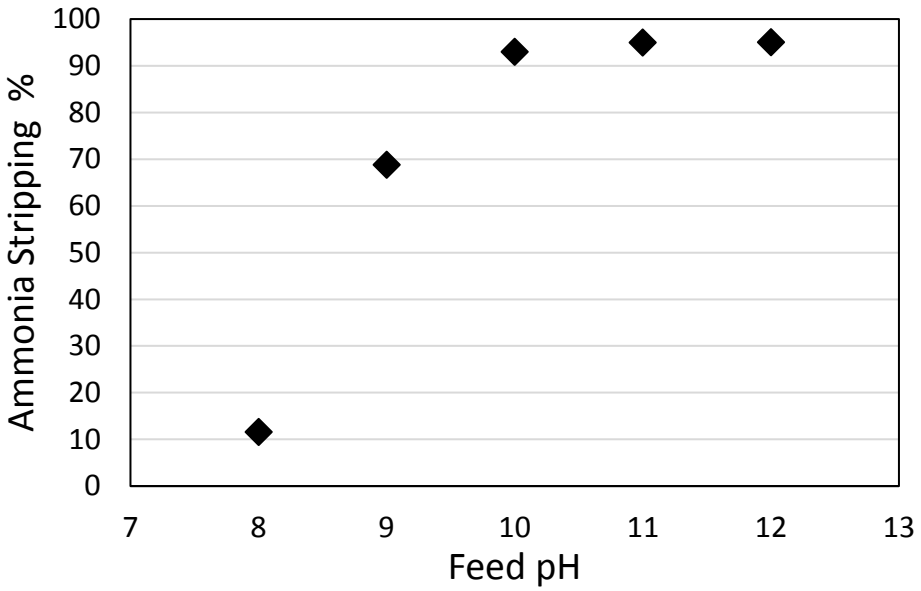

Figure 41: Ammonia stripping extent function of feed pH.

The pH of the leachate leaving the stripper was also a function of the feed pH. It is important to consider the bottom pH for two reasons. The first and most important reason is that the leachate leaving the stripper is returned to the anaerobic digestion system as shown on the overall system diagram, Figure 1. Therefore, the of the stripper liquid effluent bottom pH needs to be considered to minimize the disturbance to the anaerobic digestion system, which has a pH range of 6.8 to 8 (Gerardi, 2003). Although higher feed pH values have higher ammonia stripping extents, they also have higher liquid effluent pH values. Considering the feed pH vs. bottom pH model shown in Figure 42, feed pH at 11 and 12 should be avoided in this integrated anaerobic digestion

system. Both feed pH 8 and 9 are fine in this respect but they both lead to low ammonia stripping extents. Therefore, pH 10 is recommended for the ammonia stripping because it results in high ammonia stripping extent and minimizes anaerobic digestion pH disturbances.

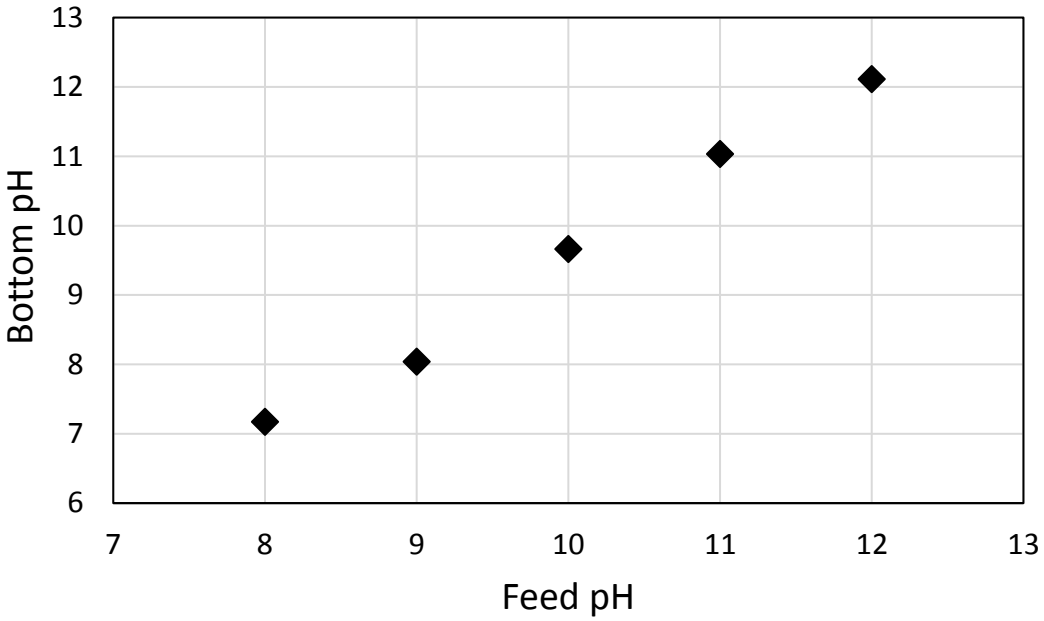

Figure 42: The stripping column bottom pH function of feed pH.

4.1.3.4 Carbon Dioxide in the Stripping Gas

The effect of the presence of carbon dioxide in the stripping gas was modeled. Whereas only air was used in the previous models, a mixture of nitrogen and CO_2 was used to study the effect of CO_2 in the ammonia stripping performance. The goal of using a mixture of nitrogen and CO_2 as a stripping gas instead of only air is to assess the feasibility of using biogas from the digester, which mainly consists of CO_2 and methane, as a stripping gas. The methane content of the biogas was neglected and replaced with

nitrogen in this model because methane has a low solubility in water. Hence, it has negligible effects.

Four stripping gas mixtures are compared in this model, each containing different CO_2 concentrations of 0, 20, 30 and 40%. The models show that the presence of CO_2 in the stripping gas has a significant effect on the stripping performance. For instance, this model shows that the ammonia stripping extent at feed pH 10 for stripping gas with 0% CO_2 is 93% whereas it is only 18% when the CO_2 % increased to 40% (Table18).

Table 18: Ammonia stripping extent as a function of carbon dioxide concentration in the stripping at different stripping feed pH.

Feed pH	CO_2 %			
	0%	20%	30%	40%
8	12	6	1	0
10	93	31	22	18
12	95	42	33	28

The ammonia stripping extent decrease as the amount of CO_2 in the stripping gas increases especially at feed pH 10 and 12 (Figure 43). At feed pH 8, the ammonia stripping extent is very low, which makes it hard see the effect of the CO_2 in the stripping performance. Therefore, the ammonia stripping extent is very close for all gas CO_2 levels at feed pH of 8.

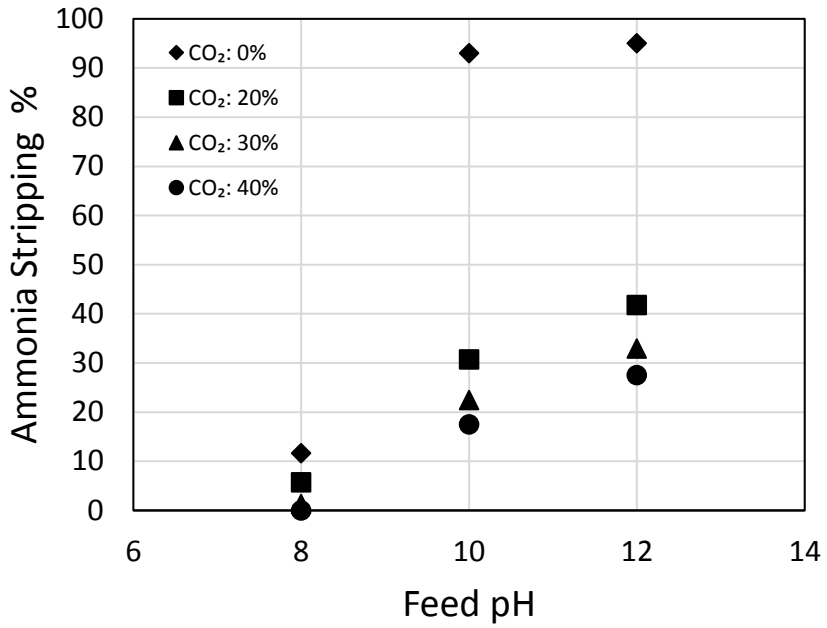

Figure 43: Ammonia stripping extent as a function of the concentration of carbon dioxide in the stripping gas at different stripping liquid feed pH values.

Higher concentrations of CO_2 in the stripping gas was considered for a liquid feed pH 10 because pH 10 was found to be the most practical stripping pH based on this model. The model result (Figure 44) shows that the ammonia stripping % significantly decreases even with a small concentration of CO_2 in the stripping gas. For example, the ammonia stripping % drops from 93% to 61% when there is only 5% of CO_2 in the stripping gas.

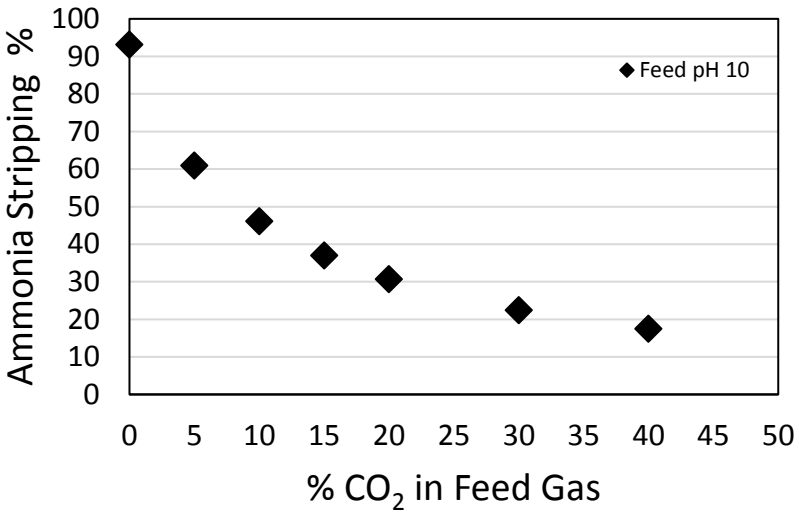

Figure 44: Ammonia stripping as a function of the carbon dioxide concentration in the stripping gas at feed pH of 10.

The decrease in the ammonia stripping performance due to the presence of CO_2 can be explained by studying the pH of the liquid in the stripping column as a function of CO_2. As shown in Figure 45, this model shows that the pH of the liquid in the stripping column decreases as the concentration of CO_2 in the stripping gas increases because CO_2 converts to carbonic acid as it dissolved in water, which may further dissociate into bicarbonate and carbonate, discharging H^+ into the aqueous solution and decreasing its pH. Figures 45 & 46 show that the pH of the bottom stream leaving the stripping column is a function of CO_2 concentration in the stripping gas, which supports the theoretical analysis of increasing the pH due to the presence of CO_2. Since ammonia and ammonium exist in equilibrium in aqueous solution and low pH shifts the equilibrium to ammonium (less volatile than ammonia), ammonia stripping decreases as the pH decreases due to the presence of CO_2.

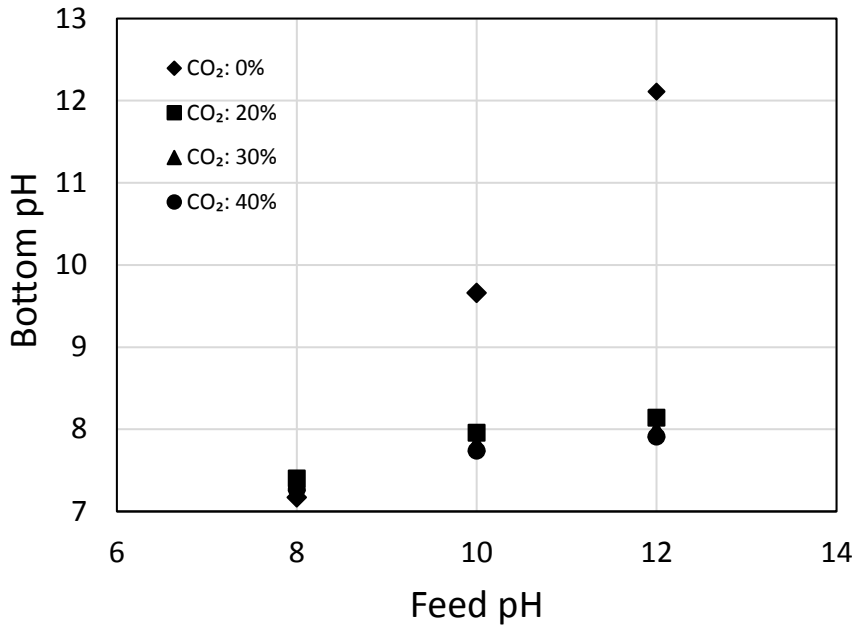

Figure 45: Experimentally determined effect of CO_2 on the stripping column pH for different feed pH.

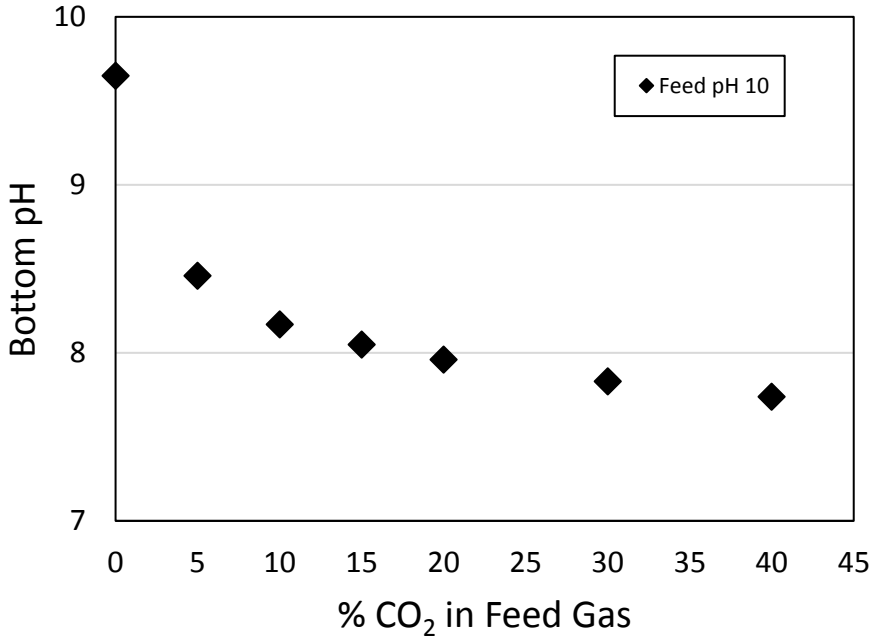

Figure 46: Experimentally determined effect of CO_2 on the stripping column pH at feed pH 10.

4.2 Ammonia Absorption Unit

4.2.1 Absorption Performance as a Function of pH and Nitrogen Concentration of the Absorber Feed.

4.2.1.1 Ammonia Absorption Experimental Objectives and Specifications

The objective of the absorption experiments was to evaluate the ammonia absorption at different absorbent feed pH values as well as at different nitrogen concentrations in the liquid absorber feed. To examine the effect of the liquid feed pH on the ammonia absorption, the ammonia absorption was measured at low feed pH (pH =2) and high feed pH (pH=7). Similarly, the effect of the nitrogen concentration in the absorber feed on the ammonia absorption was evaluated at a low level of nitrogen concentration (N=2 g/L as N) in the form of ammonium nitrate and at a high level of nitrogen concentration (N=7 g/L as N) in the form of ammonium nitrate, too.

Table 19: The nitrogen concentrations in the absorber feed.

	N level [g/L] as N	N / NH_4NO_3 ratio	NH_4NO_3 [g/L] added
High N level	7	0.35	20
Low N level	2	0.35	5.71

Table 20: Summary of the experiments.

Expt. number	NH_4NO_3 as N [g/L]	pH	Absorption %
1	2	7	82
2	2	2	90
3	7	7	70
4	7	2	82

4.2.1.2 Ammonia Absorption Experimental Result and Analysis

The result shows that neither the feed pH nor the nitrogen concentration in the absorber feed has a major impact on the ammonia absorption. The ammonia absorption in Expt.1, which represents a low feed nitrogen level (2 g/L NH_4NO_3 as N) and high feed pH (pH 7) is 82%, whereas it is 90% in in Expt. 2 at low feed pH (pH 2) for same concentration of ammonium nitrate. Comparing Expt. 1 and Expt. 2, the ammonia absorption is 8% higher at liquid feed pH 2 than at feed pH 7 for the same concentration of ammonium nitrate in the absorber feed. Considering the ammonia absorption at high level for different feed pH by comparing Expt. 3 and Expt.4, it can be seen that the ammonia absorption is higher by 15% at feed pH 2 than at feed pH 7. On the other hand, the ammonia absorption difference due to the nitrogen concentration in the absorber feed can be observed by comparing Expt. 1 and Expt. 3 at feed pH 7 or by comparing Expt. 2 and Expt. 4 at feed pH 2. Consider the high feed pH case, the ammonia absorption is 82% at low nitrogen feed whereas it is 70% for the high nitrogen. For low feed pH, the ammonia absorption is 90% with the low nitrogen feed and is 82% with the high nitrogen feed. The ammonia concentrations of the absorber gas effluent as a function of absorber liquid feed pH for low and high nitrogen concentrations were also reported (Figure 48). As explained previously (Section 3.11), the ammonia concentration of the absorber gas inlet was fixed at 2000 ppm (mole base) for all cases. On the other hand, the measured ammonia concentrations in the gas outlet were different for each tested operational condition (Figure 48).

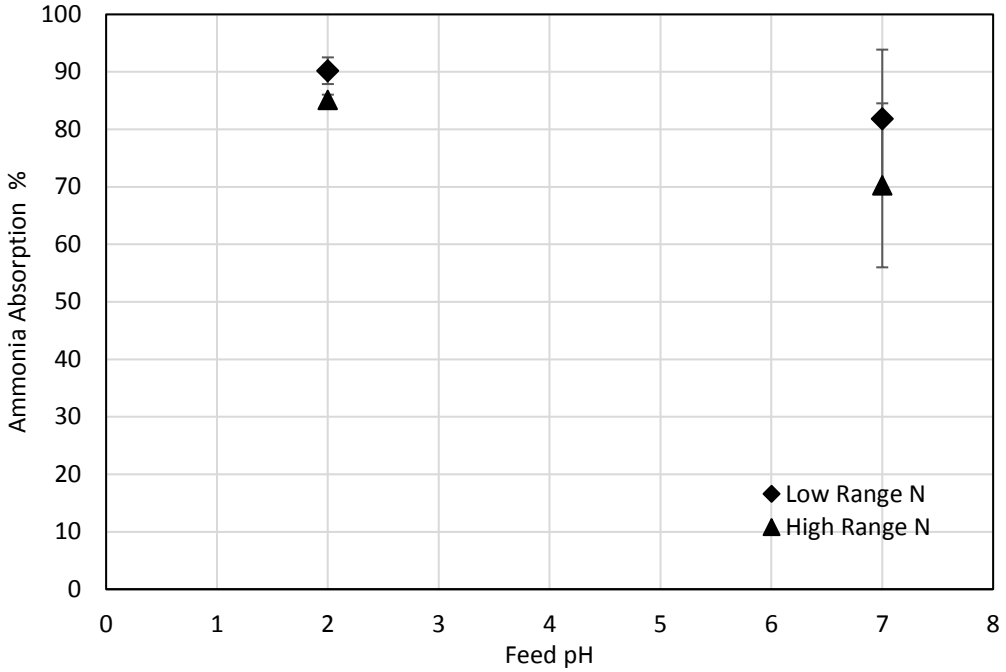

Figure 47: Ammonia absorption as a function of absorber liquid feed pH for low and high nitrogen concentrations.

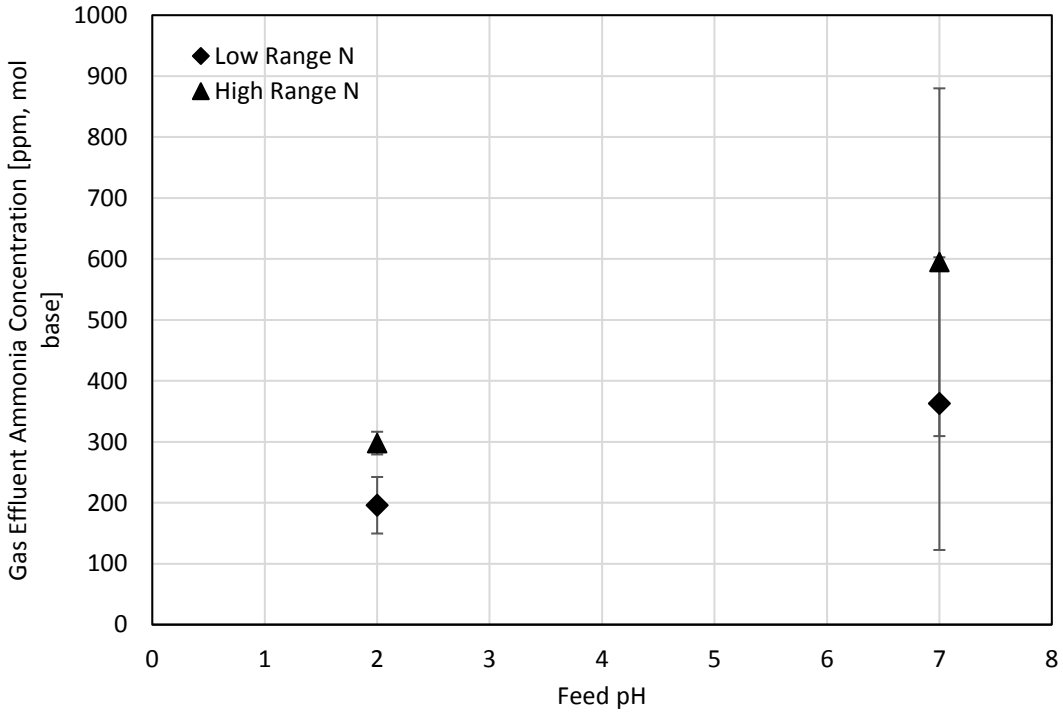

Figure 48: Ammonia concentration in the absorber gas effluent as a function of absorber liquid feed pH for low and high nitrogen concentrations.

The experimental data (Figures 47 & 48) agree with the theoretical expectation as the ammonia absorption is higher at lower pH and lower nitrogen concentration. Ammonia and ammonium exist in equilibrium in water ($NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$) which is a function of the pH. Lower liquid feed pH converts more ammonia to ammonium, which shifts the equilibrium reaction to right. Since ammonium is more the soluble form than ammonia, that increases the ammonia absorption. On the other hand, low nitrogen concentration in the liquid is expected to result in a higher ammonia absorption extent because it provides a higher driving force, increasing the ammonia mass transfer rate, which increases the ammonia absorption. The average of the triplicate runs for each experimental condition shown in Figures 47 & 48 follows the theoretical expectation since the ammonia absorption is higher at low pH and low nitrogen concentration in the liquid feed.

Considering the ammonia concentrations of the absorber gas effluent shown in Figure 49, the absorber gas effluent in the integrated anaerobic digestion (Figure 1) might need to be treated to reduce its ammonia concentration before it is released to the atmosphere based on the emission regulation.

It is very important to mention that the ammonia concentrations used in this project in the absorber gas inlet and gas outlet were above the permissible Exposure Limit (PEL). According to the Occupational Safety and Health Administration (OSHA), the PEL for ammonia is 50 ppm (OSHA, n.d.).

However, the statistical analysis shows that we cannot conclude that there is a significant difference in ammonia absorption due to the change in feed pH nor the change in the nitrogen concentration at the tested specifications. In this experiment,

each of the experimental condition shown in Table 20 was performed three times. A Two-Factor ANOVA test with replication was used to determine whether there is any statistically significant difference between the means of the four tested conditions. The sample F factor that compares pH 2 and pH 7 was 4.55 whereas the critical F factor was 5.32. This indicated that we cannot say that there is a significant difference due to the change in pH for both low and high nitrogen absorbents. The p-value for the same comparison was 0.065. Since it is greater than 0.05, the same conclusion is supported. Similarly, the test considers the variance in ammonia absorption due to the change in the nitrogen concentrations in the absorbents and shows that it cannot be concluded that there is a significant difference because the F factor was 2.36, smaller than the critical F factor of 5.32. Also, the p-value for the nitrogen concentration comparison was 0.16. Moreover, the test does not show that there is any significant interaction between the two conditions of the feed pH and the ammonia concentration affect (interaction F factor = 0.36, the critical F factor = 5.32). The interaction p-value was 0.56. Therefore, statistical tests suggest that there is no significant difference in ammonia absorption due to the change in feed pH the change in the nitrogen concentration in the absorbents. The test results are summarized in Table 21.

Table 21: Summary of the Two-Factor ANOVA test with replication.

Variation	F	P-value	F-critical
pH	4.55	0.065	5.32
Nitrogen	2.36	0.16	5.32
Interaction	0.358	0.56	5.32

4.2.2 Absorption Simulation Models with Aspen Plus

In the absorption simulation models, the ammonia absorption extent is calculated as a function of the absorption liquid feed pH.

The temperature and pressure in the absorber were 21 °C and 1 atm. The air flow rate was 40 L/ min and the liquid flow rate was 0.002 L/min for a molar ratio (L/V) of 0.66. The gas used in this model was 0.2 mol % ammonia balanced with nitrogen gas whereas the liquid was a nitrification nutrient solution. The nutrient solution was simulated to represent the nitrified solution used in this project (Table 22)

Table 22: Absorption model operational specifications.

Model Operational Condition	
T	25 °C
P	1 atm
Equilibrium stage	3
Gas flow rate	V: 40 L/min
Liquid flow rate	0.02 L/min
Molar ration (L/V)	0.66
Gas (mole %)	NH_3 0.2% N_2 99.8%
Liquid	Nitrified solution
Nutrient solution	
Component	[mg/L]
$MgSO_4$	140.41
KH_2PO_4	529.16
NaCl	90.9
$CaCl_2$	58.6

This model suggests that the feed pH has an impact on ammonia absorption in the lower pH range from pH 1 to pH 4 (Figure 49). However, the ammonia absorption is

almost constant after pH of 4. Considering the low pH range, the ammonia absorption extent at liquid feed pH of 1 is 100% but this is not practical because of the high rates of corrosion. Also, it requires a large amount of acid to achieve this pH which increases the process cost. A liquid feed of pH 2 has 76% ammonia absorption but it also corrosive and requires acid. On the other hand, a liquid feed of pH 4 to 7 has an ammonia absorption extent of 70%.

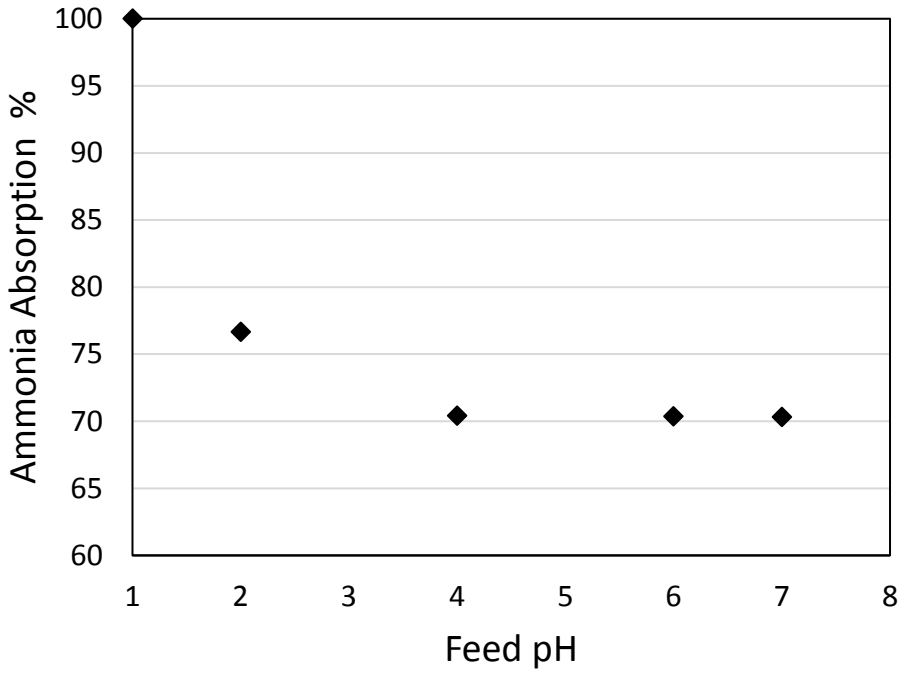

Figure 49: Ammonia absorption extent function of feed pH.

The pH of the liquid leaving the absorber was also measured as shown in Figure 50, which also has two ranges. The bottom pH increases due to ammonia absorption for the liquid feeds of pH 1 to 4 and then it is constant for liquid feeds of pH 4 to 7 at bottom pH of 11.

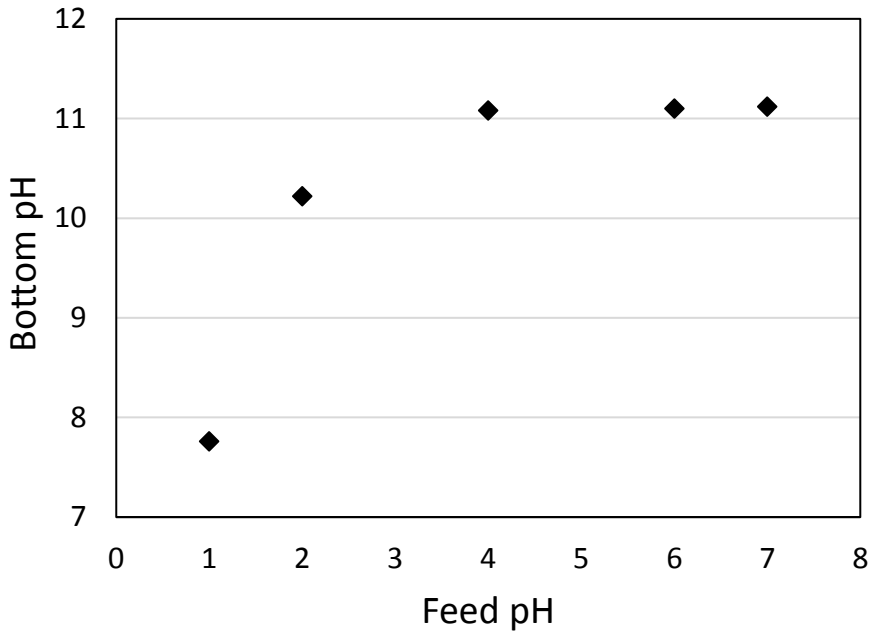

Figure 50: The absorption column bottom pH function of feed pH.

4.2.3 Absorption Overall Consideration and Recommendation

4.2.3.1 Operational consideration:

Considering the integrated anaerobic digestion system overall operation, pH of 7 was recommended for ammonia absorption since it is within nitrification pH range. Using very acidic pH for absorption negatively affects the nitrification process because the effluent of the absorber goes back to the nitrifier, shown in Figure 1. One the other hand, using high nitrogen nitrification solution increases the fertilizer production since the nitrogen is converted to ammonia nitrate fertilizer through nitrification. Therefore, the higher nitrogen level (7 g/L as N) in the absorber liquid feed is recommended considering the overall process advantages.

4.2.3.2 Assessing nitrified solution as an ammonia absorbent.

One of the main objectives of this project was to evaluate the ammonia absorption using nitrified solution. The result (Figure 48) shows that the ammonia absorption was 70% using a liquid feed of pH 4 to 7 supporting the possibility of absorption ammonia at higher pH than conventional ammonia absorption pH. Therefore, a nitrified solution with a pH 7 can be used in the absorption column as liquid feed to capture ammonia since nitrification microbial optimal pH is from 7 to 8 (EPA, 2002b). This conclusion supports the novel idea that acid can be substituted by nitrification solution in ammonia absorption in order to decrease the process cost.

5 Conclusions

This project introduced a new technology to recover nitrogen in anaerobic digestion. The digestated animal waste leachate in the anaerobic digesters which contains nitrogen is sent to the nitrogen recovery system where the ammonia is volatized in a stripping column then captured in an absorption column. Unlike the traditional ammonia recovery methods that have been reported in the literature, which use acids in the absorber to capture ammonia, a nitrified solution is used as an absorbent in this project to eliminate the cost of buying acids. Moreover, nitrification can convert the recovered ammonia to a more valuable organic fertilizer, nitrate. Therefore, one main objective of this project was to evaluate the ammonia absorption using nitrified solution as an ammonia absorbent in the absorption unit. Another important objective in this project was to assess the ammonia stripping and ammonia absorption under different operational conditions in order to provide a recommended operational condition for the ammonia recovery system.

The ammonia recovery system flow rate was the first operational condition that was considered in order to find suitable operational flow rate ranges for the liquid and gas in the stripping and absorption columns by measuring the specific liquid hold up (L_H) at different gas and liquid flow rate. The specific liquid hold up gives an indication about the hydraulic status of the column showing how stable the column is from flooding. The results show that there is a wide possible flow rate range but the flow rate that maximizes liquid-gas interfacial area while preventing flooding is just before the flooding region.

Feed pH and temperature were the other main stripping operational parameters that were analyzed. The ammonia stripping extent was calculated at several feed pH and stripping temperatures. Feed pH 8.5, 9, 9.5, 10, and 10.5 were tested and feed pH of 10 was found to be the most feasible ammonia stripping pH with ammonia stripping of 77% and HETP of 0.57 m. The ammonia stripping was also studied function the stripping temperature at 35, 50, 55, 65 °C. Among those temperatures, 50 °C has the highest stripping extent with 77% and the lowest HETP with 0.57 m.

To supplement experimental data, the ammonia stripping column was simulated with Aspen Plus. There are three stripping models which are equilibrium stages model, feed pH model and carbon dioxide model. In the equilibrium stages model, the ammonia stripping was calculated at the number of equilibrium stages of 3, 5, 7 and 10. This model shows that increasing the number of equilibrium stages has very little impact on the ammonia stripping. Therefore, 3 equilibrium stage was considered as the most practical equilibrium stage and chosen for the other models. The second model was the pH model where the ammonia stripping was calculated function of the stripper feed pH. The tested pH values were 8, 9, 10, 11 and 12. As shown by experimental data, pH of 10 was the optimal stripping pH with ammonia stripping of 93%. Although feed pH 9 provided a lower ammonia absorption (70%) than pH 10 (93%), it has some advantages over pH 10 since it would reduce chemical addition required to raise the pH, while still preventing toxicity and enhancing biogas production. The third stripping model was carbon dioxide model where the ammonia stripping was calculated function of the amount of carbon dioxide in the stripping gas. This model shows that the amount of carbon dioxide in the stripping gas has a strong impact on the ammonia stripping as the

ammonia stripping decreases as the carbon dioxide increases. For example, the ammonia stripping extent with stripping gas that contains no CO_2 is 93% while increasing the CO_2 in the stripping gas to 40% decreases the ammonia stripping from 93% to 20%.

The ammonia absorption column was the other unit that was analyzed in this project. Ammonia absorption experiments aim to study the performance of ammonia absorption at different feed pH values and different nitrogen concentrations in the absorbent, the nitrified solution. The ammonia absorption extent was calculated at feed pH 2 and feed pH 7. Although feed pH 2 provides slightly higher ammonia absorption, the statistical analysis concludes that there is not significant difference in the ammonia absorption between feed pH 2 and feed pH 7. Moreover, the ammonia absorption was calculated for two nitrogen concentrations in the absorbent which are 2 g/L as N and 7 g/L as N. Similarly, low nitrogen concentration in the absorbent has higher ammonia absorption but, statistical, there is not significant difference in the ammonia absorption between these two nitrogen concentrations. Therefore, this experiment shows that neither the feed pH nor the nitrogen concentration of absorbent has a significant impact on the ammonia absorption.

An Aspen model was generated for the ammonia absorption function of the absorber feed pH. The ammonia absorption was calculated at pH of 1, 2, 4, 6, and 7. The model shows that the ammonia absorber is 100% at feed pH 1 and 76% at feed pH 2 whereas it is constant at 70% for feed pH 4 to 7. Just like in the experimental data, the ammonia absorption is not greatly impacted by the feed pH except for pH 1.

To summarize the project main outcomes, the data shows that the ammonia stripping feed pH has a big impact on the stripping performance and suggests a feed pH of 10 as an optimal feed pH for ammonia stripping. For stripping temperature, 55 °C is recommended for ammonia stripping because it has the highest ammonia stripping comparing the other test temperatures including higher and lower temperatures. One the other hand, the ammonia absorption process is not significantly affected by the feed pH nor the concentration of nitrogen in the absorbent which answer one of the main equations in this project about the feasibility of replacing acid absorbent with nitrification solutions. Therefore, it can be concluded that a nitrification solution can replace the traditional acid absorbents in ammonia absorption.

Further recommendations for future work, whereas the focus in this project was on the nitrogen recovery system, it would be very beneficial to analysis the overall system proposed in Figure 1. The overall process shown in Figure 1 consists of three sub-systems: (1) anaerobic digestion (2) the nitrogen recovery system (stripper and absorber) and (3) nitrification system. Each sub-system has its optimal operational conditions including temperature and pH. When connecting the three systems as proposed in this project, suitable operational conditions for each system is needed to be found considering the overall system performance and economy. In this project the three systems were separate, and each system was running independently. For future work, it would be very advantageous to have the three systems connected as one system as shown in Figure 1. Connecting the systems would allow consideration of overall system advantages. For example, it would provide the opportunity to study the benefit of the ammonia removal to the anaerobic digestion system which reduces its

ammonia toxicity. It would also allow to identify the amount of ammonia needed to be removed from the anaerobic digestion to prevent ammonia toxicity in anaerobic digestion. Another recommendation is that it would be very beneficial to study the economic feasibility and focus more on the financial considerations for the overall system. Although general economic recommendations were considered and analyzed in this project including the process design and operational system such as considering the number of equilibrium stages, temperature and feed pH, exact costs were not calculated. For example, increasing the feed pH in the stripping requires a base which increases the process cost, so a trade-off between the cost and ammonia stripping performance was analyzed in this project and a pH of 10 was recommended even though a pH of 10.5 provided a higher ammonia stripping. However, the exact cost of the base versus the profit of the ammonia recovered was not calculated in this project. Also, it would be interesting to compare the process cost and benefits of ammonia recovery using nitrifier which produces organic fertilizer (used in this project) versus other traditional methods such as absorption with acid which does not allow to produce organic fertilizer. Therefore, an overall operational and economic analysis would provide integrated outcomes for the whole system connected. Considering the system design, one interesting suggestion would be to replace the ammonia absorber (used in this project) with ammonia adsorption column. An organic material would need to be considered to fill the adsorption column in order to keep the recovered ammonia organic. One another design recommendation in the integrated anaerobic digestion system is that the pH of the stripper effluent, which is returned to the anaerobic digestion system, might need to be adjusted to be within the anaerobic digestion pH.

One way that can be considered is to bubble the stripper effluent with biogas which contains CO_2 in order to reduce the stripper effluent stream pH. Another way that might reduce the anaerobic digestion pH disturbance is to consider lower stripping pH that this work's recommended stripping pH (pH of 10). However, lower stripping pH would provide a lower ammonia stripping.

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