A CURIOUS INSIGHT INTO REMOVAL AND RECOVERY OF AMMONIA FROM STRUVITE THERMAL DECOMPOSITION UNIT OUTLET BY ACIDIC ADSORPTION

by

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Abstract

In this study investigated the recovery of ammonia from the hot and humid gas outlet of a struvite thermal decomposition unit. Based on the project objectives and the initial studies, adsorption of the ammonia by oxalic acid dihydrate was selected as the ammonia removal method. Oxalic acid’s solid form not only would reduce the energy loss through adsorption, but also could be a potential carrier for the final product that could be used as a nitrogen fertilizer. This research presents experimental stages specifically designed for recovering the ammonia and energy of this stream. Experiments started in ambient temperatures and humidity to gain a good understanding of the process. Later, it evolved to simulate the actual conditions of the struvite thermal decomposition unit outlet.

During the investigation phase, factors such as flow rate, adsorbent crystal size, and contact time were recognized as the most influential parameters for this process. The efficiency of ammonia removal could be optimized to stay above 90% by controlling these factors in a two-hour period. In the next phase, as the struvite thermal decomposition unit had output conditions of 80°C and relative humidity of 80%, experiments were continued by accommodating these conditions. At this stage, difficulties were observed in the stability of initial adsorbent. This led to a substitution of this adsorbent with anhydrous oxalic acid and potassium tetraoxalate dehydrate. The results indicated a high capacity and potential for ammonia adsorption. Despite the adverse effects of high temperature on adsorption processes, ammonia removal efficiency could be kept above 93% at all times, with modifications in the reactor for setting a good range of contact times for the adsorption. Although ammonia removal from the stream could achieve high efficiencies the ammonia capture in the adsorbents never exceeded 10-15% of the maximum theoretical adsorption. This suggested that the adsorption is only occurring in the surface layer of the adsorbents and the ammonia molecules are not penetrating and reacting with the total acid mass. Therefore, it is recommended that further research be continued, to gain new insight into this problem.
Preface

This thesis is original, unpublished, independent work by the author, Neshat Basiri.
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<tr>
<td>AGMD</td>
<td>Air Gas Membrane Distillation</td>
</tr>
<tr>
<td>ANAMMOX</td>
<td>Anaerobic Ammonium Oxidation</td>
</tr>
<tr>
<td>B.C.</td>
<td>British Columbia</td>
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<tr>
<td>BNR</td>
<td>Biological Nutrient Removal</td>
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<tr>
<td>°C</td>
<td>Degrees Celsius</td>
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<td>C</td>
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<td>CO₂</td>
<td>Carbon Dioxide</td>
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<tr>
<td>Cm</td>
<td>Centimeter</td>
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<tr>
<td>DCMD</td>
<td>Direct Contact Membrane Distillation</td>
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<tr>
<td>FBR</td>
<td>Fluidized Bed Reactor</td>
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<tr>
<td>g</td>
<td>gram</td>
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<tr>
<td>G</td>
<td>Gibbs Energy</td>
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<tr>
<td>H</td>
<td>Enthalpy</td>
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<td>K</td>
<td>Potassium</td>
</tr>
<tr>
<td>LPM</td>
<td>Liter per Minute</td>
</tr>
<tr>
<td>mm</td>
<td>millimeter</td>
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<tr>
<td>N</td>
<td>Nitrogen</td>
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<tr>
<td>NH₃</td>
<td>Ammonia</td>
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<tr>
<td>NH₄⁺</td>
<td>Ammonium ion</td>
</tr>
<tr>
<td>OH⁻</td>
<td>Hydroxide</td>
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<tr>
<td>pH</td>
<td>Power of Hydrogen</td>
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<tr>
<td>RH</td>
<td>Relative Humidity</td>
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<tr>
<td>S</td>
<td>Entropy</td>
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<tr>
<td>SGMD</td>
<td>Sweeping Gas Membrane Distillation</td>
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<tr>
<td>TOC</td>
<td>Total Organic Carbon</td>
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<tr>
<td>Acronym</td>
<td>Description</td>
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<td>---------</td>
<td>----------------------------------</td>
</tr>
<tr>
<td>UBC</td>
<td>University of British Columbia</td>
</tr>
<tr>
<td>USD</td>
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<tr>
<td>VMD</td>
<td>Vacuum Membrane Distillation</td>
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<tr>
<td>WWTP</td>
<td>Wastewater Treatment Plant</td>
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<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
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I would like to leave the following space in memory of Frederic Koch, a great mind and a kind heart not beside us anymore…
This thesis is dedicated to my parents

Esmaeil Basiri and Marjan Fardad

For their endless love, support and encouragement
Chapter 1: Introduction

Ammonia has been one of the key players in the agricultural history of mankind. It became more and more important with the population growth and the corresponding food demand. As industrial processes were developed for addressing this demand and increasing amounts of ammonia were produced, ammonia started to switch sides from being a precious food fertilizer that will increase the food production and quality, to a pollutant that can decrease the air and water quality in many ways. This pollution was not due to industrial processes of ammonia production that involved huge amounts of fossil fuel consumption and greenhouse gas emissions, but also due to the excessive loss of ammonia in nature that would end up over fertilizing aquatic environments and trigger eutrophication, this increases the water toxicity levels and influences the overall balance of ammonia in the environment.

In recent years, a novel approach to solve this problem was applied to this cycle. Since a lot of ammonia in food ends up in the municipal wastewater streams, it was suggested to recover this ammonia in a form that could be reused as fertilizers and close the nitrogen cycle by this method (James D. Doyle & Parsons, 2002). The path for doing so was through recovering ammonia in the form of struvite pellets from wastewater treatment plants. Struvite was previously known and studied widely as a problem for the WWTPs. It would form in the WWTPs pipes and pumps and cause maintenance issues resulting in costly treatments, replacements and plant shutdowns (Borgerding, 1972). Therefore, recovering this struvite before formation in the pipeline under specific conditions and in the desired forms for fertilizer application would not only provide a valuable product, but also eliminate a common WWTP maintenance problem.

In most cases these struvite pellets consist of 1:1:1 molar ratio of ammonia: phosphate: magnesium. Since the total amount of ammonia in municipal wastewaters is more than phosphate and magnesium, this process could only remove an average between 5% and 10% of the total amount of existing ammonia in the stream (Wilson, 2013). Different techniques have been employed to increase this removal efficiency and recover as much ammonia as possible. One of these techniques was the thermal decomposition of struvite that could release ammonia
from struvite pellets with heating and return the resulting newberyite (that contains phosphate and magnesium) to the wastewater stream to form more struvite pellets, while removing a higher percentage of ammonia. This process had a gas outlet that was a hot and humid air stream containing low concentrations of ammonia (Farhana, 2015).

The current study was based on removal of this ammonia from the gas stream exciting the struvite thermal decomposition unit, and recovery of its energy content and ammonia as a potential product. The importance of these objectives are not only the elimination of ammonia discharge to the atmosphere from struvite thermal decomposition unit, but also the possibility of added economic value to the whole removal and recovery process, by providing additional products and energy recovery.

In order to do so, different options were considered and adsorption by an organic acid, in solid form, was the one chosen due to the benefits it could provide. In the search for an acid with these characteristics, oxalic acid dihydrate was selected. Since this was a novel approach, and there was not any data available about this specific adsorption process, numerous experimental procedures were applied to investigate the parameters influencing this process as well as optimizing its performance. In this chapter, the background and existing literature about this matter will be presented in detail.
Chapter 2: Background and Literature Review

2.1 Ammonia

Ammonia is an alkaline gas having an atom of nitrogen bonded with three hydrogen atoms. With a molecular weight of 17.03, this colorless gas stands lighter than air. Ammonia holds two abundant elements on earth together, yet complicated in a way. Despite the fact that 78% of the atmosphere is nitrogen, these nitrogen atoms are bonded strongly together with a triple bond that requires great energy input (226 kcal/mole) to break and be available for new bonds (Pauling, 1960). The natural formation of ammonia is through decomposition of organic materials, volcanic activities and animal wastes. Ammonia has been known from the ancient times in salt forms such as ammonium carbonate, ammonium chloride and ammonium nitrite (Appl, 1999). In the present, ammonia is one of the most widely produced chemical compounds all around the world due to its high demand. The following section focuses on different applications of this compound starting with the most important one that has been the main driving force for its industrial production throughout the years.

2.2 Applications of ammonia

2.2.1 Agricultural application of ammonia

Nitrogen is one the essential nutrients for the agriculture. Justis von Liebig was the first to analyze the minerals essential for the plant growth and emphasize the importance of nitrogen for plants in his book in 1840 (Appl, 1999). Nitrogen converts to amino acids inside plants. These amino acids are the building blocks of proteins, which will be used in production of enzymes, structural parts of plants and also the stored protein in the plant that gives it the food value. Also, it combines with the chlorophyll to utilize the sunlight as the plant's energy source. Therefore, plants cannot grow without nitrogen and nitrogen deficiency will result in shorter and stunted plants that are weaker, grow slower and have standability problems (Zhao et al., 2005).
Although there is plenty of nitrogen in our environment, it is the N\textsubscript{2} gas form that cannot be consumed directly by most of the organisms. Also, most of the nitrogen in the soil is tied to organic matter and cannot be consumed by plants. Therefore, this nitrogen must be transformed to other forms called “reactive nitrogen” to become biologically functional.

After discovery of the effect of nitrogen fertilizers the demand for them increased rapidly. The earliest nitrogen fertilizer source was ammonium sulfate recovered as a byproduct of the destructive distillation of coal, which was not sufficient for the existing demand. The first industrial process developed for nitrogen fertilizer production in 1898 was the Frank – Caro calcium cyanamide process. However, the supply from this process not only could not cover the demand, but also could not compete with the cheap, natural, sodium nitrate supplied by Chile. In 1898 Sir William Crooks addressed this problem in his famous presidential speech saying: “It is the chemist who must come to the rescue of the threatened communities. It is through the laboratory that starvation may ultimately be turned into plenty. Before we are in grip of actual dearth the chemist will step in and postpone the days of famine to so distant a period that we, our sons and grandsons may live without undue solicitude for the future.” (Appl, 1999)
In Figure 2-1, the left axis is presenting the population in billions, and the right axis is presenting nitrogen production in teragrams of nitrogen per year through different sources. In the last 50 years the human population has more than doubled. By 2050 there will be at least nine billion people living on this planet as reported by The United Nations. One of the basic needs of this population will be food. Since most of the food required for the growing population should be produced by increasing the production over the existing farmland, fertilizers and agricultural practices are becoming more and more important.

### 2.2.2 Ammonia as fuel

As of today, the main source of energy for most industries all around the world comes from fossil fuel sources. Although being cheap and efficient, at this stage the concerns about alternative fuel options are increasing due to the fact that fossil fuels are not renewable. Also we are consuming the last portions of our fossil fuel sources at accelerated rates. Coal, oil and natural gas are all made through natural processes and their reproduction rate is not comparable...
with their extraction and depletion rates. On the other hand, environmental and ecological problems associated with their usage, including global warming, acid rains, air and water pollution, are pushing mankind to look for a sustainable, safe and renewable replacement for fossil fuels.

One of these alternatives is ammonia. The main reasons include it’s low production cost, availability and ease of handling, storing and distributing processes in comparison to other viable and proposed options. This is because ammonia has a high ignition temperature that makes it a safer fuel in terms of fire hazard. Moreover, ammonia fuels are carbon free. Ammonia’s high hydrogen density makes it a fuel that could generate high energy content for its unit of volume. Ammonia can store 30% more energy by volume than liquid hydrogen (MacKenzie & Avery, 1996). It can also be stored safely in low pressures and room temperatures (Nozari & Karabeyoğlu, 2015). Having similar properties to liquid propane, the same infrastructure for transport and storage of widely used liquid propane can be used for ammonia with minor material modifications (Reiter & Kong, 2011). The first application of ammonia as fuel was in 1942 in Belgium for public motorbuses, where ammonia vapor and coal gas were used together to run these buses (Kroch, 1945). Ammonia is usually combined with other compounds to provide a better combustion performance. Also it is mostly used in fuel cells and low speed engines such as internal combustion engines, gas turbines and boilers. It has been implemented for sports cars (Marangoni Toyota GT86 Eco Explorer) having dual fuel systems where the engine could use ammonia at lower speeds (engine speed under 2800 rpm) (Fumanelli, 2013). Ammonia and air mixtures with concentrations of 16-25% have been used for piston engines with modifications to fuel and ignition system (Zamfirescu & Dincer, 2008).

2.2.3 Other applications of ammonia

Although most of the ammonia produced goes into agricultural applications, there is still a huge amount of ammonia used in different industrial sectors. Here, a brief explanation of different properties of this compound that corresponds to its various applications will be given.
Ammonia has a pyramid configuration with the nitrogen atom placed at the apex. Ammonia and water share a similar electron configuration and bond angle that explains their similarity in many reactions. The diamagnetic characteristics of this compound make it a good solvent able to dissolve many substances. Therefore, liquid ammonia is used as an alkali metal solvent in industry (Johnson & Fernelius, 1929). Application of ammonia in the textile industry is another common use of ammonia. Fibers treated with liquid ammonia have shown significant abrasion resistance increase. Anhydrous liquid ammonia is applied for flame-retardant finishing of cotton and polyester (Deo, 2001). Ammonia has a sharp and distinctive odour that is used for preventing and treating fainting. It is also used in sulfa drugs manufacturing that are mostly antibacterial. This is because the sulfonamide can inhibit folate synthesis enzyme that eventually prevents bacterial growth and reproduction (García-Galán et al., 2008). There has been an increasing interest in application of ammonia as a refrigerant, due to its low boiling point and high heat of evaporation. Economic and environmental considerations make ammonia a competitor to the conventional CFC refrigerants (Critoph, 1996). The steel industry, plastic manufacturing, water purification and explosive material production are some of the other industrial sectors consuming ammonia. Ammonia is also used in some cleaning solutions for household purposes. These types of solutions usually contain about 5-10% ammonia. A higher percentage of ammonia is only used in industrial processes, as it is corrosive and safety considerations are required for its handling.

2.3 Industrial process for ammonia production

The ammonia required for satisfying its demand is mostly produced through an industrial process developed for ammonia production in great quantities over the years. Ammonia is the second largest synthetic chemical product. In 1908, Fritz Haber presented the process for ammonia production. Five years later in 1913, Carl Bosch and his team of engineers could design the industrial scale of the process and build the first ammonia plant (Appl, 1999). The ammonia production process was a really important industrial step for mankind, as it was one of the very first catalytic, high pressure and high temperature processes industrialized worldwide. The Haber–Bosch process changed the world for good with its simple fundamental reaction of hydrogen
and nitrogen atoms on an iron catalyst. This process employs natural gas as a hydrogen source and the atmospheric nitrogen gas as a nitrogen source, to produce ammonia in temperatures about 400-450°C and pressure of 100-300 atm (King & Woodruff, 1982). This is the most widely used process in the fertilizer production industry. The process has been modified and improved over years in the sense of catalyst modifications, reactor configuration, switch in raw material etc. However, the basic process sequence has remained unchanged.

2.4 Ammonia as a pollutant

In nature, nitrogen compounds exist in the atmosphere and water, but can be handled by natural processes. For instance, ammonia is a byproduct of fish metabolism, and it also exists in its urea. However, it is converted to nitrite and later to nitrate and gets consumed by plants and algal cultures available in the water. It can also go through denitrification, be converted to nitrogen gas, leave the water as bubbles and enter atmosphere. Figure 2-2 presents the simplified nitrogen cycle and its most common naturally existing forms. This simplified version can help in understanding the close connection between different forms of nitrogen. The increase in the amount of these compounds and the excessive amount of nitrogen that is entering the system by human activities will disturb the natural cycle.

Figure 2-2 Simplified nitrogen cycle and transformation between its forms
2.5 Nitrogen loss in the environment

The amount of ammonia applied for the agricultural purposes exceeds the amount actually consumed by the crops. This excess amount will then get transferred to soil, water and air; that would mean a loss of ammonia to these environments. This loss of ammonia continues to grow in the sequences after the consumption by plants until they are actually consumed by humans in different forms of food. Figure 2-3 demonstrates the loss of nitrogen in each step from applying to the agricultural lands until consumed by human beings. Crops take up nitrogen existing in the soil and accumulated from last years as well as the nitrogen from fixation and fertilizer source. Assuming recycling of nitrogen in manure after the feed stage, residues of crops and meat byproducts (green arrows), over 80% of the applied fertilizer is eventually lost to the environment (red arrows).

![Figure 2-3 Percentage of nitrogen loss through different stages from application on farm land to consumption by human (Braun, 2007)](image)

There are various types of fertilizers for providing nitrogen. Most of these fertilizers are either ammonium based or nitrate based. Anhydrous ammonia, ammonium nitrate, ammonium sulfate and N solutions are some of the examples of commercially available nitrogen fertilizers. Urea is also a common fertilizer that decomposes to ammonia and carbon dioxide in aerobic soil and to
dinitrogen, nitrous oxide, nitric acid and nitrite in anaerobic soils. The major mechanisms for loss of nitrogen in the environment include volatilization, denitrification, runoff, and leaching (Datta, 1986). Nitrogen fertilizer’s reaction and efficiency in the soil is mostly governed by temperature, moisture, pH, texture, buffering capacity and organic matter content of the soil. The efficiency of fertilizers also depends on their physical forms and application methods (Russel, 1979).

Livestock manure is another source of ammonia release to the environment. Ammonia loss to the atmosphere from manure can range from 10% to 99% of the total available ammonia in the manure, depending on the conditions. However, the highest rate of volatilization occurs in the first 6 hours (Hoff et al., 1981). Ammonia loss during storage and after application of manure to the soil as a fertilizer is a common handling problem of manure. Soil pH and temperature are the major factors affecting the rates of this loss. For instance, under acidic conditions, the ionized form of ammonia dominates. This form of ammonia is relatively non-volatile and the loss through vaporization declines (Sommer & Hutchings, 2001). Moreover, it was proven that ammonia loss was reduced when the manure was injected beneath the soil surface layer (Hoff et al. 1981).

There is also a great amount of ammonia released to air, water and soil from industries other than agriculture. The metal industry, petroleum extraction and refineries are among those. Table 2-1 summarizes annual ammonia release from some of the top industrial sources in Canada.
Table 2-1 Top industries in ammonia release in Canada after fertilizer industries based on data gathered in 1996 (Environment Canada, 2001)

<table>
<thead>
<tr>
<th>Industry</th>
<th>Location</th>
<th>Ammonia release (tonnes/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shell Scotford refinery</td>
<td>Fort Saskatchewan, Alberta</td>
<td>2488</td>
</tr>
<tr>
<td>Petro Canada refinery</td>
<td>Edmonton, Alberta</td>
<td>1718</td>
</tr>
<tr>
<td>Imperial Oil Limited Strathcona</td>
<td>Edmonton, Alberta</td>
<td>1130</td>
</tr>
<tr>
<td>Algoma Steel in Sault Ste Marie</td>
<td>Ontario</td>
<td>676</td>
</tr>
<tr>
<td>Cobalt Refinery Company</td>
<td>Fort Saskatchewan, Alberta</td>
<td>528</td>
</tr>
<tr>
<td>Inco Nickel Refinery</td>
<td>Copper Cliff, Ontario</td>
<td>297</td>
</tr>
<tr>
<td>Stelwire</td>
<td>Hamilton, Ontario</td>
<td>245.5</td>
</tr>
<tr>
<td>Stelco refinery</td>
<td>Hamilton, Ontario</td>
<td>182</td>
</tr>
<tr>
<td>Dofasco refinery</td>
<td>Hamilton, Ontario</td>
<td>180</td>
</tr>
</tbody>
</table>

The average human body needs roughly 2.0 grams of nitrogen per day for its amino acid and protein balance. However, most humans consume much more nitrogen than would be needed. The typical American diet supplies approximately 13 grams of nitrogen per day (Minnis, 2009). Therefore, about 11 grams will go into the waste stream. Kitchen waste, yard and pet waste, and certain soaps and detergents containing nitrogen and can contribute to nutrient pollution, if not properly used or disposed. The average concentration for ammonia in sewage entering wastewater treatment plants is estimated to be about 14 mg/L in Canada contributing to a total ammonia load of 62,000 tonnes per year to aquatic systems (Environment Canada, 2001). The overall ammonia release through municipal wastewater shown in table 2-2 far overweighs the industrial discharge in each province.
Table 2-2 Ammonia loading rate in municipal wastewater for top 12 cities in Canada in 1995 or 1996

(Environment Canada, 2001)

<table>
<thead>
<tr>
<th>City</th>
<th>Ammonia loading (tonnes/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Montreal, QC</td>
<td>6128</td>
</tr>
<tr>
<td>Toronto, ON</td>
<td>5938</td>
</tr>
<tr>
<td>Vancouver, BC</td>
<td>5741</td>
</tr>
<tr>
<td>Winnipeg, MB</td>
<td>2152</td>
</tr>
<tr>
<td>Edmonton, AB</td>
<td>1946</td>
</tr>
<tr>
<td>Hamilton, ON</td>
<td>1499</td>
</tr>
<tr>
<td>Longueuil, QC</td>
<td>1121</td>
</tr>
<tr>
<td>Calgary, AB</td>
<td>996</td>
</tr>
<tr>
<td>Quebec City, QC</td>
<td>667</td>
</tr>
<tr>
<td>Victoria, BC</td>
<td>377</td>
</tr>
<tr>
<td>Burlington, ON</td>
<td>370</td>
</tr>
<tr>
<td>Saskatoon, SK</td>
<td>352</td>
</tr>
</tbody>
</table>

2.6 Eutrophication

When a body of water is supplied with excess nutrients, it is called eutrophic. The term eutrophic means well nourished and eutrophication is the process in which a water body is receiving excessive quantities of nutrients (nitrogen and phosphorous). In general, excessive amounts of nitrogen compounds entering water bodies can lead to anoxia, hypoxia and alteration of food web structure and biodiversity. Today, eutrophication is one of the most widespread water quality issues in many nations. One of the common effects of eutrophication is promotion of plant and algal growth. Increased growth of these species will limit the access of other existing species in the water body leading to their extinction. This process is accelerated by sun light blockage due to algal growth on the surface and the possible poisonous compounds produced by them. The result is a switch from the existing species to creatures adapted to this new
environment that, in most cases, are not desirable species for the area. Also the water bodies would lose the amenities and services they used to provide, and there are high costs associated with the cleaning of these algae from their surfaces (Bell, 1992). One of the recent examples of the economic loss due to algal bloom clean ups were in Qingdao, China where the government had to spend $87.3 million to clean up the sailing venue for the Olympic games in summer 2008 (Wang et al., 2009).

2.7 Toxicity of ammonia

Depending on the type of nitrogen compound, it can have different effects on fish, humans and other creatures (Conley et al., 2009). In general human are exposed to ammonia through inhalation. Inhalation of high concentrations of ammonia can cause immediate burning of the respiration system. Ammonia also can have irritating effects in lower concentrations in contact with skin or eyes. Ammonia interacts with moisture available in the cells and causes necrosis of tissues through disruption of cell membrane lipids continued by an inflammatory response (Amshel et al., 2000).

In aquatic systems, there is a balance between the ionized and un-ionized form of ammonia that is controlled mostly by pH and temperature. As the toxicity of ammonia in the un-ionized form is more than hundred times greater than the ionized form it would receive more attention as well. The reason for this higher toxicity level is that the ionized ammonia cannot easily cross fish gills and is less bioavailable. However, the un-ionized form can pass the gills and when inside the fish, transforms to the ionized form and causes cellular damage. Ammonia can affect the central nervous system of fish and result in convulsion and death. Even in lower concentrations, ammonia will have an adverse effect on reproduction, and growth of fish. As the temperature and pH increase in the water, the equilibrium equation between \( \text{NH}_3 \) and \( \text{NH}_4^+ \) moves toward the formation of \( \text{NH}_3 \). One unit increase in pH will increase the \( \text{NH}_3 \) to \( \text{NH}_4^+ \) ratio by ten times. Hardness, duration of exposure, fish type and life stage are other factors that can affect the toxicity level of ammonia on fish (Reed et al., 2009).
2.8 Ammonia discharge criteria

There are two types of toxicity to consider when the ammonia discharge criteria for a specific water influent to a water body are being set. Acute toxicity corresponds to a concentration of ammonia that can be acutely lethal to fish, while chronic toxicity is related to the concentrations that could affect fish reproduction and growth. Both of these concentrations depend on factors such as pH, temperature and aquatic population, and need to be calculated for each case. There are several methods to decide the safe concentration for ammonia in discharges. One approach for this calculation is through weekly sampling of the effluent and analyzing the ammonia concentration and pH to obtain the plot presented in Figure 2-4. The effluent is approved when the data points fall below the curve indicating the threshold for acute concentration of ammonia vs. pH. In order to meet these criteria, in most cases, wastewater needs to be treated to a target level. There exist various treatment methods for reducing the overall nitrogen and ammonia in the effluent, some of which will be discussed in the following sections (Environment Canada, 2016).

![Figure 2-4 Threshold acute concentration for ammonia vs. pH](Environment Canada, 2016)
2.9 Paradigm shift from nitrogen removal to nitrogen recovery

Ammonia production in large quantities, although required for satisfaction of increasing demand, have caused many problems, including pollution through excess ammonia entering the environment, as well as pollution from fossil fuels used for industrial ammonia production processes. That is why, in the switch towards a more sustainable world and to maintain the balance in the environment, humans should develop viable ideas to control the excess nitrogen input to the environment. Throughout time, different nitrogen removal methods have been developed. These methods differ widely in their concepts and conditions, from physical treatments (aeration and stripping) to chemical treatments (lime treatments and ion exchange) and biological technologies (nitrification/ denitrification and Anammox) (Değermenci et al., 2012). Each method had its own application depending on the case conditions. Moreover, all these methods come with advantages and disadvantages. For instance, air stripping has simple operation and high efficiencies, but the air used in the process cannot be discharged directly to the atmosphere due to its high ammonia content, thus requiring a post treatment (Dapena-Mora et al. 2004). Biological methods although economically favored, especially when ammonia concentrations are high, require large tanks, long retention times, long recovery and bacteria regeneration times (Peng & Zhu, 2006).

Most methods transfer nitrogen from one phase to another, which simply means delaying the problems instead of solving them. For instance, in biological nitrogen removal processes that are considered one of the most environmental friendly methods applied in the WWTPs for nitrogen removal, nitrogen in the wastewater ends up either in the atmosphere in the form of nitrogen gas or in the waste sludge that is considered the most complicated waste of the treatment plant (Wiesmann, Choi, & Dombrowski, 2007). This can be translated to the fact that additional energy and effort was employed to un-fix the nitrogen and release it to the atmosphere or introduce highly concentrated nitrogen sludge to the environment (that needs to be dealt with).

One of the novel approaches to solve this problem is to recover nitrogen from wastewater in a form that can be applied as fertilizer. This approach will not only eliminate the additional costs
of reproducing nitrogen in fixed forms for fertilizing applications but also recover some treatment costs by adding a valuable product to the process. Therefore, scientists have been working on developing economical and industrial scales of this process that can be employed in existing and new treatment plants (Booker et al., 1999, Lobanov & Poilov, 2006, Mavinic et al., 2007).

2.10 Struvite precipitation

Struvite, magnesium ammonium phosphate hexahydrate has been long known as a problem. It forms according to the chemical reaction below:

\[
Mg^{2+} + NH_4^+ + H_2PO_4^- + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O + 2H^+ \tag{1-1}
\]

This white to yellowish crystalline mineral was first defined in the 18th century, when a Swedish geologist first named it after Stuve, a Russian diplomat and naturalist (Rodman, 1999).

As the discharge criteria become more and more stringent, there will be higher concentrations of nitrogen and other pollutant/nutrients available in the sewage sludge resulted from treatment. The combination of the three ions, ammonium, magnesium and phosphate, that are highly concentrated in the sludge resulted from the nutrient removal process, especially biological nutrient removal (BNR), forming struvite (Booker et al., 1999). This struvite formation in the pipes and pumping systems will eventually cause problems such as pressure drop in the line and reduction in the pipe diameter, sometimes to the blockage point. This will eventually increase the energy cost due to the extra pumping energy required and the plant capacity reduction due to the decrease in flow rate. Sometimes, this fouling is so severe that it requires replacement of the pipes, which is a time consuming, expensive and disruptive process (James D. Doyle & Parsons, 2002). Some examples of the impact of struvite formation in pipes and pumps at WWTPs have been listed in Table 2-3.
### Table 2-3 Examples of struvite formation in WWTPs

<table>
<thead>
<tr>
<th>Process affected</th>
<th>Result</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sludge supernatant system</td>
<td>Struvite reported to foul pipe, pumps, aerators and screens. 5.6 km of piping were replaced.</td>
<td>Sacramento, California, USA&lt;sup&gt;a)&lt;/sup&gt;</td>
</tr>
<tr>
<td>Digester effluent pipes</td>
<td>150 mm pipe diameter reduced by a value in the range of 8.81 mm to 69.43 mm.</td>
<td>Ponggol, Singapore&lt;sup&gt;b)&lt;/sup&gt;</td>
</tr>
<tr>
<td>Central discharge line</td>
<td>150 mm rubber pipe reduced to 60 mm in 12 weeks.</td>
<td>Coleshill, UK&lt;sup&gt;c)&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

- a. This data have been taken from (Ohlinger & Mahmood, 2003)
- b. This data have been taken from (Bhattarai, Taiganides, & Yap, 1989)
- c. This data have been taken from (J.D. Doyle, Philp, Churchley, & Parsons, 2000)

Dumping of sewage sludge at sea is now prohibited and it requires treatment and safe disposal. Recovery of struvite will not only reduce the nitrogen and phosphorous content of the sludge, but also its volume. Struvite contains ammonium and phosphate that are two key nutrients for the agricultural growth and it has been studied and proven to be a good, slow release fertilizer (Bridger, Salutsky, & Starostka, 1962). Previous research has shown that struvite pellets can provide prolonged release and low leaching rates and there is good potential to substitute current fertilizers used for various applications such as peat, potted plants, forest out planting, turf, orchards and ornamentals (Lunt et al., 1964, Gaterell et al., 2000). Since phosphorus is one of the main components of struvite the attention and push for industrialization of a process for struvite recovery, as a fertilizer, is increasing everyday. As mentioned before, there is a huge industrial background and process development history behind ammonia and other nitrogen sources for fertilizers. However, in the case of phosphor, there does not yet exist a process for its production from other abundant elements; the consumption is directly from natural sources that are diminishing and losing their purity over time (Rahaman et al., 2014). An economically reasonable process to recover struvite from wastewater treatment plants, as a fertilizer, has been a challenge for years. Resolving this puzzle, however, would be a great accomplishment, as it will overcome multiple problems simultaneously.

A successful pilot scale fluidized bed reactor for effective struvite recovery from wastewater was developed in UBC Civil Engineering in 2003. This method recovers struvite through controlled
crystallization. Successful recovery of struvite crystals and their quality is very dependent on conditions such as temperature, pH, molar ratio, degree of super saturation, kinetics and presence of seed crystals (Booker et al., 1999, Adnan et al, 2003).

2.10.1 Ammonia recovery through struvite precipitation

Municipal wastewater is usually very high in ammonia. As the molar ratio of ammonia, magnesium and phosphate in struvite structure is 1:1:1, in order to remove the ammonia through this process, additional phosphate and magnesium should be added to this water stream. Previous work in this area has shown ammonia removal of only about 15% to 20% through struvite precipitation, whereas phosphorus was removed above 90% (Adnan et al., 2003). Therefore, a search for improvements in this technique, in order to achieve higher ammonia removal, was initiated. Different types of reagents as sources of magnesium and phosphate have been tested on different types of wastewater streams. These studies have focused on optimization of the process for maximum ammonia removal with available sources. For instance, Celen & Türker, in an study in 2001, could achieve more than 90% ammonia removal from anaerobic digester effluent of molasses industry with about 1400 mg/l initial ammonia concentration through external addition of MgCl₂ and H₃PO₄. In another study performed on landfill leachate with initial ammonia concentration of 2750 mg/l, application of MgCl₂.6H₂O and Na₂HPO₄.12H₂O resulted in 92% ammonia removal (Li & Zhao, 2003). However, direct addition of these valuable ions in the required large quantities did not make economic sense, and alternative methods to precipitate more ammonia were needed. At this point, application of the struvite pellets was suggested. The idea behind this was to add a second stage to the process where ammonia could be removed from the formed struvite pellets in the first stage. The outlet of this added stage is then recycled to the main stream as a source of magnesium and phosphate, to form more struvite pellets (Zhang et al., 2004, Wilson, 2013).
2.11 Phase transition of struvite

Struvite can be decomposed to different products, depending on the variables that control the process. Ultimately, the desired format for our application would be transformation of struvite pellets to newberyite that does not hold any ammonia in its structure. This is because residual ammonia in the product will significantly reduce ammonia removal efficiency of this recycling stream. Another requirement for the desired product would be lower stability in comparison to struvite that would facilitate the dissolution of this product and formation of more struvite pellets (Farhana, 2015). Stability and solubility of struvite crystals are very dependent upon the environmental pH, temperature and ionic composition. Although this will provide difficulties in purification of the desired phase, it will provide the advantage of producing the goal product with control on the stream. One of the control factors on the crystals is the rate of heating. For instance, thermal decomposition of struvite in water with heating results in bobierrite ($Mg(PO_4)_2 \cdot 8H_2O$), while the heating in boiling water results in loss of 5 moles of water and formation of dittmarite (Bhuiyan, Mavinic, & Koch, 2008). The following sections explain the wet and dry process for struvite decomposition.

2.11.1 Wet process

The concept of this type of ammonia removal from struvite is based on ion interactions and balance. Struvite can be dissociated in an aqueous alkaline or acidic environment. In the case of an alkali environment, the increased concentration of $OH^-$ will result in conversion of $NH_4^+$ to $NH_3$ based on the following equation. Ammonia in this form can be separated from the stream by heating and subsequent vaporization.

$$NH_4^+ + OH^- \rightarrow NH_3 \cdot H_2O$$

In acidolysis however, by preparing an acidic environment for the struvite pellets, a phase transition occurs. This is because at lower pH, around 4 to 5, favored conditions for newberyite formation are provided. Both methods have been tested successfully and ammonia removal
efficiencies up to 96% have been achieved (He et al., 2007). Moreover, application of the resulting magnesium and phosphate compounds has been tested in the recycling streams for struvite reformation and the effectiveness of these processes has been observed (Zhang et al., 2004).

2.11.2 Dry process

One of the advantages of the dry process for ammonia removal over the wet process is that less energy is required for heating of solid struvite pellets in air in comparison with liquid. However, previous work in this area indicated a limitation in ammonia removal from struvite structure with increase in temperature. In thermal decomposition of struvite, heating can result in extensive water removal from the struvite structure. This will release water and entrap the ammonia into the structure of a new substance called dittmarite. Previous experiments performed with the objective of releasing ammonia from dittmarite by heat have mostly failed. One solution proposed was to control the thermal decomposition in way that struvite goes through the second reaction where newberyite would be produced. In order to do so, le Chaterlier’s principle was used. It was decided that complete ammonia removal could only be achieved by controlled water removal. Therefore, during thermal decomposition, if the water vapor pressure could be kept higher than the equilibrium water vapor pressure at the surface of the struvite crystal at any temperature, a second reaction would dominate the struvite thermal decomposition.

\[
\begin{align*}
MgNH_4PO_4 \cdot 6H_2O & \rightarrow MgHPO_4 \cdot 3H_2O + 3H_2O + NH_3 \\
MgNH_4PO_4 \cdot 6H_2O & \rightarrow MgNH_4PO_4 \cdot H_2O + 5H_2O
\end{align*}
\] (1-3) (1-4)

Although the source of struvite and its surface and physical conditions prove to be important factors in the efficiency of ammonia release from struvite through thermal decomposition, humidity and temperature could control this process. It was shown that providing temperatures about 80 to 85°C and 95% relative humidity, ammonia could be fully removed from struvite pellets in 2 hours (Farhana, 2015).
2.12 Thermal decomposition unit outlets

As presented in Figure 2-5, the thermal decomposition unit receives hot air and steam input and turns the struvite pellets to newberyite pellets. The outlet from this unit consists of two streams; a solid product and a gas stream. The solid product consist of newberyite pellets that are transferred to the struvite precipitation fluidized bed reactor, to extract more ammonia from the ammonia rich stream coming into the unit and converted to struvite pellets, again. The gas stream is a hot water vapor and ammonia gas with low concentration of ammonia and high temperature. This gas can be very valuable in terms of ammonia and energy recovery. Ammonia can be recovered as fertilizer or potential fuel. Different options for recovery and separation of ammonia and moisture from the air will be discussed in the following sections. Both products are very important in terms of adding economic value to the overall process.

Figure 2-5 Struvite thermal decomposition process flow diagram (Modified from (Farhana, 2015))
2.12.1 Options for gas stream recovery

The main obstacle in this case is the low concentration of ammonia in the stream and presence of water vapor. Added to that there is the tendency to preserve the energy value of the stream. One main decision at this point is whether or not to separate the vapor and ammonia. The ammonia and vapor stream can go through an absorption/adsorption process and the product can be used as a fertilizer. Many industries apply ammonia for neutralization of their waste effluents containing acids. This results in large quantities of ammonium salts such as ammonium sulfate, ammonium phosphate or ammonium nitrite, that can be used as fertilizers.

The stream can also be concentrated, and ammonia in water can be used as a working fluid in Kalina engines. In the mid 1800’s the application of power cycles to produce power by passage of high temperature and high-pressure fluids through a turbine became very popular. The Kalina cycle is an improved version of this thermodynamic process for obtaining mechanical power from thermal energy. This cycle uses a mixture of two fluids with different boiling points as the working fluid. During evaporation one of the fluids will evaporate more than the other and the mixture ratio will change constantly. This will result in a non-isothermal evaporation and condensation process with 10% to 50% higher efficiencies in comparison to single fluid systems. The ammonia and water mixture holds multiple advantages as the working fluid for a Kalina cycle. This includes low operational costs due to the availability of ammonia and its low boiling point, resulting in a higher pressure at the turbine inlet and lower circulating mass flow (Ogriseck, 2009).

On the other hand, if ammonia and vapor separation is chosen, the product can be pure ammonia to be used as fuel gas. Application of ammonia as a fuel gas was first limited because of its low energy density and toxicity. However, in the search for sources that can produce minimal or zero CO₂, ammonia could see a lot of attention by the scientific community. Partial cracking of ammonia increases its performance as a fuel. Experiments show 28% dissociation of ammonia would increase its performance to be approximately equal to the burning velocities of methane and propane with even higher efficiencies and stability (Verkamp, Hardin, & Williams, 1967).
Also, another study showed ammonia gas could be blended with methane or hydrogen for running a gas turbine (Valera-Medina et al., 2015). In the case of aiming for a final product as a fuel, pressurizing and liquefying the ammonia could be an option as well. In order to separate the ammonia from the gas stream, there are multiple applicable procedures. The criteria for this case can narrow down the options as well as make this separation process challenging. In this section, different options will be discussed.

2.12.1 Ammonia absorption

Ammonia absorption with acidic solutions has been used frequently as a separation process after the ammonia stripping units. In many of these units, the gas after passing through the acidic medium will be recycled to the stripping unit to make a closed loop. One of the commonly used acids for this purpose is sulfuric acid due to its capability of ammonia uptake for fixed ammonium salt formation and its fast reaction with ammonia (Katehis, Diyamandoglu, & Fillos, 1998). Full absorption can be achieved if the flow rate and absorption column height are set to be able to accommodate 100% absorption. The ammonium sulphate formed in this process could be used as liquid fertilizer (Swartz et al., 1999; Bauer & Chowdhury, 1981). Tao & Ukwuani (2015) in a study could recover high purity ammonium sulphate crystals from dairy manure and manure digestate with high concentrations of ammonia through coupling of thermal stripping with sulfuric acid absorption. This was because thermal stripping could increase ammonia volatilization by heating in comparison to air stripping. In this investigation the recycling of ammonia recovered manure to the main stream could help in heat recovery and economic reasonability. The authors could estimate a price for the final product that was economically promising, due to the high quality of the final product and energy saving techniques applied.

2.12.1.2 Ammonia adsorption

Activated carbon has long been known as an effective adsorbent for various materials due to its structure, high surface area and pore volume. However, in the case of ammonia having low interaction energies, it has not shown a good performance and effective removal. Activated
carbon efficiency could be increased by treating it with acid or addition of heteropolyacids and metal oxides to the pores. Using nanoporous carbons treated with nitric acid scientists could improve ammonia adsorption by carbon from 10 mmol/g to 17 mmol/g in 1 bar and 25°C (Qajar, Peer, Andalibi, Rajagopalan, & Foley, 2015). Various researchers have studied adsorption of ammonia by zeolites. Zeolite has high selectivity for ammonia adsorption and it combines adsorption and ion exchange features for ammonia removal. In a study in Turkey, where natural zeolites exist in large quantities, experiments on ammonium ion adsorption from wastewater by natural zeolites in batch and continuous modes were carried out. In this study, the adsorption efficiencies were improved by washing the zeolite samples with nitric acid before performing the experiments. They concluded this method could achieve 100% removal when applied to low influent ammonia concentrations. Beside the quality and purity of the zeolite that was playing an important role, this high efficiency needed optimization of conditions affecting the process such as pH, temperature and flow rate (Sarioglu, 2005). However, the ammonia adsorption capacity of zeolites decreases intensively for humid conditions (Glover et al., 2011). In another recent study, ammonia adsorption by sulfuric acid treated zirconium hydroxide was tested. In this study, sulfuric acid treatment could create a platform for ammonia adsorption and ammonium sulfate formation where zirconium hydroxides are in general known for acidic gases adsorption. Although the adsorption capacity was found to be complex, it was very dependent on pH, surface area, and the amount of sulfate present on the adsorption surface (Glover et al., 2012).

### 2.12.1.3 Membrane distillation

Membrane distillation is a membrane based thermal separation process. It is different from other membrane processes due to its driving force being the difference in vapor pressure rather than an applied absolute pressure difference, concentration gradient or electrical potential gradient. This process employs a hydrophobic microporous membrane for separating vapor-liquid/liquid-liquid phases in equilibrium. The hydrophobic nature of the membrane prevents liquid passage and therefore allows for formation of a fixed interface at pore entrances. This will lead to transfer of more volatile components from the feed to the permeate side (Lawson & Lloyd, 1997, El-Bourawi et al., 2006). There are four common types of membrane distillation and they differ
mostly in their method for condensation of the molecules transferred to the permeate side. If the condensation is through direct circulation of a cold liquid it is referred to as direct contact membrane distillation (DCMD). Where condensation occurs over a cold surface separated from the membrane surface by an air gap it is called air gap membrane distillation (AGMD). Sometimes they use techniques such as application of vacuum (VMD) or sweeping gas (SGMD) for removal of the transferred molecules are used. The advantage of this technique is its low required temperature and pressure. Ammonia separation from water has been tested with different techniques. Each method has its advantages and disadvantages. The efficiencies and separation performance are very dependent of the membrane characteristics and operating conditions that can affect the vapor pressure of components such as pH, temperature and initial concentration. However, a study comparing VMD, DCMD and SGMD indicated that under the same operating conditions VMD shows the highest mass transfer coefficient but lowest selectivity, DCMD gives the highest selectivity and moderate mass transfer coefficient, and SGMD has the lowest mass transfer coefficient and moderate selectivity (Ding et al, 2006). Applying VMD has shown that higher than 90% separation efficiencies can be achieved if the pH is adjusted and temperature is high (EL-Bourawi et al., 2007). In another study, ammonia removal was done by SGMD and the results showed up to 97% removal in optimized operating conditions. The significance of the later study is the low ammonia initial concentrations used, since it is known that the high feed concentrations influences the removal efficiencies significantly (Xie et al., 2009).

### 2.12.1.4 Ammonia stripping

Gas stripping in the field of wastewater treatment can be defined as a process to remove volatile and semi-volatile contaminants from wastewater to a gas phase. This process is typically performed with countercurrent passage of the liquid phase and air through a packed column. As the liquid phase is distributed over the packing media, it breaks into small droplets, which increases the surface area for mass transfer. Since ammonia is partially present as a dissolved gas, it can be transferred to the air coming from the bottom of the stripping tower. This method can tolerate solids in the stream and requires relatively lower energy input. Moreover, it has been
implemented for various wastewater effluents successfully. Stripping takes advantage of the lower boiling point and higher vapor pressure of ammonia relative to water. This helps to minimize the water evaporation associated with distillation, and result in diminished energy consumption due to water evaporation (Tao & Ukwuani, 2015). The driving force in ammonia stripping is the difference between the saturation concentration and the actual concentration. This process is dependent on temperature and pH conditions, as they will define the Henry’s law constant for ammonia saturation in water. Henry’s law constant is a property of solute/solvent system based on the ratio of contaminant at equilibrium in the liquid phase to the contaminant in the gaseous phase. The value of this constant decreases at higher temperatures and lower ionic strengths (Smolen, Manley, & Poling, 1991). Therefore the driving force will be increased at higher temperatures and higher pH values. Ammonia stripping is one of very-well, established technologies in the ammonia removal field. There have been various research projects defined for optimization of this process for different ammonia containing streams. For instance, ammonia removal of 90% for anaerobically digested animal manure effluent, stripped with air in 35°C and pH=10.3, has been achieved (Jiang et al., 2014).

2.13 Method applied in this research

Responding to the first goal of this project, being the removal of ammonia from the gas stream, acidic absorption/adsorption was chosen. Acids such as sulfuric or nitric acid could be applied for ammonia absorption from the struvite thermal decomposition unit outlet gas. This process will be very similar to the absorption units connected to ammonia stripping units in industrial scale processes. However, due to the very low concentration of ammonia in the stream we are working on, this method will have high cost and at the end of the process we will have huge amounts of diluted ammonia solution that is hard to handle, store and transfer. Considering a further crystallization process adds to the cost since it requires large heat and energy input. Also this is in conflict with another objective of this project being energy recovery from the hot and humid stream to improve the economic status of the struvite crystallization and recrystallization process.
Therefore solid form adsorbents will be a beneficial option for ammonia recovery with which we can achieve a concentrated product that is easier to handle (already in the solid form). In the search for an appropriate and efficient adsorbent, one of the major considerations was to look for a compound that could generate a strong bond with the ammonia, possibly a chemical bond, after which we still maintain the high temperature and humidity of the gas for further energy reuse. As discussed before, ordinary adsorbents like activated carbon are not efficient adsorbents for ammonia specifically unless treated. At the same time, many adsorbent options require a recovery process, which involves steam passage through them. However, in this case steam is actually the input to the adsorbent. Another consideration was to find a compound that could have an immediate market use, not just an adsorbent for ammonia removal that requires further processing for ammonia separation.

2.14 Gas-solid adsorption

When studying a new process that includes a chemical reaction, thermodynamics and the kinetics of the reaction will be one of the main aspects to be considered, since thermodynamic analysis will decide on the possibility of a reaction, and kinetic analysis can help in predicting the rate of the reaction. There are some principles connecting these two analyses. A kinetically possible change must be thermodynamically possible. However, a thermodynamically possible change may or may not be fast enough due to the process kinetics. This translates to the fact that sometimes a reaction is thermodynamically possible, but the rate is approximately zero and the time required for that reaction to take place tends to infinity (A. Myers, 2004). Moreover, later in this section, a brief explanation of the mass and heat transfer and their importance for us will be discussed.

2.14.1 Thermodynamics

Adsorption of a gas to a solid surface comes with a decrease in its entropy (S) (Birdi, 2015). This is because the gas atoms are losing their degrees of freedom and being fixed to a solid surface. A process is considered thermodynamically possible if the free energy change throughout the
process is negative. In order to have the free energy change as a negative value based on the following equation, the change in the enthalpy (H) should be negative and large enough to overweigh the term of entropy and result in a negative change free Gibbs energy (G).

\[ \Delta G = \Delta H - T \Delta S \]
\[ \Delta G < 0 \rightarrow \text{T} \text{hermodynamically possible reaction} \]

The enthalpy of adsorption is negative as it is an exothermic process. Also the change in enthalpy depends on different factors, but in general the change will be higher when there is chemisorption happening, in comparison to physical adsorption. This is simply because there are stronger bonds between the gas and solid atoms in chemisorption. In most cases, physical adsorption only involves the molecular interaction forces. Therefore, the enthalpy change of chemisorption is generally greater than the enthalpy change in physical sorption. However, in many chemisorption cases, there is only one layer of adsorbate chemically bonded and under certain conditions physical adsorption on the top of the chemisorption layer is a possibility (Clark, 2012). This extra layer, although not having the proper chemical bond, can increase the ammonia removal from the gas.

Moreover, temperature influence on this equation can be discussed. As the change in entropy for this process is negative, the higher the temperature is the higher the second part of the equation becomes. The first negative term will be summed with a bigger term that could risk the negative results for change in Gibbs free energy change. This explains why high temperatures are not in favor of this reaction, and this is why the first set of experiments was designed at lower temperatures, to investigate the possibility and operating conditions of the process.

Despite the importance of the thermodynamic analysis, they require batch studies to obtain adsorption isotherms. These isotherms can be later compared with some known adsorption models that will make interpolation and extrapolation possible. However, these fittings usually come with a number of assumptions and most of them are valid for physical adsorption. As a
result, matching this information later with the experimental data of continuous adsorption in this case, might not provide meaningful data interpretation.

On the other hand, this process was designed as a part of an already existing industrial process with known conditions and continuous flow. Therefore, it was decided to skip the batch test and isotherm study step and start with studying the process in a continuous mode, using a simplified bench setup that simulates the actual technological process.

2.14.2 Heat and mass transfer

Adsorption is the process that takes place when a fluid is passing through an adsorbent bed, at least one of the components of the fluid is captured by the adsorbent bed, and the mass flux can be observed at the solid-fluid interface. When a chemical reaction is involved, there is also a reaction happening on the solid surface. Understanding the mass and heat transfer of a process can help in resolving efficiency problems, and in calculating the overall efficiency of the process. The mass transfer and the reaction rates are very dependent on the process conditions such as temperature, pressure and the interface conditions. To start with, one of the major factors would be the solid surface. Theoretical analysis of most surfaces assumes a homogenous surface for the adsorbent. However, in reality, most surfaces are heterogeneous with surface vacancies, corners, kink edges, and steps, unless they are specially designed and modified for surface analysis in laboratories. Adsorbent porosity is another factor that not only affects the total available surface for reaction but also influences the fluid movement.

The adsorption process usually involves heat exchange. Heat is not a state function. Its value depends on both experimental conditions and the measurement method, and it can provide useful information for surface studies of an adsorption (A. Myers & Monson, 2002). Mass and heat transfer can occur simultaneously. The heat transfer may be due to an externally imposed temperature difference or the evolution of heat due to adsorption that can happen when a substance is moving from a phase to another. In this case, the heat transfer has a part from the temperature driving force and another part from the heat transferred by diffusing matter.
2.14.3 Breakthrough

In a simplified manner, in an adsorbent column with an up flow direction, the mass transfer zone is moving from the lowest part to the highest part. The mass of adsorbent beneath the mass transfer zone is assumed to be the used portion of the adsorbent, and the portion above would be the unused adsorbent mass (Figure 2-6). As soon as the mass transfer zone reaches the highest part of the adsorbent column, the adsorption efficiency decreases significantly and the inlet and outlet concentrations tend to equalize. However, in a real process, it may not be as straightforward, and total adsorbent mass can be partially involved in the adsorption. A higher flow will generally decrease the break point time and the breakthrough curves will become steeper with increasing flow rate.

![Movement of mass transfer zone in an adsorbent column](image)

2.15 Evaluation of oxalic acid as an adsorbent

After reviewing different adsorbents having a list of requirements and preferences, it was decided to look for an organic acid in solid form. This could make the application of the final product as a fertilizer possible. The acidic and oxygen containing functional groups can provide numerous sites for ammonia adsorption (Yun-long et al., 2015). Knowing one of the main characteristics of slow release fertilizers is their low solubility in water (Yamamoto, Pereira, Mattoso, Matsunaka, & Ribeiro, 2016), different ammonium salt’s solubility was investigated;
this is because the gradual release of fertilizer is depended on its solubility in the soil moisture. Putting these two properties together, oxalic acid was a candidate. Ammonium oxalate has 2.269 g/100g water in 0°C; this value increases up to 4.995 in 25°C, which is very low in comparison to many other common ammonium salts applied to soil as fertilizers (Hill & Distler, 1935). For instance, ammonium sulfate has 70.6g/100g water solubility in cold water. This measure increases up to 118.3g/100g water for ammonium nitrate (Perry & Green, 1999). Moreover, oxalic acid not only is in solid form at room temperature, it can stay in this phase up to about 100°C, which is a great advantage for this specific process. Oxalic acid is the simplest dicarboxylic acid with relatively low molecular weight that increases the ammonia percentage in the final product. The ionization constant of oxalic acid shows it is a strong acid able to perform fast chemical reactions (Riemensschneider & Tanifuji, 2012). Having a dibasic character, for each mole of oxalic acid, two moles of ammonia can be adsorbed.

2.16 Properties of oxalic acid

Oxalic acid has anhydrous and dihydrate forms. Anhydrous oxalic acid has a α-form and a slightly more stable β-form. This form does not usually exist in nature because of its hygroscopic character. It adsorbs moisture in the environment and forms dihydrate oxalic acid. Although the transformation of anhydrous form to dihydrate form is very common in existence of moisture, they are classified as dicarboxylic acids and generally expected to have hydrophilic and hygroscopic properties (Kerminen et al., 2000). The anhydrous form of oxalic acid is produced by azeotropic distillation of dihydrate oxalic acid with benzene or toluene in industrial scales. Oxalic acid is easily esterified and these esters react relatively easily with water and ammonia (Table 2-4).
Table 2-4 Properties of different form of oxalic acid

<table>
<thead>
<tr>
<th>Property</th>
<th>Dihydrate oxalic acid</th>
<th>Anhydrous oxalic acid ((\alpha)-form)</th>
<th>Anhydrous oxalic acid ((\beta) -form)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight</td>
<td>126.07</td>
<td>90.04</td>
<td>90.04</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>101.5</td>
<td>189.5</td>
<td>182</td>
</tr>
<tr>
<td>Density (g/cm(^3))</td>
<td>1.653</td>
<td>1.900</td>
<td>1.895</td>
</tr>
</tbody>
</table>

There are several industrial processes developed for oxalic acid production. The raw material for most of them includes carbohydrates, olefins and carbon monoxide. Three traditional processes for production of this acid are the sodium formate method, alkali fusion of cellulose, and isolation of oxalic acid as a byproduct of carbohydrate fermentation. There are four more current methods industrially used for oxalic acid production; oxidation of carbohydrates, oxidation of ethylene glycol, oxidation of propene and synthesis of oxalic acid from carbon monoxides. Its most common applications are in metal treatment, textile treatment, bleaching agent and chemical uses such as preparation of esters and salts (reducing and complexing agent). China, Spain and France are the biggest producers of this acid (Riemensschnieder & Tanifuji, 2012).

2.17 Theoretical background of ammonia adsorption by oxalic acid

A phase diagram shows various phases of a system. Based on the information obtained from the literature on oxalic acid, ammonium oxalate and water, and their equilibrium, a ternary phase diagram can be attained (The data can be found in Appendix B). A phase diagram for a pure compound is usually studying its behavior at different temperatures and pressures. With the added dimensions of variation coming from the multiple compounds in the ternary phase diagram, it is usually presented in a triangular shape as the simplest form. However, eliminating the temperature and pressure variation makes it possible to draw the phase diagram on an ordinary perpendicular axis. Having the weight percentages of the triple compound at 30°C and 45°C, the diagram for 75 °C was extrapolated. Although there will be an uncertainty in the extrapolation based on two lower temperatures, the most important part of the diagram for our analysis, that is the equilibrium between solid phases, would undergo the least impact from these
uncertainties and therefore is still reliable. Table 2-5 presents a list of most possible solid phases in this ternary system;

Table 2-5 List of possible solid states in the phase diagram

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mw</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{C}_2\text{O}_4$</td>
<td>90.03</td>
</tr>
<tr>
<td>$\text{H}_2\text{C}_2\text{O}_4\cdot\text{2H}_2\text{O} \ (\text{S1})$</td>
<td>126.07</td>
</tr>
<tr>
<td>$\text{NH}_4\text{C}_2\text{H}_2\text{O}_6 \ (\text{S5})$</td>
<td>197.10</td>
</tr>
<tr>
<td>$\text{NH}_4\text{C}_2\text{H}_2\text{O}_5\cdot\text{2H}_2\text{O} \ (\text{S2})$</td>
<td>233.13</td>
</tr>
<tr>
<td>$\text{NH}_4\text{HC}_2\text{O}_4 \ (\text{S6})$</td>
<td>107.07</td>
</tr>
<tr>
<td>$\text{NH}_4\text{HC}_2\text{O}_4\cdot0.5\text{H}_2\text{O} \ (\text{S3})$</td>
<td>118.08</td>
</tr>
<tr>
<td>$(\text{NH}_4)_2\text{C}_2\text{O}_4$</td>
<td>124.10</td>
</tr>
<tr>
<td>$(\text{NH}_4)_2\text{C}_2\text{O}_4\cdot\text{H}_2\text{O} \ (\text{S4} \ (\text{Oxammite}))$</td>
<td>142.11</td>
</tr>
</tbody>
</table>

As labeled in the diagram, the 100% on the Y-axis is representing pure oxalic acid and the 100% on the X-axis would be pure anhydrous ammonium oxalate. Their intersection in the origin is representing pure water point. Therefore, the line connecting the 100% points would be the anhydrous line on which the compounds will have absolutely no water in their structure. Also the intersection points that are labeled as pure points of different solid compounds are calculated based on their molecular weight proportions, and are fixed points that will not be affected by our extrapolations.

For instance,

$$\frac{\text{Anhydrous oxalic acid}}{\text{Oxalic acid dihydrate}} \times 100 = \frac{90.03}{126.07} \times 100 = 71.4\%$$

Therefore the exact point for oxalic acid dihydrate will be

$$X = 0 \text{ and } Y = 71.4$$

For every solid, this coordination was calculated based on the amount of ammonium oxalate and oxalic acid available in their structure. This coordination will not change with temperature. Also based on the data from literature it was known which solid phases are in equilibrium with each other, and they can be seen as small triangles in the graph (Figure 2-7).
The most important part of this phase diagram for this analysis is between the anhydrous line and the line connecting S1-S2-S3-S4. If the composition point in our system goes below this line, liquid formation in the system can be observed, due to melting of the crystals.

Using this diagram, it can be predicted how the process would affect the material formation from the starting point. Depending on what substances are initially inserted and formed in the reactor, we can actually track which way we are going until the final oxamnide product that is the most desired outlet we are expecting. The higher the humidity in the system, the closer we would be to the line connecting S1-S2-S3-S4 and hydrous product will be formed.

### 2.18 Market and application of final product

Oxalic acid naturally occurs in many plants such as Spinach, Rhubarb, Chard, Parsley, beets and tea. It is formed through oxidation of carbohydrates by fungi or bacteria. Humans, and most
other mammals have small amounts of oxalic acid in their urine. Oxalic acid is not flammable and self-inflamatory up to 400°C. It has low toxicity for fish and bacteria (Riemensschneider & Tanifuji, 2012). In this project, by passage of a hot stream of ammonia and water through an oxalic acid bed, the expected salt to be formed is ammonium oxalate. Ammonium oxalate is a complexing agent that begins to decompose above 70°C, and by losing its water transforms to anhydrous ammonium oxalate. It will stay in this form up to temperatures about 200°C. However, with a further increase of temperature, it decomposes to gaseous products including carbon monoxide, carbon dioxide, ammonia, formic acid and oximde that could be in other phases depending on experimental conditions (Erdey, Gál, & Liptay, 1964).

In 1953, the United States patent office released a document discussing an optimized process for oxamide (\((\text{NH}_2\text{H}_2\text{C}_2\text{O}_2)\) formation by pyrolysis of ammonium oxalate (\((\text{NH}_4)_2\text{C}_2\text{O}_4)\) (Daniel, J. J., & James, B. L., 1953). Oxamide has proven to be a good long-term fertilizer due to its ability for gradual nitrogen release throughout the vegetation period, in a form that plants can use easily. The low aqueous solubility prevents wash out by rainfall, and increases its potential as a rice fertilizer (Dllz & Steggerda, 2000; Riemensschneider & Tanifuji, 2012). Pyrolysis of ammonium oxalate to oxamide is carried out by the addition of an acidic phosphorous-containing catalyst to ammonium oxalate, and heating it to temperatures between 155°C and about 220°C. The challenge in this reaction is controlling the reaction and leading it to the desired product. Common by products of this reaction at high temperatures are ammonia, formic acid, carbon monoxide and carbon dioxide. Application of the catalyst and control of temperature could minimize the competitive reactions, and result in high purity oxamide in about two hours (Daniel, J. J., & James, B. L., 1953).

Purely based on material cost, the price for oxalic acid is 1000 USD/ton, whereas the price for oxamnitr (ammonium oxalate) is 3800 USD/ton. These prices are based on online offers from various suppliers. Although oxalic acid is not inexpensive, at the end of this process, we will have an added value product, that has its own market due to its specific applications.
2.19 Research objective

The main purpose of this study was to establish an effective process for treating the outlet gas from the struvite thermal decomposition unit and understand the details of this process, the optimal conditions and reactions involved with it. This process was designed considering the three main objectives listed below, based on priority:

- removing the ammonia from the gas stream;
- producing a marketable by-product; and
- recovering the high energy of the hot gas stream.

Each of these objectives can benefit the entire N recovery process in terms of increasing its efficiency, as well as its cost effectiveness. These objectives are met by adding a new product to the line, and recycling the energy from the hot and humid stream that can be used for heating in the thermal decomposition unit.

As a novel process, in order to explore its behaviors and the effects of different parameters on it, the first set of tests was designed to explore the fundamental theory’s possibility and to give us an idea of how this procedure can be improved to the desired level. These experiments were designed to answer the following questions:

- Is oxalic acid a possible adsorbent for ammonia?
- What is the difference between the stoichiometry values and the experimental results?
- What are the adsorption ranges and limitations?
- What are the main process parameters that can affect this adsorption?

Later, the experiments were targeted to different parameters, to step-by-step increases in the efficiency of the system, as well as moving toward the real conditions in the struvite decomposition reactor outlet gas. In this stage, the answers for the following questions were investigated.
• How the adsorption process might be optimized?
• What is the effect of high temperatures and humidity on the adsorption process?
• What are the other possible adsorbents?
• What are the different compounds that form throughout the process?
Chapter 3: Materials and Methods

Due to the lack of literature data regarding ammonia gas adsorption on solid oxalic acid, a set of preliminary tests was performed to establish an experimental range of conditions that were believed to influence the process efficiency and kinetics. The experiments were modified, stage-by-stage, as we moved from understanding the process to optimizing the process and identifying a potential optimal range of operation for the proposed technology. In this chapter, detailed explanation and mapping of the process components and the material involved in different stages of the process will be discussed.

3.1 Process components:

In this section, the focus is mostly on explaining different components of the experimental set up. As more experiments were performed, the collected data helped in developing the process and adding/removing different components to it. The whole experimental process could be divided into three stages. Each stage and the detailed explanation of its set up will be described in the following sections.

3.1.1 Flow rate range

There is a lower and higher boundary for the flow rate. We do not want to go so high that the crystals become suspended and the fixed bed is transformed to a fluidized bed. At the same time, the flow rate cannot be so low that the results become not representable of the actual operating conditions in the struvite decomposition reactor that we are trying to simulate. Moreover, there was also an instrumental boundary for the flow rate, as the connections and setup could not tolerate or stabilize for more than 4 LPM, and 6 LPM in some cases. More details on the positioning and reasoning of the flow meters are provided in the following sections.
3.1.2 Adsorbent quantity

Initially it was calculated from the stoichiometric proportions that for the concentration of ammonia coming in, 6 grams of oxalic acid as the adsorbent would be enough. However, when initially started, quantities as high as 50 grams of oxalic acid were tested as well to observe the effect of this excessive adsorbent dose on the continuous removal efficiency.

3.1.3 First stage

The first stage also could be recognized as a process feasibility check stage. It has the simplest design, running under room temperature conditions at all times. In this stage, twenty-four experiments were performed with different flow rates (2 LPM, 3 LPM and 4 LPM) and different amounts of adsorbent in line (6g, 10g, 20g, 30g, 40g, 50g).

3.1.3.1 Set-up

A lab-scale set up was designed and assembled in the UBC Civil Engineering Environmental Laboratory (see Figure 3-1). The set up consisted of three main units. The first unit was the ammonia and air generator that was the input stream for the experiments. This part was, in fact, simulating the struvite thermal decomposition unit outlet. Connected to this unit was the adsorption unit where the main reaction that was under investigation was taking place. The last unit was the sulfuric acid trap that could collect all of the ammonia not adsorbed in the reactor, as well as providing an opportunity for monitoring the process.
3.1.3.1.1 **Inlet stream generator**

As presented in Figure 3-1, the air inlet passes through a pressure regulator that has been set on 5 psi. This air inlet then enters a 500 ml sealed jar that holds about 300 ml of the ammonia solution. The air is pushed through a ceramic diffuser into the jar, and the resulting bubbles facilitate and intensify the liquid to gas phase transport of ammonia in the solution. There is an outlet from this jar that will let the gas stream pass from the jar to the flow meters. Liquid passage through the flow meters would wet the flow meter measurement ball; in this case, the experiment must be stopped and the flow meter disassembled and dried properly. In order to prevent the liquid entering the flow meters, a trap jar was connected to the line between the ammonia solution jar and the divider before the flow meters. This jar simply prevents the passage of liquid and captures it, if necessary.

The stream is then divided into two lines. The two lines were designed similarly, with the only difference being that one will have an adsorption reactor attached. This was done in order to have a better and more accurate understanding of the ammonia inlet concentration. One line (blank line) had no adsorption unit and all the ammonia entered in captured in the absorption
unit, while the other line had the adsorption unit and the outlet is captured as well, and can be compared to the blank line.

In order to accommodate this comparison, the lines were designed to be identical as much as possible in terms of the material, equipment, spacing, and flow rate.

- Two flow meters were identical and set to pass the same flow for two lines in all experiments.
- Sulfuric acid solution was prepared in the accumulative volume of the four containers in the absorption unit and the same amount was poured into all four containers at the beginning of each experiment.
- The same tubing and equipment were used for both lines.
- The spacing for the units and parts were tried to be identical to minimize the difference in flow resistance between two lines.

Although the above considerations were undertaken, there would always be a difference between the lines due to the existence of adsorption unit on the main line.

3.1.3.1.2 Adsorption unit

As explained above, the gas stream in the main line entered the reactor, which was a special glass Buchner funnel with a 64 mm inside diameter. The reactor had a ceramic diffuser sealed and attached in the bottom, that would facilitate the distribution of ammonia and air stream throughout the absorbent layer sitting on it and provide a uniform flow of adsorbate.

For every experiment, the required adsorbent was weighed and spread to an even height on the circular ceramic diffuser. This height was recorded for later analysis of contact time. The outlet from this unit passed through another tube on the top, towards the absorption unit.
3.1.3.1.3   Sulfuric acid trap

The sulfuric acid trap (absorption unit) consisted of two back-to-back Erlenmeyer flasks. The flasks were 500-milliliters of volume and made out of plastic. The reactor outlet entered the first flask, which held 500 milliliters of sulfuric acid. This acid had the capacity to absorb the ammonia in the stream. Therefore, the analysis of the amount of ammonia in this flask helped to understand the adsorption performance, as well as the process rate (Figure 3-2).

Figure 3-2 Absorption unit of experimental set up

3.1.4   Second stage

After the initial phase, and for further improvement to the system performance a new reactor was designed to replace the old one. All other parts of the system were identical, except for the reactor and its fixtures. The initiative for this design modification was to increase the contact time between the input stream and adsorbent by decreasing the reactor diameter and, subsequently, increasing the mass transfer column height.
The new reactor had a 27 mm inside diameter (with a total volume of 5 ml) and was made of plastic. Similar to the previous reactor, a diffuser system was designed for this reactor at the bottom. This layer not only helped the distribution of the gas input to the reactor, but also provided a platform for the adsorbent and prevented its leakage to the connected tube at the bottom.

In this stage flow rates of 2 LPM and 3 LPM were applied. Since the reactor and the connections could only perform up to maximum flow rate of 3 LPM. The initial experiments used 6 grams and 10 grams of adsorbent (oxalic acid). Later, it was decided to use four layers of 6 grams (total of 24 grams) in order to investigate the performance of adsorbent and distribution of ammonia adsorption in the adsorbent column.

3.1.5 Third stage

In this stage, the experimental set up was modified to provide high temperature conditions close to the actual struvite decomposition unit outlet (see Figures 3-3 and 3-4).
Figure 3-3 Schematic view of experimental set up for third stage
3.1.5.1.1 Final set-up:

The final set up consisted of two lines (see Figure 3-3). One line was at room temperature acting mainly as the blank line, and the other line acting as the main line under the high temperature conditions. The air, after passing a pressure regulator that fixed the pressure to 10 psi, entered the ammonia solution container. This was the highest pressure that could be tolerated by the ammonia solution container. There were traps before and after this container, as there were flow meters before and after, to monitor the flow. The traps prevented the entrance of any liquid to the flow meters, as it would affect their performance. Also in that case, cleaning and drying would be required, thus interrupting the experiment.
The ammonia solution outlet then was divided into two lines that enter the same type of flow meters and usually set for passage of the same flow. The cold line followed the routine of the previous set up. This line was for measuring the amount of ammonia entering the system in each run. There were two sulfuric acid flasks with 500 ml volume back to back, to collect the ammonia.

The hot line passed through a chamber in which the ammonia and air inlet were mixed with hot steam, which provided heat and humidity. The chamber was also heated by a circular heat element around it. The humidity and temperature were monitored continuously with a probe. The continuous monitoring helped to control and keep the temperature and humidity in a constant range. This manual control was exerted through the valve for the steam inlet, as well as the temperature control for the heat element.

Where required, the tubes were heat resistant and isolated. Also a jacket that provided the hot water passage surrounded the reactor. The water in the jacket was heated up to 80ºC. This was the temperature used in almost all the high temperature experiments, which works as it was close
to the conditions of the struvite thermal decomposition unit outlet. Temperature in the jacket was kept a few degrees higher than the temperature inside the reactor, in order to prevent water condensation.

The reactor outlet entered two, back-to-back sulfuric acid flasks with 500 ml volume, where the ammonia still remaining in the stream is absorbed by the sulfuric acid and monitored. The adsorption in the reactor was measured by comparing the results for the ammonia analysis of the hot and cold lines, respectively.

### 3.1.5.1.2  The reactor

The reactor had a cylindrical configuration made out of glass, with an inside diameter of 13 mm. As the reactor was surrounded by a jacket with a diameter of 15 mm connected to a heated water bath of 80°C (VWR Scientific-1130A), the gas stream passed through the heating chamber to heated reactor. However, at the very top point of the reactor, although isolote tubing was used, there was temperature drop. This could have resulted in condensation of the gas when passing the reactor. Therefore, a small piece of cotton was always placed at the top of the reactor; this had two possible advantages. The first is to adsorb any droplets from possible condensation, and the second is to prevent any adsorbent particle passage from the reactor in case of high flow rate disturbance.

For a similar reason, a small piece of cotton was also installed in the bottom of the reactor. This was initiated after observing some oxalic acid melting during the high temperature experiments. The cotton could hold the possible droplets of oxalic acid in this case and prevent their passage to the entrance of the reactor, where the acid could solidify and clog the reactor entrance.
3.1.5.1.3 The probe

During the actual experiments, temperature and humidity were monitored online with a Fisher Scientific certified traceable digital hygrometer/thermometer: 11-661 – 7B probe. This probe constantly monitored humidity and temperature. It worked for a temperature range of -40°C to +104°C with accuracy of 0.1°C and humidity range of 10% to 95% with 0.01% accuracy (the reading could have between 3.5 to a maximum of 10 seconds delay). There was a special port installed for this probe on the heating chamber and the port was equipped with a circular rubber edge that facilitated connecting and disconnecting of the probe, as well as sealing the connection (see Figure 3-6).

![The hygrometer/thermometer probe](image)

**Figure 3-6 The hygrometer/thermometer probe**

3.1.5.1.4 Steam generator

Since the struvite decomposition unit outlet conditions were simulated for these experiments, in order to reach the required humidity, a steam generator was connected to the heating chamber. This was a household-scale, steam generator with water storage capacity of 600 ml. At the beginning of each experiment, it was filled with distilled water. Distilled water usage was
preferred as it was important not to lose the capacity due to precipitation and scale buildup in the steam generator tank. The steam coming from this small steam generator could not be controlled to desired flow rates. Therefore, a valve was introduced at the connection of steam generator to the heating chamber, that could be manually controlled with respect to the online humidity monitoring by the probe.

3.2 Sampling

Each experiment ran for two hours, and following samples were taken for each;

- Every fifteen minutes, 3-5 ml of sample was taken from each sulfuric acid flask. These samples were taken without interrupting the experiments. For doing so, a tube was connected to each flask, and connected to the tube was a syringe through which the samples could be removed. These samples were analyzed later for ammonia concentration.

- After each experiment, the adsorbent was taken from the reactor and 1 gram of it was dissolved in 1000 ml volumetric flask using distilled water. The collected adsorbent crystals were thoroughly mixed before taking a 1gram sample in order to make sure it would be a valid representative of the adsorbent bulk. Duplicate samples of this diluted solution were later analyzed for ammonia concentration. This analysis was performed in the UBC Environmental Engineering Laboratory.

- Due to the high temperature and humidity in the heating chamber, there was usually a condensed liquid waste collected in the heating chamber. In order to determine the degree of condensation, as well as for the mass balance calculations, 5 ml samples of this liquid was collected after the experiments and analyzed for ammonia content after 10 times dilution.
• In some experiments, another one gram of the adsorbent sample was separated for XRD analysis, that could indicate more detailed understanding of the material formed in the adsorbent.

3.3 Preparation of solutions

There are number of solutions that were repetitively prepared for these sets of experiments. The initial material and the methods for obtaining the required dilution, as well as the reasons behind choosing the specific concentrations, will be explained further.

3.3.1 Ammonia solution preparation

The input for the process was an air stream containing ammonia and water vapor. The input was generated by air stripping of an aqueous ammonia solution of a certain concentration, which was prepared by dilution of a stock ammonia solution in distilled water. The initial ammonia solution used for preparation of these diluted solutions was 28% - 30% ammonium hydroxide by Fisher Scientific (CAS 1336-21-6). The concentrations were based on the liquid-gas equilibrium concentration for ammonia and air. Since air was passing through the ammonia solution, it provided an additional energy for the ammonia molecules in the liquid phase to escape through the liquid-gas interface and enter the gas phase in the above section of the jar. Ammonia vapor pressure in the gas phase, at equilibrium with the aqueous ammonia solution at known temperature and pressure, was be calculated from the concentration of the ammonia in the aqueous solution. This corresponded to the ammonia concentration in the gas stream that was entering the process. However, the uncertainties added from the pressure change imposed by the downstream connections made it difficult to calculate the exact amount of ammonia coming in every second. In this case, it was decided to add a blank line to the process in order to be able to monitor the ammonia inlet.

Based on the data from struvite thermal decomposition experiments carried out previously (Farhana, 2015), the concentration of ammonia in the gas stream outlet of the decomposition
process was expected to be within the range of 300ppmv -500ppmv, or 0.03%-0.05% by volume. From the liquid-gas equilibrium data for aqueous ammonia solutions (Perman, 1903), ammonia vapor pressure that corresponded to this concentration would be created above a solution of approximately 0.05% NH$_3$ by weight, at room temperature (20°C -22°C). Hence, the initial ammonia solution (28%-30% by weight) was diluted 500 times to give the desired concentration of 0.05%-0.06% (by weight). In addition, another ammonia solution, which was 10 times more concentrated, was used in some preliminary experiments, in order to establish the process possibility in principle, and to determine which operating parameters had the most effect. The latter solution was prepared by dilution of the initial stock solution 50 times; this resulted in NH$_3$ concentration of 0.5-0.6% (by weight). The gas phase in equilibrium with this solution was expected to contain 0.3-0.5% NH$_3$ by volume (or 3000ppmv-5000ppmv).

3.3.2 Sulfuric acid solution preparation

As explained in section 3.1.3.1.3, the absorption segment of the process used a strong acid to capture the ammonia escaped from the adsorption unit, to determine process efficiency and rate. This absorption unit required about 2 liters of diluted sulfuric acid per run. This sulfuric acid was prepared from an initial solution of 95-98% sulfuric acid by Fisher Scientific (CAS 7664-93-9) and diluted to the concentration of 0.05 molar under the fume hood. The sulfuric acid concentration was calculated based on stoichiometric absorption of ammonia by sulfuric acid, assuming a situation where all the input ammonia could escape the adsorption process. This decision was made as experiments were running a blank line simultaneously, where all the inlet ammonia was transferred directly to the absorption unit. Also, this could control any possible ammonia escape from the set-up, as continuous release of ammonia could be a safety issue in a closed environment. The diluted sulfuric acid solutions was divided and poured into four 500 ml Erlenmeyer flasks in the absorption unit.
3.4 Adsorbents preparation:

3.4.1 Oxalic acid dihydrate (C$_2$H$_2$O$_4$.2H$_2$O)

Oxalic acid dihydrate is a dicarboxylic acid formulated as C$_2$H$_2$O$_4$.2H$_2$O. The oxalic acid dihydrate used for this experiments were from Fisher Scientific with the code of A219-500 and chemical abstracts service number of CAS 6153-56-6. This substance is corrosive and toxic, and safety considerations should be taken when dealing with it.

3.4.2 Anhydrous oxalic acid (C$_2$H$_2$O$_4$)

Anhydrous oxalic acid is the dehydrated form of oxalic acid that, in many cases, is produced industrially from further processing of oxalic acid dihydrate. It starts melting and decomposing at the same temperature of about 188-191°C. The anhydrous oxalic acid applied to the experiments here was from Fluka Chemika with molecular weight of 90.04 and product code of 75688 and European community number of EC 2056343.

3.4.3 Potassium tetraoxalate dihydrate (KHC$_2$O$_4$.H$_2$C$_2$O$_4$.2H$_2$O)

This salt was initially chosen due to its higher melting point in comparison to oxalic acid. Also, having three hydrogen atoms in its structure makes it a good candidate for adsorption purposes. The potassium tetraoxalate dihydrate used in this project is from Fluka Analytical with the code of 60594-500, molecular weight of 254.19 and CAS 6100-25-5.

In total, three adsorbents were used in the experiments. Initially the focus was on oxalic acid dihydrate. Later, as the process evolved and more knowledge was gained on the interaction of oxalic acid and ammonia, anhydrous oxalic acid and potassium tetraoxalate dihydrate were also tested as potential adsorbents for this process. These adsorbents were generally passed through a sieving process, before being loaded to the reactor.
3.4.4 Sieving method

The sieving of adsorbent particles was done using the Tyler test sieve shaker (Ro-Tap model RX-29) using uniform mechanical motion to provide the most consistent results (see Figure 3-7). This shaker was properly installed on a foundation capable of supporting 200 lbs in the UBC Geotechnical laboratory. As presented in Figure 3-7 the main parts of the shaker were;

- a hammer that provides the tapping energy;
- sieve plates carried that hold the stacked sieve plates and provide the circular motion; and
- a cover that was closed and fixed during the time the shaker was running for safety purposes as well as preventing dust and particle dispersion.

Figure 3-7 Schematic view of Ro-Tap RX-29 shaker (Adopted from Hayer Tylor Inc website)
Seven sieve plates were employed with mesh openings of 149, 250, 420, 500, 600, 833, 1000 and 2000 micrometers. However, in the later sieving processes smaller collections of plates were used, as there was a specific targeted crystal size. The sieves were stacked on top of each other with the plate having the largest mesh opening being on top and a pan plate on the bottom. This pan plate will collected the fine material that passed through the smallest mesh in the stack.

This sieving process was used for two purposes. One was to understand the crystal size distribution for a specific adsorbent, and the other was to separate a specific crystal size portion of the adsorbent, to continue the experiment with that crystal size range. When it was the case of understanding the crystal size distribution of the adsorbent, the amount of adsorbent had to be large enough to represent the adsorbent pack. However, this amount could not be so large that the sieving process encountered overloading. Overloading is when a fine particle, that should pass all the seven sieves, could not pass at least one due to the blocking of mesh by the overloaded sample.

After loading the proper amount of adsorbent to the top sieve plate, the stack was fixed and tightened properly with designed fixtures. The tapping hammer handle was then placed and the time was set. At this point, the start button was used to start the shaker after the cover was closed and fixed. The shaker was set for five minutes.

When the timer went off, the stack was unloaded from the shaker, and each plate was carefully emptied to a clean measuring disk. The sieving meshes were cleaned with a bristle brush to minimize the loss of material initially loaded to the sieves. The collected sample from each plate was then measured on a scale. This step was repeated for each plate, so that the distribution of the adsorbent crystal size could be assessed. This distribution assessment was later used to choose the optimal size range to separate and work with.
3.5 Struvite

As discussed previously, the goal of these experiments was to simulate the conditions and the outlet stream of a struvite thermal decomposition unit, and to design an appropriate process to not only deal with this stream, but to also recover the energy and ammonia as valuable by-products. Although in most of the experiments the simulation for the ammonia stream input was done by passing air through an ammonia solution purely made in the laboratory, in the final stages, application of struvite pellets previously synthesized in pilot-scale struvite crystallizers was tested. The struvite pellets with diameters 0.5-1.0 mm were collected from a pilot scale struvite crystallizer at the WWTP in Penticton, BC. The ammonia removal with heating also depended on the porosity, hardness and structural composition of the pellets. Previous studies had shown the pellets of this size and source to be the best for ammonia removal through heating in the decomposition reactor (Farhana, 2015).

3.6 Analysis methods

3.6.1 Ammonia detection method

The result of this analysis were most reliable if done within 24 hours after the sampling. However, the samples could be preserved for up to 28 days at 4°C (APHA, 1999). The method employed for this analysis was 4500-NH$_3$-H (APHA, 1999), which is an automated flow injection method using the measurement of peak absorbance of intensified blue color produced by the Berthelot reaction, to access the concentration of ammonia in the original sample. The buffer used is a solution containing disodium ethylenediamine tetraacetate and sodium hydroxide. Ammonium chloride in distilled water was used as a calibration standard solution (APHA et al., 1999). The calibration range of this method was between 0 to 50 mg/l. Therefore, samples that were expected to have higher concentrations of ammonia were always diluted in advance to stay within the calibration range. Also, required samples were filtered through glass wool to prevent blockage of the instrument injector by particles.
3.6.2 Potassium detection method

Potassium detection was done using a Varian SpectroAA 220 Fast Sequential Atomic Absorption Spectrophotometer. This method uses KCl for preparation of standards; therefore, standards of 0.1, 0.5, 1.0, 2.5, 5.0, 10.0 and 15.0 mg/L were prepared as well as a 5 g/L Cs\(^+\) solution as an ionization suppressant. Prior to analysis, a drop of nitric acid was added to the samples and well mixed. Fresh deionized water was provided for auto-sampler rinsing before each set of analyses. The potassium lamp was optimized, warmed up and different flame angles were used during the analysis.

3.6.3 X-ray diffraction (XRD) analysis

XRD is a rapid analytical method to identify a crystalline material. The sample for this test should be finely ground and homogenized. Using the X-ray diffraction angle and relating it to the wavelength of electromagnetic radiation, as well as the lattice spacing in the sample, the average bulk composition of the sample can be obtained. For these tests, a Bruker D8 advanced x-ray diffratometer in UBC department of Chemistry was used. The software associated with this instrument holds a database of various substances and their peaks.

One of the important factors in XRD analysis is having a proper material reference for the XRD analyzer database. Every compound in the database has an assigned graph with specific peaks and intensities. When running a sample, the possible available compounds must be identified and selected from the database. The test will provide the crystal analysis of a sample and try to match as many compound peaks from the chosen list as possible. Later, it can be seen on the final graph, which peaks are matching clearly to estimate the intensity and percentage of that specific compound in the sample.

In case a required compound was missing from the database, the data can be gathered from the literature and added to the database. In our case, we needed to add the oxalic acid that had two different structures and ammonium tetraoxalate. Oxalic acid is a polymorph, and its crystals,
although having the same compositions, can have different structures. That is why oxalic acid graphs are separated as alpha oxalic acid and beta oxalic acid.

3.6.4 Total organic carbon (TOC) analysis

Total organic carbon is one of the measures that can indicate the total amount of organic carbon in the sample. TOC analysis targets organically bonded carbon. This measure was applied to the adsorbent samples collected at the end of the experiment, to help identifying the material formed during the process by indicating the carbon content. The method applied was the 5310 B (APHA et al., 1999), which employs high-temperature combustion for breaking down the organically bonded carbons to form CO$_2$. Later, this carbon dioxide could be measured either by a nondispersive infrared analyzer or a coulometric titrator. Many samples contain inorganic carbon that could interfere in the results of the TOC. Acidifying the samples to a pH of about 2 or less can help eliminate this interference (APHA et al., 1999).
Chapter 4: Results and Discussion

4.1 Introduction

The purpose of this research was to remove ammonia from the thermal decomposition unit gas outlet. In order to achieve this goal, a series of experiments was run on different experimental setups. In this chapter, the results obtained from those experiments along with the understandings and conclusions from the results were presented. In order to better understand the overall effect of each parameter on performance of the process, results from different stages previously explained in the material and methods chapter have been assembled to present the influence of different parameters on the efficiency of the process.

4.2 Effect of different experimental parameters on efficiency

4.2.1 Flow rate effect on the efficiency of ammonia removal

As one of the objectives of the initial experiments, the effect of flow rate on adsorption performance was investigated. In order to understand the relationship between different flow rates and the amount of ammonia entering the system, analyses were based on data collected from the 2\textsuperscript{nd} flask (this is the first flask in the blank line as previously mapped in Figure 3-1). Figure 4-1 represents the amount of ammonia input to the system for the same flow rate in different runs. This figure is specifically from 3LPM runs on the first stage setup, having 20, 30 and 40 grams of oxalic acid in line as the adsorbent. The slight difference between the amounts of ammonia coming in for the same flow rate is due to inaccuracy imposed by the flow meter. This means there can be a slight difference between the actual and recorded flows. For instance, two runs with the flow rate recorded as 2LPM may have in fact flow rates of 2.05 and 1.95. Also, the data presented here (ammonia concentration in the 2\textsuperscript{nd} flask samples) were obtained from samples diluted 25 times to fall in the calibration range of the analytical method applied. This could contribute to errors translating into differences between the amounts of ammonia for the same flow rate, at the same time point.
Due to the change in the setup at each stage of the experiments, the total amount of ammonia passing through the system might change slightly for the same flow rate. The data presented in Figure 4-2 was gathered from the blank line’s first flask for different flow rates, in different stages. This was a good representative of the total amount of ammonia, as the second flask in the absorption blank line had negligible absorption compared to the first flask, and most of the ammonia was absorbed almost immediately in contact with the sulfuric acid in the first flask. The concentrations reported in Figure 4-2 are an average of the slightly different concentrations obtained for each flow rate in the specific stage after 2 hours of the experiment.

<table>
<thead>
<tr>
<th>Time (mins)</th>
<th>20 gr Oxalic acid</th>
<th>30 gr Oxalic acid</th>
<th>40 gr Oxalic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
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<td>0</td>
<td>0</td>
</tr>
<tr>
<td>15</td>
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<td>15</td>
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<tr>
<td>120</td>
<td>120</td>
<td>120</td>
<td>120</td>
</tr>
</tbody>
</table>

Figure 4-1 Ammonia concentrations in 2nd flask (blank line) for flow rate of 3 LPM – 1st stage set up
As shown in Figure 4-3, independent from the amount of adsorbent in the line, an increase in flow rate corresponded to an increase in the amount of ammonia coming into the reactor and that would be in contact with the adsorbent. At the same time, an increase in the flow rate resulted in lower contact time values, not favorable for adsorption efficiency.
Breakthrough is one of the adsorption process aspects that are highly affected by flow rate adjustments. As discussed in Section 2.14.3, breakthrough is the situation where the output concentrations increase suddenly. In the data obtained from the experiments performed, breakthrough was observed in some cases and, with the breakthrough, a decrease in adsorption efficiency was observed over time. This decrease was amplified with an increase in flow rate. Figure 4-4 summarizes the flow rate impact on adsorption efficiencies. Here, Ct represents the concentration of ammonia in the first flask after the adsorption unit at each time point. Here C₀ represents the concentration of ammonia in the second flask (first flask on the blank line) at each data point. Therefore, (C₀ – Ct) / C₀ will be the fraction of ammonia adsorbed relative to the ammonia input at each time point (i.e., percent removal).
Figure 4-4 Effect of flow rate on adsorption efficiencies in the 1st stage with 20 g oxalic acid in line

As indicated in Figure 4-4, the highest adsorption efficiency point belongs to the lowest flow and earliest data point. This is because of the freshness of the adsorbent in the beginning of the process and higher contact time provided, due to the lower flow rate. The adsorption efficiency had a steeper reduction with increase in flow rate and, as the process continued, the adsorption efficiency stabilized and became linear. It is important to mention that, even at the highest flows, the efficiency remained above 90% at all times, indicating that the adsorption process was promising under the tested conditions.

4.2.2 Adsorbent quantity effect on the efficiency of ammonia removal

As presented in Figure 4-5, the oxalic acid adsorbent had a higher percentage of ammonia capture on a gram-to-gram basis at the lowest adsorbent dose. Since the equilibrium state was not achieved and the adsorbent was still adsorbing ammonia. Assuming the same amount of ammonia was passing through the adsorbent column at a specific flow rate, as the amount of adsorbent increased the captured ammonia would have become more dispersed in the higher quantities than lower quantities; thus the overall ratio would decrease with an increase in
adsorbent dose. However, the overall amount of ammonia adsorbed would still be higher in higher quantities of oxalic acid. For instance, in Figure 4-5, 40 grams of oxalic acid, although having the lowest ammonia to oxalic acid ratio, had the highest overall amount of ammonia at 149.6 mg, followed by 84.6 mg in 20 grams, 55.2 mg in 10 grams and 33.42 mg in 6 grams of oxalic acid, respectively. Increase in the amount of adsorbent on-line would increase the total amount of ammonia capture. However, at some point even though the total amount of ammonia is more in comparison to lower mass of adsorbent, but it is not concentrated in the adsorbent and a portion of the adsorbent could be unused. This would result in waste of adsorbent and decline in the ammonia percentage in the final product. Therefore, it is required to find the optimum amount of adsorbent for any specific ammonia load.

![Figure 4-5 Ammonia captured in each gram of oxalic acid adsorbent for the first stage experiments with 2LPM flow rate.](image)

It can be argued that the bottom layers of oxalic acid may have captured higher values of ammonia in comparison to the upper levels. This is a valid argument, knowing the oxalic acid column was not reaching its highest capacity of adsorption in the two-hour time frame. However, after the experiment and before taking the sample from the adsorbent to analyze, it was mixed to confirm that the sample would be a good representative of the total adsorbent column. This was
another motivation for performing layered adsorbent experiments, where samples could be taken from different layers of an adsorbent column, and a better analysis of the distribution of ammonia in adsorbent could be obtained.

As indicated in the previous section, the ammonia removal from the gas stream achieved higher than 90% efficiency in most experiments. At the beginning of the experiments, as the adsorbent was fresh, the efficiency of adsorption seemed to be higher and similar for different quantities of adsorbent. With time, as the sites of the adsorbent were occupied by ammonia, the efficiency would drop. This drop in efficiency was more intense in lower quantities of adsorbent, as can be observed in Figure 4-6; this was due to the fact that, as the quantity of the adsorbent increased, the number of active sites also increased, and the adsorption continued to have high efficiencies for longer times.

![Figure 4-6 Effect of adsorbent quantity of adsorption efficiency in the first stage having 3 LPM flow rate](image)

At this point, good efficiencies of adsorption had already been achieved; however, the ratio of ammonia captured per gram of oxalic acid in the reactor was in a range of 3.03-5.57 mg/g of
oxalic acid, which is still too low to be used as a direct product. Therefore, the experiments were modified to increase this ratio, as well as attempt to maintain the high removal efficiency.

4.2.2.1 Understanding the adsorption gradient throughout the adsorption column

In order to better understand what happens in the adsorption column and the gradient dispersion of ammonia capture throughout the adsorbent column height, the adsorbent was separated into 4 layers by plastic mesh. This provided the opportunity to take samples from 4 different heights of the column. The results of this analysis at different flow and adsorbent conditions indicated a trend of highest to lowest ammonia concentrations, from bottom to top of the column. This triggered the idea of recycling the upper layers.

In these experiments, 24 grams of oxalic acid was separated into 4 layers of 6 grams. The oxalic acid used for these tests was from a selected crystal size range of 250 to 500 micrometers. Due to the higher resistance of 24 grams of adsorbent in the second reactor, the inlet pressure was set to a higher amount of 7.5 psi, to obtain the desired flow rates.

Also, in these experiments, the ammonia input solution was diluted 10 times. This dilution was established since the theoretical amount of ammonia in the gas phase, in balance with the ammonia solution input at this dilution ratio, was closer to the struvite thermal decomposition reactor outlet.

Moreover, a recycling technique was implemented in these test series, where the upper layers were collected carefully and used again in the next experiment under the same experimental conditions. In this recycling procedure, the experiments were repeated four times. The first run had four layers of fresh oxalic acid. For the second run, Layer 4 was removed and analyzed while the other layers were shifted down and 6 grams of fresh oxalic acid was added on top as the new layer 1. Therefore, the results shown in Figure 4-7 are for the layers after they reach the layer 4 position. For example, 1.89 mg ammonia reported for the flow rate of 2 LPM and layer 1 indicated the amount of ammonia adsorbed in each gram of the 6 grams initially positioned in
layer 1, after being in the reactor for four experiments and being moved from layer 1 to 2, 3 and eventually 4. The results for the blank line indicated an average accumulative value of about 25 and 30 mg/l of ammonia passing through the system for the flow rates of 2 LPM and 3 LPM, respectively. Figure 4-6 represents the layer positioning as well as the result of ammonia concentration analysis in these layers.

<table>
<thead>
<tr>
<th></th>
<th>2LPM</th>
<th>3 LPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layer 1</td>
<td>1.89 mg/g adsorbent</td>
<td>1.63 mg/g adsorbent</td>
</tr>
<tr>
<td>Layer 2</td>
<td>1.75 mg/g adsorbent</td>
<td>2.76 mg/g adsorbent</td>
</tr>
<tr>
<td>Layer 3</td>
<td>2.50 mg/g adsorbent</td>
<td>1.37 mg/g adsorbent</td>
</tr>
<tr>
<td>Layer 4</td>
<td>3.56 mg/g adsorbent</td>
<td>2.49 mg/g adsorbent</td>
</tr>
</tbody>
</table>

**Figure 4-7** Position of layers and the final amount of ammonia adsorbed in each layer for 2 LPM and 3 LPM flow rates in the second stage setup (modified for layer experiment)

As shown in Figure 4-7, the 4\(^{th}\) layer that had been in the reactor only once showed the highest concentration of ammonia. Initially, it was assumed as the layers was not capturing ammonia to their highest capacity, and this could work as a recycling method, where the adsorbent could be used multiple times and higher concentrations could be captured. However, the experimental data showed the opposite. The main reason for this can be the fact that chemisorption happened mostly in the first layer, and the adsorption continued as physical adsorption on the first layer. Also, in crystals and porous adsorbents, there is usually a specific amount of capture that occurs through pore diffusion. This increased the chances of escape when the pressure was reduced in between the runs and the layers were being replaced, as well as in the next run where the flow can help the “un bonded” ammonia to exit.

Here, another thing to notice is the lower amount of ammonia coming in. The ammonia solution as mentioned before was diluted 10 times. Therefore, the mg/g adsorption quantities reported in
Figure 4-7 should not be compared to the results of other experiments, without adjustments. Moreover, the total amount of ammonia coming in, as recorded by the second flask results, was decreased even more than the 1/10 ratio in comparison to the average mg/l concentrations presented in Figure 4-2. This decrease in the amount of ammonia passing through the system resulted in a decrease in concentrations for the 3rd and 4th flask, where all the data obtained showed zero or negative. The negative values were due to the interference of the acidic samples with the buffer used in the analytical method applied. Since the concentrations were negligible and the 3rd and 4th flask were not reducing the ammonia concentration (because all the excess ammonia was already absorbed in the first flasks in each line), flasks 3 and 4 were removed.

At this point, the next phase of experiments continued, mostly with six and ten grams of adsorbent. Moreover, the increase in efficiency with increase in adsorbent dose should make economic sense. However, in most cases, doubling the amount of adsorbent resulted in only about a 2% increase in adsorption efficiency. The decision of whether this increase is economically acceptable or not, depends on the flexibility and demand of the market for the final product.

4.2.3 Crystal size effect on the efficiency of ammonia removal

A major effective parameter in the efficiency of adsorption processes is the surface area of the adsorbent that provides the adsorption sites. Any increase in the surface area or the contacting area of the gas and solid phase can have large effects on the adsorption rate and efficiency. Therefore, one of the approaches to increase the process performance was to think of different ways of increasing the surface area of the adsorbent.

Since the adsorbent here was oxalic acid crystals, the smaller the crystal size, the larger the surface area would be. However, there would be a limit for this decrease in crystal size since after some point, the crystal size would be too small and the oxalic acid would act like a powder that could make a cake with small amounts of moisture. This caking would have a negative effect as the passage of the gas would be blocked, the flow rate would change, and the pressure
on the system would suddenly increase. Moreover, in these experiments, the design was based on a fixed bed reactor and with a decrease in crystal size, after a point, the reactor might switch to a fluidized bed (not the target of these experiments). Additionally, it would have required a more accurate and sensitive flow meter, for flow control.

Figure 4-8 Oxalic acid crystal size distribution

As explained in section 3.4.4, oxalic acid was sieved with the tap shaker, and the crystal distribution presented in the Figure 4-8 showed a peak between 200 and 400 micrometers. After this analysis, it was decided to continue with crystal size portion of 250-500µm. Figure 4-9 represents the effect of this decision on the data obtained from first flask in line, after the adsorption unit with a flow rate of 2 LPM and 10 grams of oxalic acid in the first stage reactor. The results indicate that, after the sieving process more ammonia had been adsorbed in the adsorption unit and less had escaped from the adsorption unit; the efficiency improved from 96.6% to 98.9%. Also, a more important result would be the delay of breakthrough as the adsorption capacity had increased. Figure 4-9 compares the performance of oxalic acid with crystal size ranging from 0 to about 2000µm, with a crystal size range of 200 to 500µm under same experimental conditions. This graph shows that sieved oxalic acid could provide better adsorption due to increased surface area provided by smaller crystal size range. Therefore,
smaller concentrations of ammonia was detected in the 1\textsuperscript{st} sulfuric acid flask after the adsorption unit, in comparison to the previous experimental run with same flow condition (2LPM) and mass of oxalic acid (10 grams).

![Graph showing ammonia concentration over time](image)

**Figure 4-9** Effect of crystal size change on the adsorption for 2LPM flow rate and 10 g of oxalic acid in first stage

### 4.2.4 Contact time effect on the efficiency of ammonia removal

In most of the experiments performed, the overall experimental time was two hours. Figure 4-10 shows the difference between the amount of ammonia in the first flask, representing the ammonia coming into the system, and the amount of ammonia in the second flask, that represents the ammonia remaining in the stream after the adsorption unit. This difference is an estimate of the amount of ammonia adsorbed by the reactor. It can be seen that the slope for all the flow rates are slightly decreasing with time. Assuming a similar amount of ammonia passing through the system in every 15 minutes it can be concluded that the concentrations in flask one is increasing. This shows decrease in adsorption capacity of the adsorbent over time and increase in the amount of ammonia escaping from the reactor.
Concentration difference between flask 1 and 2 in each time point for 40 g oxalic acid in line at first stage reactor

With a decrease in the removal efficiency and adsorbent capacity there will be a point in adsorption process that the concentration of adsorbate (ammonia in this case) will start increasing intensely. This point as called breakthrough, is very dependent on the flow rate, adsorbent quantity, capacity and contact time between the adsorbent and adsorbate. During the different phases of experiments, breakthrough never happened within the first 30 minutes of the experiment. Here, the results for increasing contact time, in order to delay the breakthrough and increasing the process efficiency, will be discussed.

In a continuous system such as the one employed here, the average contact time is dependent on the height of the adsorbent column and the flow rate. In order to calculate the contact time for each run, the following method has been used.
Contact time $= \frac{H}{U}$ (2-1)

$U = \frac{\text{Flow}}{A}$ (2-2)

Where $H$ is the height of Oxalic Acid in reactor, $U$ is the velocity and $A$ is the reactor cross sectional area. Table 4-1 summarizes contact time values for different flow rate and reactors.

<table>
<thead>
<tr>
<th>Reactor</th>
<th>Reactor Diameter (mm)</th>
<th>Mass of Oxalic Acid (g)</th>
<th>Height of Acid Layer (mm)</th>
<th>Contact time for 2LPM flow (seconds)</th>
<th>Contact time for 3 LPM flow (seconds)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor 1</td>
<td>64</td>
<td>6</td>
<td>1.5</td>
<td>0.14</td>
<td>0.09</td>
</tr>
<tr>
<td>Reactor 1</td>
<td>64</td>
<td>10</td>
<td>2</td>
<td>0.19</td>
<td>0.13</td>
</tr>
<tr>
<td>Reactor 2</td>
<td>27</td>
<td>6</td>
<td>13</td>
<td>0.22</td>
<td>0.15</td>
</tr>
<tr>
<td>Reactor 2</td>
<td>27</td>
<td>10</td>
<td>22</td>
<td>0.38</td>
<td>0.25</td>
</tr>
<tr>
<td>Reactor 3</td>
<td>15</td>
<td>10</td>
<td>60</td>
<td>0.32</td>
<td>0.21</td>
</tr>
</tbody>
</table>

As noted here, there was an increase in the contact time value from the reactor we started with in the first stage and the second reactor. The final reactor that was adjusted for high temperature experiments maintained a similar contact time range as the second reactor. Although the height of the adsorbent column increased, the contacting surface decreased due to the smaller diameter of the reactor resulting in a similar contact time value. As the third reactor was performing under a very different experimental condition (high temperature and humidity) a direct comparison of the contact time effect on the results is not possible. Figure 4-11 presents the total amount of ammonia adsorbed in the oxalic acid in reactor 1 and 2. Putting different experimental flow rates and adsorbent quantity together with the calculated contact time, it was observed that an increase in the contact time was resulted in an increase in total amount of ammonia captured in adsorbent (see Table 4-2).
Figure 4-11 Comparison of the total amount of ammonia adsorbed by the adsorbent column in reactor 1 and reactor 2 at 2 LPM and 3 LPM flow rates

Table 4-2 Relationship between contact time and total amount of ammonia captured in the adsorbent

<table>
<thead>
<tr>
<th>Flow rate</th>
<th>2 LPM</th>
<th>3 LPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount of Adsorbent</td>
<td>6 g</td>
<td>10 g</td>
</tr>
<tr>
<td>Total amount of ammonia in the adsorbent after the process (mg)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Calculated contact time for each scenario (s))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reactor 1</td>
<td>33.42 (0.14)</td>
<td>55.2 (0.19)</td>
</tr>
<tr>
<td>Reactor 2</td>
<td>65.7 (0.22)</td>
<td>95.6 (0.38)</td>
</tr>
</tbody>
</table>

As presented in the Table 4-2, the larger total adsorption values are in most cases tied to a larger contact time values that is due to higher mass of adsorbent (height of adsorbent column) or lower flow rate. This data confirms the improved adsorption parameters by modification of the reactor (switching from reactor 1 to reactor 2).
At this point, a test was specifically performed to establish the influence of contact time on the efficiency and total ammonia adsorption. For this purpose, 6 grams of oxalic acid, low flow rate (0.5 LPM) and long experiment time (8 hours) was used. Low flow rate was applied to the system to increase the contact time and long experimental time was provided to observe the efficiency in higher contact time values. Theoretically, the total amount of ammonia passed through the system in this condition, should be the same as the amount of ammonia passed through the system at flow rate of 2 LPM in a 2-hour time span. In this test, Figure 4-12 Efficiency performance comparison of experiments with similar total ammonia passage and different contact time.

The test resulted in high ammonia concentrations captured in the adsorbent. The highest mg/g values achieved in this reactor (in the previous experiments with 2-hour experimental time), were about 10 mg/l. In this experiment 17.25 mg/l of ammonia could be adsorbed in the oxalic acid. However, Figure 4-12 shows the efficiency \(^{((C_0 - Ct) \times 100/C_0)}\) decreased under 80% after the first two hours. The efficiency continued to decrease to about 68% over the total eight hours. It is important to note, although the efficiency for the 2 conditions with similar total ammonia passage are presented in Figure 4-12, direct comparison of this data would not be accurate, since
the sample points are representing 15min ranges for 2 LPM – 2hr test, and 60 mins ranges for 0.5 LPM – 8hr test.

4.2.5 Temperature effect on the efficiency of ammonia removal

Since the actual conditions for the ammonia adsorption in the struvite thermal decomposition reactor included high temperature and humidity, the next step was to investigate the adsorption under these conditions. Adsorption processes are, in general, exothermic. High temperature normally does not favor adsorption processes. Previous studies on ammonia adsorption, with different adsorbents, showed that adsorption rates and efficiency decreased with an increase in temperature (Holm & Blackburn, 1962).

As explained in Section 3.1.5, a new setup was designed for applying higher temperatures. This new setup could not accommodate two lines of heated outlet gas and the flow rate would have been different for different temperatures. A blank line was established at room temperature, whereas the main line maintained temperatures around 80 °C. Since the lines had different temperatures, the adsorptions would be expected to differ, even with all the other conditions being the same. In addition, in order to monitor the system performance, a blank test was run.

In this blank test there was no oxalic acid online and the ammonia air combination entered the system in both lines with the same flow rate. The only difference between the lines was:

- Cold Line: Flow entered the line directly from the ammonia jar through the flow meter.
- Hot Line: Flow passed through a chamber with temperature set at 80 °C and humidity in the range of 75-85%.

As the Figure 4-13 presents, although both lines had the same flow rate, there was a difference in the concentration of ammonia going through the lines; the high temperature line indicates the passage of about 35% to 45% less ammonia. This difference increased with an increase in flow rate. The main difference between low and high temperature was the change in gas volume.
Gases expand upon heating, if pressure is constant. Therefore, the flow rates cannot be identical. Also, one of the streams passed a line with a heating chamber and a reactor, adding to the line resistance for flow and, therefore, head loss. Additionally, gases behave very differently from liquids, in terms of relation between viscosity and temperature. For a gas, with an increase in temperature, there will be an increase in the movement of molecules and they will start colliding. As the collision between gas particles increase, the velocity of the gas decreases (Perry & Green, 1999). Last but not least, temperature can influence the absorption of ammonia in the sulfuric acid flasks, which will be reflected in the samples taken, and the data obtained. The blank test results can help to understand the effect of temperature on the adsorption. The experiments done on the final setup in high temperatures will have their blank lines in low temperature and their adsorption line (mainline) in high temperature and high humidity. Using the results from Figure 4-13, the blank line for each of those experiments can be normalized to project the data in high temperature. According to the results obtained here, by applying this correction there will be a reduction in the values obtained for blank line.
The next step was to examine the system performance with the adsorption unit on line. In this setup, flows could be increased to 6 LPM, thus more representative of the actual flow rate in the struvite decomposition unit outlet. Also, with increase in the flow, it is easier to maintain a stable humidity and temperature in the system. As explained before, both temperature and humidity in the heating chamber were monitored and manually adjusted within the range. The tests were done on 10 grams of oxalic acid under 2, 3, 4 and 6 LPM flow rates. For final results, the values obtained from the raw data for the second flask were reduced by 40%, based on what was observed in the blank test runs.

Figure 4-13 High temperature setup blank runs
In Figure 4-14, the ammonia concentration in the first flask for 3 LPM and 6 LPM is presented as the lowest and highest flow rates applied (the experiments for 2 LPM did not resulted in stable data and the system temperature and humidity were unstable for flows that low). Since the previous setups had different design, reactor size and contact time, the data was not directly comparable. Moreover, the previous setup could not tolerate flow rates higher than 4 LPM. However, comparing the proportional average difference of the ammonia not adsorbed in the adsorbent (the data from flask 1) between 3 LPM and 6 LPM flow rates indicated similar Ct/flow rate proportions. Efficiency \( \left( \frac{(C'_0 - C_t) \times 100}{C'_0} \right) \) was calculated using concentrations form flask 1(Ct) and normalized concentrations from flask 2 to project the effect of temperature \( (C'_0) \). The efficiency analysis shows an interesting pattern. Both flow rates had a decreasing trend in their efficiency but the 3 LPM flow rate starts off with a higher efficiency in the beginning and ends with a lower efficiency, in comparison to 6 LPM flow rate. This difference is very small but one possible explanation for that could be the better stability of the system, at higher flow rates.
The results overall, indicated that the removal efficiency of ammonia from the gas stream remained above 93% at all times. However, after the first hour, signs of breakthrough can be observed, resulting in a sudden increase in the ammonia concentration in this flask. On the other hand, breakthrough is a situation where the adsorbate is passing the adsorbent without much adsorption and the increase in the ammonia concentrations will continue. As seen in the Figure 4-14 it reached a constant slope again around 100 minutes.

To further investigate the adsorption process, the oxalic acid in the reactor was separated into 4 layers of 2.5 grams and each layer was analyzed separately, after the experiment. This was done for both 4 LPM and 6 LPM flow rates. Figure 4-15 presents the data from analyzing samples taken from each layer, layer 1 being the top layer and layer 4 being the bottom layer. Each layer shows the capacity for taking around 24 mg/g of oxalic acid, if the flow rate and other effective conditions could be controlled in a way that the ammonia dispersion happens evenly in the adsorbent height. The results indicate an improvement in the amount of ammonia actually captured in the oxalic acid in comparison with the results from similar test performed using reactor 2 with lower temperature and humidity. However, this cannot be directly related to temperature and humidity. One reason could be improvements in the contact time between the ammonia stream and adsorbent. Furthermore, the fact that the heating chamber decreased the flow rate entering to the reactor, also had an effect on the adsorption performance.

Another possible explanation for this can be formation of a thin liquid layer at the surface of the oxalic acid crystal, due to partial melting of oxalic acid at the surface. If this were the case, the liquid layer would provide a platform for absorption instead of adsorption. This, of course, adds to the complexity of the process, but could facilitate the ammonia capture by oxalic acid.
The primary absorbent for the experiments was oxalic acid dihydrate. That had its advantages and disadvantages. One of the disadvantages was the reaction of oxalic acid to high temperature and humidity. In this case, since the experiments were run with the intent of simulating the actual struvite thermal decomposition unit outlet, for most of them the temperature was set to 80 °C and the RH could go above 80%. However, with the oxalic acid dihydrate, this resulted in slight melting at some points of the experiment. This caking will result in limitation in the product application, as well as difficulties in handling. Moreover, caking can block the flow path and increase the pressure in the system, which will influence the process. At this point, it was decided to investigate the process performance with two other adsorbents; Anhydrous Oxalic acid and Potassium tetraoxalate dihydrate.

4.2.6 Adsorbent effect on the efficiency of ammonia removal

The primary absorbent for the experiments was oxalic acid dihydrate. That had its advantages and disadvantages. One of the disadvantages was the reaction of oxalic acid to high temperature and humidity. In this case, since the experiments were run with the intent of simulating the actual struvite thermal decomposition unit outlet, for most of them the temperature was set to 80 °C and the RH could go above 80%. However, with the oxalic acid dihydrate, this resulted in slight melting at some points of the experiment. This caking will result in limitation in the product application, as well as difficulties in handling. Moreover, caking can block the flow path and increase the pressure in the system, which will influence the process. At this point, it was decided to investigate the process performance with two other adsorbents; Anhydrous Oxalic acid and Potassium tetraoxalate dihydrate.
4.2.6.1 Melting test for the adsorbents

In order to check the temperature resistance of these three adsorbents, three glass vials were filled to almost half with three adsorbents and put in the oven set on 100°C for a day. They were monitored observe the effect of temperature. The oxalic acid crystals were fully melted after a day. However, anhydrous oxalic acid and potassium tetraoxalate dihydrate maintained their solid state at all times. There was a slight caking in the anhydrous oxalic acid sample; however, that could be explained by the fact that anhydrous oxalic acid can absorb moisture in the environment and there is a chance that some oxalic acid dihydrate might have formed in between the anhydrous oxalic acid crystals, that would start melting and create the caking condition. With this experiment, it was proven that the two new adsorbents could provide better stability in higher temperatures. In order to investigate further, six experiments were designed to compare the performance of the adsorbents. Moreover, in these experiments for tracking the adsorption distribution in adsorbent height, the adsorbents were divided in four layers, that could be separately analyzed at the end of the experiment. All experiments were performed having ten grams of adsorbent in the reactor, divided to 4 layers of 2.5 grams each.

4.2.6.2 Adsorbent characteristics

Initially, oxalic acid dihydrate was chosen as the potential adsorbent for the process under investigation. The reasons for this decision, along with the general properties of oxalic acid, have been discussed in Sections 2.16 and 2.17. In this part, the main focus was on two new adsorbents that were tested as possible alternatives to the oxalic acid dihydrate.

Table 4-3 presents the most important properties of all three adsorbents that were compared. In this table, the theoretical ammonia uptake (that was calculated through stoichiometric proportions and based on the molecular weight of each adsorbent) is also presented. These theoretical values, however, do not always match with the experimental data, as there are other parameters influencing the adsorption process. These parameters can vary from experimental
conditions that affect the adsorption process, such as temperature and flow rate to molecular reactions and behaviours that could limit the ammonia uptake by the adsorbent.

Table 4-3 Properties of different adsorbents used in the experiments

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Dihydrate oxalic acid</th>
<th>Anhydrous Oxalic acid</th>
<th>Potassium tetraoxalate dihydrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C₂H₂O₄·2H₂O</td>
<td>C₂H₂O₄</td>
<td>KHC₂O₄·H₂C₂O₄·2H₂O</td>
</tr>
<tr>
<td>Molar mass (g/mol)</td>
<td>126.07</td>
<td>90.03</td>
<td>254.19</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>1.653</td>
<td>1.90</td>
<td>1.85(ab)</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>101-102</td>
<td>189-190</td>
<td>143(b)</td>
</tr>
<tr>
<td>Theoretical ammonia uptake per gram (g)</td>
<td>0.270</td>
<td>0.378</td>
<td>0.201</td>
</tr>
</tbody>
</table>

a. (Haas, 1964)
b. (Emsley, Jones, & Kuroda, 1981)

Since crystal size was one of the influencing parameters on adsorption, an attempt was made to have similar crystal sizes for all the comparative experiments, between different adsorbents. However, potassium tetraoxalate dihydrate crystals were generally smaller than the oxalic acid dihydrate and anhydrous crystals and they passed the sieve tray of 250 micrometer. Therefore, a smaller crystal size range was used for the experiment on potassium tetraoxalate dihydrate. Figure 4-16 shows crystal size distribution for this material.
In order to minimize the effect of a change in size, (which will affect the comparison of the data achieved for different adsorbents) the second largest range was chosen as the range under investigation. That means that the crystal size of 149-250 (outlined in the Figure 4-16) was used.

4.2.6.3 Performance comparison of adsorbents

Due to the conditions and the various factors that affect a process, theoretical calculations have always been an estimate or a starting point and they always require experimental data for modification and support. Here, the results of the experiments designed to investigate the performances of the three adsorbents, are presented.

The results for 4 LPM experiments showed a removal efficiency of 98% and higher, at all times, for all three adsorbents. However, a closer examination of ammonia concentration difference between flask 1(mainline) and flask 2 (blank) shows that the potassium tetraoxalate dihydrate had the highest ammonia removal, of the three (see Table 4-4). Although in all three experiments, the flow rate was set at the same level, the results show that there was a higher

Figure 4-16 Potassium tetraoxalate dihydrate crystal size distribution
passage of ammonia through the reactor when potassium tetraoxalate dihydrate was on line. This was attributed to inaccuracy of the flow meter. As previously presented in Figure 4-1, same flow rate setting on the flow meter could result in slightly different amount of ammonia passed through the system overall. The errors introduced by dilution in the results of second flask also play an important role in this difference. Despite the fact that the highest amount of ammonia entered the adsorption unit (flask 1), the least ammonia concentration in the absorption unit (flask 1) reported belonged to potassium tetraoxalate dihydrate. Table 4-4 compares the results for the last sample point in three experiments, based on the data gathered from the absorption unit.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>1&lt;sup&gt;st&lt;/sup&gt; flask (mg/l)</th>
<th>2&lt;sup&gt;nd&lt;/sup&gt; flask (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxalic acid dihydrate</td>
<td>1.12</td>
<td>505</td>
</tr>
<tr>
<td>Anhydrous Oxalic acid</td>
<td>1.42</td>
<td>525</td>
</tr>
<tr>
<td>Potassium tetraoxalate dihydrate</td>
<td>0.26</td>
<td>620</td>
</tr>
</tbody>
</table>

In these experiments, there were 10 grams of adsorbent in the reactor. Applying the results from layered analysis of the adsorbents can give us the overall amount of ammonia captured by each adsorbent.

This number is smaller than the number obtained from the analysis of the absorption unit itself based on the difference between the ammonia in the blank line and the flasks after the adsorption unit. For instance, in the 4 LPM run, with 10 grams of potassium tetraoxalate dihydrate, the total average amount of ammonia capture in the 10 grams of acid (based on the ammonia concentration in analysis of each layer of the adsorbent) was 53.83 mg. The fact that the blank line was not in the same temperature and not going through the same path, can influence the results. Therefore, the result from the analysis of the ammonia concentration in the blank line should be normalized (Figure 4-13) to represent the ammonia passage in high temperature.
According to the initial blank tests for high temperature unit, the actual results for the 2\textsuperscript{nd} flask should be reduced by 45\% (see hot and cold line results for 4 LPM flow rate in Figure 4-13), in order to be adjusted to the 80°C temperature condition applied to the experiment. Therefore, 620 mg/l reported here will be reduced to 340 mg/l. Since the amount absorbed in the 3\textsuperscript{rd} and 4\textsuperscript{th} flasks were negligible and the total volume of sulfuric acid in the flask 2 was 500 ml, it can be assumed that the total ammonia passing through the system in 2 hours was about 170 mg. There is still a big difference between this final number and the ammonia actually captured in the adsorption system. One of the explanations for this huge difference (170mg - 53mg = 117mg) is the absorption happening in the heating chamber before the adsorption unit that could limit the amount of ammonia entering the adsorption unit. Analysis of the liquid samples from this chamber indicated average ammonia concentration of about 55mg/l. Other influencing factors could be possible leakages in the reactor entrance, experimental and sample analysis errors.

Another point of interest in these experiments is the breakthrough during the experiments. As previously discussed, breakthrough will happen at an earlier point at higher flow rates. Figure 4-17 is comparing the results for oxalic acid dihydrate and anhydrous oxalic acid. As previously presented in Table 4-4, anhydrous oxalic acid has higher theoretical uptake capacity for ammonia due to the absence of water in its structure. Therefore, although a breakthrough can be observed for oxalic acid dihydrate, anhydrous oxalic acid performed with high efficiencies in the 2hour time span despite the increase in flow rate. The implication of these results on the practical application of this process, would be decreased number of adsorbent replacement cycles for anhydrous oxalic acid in comparison to oxalic acid dihydrate.
4.2.6.4 Capacity test

As presented in Figure 4-18, the bottom layer (labeled as layer 4) had the highest ammonia captured in all three adsorbents. The captured ammonia amount decreased gradually, going from layer 4 to 1 for oxalic acid dihydrate. However, in the case of anhydrous oxalic acid and potassium tetraoxalate dihydrate, there was a big difference between the amount of ammonia adsorbed in the bottom layer and the other three layers. The results of these experiments proposed the idea that the new adsorbents might have higher capacities compared to oxalic acid dihydrate; after the two hours, the upper layers of these adsorbents still had high capacities to adsorb more ammonia from the incoming stream. In Figure 4-18 each column represents the total amount of ammonia captured by specific layer of each adsorbent. All the adsorbent were used in quantity of 10 grams and divided into 4 layers of 2.5 grams. The interesting point observed in this data, was the loss of ammonia. In case of oxalic acid dihydrate, the mass transfer zone has moved through the adsorption reactor and almost reached the top layer in the 2-hour experimental time. However, in the other two adsorbents it seems the mass transfer zone is still in the bottom layer and there might be higher capacities for adsorption of ammonia in the bottom
layer as well as the layers above it. Combining the results obtained here, with the results from the absorption unit and the blank line (Table 4-5), there had been a clear leakage before the adsorption reactor that prevented the passage of the same amount of ammonia from these two adsorbents, in comparison to oxalic acid dihydrate.

![Graph showing ammonia adsorbed in each layer of the three different adsorbents](image)

**Figure 4-18 Ammonia adsorbed in each layer of the three different adsorbents**

In order to investigate this theory, a capacity test was performed. In these tests a higher concentration of ammonia solution was employed. This ammonia had 2% concentration of ammonia that was four times higher than the highest ammonia concentration for the ammonia solution in all the previous tests. In these experiments, the actual adsorbent samples were the main focus. Two grams of each adsorbent were put in the reactor and run under the 80°C and 80% humidity for two hours, with flow rates of 6 LPM. The adsorbent was then collected right after the experiment. Almost half of the collected sample was sent for an XRD analysis and the rest was diluted for chemical analysis (that included ammonia and TOC analysis) and, in case of the potassium tetraoxalate dihydrate an additional potassium analysis was performed. These results, presented in Section 4.3 (see Table 4-7), could help to clarify what happens during the process and what compounds are forming during the experiment.
4.3 Analysis of material formation throughout the process

One of the main aspects of understanding a process, in order to optimize it, would be the understanding of sequence of material formation. Having a theoretical background for the possible compositions and substances that can form during the adsorption process of capturing ammonia by the three adsorbents can help to understand the results of the performed analysis on the correct platform and understand this adsorption process.

In this case, the process is based on interactions between three key compounds; ammonia, oxalic acid and water. Initially, the process was assumed to take place based on the following reaction:

\[ H_2C_2O_4 \cdot 2H_2O + 2NH_3 \rightarrow (NH_4)_2C_2O_4 \cdot H_2O + H_2O \]  \hspace{1cm} (3-1)

\((NH_4)_2C_2O_4 \cdot H_2O\) or ammonium oxalate is not itself a widely used chemical. This is mainly because of the cost associated in producing ammonium oxalate and, in general, oxalate compounds. However, if it can be produced at low cost it will have an instant market as it can be heated in a simple process to transform to oxamide. Oxamide, as previously explained in Section 2.18 has been proven to be a superior, slow release fertilizer.

Previous, early work investigated the decomposition of ammonium oxalate monohydrate to oxamide, under 170 -200°C (Daniel, J. J., & James, B. L., 1953). The main issue with oxamide application as a slow release fertilizer, after its cost, is the difficulties assigned to forming a granular oxamide. Oxamide is in powder form and because of the hard and rigid characteristics of its surface, the oxamide powder particles do not adhere to each other to form granular oxamide. The common industrial practices of granulating, such as the rolling granulating process or the fluid granulating process, usually fail in producing granular oxamide with desired a hardness. On the other hand, the melt injection process cannot be used either, as oxamide decomposes under the required temperatures for this method. However, in 1989, a patent was
issued for work showing that when bonded to polyvinyl alcohol in a weight part ration of 0.2-10/100, it can be applied as a proper, slow-release fertilizer (Yutaka et al., 1989)

Although initially the main product was ammonium oxalate, after some analysis on the samples, it was obvious that not all the product was in ammonium oxalate form. In the following sections this will be explained in more detail and the different analysis can lead us to a better picture of the material formation during the adsorption of ammonia by adsorbents.

4.3.1 XRD analysis

Table 4-5 summarizes the compound list in each adsorbent before and after the adsorption process.

Table 4-5 Changes in the adsorbent composition after the process

<table>
<thead>
<tr>
<th>Initial phase composition of adsorbents before the process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxalic acid dihydrate</td>
</tr>
<tr>
<td>Oxalic acid anhydrous</td>
</tr>
<tr>
<td>Potassium Oxalate</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Phase identified in the adsorbent sample after the process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen oxalate hydrate (COOH2).2H2O</td>
</tr>
<tr>
<td>Beta oxalic acid</td>
</tr>
<tr>
<td>Alpha oxalic acid</td>
</tr>
<tr>
<td>H2C2O4</td>
</tr>
<tr>
<td>Ammonium hydrogen oxalate hydrate NH4H2O(C2O4)2.2H2O</td>
</tr>
<tr>
<td>Ammonium tetraoxalate</td>
</tr>
<tr>
<td>NH4H2O(C2O4)2.2H2O</td>
</tr>
<tr>
<td>Ammonium tetraoxalate</td>
</tr>
<tr>
<td>NH4H2O(C2O4)2.2H2O</td>
</tr>
<tr>
<td>Hydrogen oxalate hydrate (COOH2).2H2O</td>
</tr>
<tr>
<td>Oxammite</td>
</tr>
<tr>
<td>C2H8N2O4.2H2O</td>
</tr>
</tbody>
</table>

XRD analysis can help qualitatively identify composition in the sample however it is not a proper indication of the intensity and measures of those compounds. It can only indicate which compounds have higher percentage in the sample but it is still incapable of giving any concentration measures. As noted in Table 4-5, XRD analysis clearly showed for oxalic acid dihydrate, the most common phase formed during the adsorption is ammonium tetraoxalate. This was in agreement with the phase diagram. Ammonium tetraoxalate was the 1st ammonium
oxalate that forms in interaction of ammonia with oxalates (see Figure 2-7). For anhydrous oxalic acid, beside the oxalic acid itself and ammonium tetraoxalate, formation of Hydrogen oxalate hydrate can be observed. This indicates water adsorption during the process, which is later confirmed by the chemical analysis as well. The analysis for solid phase of the experiment done by application of potassium tetraoxalate dihydrate shows that it was the only adsorbent that could result in the ultimate product (Oxammite).

4.3.2 Chemical analysis

Based on the results gathered from analyzing the same samples separately for nitrogen, potassium and carbon, Table 4-6 can be produced. In this table, the amount of ammonia, oxalate and water was calculated based on mass ratio and the chemical analysis. The results presented here show water adsorption by anhydrous oxalic acid, a result that could explain the slight melting of anhydrous oxalic acid adsorbent during the process. The melting point for the anhydrous form of oxalic acid is way beyond the temperature ranges that are being experienced during these experiments. However, if with water adsorption, a portion of anhydrous oxalic acid turns to oxalic acid dihydrate due to its melting point of 90°C, melting could be expected. On the contrary, oxalic acid dihydrate loses water during the process. Here it can be argued that the anhydrous form in the beginning of the process is adsorbing the moisture coming into the system by the imposed humidity; whereas the dihydrate form is more sensitive to the heat applied by the high temperature and loses water during the experiment.

Also, the results from chemical analysis indicate that we could only reach a maximum adsorption of 16% of possible theoretical adsorption (see Table 4-7). However, both oxalic acid and potassium tetraoxalate dihydrate show promising performances; further investigations could help by comparing these two adsorbents. In these experiments different crystal sizes were used for those two adsorbents and performing a same, crystal size experiment could better assist the decision matrix. The economical and market aspect also plays an important role, as potassium tetraoxalate dihydrate is more expensive.
Table 4-6 Results from chemical analysis of the adsorbents after process

<table>
<thead>
<tr>
<th>Adsorbent after the process</th>
<th>N (mg/l)</th>
<th>K (mg/l)</th>
<th>C (mg/l)</th>
<th>H$_2$O Before (mg/g)</th>
<th>H$_2$O After (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxalic acid dihydrate</td>
<td>37.15</td>
<td>0</td>
<td>199.79</td>
<td>286</td>
<td>220</td>
</tr>
<tr>
<td>Anhydrous Oxalic acid</td>
<td>17.6</td>
<td>0</td>
<td>226.07</td>
<td>0</td>
<td>145</td>
</tr>
<tr>
<td>Potassium tetraoxalate dihydrate</td>
<td>21.8</td>
<td>163.5</td>
<td>194.06</td>
<td>142</td>
<td>95</td>
</tr>
</tbody>
</table>

Table 4-7 Comparison of ammonia adsorption in adsorbents based on their maximum theoretical adsorption capacity

<table>
<thead>
<tr>
<th>Adsorbent after the process</th>
<th>N (mg/l)</th>
<th>Max N (mg/g)</th>
<th>Ratio of the actual to maximum possible adsorption (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxalic acid dihydrate</td>
<td>37.15</td>
<td>222</td>
<td>16</td>
</tr>
<tr>
<td>Anhydrous Oxalic acid</td>
<td>17.6</td>
<td>378</td>
<td>7</td>
</tr>
<tr>
<td>Potassium tetraoxalate dihydrate</td>
<td>21.8</td>
<td>201</td>
<td>13</td>
</tr>
</tbody>
</table>

The first part of the Table 4-8 presents the theoretical molar ratios in different oxalates. The second part shows the results obtained from the chemical analysis done on the samples taken from different adsorbents, after each experiment. With this table the results obtained from chemical tests can be compared to different oxalates, keeping in mind that, the initial target was to have oxammite as final product due to its proven value as a slow-release fertilizer. This comparison, along with the appropriate phase diagram, can help position the final product for each condition and adsorbent. Based on that, optimizing of the process path as much as possible, should be possible. The reason for having two samples of potassium tetraoxalate dihydrate is that the first one was taken right after the experiment and kept in a desiccator, thus protecting it from adsorbing any environmental moisture it might be exposed to. However, the second one was prepared a day later and, as can be seen, it actually adsorbed moisture quite readily.
Table 4-8 Composition analysis of adsorbents after the process related to mol of species/mol of C$_2$O$_4$$^{2-}$:

<table>
<thead>
<tr>
<th>Compound</th>
<th>NH4</th>
<th>K</th>
<th>C2O4</th>
<th>H2O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxalic acid dihydrate</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Anhydrous oxalic acid</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Ammonium hydrogen oxalate hydrate</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0.5</td>
</tr>
<tr>
<td>Oxammite C$_2$H$_8$N$_2$O$_4$·2H$_2$O</td>
<td>2</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Ammonium tetraoxalate NH$_4$H$_3$(C$_2$O$_4$)$_2$·2H$_2$O</td>
<td>0.5</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Potassium tetraoxalate dihydrate</td>
<td>0</td>
<td>0.5</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

(Part 2: Composition of Adsorbent After Process)

<table>
<thead>
<tr>
<th>Compound</th>
<th>NH4</th>
<th>K</th>
<th>C2O4</th>
<th>H2O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxalic acid dihydrate</td>
<td>0.32</td>
<td>0.00</td>
<td>1.00</td>
<td>1.47</td>
</tr>
<tr>
<td>Anhydrous Oxalic acid</td>
<td>0.13</td>
<td>0.00</td>
<td>1.00</td>
<td>0.88</td>
</tr>
<tr>
<td>Potassium tetraoxalate dihydrate 1</td>
<td>0.19</td>
<td>0.52</td>
<td>1.00</td>
<td>0.67</td>
</tr>
<tr>
<td>Potassium tetraoxalate dihydrate 2</td>
<td>0.19</td>
<td>0.52</td>
<td>1.00</td>
<td>0.88</td>
</tr>
</tbody>
</table>

4.4 Struvite pellets employment as ammonia source

At this point, it was decided to run the test with the actual struvite pellets previously collected from struvite pilot plants. At this stage, this experiment was performed using the existing set up with a slight modification of the settings. The results from this test could provide information that could help further development and optimization of this process.

4.4.1 Type of the applied struvite

For this purpose, the pellets from the Penticton B.C. treatment plant with a size range of 0.5 to 1 mm, was selected. Even having the same pellet size based on hardness, porosity and structural composition, struvite pellets can behave differently in terms of ammonia release by heating. Previous experiments performed on different struvite pellets, with varying sizes and sources in the struvite thermal decomposition pilot-scale set up, indicated that the Penticton WWTP pellets of this size could achieve higher than 94% ammonia removal, after 2 hours, under optimum
conditions. The porous and soft surface of these pellets makes it easier for the gas stream to reach its core and extract the ammonia from it.

The optimum conditions that resulted in higher than 94% ammonia removal from the Penticton B.C. struvite pellets were 80°C and 95% RH. However, in this experiment the humidity was set to lower amounts, as the adsorbent was reacting to this high humidity and melting was observed. Therefore, the ammonia extraction percentage could be affected by this change. Moreover, the pilot plant reactor design and flow control differences have an important influence on the final ammonia extraction efficiencies (Farhana, 2015).

### 4.4.2 The change in process and performance of struvite pellets

Due to the way the set up was designed, it was not possible to perform the blank line and main line with the adsorbent on the line simultaneously, when struvite pellets were the ammonia source. Therefore, this experiment was performed as multiple runs, with only one absorption line working. In the blank run, four grams of the struvite pellets were placed in the bottom of the reactor and were blocked there with a small cotton ball. The inlet jar that was always the source for ammonia was filled with distilled water this time and the flow rate was set for 6 LPM. The experiment was run for 2 hours at 80°C and 80% RH. Samples were taken every fifteen minutes to monitor the ammonia extraction from the struvite pellets and their performance as the ammonia source.
Figure 4-19 Comparison of ammonia input by struvite pellets vs. the synthetic ammonia source at 6 LPM flow rate in 3rd stage setup

In the next run, in addition to four grams of struvite pellets, ten grams of sieved oxalic acid in the range of 250µm-500µm was placed in 4 layers, of 2.5 grams each. This could help in analyzing the ammonia adsorption throughout the adsorbent column. The results for ammonia input concentrations (Figure 4-19) as well as the ammonia concentration analysis of the oxalic acid layers are presented here (Figure 4-20).

The results from these tests indicated that the amount of ammonia passing through the system, when the ammonia source was switched to struvite pellets, was about 1/10 of the average amount for the total ammonia passage through the system, with synthetic ammonia solution source at the same flow rate.

However, taking a closer look it can be seen the overall results have been improved. Comparing the results of this test with the previous 6 LPM and 10 grams oxalic acid adsorbent test with ammonia solution jar (see Figure 4-19), it can been seen that, after 120 minutes of ammonia
passage through the same amount and type of adsorbent, not only was a higher ammonia concentration captured in the adsorbent bottom layer, but also the break out had not yet happened. By comparison, a breakout did happen in the previous tests after the first 90 minutes. These results suggest that, in a longer test run, the upper layer of the adsorbent can still adsorb more and more ammonia before reaching the break out point. Also, at all times during this 120 minutes run the removal efficiency remained above 93% and went as high as 99.2%. These runs indicate, with the same contact time values, a more stable flow rate containing lower amounts of ammonia could result in better accumulation of ammonia in each layer of the adsorbent. This not only increase the value of the final product by increased ammonia content but also result in lower number of adsorbent replacement.

![Figure 4-20](image.png)

**Figure 4-20** Comparison of ammonia capture in the adsorbent for different ammonia source

One important difference between these two experiments that could result in better performance of adsorbent when struvite is the ammonia source, rather than the synthetic ammonia source, was the stability of ammonia input. In the later, the ammonia was generated in a system outside the reactor, under different temperature and pressure conditions. This ammonia then travelled through a heating chamber that according to the previous experiments, could limit the ammonia passage due to condensation and possible leakage. However, when ammonia source was struvite,
the same conditions were applied to ammonia generator and adsorbent, since they were both placed in the same container (reactor). In this case, the ammonia input into the adsorbent remained in continuous low concentrations, whereas the synthetic scenario could push in pulses of high and low concentration to the adsorbent that resulted in performance decline.

4.5 Sources of error

Some of the content in this section may have been previously mentioned. However, it is useful to have the results summarized in total. The data, for the most part of this thesis, were obtained through different experimental sets, as very little literature was available for this specific adsorption process. Experimental data could always have errors introduced for different reasons;

- The solutions used in this process, such as the ammonia solution or the sulfuric acid solution, were all diluted versions of the existing solutions in the lab and this dilution was performed every time for each experiment; this could introduce some error to the overall process results.
- The samples, had slightly different timing, as they were taken by the syringe one after the other.
- The samples for the second flask, and when needed some other samples, were diluted and dilution always can introduce error to the results.
- The flow meter had a minimum accuracy of 0.2 LPM. Therefore, it could not be accurately set for the required flow rate, and there may have been slight unmeasured varieties for the reported flow rates in different experiments. In order to minimize this error, experiments with the same flow rate were performed sequentially as much as possible.
- The tubings were cleaned as much as possible, but since there were some parts of the set up fixed, the tubing could not be cleaned fully after each experiment.
- Since samples were collected at different times and sent for analysis later, sometimes the samples could remain in the racks 1-2 days and this could introduce water from the environment or loss of water in some cases.
• In some cases, when humidity was added to the experimental conditions, time should have been given to the adsorbent samples for drying in order to weight (the dried samples; however, this could risk changing results, due to water adsorbance or loss from the environment.

• Throughout the experiments, there could have been a situation where the crystals of adsorbent could lose the captured ammonia to the passing stream. This is the situation where the ammonia adsorbed is either not chemically bonded and low energy physical bonds are holding it to the adsorbent or the incoming stream could have released the ammonia captured in between the crystals (Perry & Green, 1999).

• In some cases, negative amounts of ammonia were reported for the sulfuric acid capture unit samples. However, this was due to the low amounts of ammonia in that sample vial and interference of the analysis method buffer. For negative results, it was assumed as zero ammonia concentration for that sample.

• Although an attempt was made to mix the solutions or the adsorbents, either through aeration or hand mixing, there may have been some samples were are not exactly representative of the bulk.

• During the high temperature runs, due to occasional condensation happening in the heating chamber, excessive resistance and sudden changes in flow rates were observed.

• Condensation could affect the flow rate, and there was a difference due to this effect, between the flow in the blank line and main line, in high temperature experiments.

• Although control of leakage was done for every experiment, leakage from the connector between the heating chamber and reactor was sometimes observed, due to the high temperature effect on the plastic connector.
Chapter 5: Conclusions and Recommendations

5.1 Summary and conclusions

In this project, the idea of adsorbing the low concentrations of ammonia existing in the struvite, thermal decomposition unit, outlet stream onto a solid adsorbent, (oxalic acid) was investigated through experiments designed and modified, stage-by-stage. The first setup was the most basic setup working at room temperature conditions. In this setup the flow rate was the first parameter investigated. The set up could handle flow rates between 2 LPM and 6 LPM. Primary experiments validated the possibility of eliminating ammonia from the stream with high efficiencies (higher than 90%). Being able to achieve ammonia removal from the stream would enable the stream to be reused for its high energy content due to its humidity and high temperature, in the overall process without further processing.

While imposing different flow rates and observing the influence of flow rate on the ammonia removal efficiencies, it can be concluded that the adsorption starts with higher rates, as more adsorbent sites are available at the beginning of the process and the concentration driving force is at the highest point, for the mass transfer between gas and solid. This adsorption rate gradually decreased with occupancy of the adsorption sites (Ghorai & Pant, 2005). An increase in the flow rate will increase the rate of ammonia coming in, with a decrease in the contact time between the ammonia molecules and the adsorbent surface. This will result in an increase in the number of ammonia molecules escaping from the reactor without having a chance to bond with the adsorbent and become adsorbed; eventually, this will decrease the removal efficiency. In order to accommodate higher flow rates of the actual struvite thermal decomposition unit (that would be the feed to this process), other parameters could be optimized without jeopardizing ammonia removal efficiencies.

One of these parameters was the adsorbent quantity and quality. One major parameter in any adsorption process is the contacting surface area, provided for the two phases. In order to increase this surface area, multiple procedures can be employed. One is to increase the total
amount of adsorbent. This approach increased the total amount of ammonia stored in the oxalic acid; however, the concern was the very low concentration of ammonia in each gram of acid. Since oxalic acid is expensive, it required finding the optimum amount of acid that could be loaded to the reactor. Further analysis indicated the maximum adsorption happening in the lower parts of the adsorbent column loaded to the reactor. After performing layered experiments, the experiments were mostly continued with adsorbent quantities between 6 and 10 grams.

Another approach for increasing the surface area between the ammonia in the input steam and the adsorbent was to use smaller crystals of the oxalic acid. After sieving the oxalic acid, the crystal size range of 250-500µm was chosen to continue the experiments. The main reason for this decision was that this crystal size was big enough to maintain a fixed bed condition, within the range of flow rates imposed to the system, and a high percentage of this fraction was available in the laboratory. Although this increased, the ratio of ammonia in the oxalic acid and the experiments continued with this specific crystal size, the mass ratio of the ammonia captured in each gram of oxalic acid was still very low.

The next step in further optimizing the process was to change the reactor configuration in order to increase the contact time. The new reactor provided almost 3 times longer contact time between the two phases (gas stream and adsorbent). This resulted in an increase in total amount of ammonia captured by the oxalic acid adsorbent. However, the increase was still far from satisfactory. Therefore, a special experiment was designed with long experimental time and a low flow rate, to provide an exaggerated contact time value to the system. Although the overall amount of ammonia adsorbed in the oxalic acid increased, the analysis of the adsorbent from this test indicated an efficiency drop, after two hours of experimental run.

At this point, it was decided to move to the high temperature and humidity conditions, to investigate their influence on the process. The third stage setup had additional compartments to provide temperatures around 80°C and RH, in required ranges. One of the design limitations was the unavailability of heating and adding humidity to two lines. Due to this limitation, a set of blank experiments were run, in order to have a base for comparing the results with adsorbent in
line, and to understand the direct effect of temperature of the flow rates and adsorption. This indicated about 35%-45% (depending on the flow rate) difference in the data reported for the same flow rate, at two temperatures. The concentration of ammonia in the sulfuric acid captures where always lower in high temperature (80°C) in comparison to low temperature (room temperature; 20°C) in the same flow rate. The purpose of these blank tests was to normalize the later experiment results (since the blank line for the experiments was in room temperature) to project the effect of temperature.

Having the blank runs, the experiments with 10 grams of oxalic acid dihydrate began on the 3\textsuperscript{rd} stage setup. The results from these experiments indicated better stability of humidity and temperature values during the experiments for higher flow rates. The data collected from ammonia concentration analysis, and ammonia captured in the adsorbent, indicated an increase in mass ratio of ammonia adsorbed in the oxalic acid dihydrate, while still maintaining the high efficiency of removal in comparison to experiments performed with similar flow rate and adsorbent dose at lower temperature. The efficiency of ammonia removal from the stream never dropped below 93% (based on the results from acid capture).

Although the results improved in the high temperature setup, a new problem was introduced. High temperature and humidity led to slight melting and eventually caking of the adsorbent in the reactor. In the search for another similar adsorbent with a higher melting point, two candidates were chosen. Both anhydrous oxalic acid and potassium tetraoxalate dihydrate have higher melting points. This could eliminate the melting possibilities during the adsorption process. The initial experiments indicated both potential adsorbents could perform high removal efficiencies, these experiments also proposed the possibility of higher capacity of adsorption with these adsorbents.

In order to validate this hypothesis, capacity tests were performed, followed by chemical analysis, TOC and XRD. The results provided an estimate of the material formed during this process, and indicated that not all the product is purely ammonium oxalate. Although ammonium hydrogen oxalate, ammonium tetra oxalate and oxammite were among the identified formed
compounds, initial adsorbents and other compounds were also available. The molar ratio data analysis, along with the phase diagram, also lead us to the conclusion that the experimental conditions were not optimized in a way to confirm the process of the direct line from oxalic acid to ammonium oxalate.

A more important conclusion was the fact that efficiencies of adsorption on the adsorbents (based on ammonia adsorbed in each gram of adsorbent) could not exceed more than 10-15% of the maximum theoretical estimates. This brings us to consider the limitation of ammonia penetrating into the adsorbent crystals and getting adsorbed to the total mass. The results proposed that ammonia was mostly adsorbed to the surface of the crystals; this limited the adsorption mass ratio.

The final part of the experiments was to apply struvite pellets as the ammonia source, and to observe the interactions between the released ammonia with this process. The results from this part showed that ammonia passing through the process, having struvite pellets as the ammonia source, was lower than ammonia solution source. This could have been the influence of operating condition such as lower RH combined with a change in design. As the high ammonia releases of the struvite pellets were optimized in a fluidized-bed, pilot-scale reactor, the removal efficiencies in this scenario were higher than 93% at all times and reached as high as 99.2% towards the end of the experiment. This was an indicator of available capacity for continuing this process, with higher adsorption rates.

As a result of this research, it is possible to optimize a novel ammonia removal process, which this adsorption process was a part of. By removing the ammonia from the hot and humid stream coming from the struvite thermal decomposition unit, it can be possible to reuse this stream and its energy. This will allow for significant reduction in operating costs for ammonia recovery using struvite thermal decomposition technology. Also, this work explored various options for recovery of ammonia as a valuable ammonia-containing product.
In summary, the most important objective of this research to design and develop a process for removing ammonia from the struvite thermal decomposition unit was met successfully. As mentioned before in search for a valuable by-product from this eliminated ammonia different adsorbents were investigated. These adsorbents (although they could satisfy the ammonia removal efficiencies along with stream energy conservation during the process), could not be concentrated with ammonia to satisfy the second objective of this research (producing a marketable product).

5.2 Recommendations for future work:
5.2.1 Application of an adsorbent carrier

One of the main concerns with the experiments was the limitation of actual mass ratio of ammonia capture in the adsorbents. With existing settings and conditions, we could efficiently remove ammonia from the input gas stream (simulating the struvite thermal decomposition unit outlet gas) and reuse this gas. However, different approaches to increase the mass ratio of ammonia adsorbed to the adsorbent mass, could not improve it more than 10-15% of the possible theoretical adsorption.

The reason is that ammonia gets adsorbed on the exterior surface of adsorbent crystals, and it cannot get inside. This is why all the mass of the oxalic acid cannot be utilized. Since most of the ammonia adsorption happens at the surface of the crystals, a media or carrier can be covered by a layer of adsorbent to replace the adsorption column, and minimize the adsorbent required in an efficient way. In doing so, one of the challenges could be the application and market for the product. This is largely dependent on the media chosen for this purpose. Unlike typical adsorbents it would not be possible to desorb ammonia from this media/carrier. Therefore, the media/carrier would not be reusable and it has to be valuable to the market.

In order to use this product (media with a layer of ammonium oxalate) directly as a fertilizer, it must be biodegradable. Woodchips are potential biodegradable carriers. Woodchips are among the several types of slow release fertilizers formulated over the past decades. To manufacture
these fertilizers, pressurizing methods are generally used to impregnate nutrient solutions in woodchips. Later, in contact with soil nutrients, ammonia will enter the soil solution through diffusion and capillary phenomena over a long period of time. The decomposition of the woodchips can also increase the organic matter content of the soil (Ahmed & Chun, 2007 and Ahmed et al., 2011)

One of the concerns with this method would be the possibility and efficiency of ammonia adsorption by the woodchips impregnated with an acidic solution. This, of course, would require further study and experimental proof; however, a similar process has been reported in the literature, where ammonia was removed from air streams and biogas by wood-shavings and anaerobically digestion bio-solids impregnated with sulfuric acid (Guo, Tak, & Johnson, 2009).

5.2.2 Energy recovery from the system

One of the main reasons behind choosing an adsorption process, over an absorption process, was the ability of adsorption for preserving the heat content of the incoming hot stream. In the experiments performed, although the whole line up to the absorption unit was not thermally insulated, the first flask right after the adsorption unit (flask 1) would always get heated. Keeping in mind the high heating capacity of the sulfuric acid solution, it can be concluded that a high heat transfer is required in order to have the glassware and the solution heated. This was observed in all the high temperature experiments. This indicated that the stream still held its heat content after the adsorption unit and the ammonia was removed without energy disruption in the stream.

The heat capacity of a solution depends on the components of the solution and their molar ratio. In this case it will refer to the moles of sulfuric acid and water in the solution and their heat content. The heat capacity of sulfuric acid solutions, based on their molality, is shown in Appendix C. These values are for 20°C (that is close to the temperature in the environmental laboratory where all the experiments took place). Knowing the molality of our solution and modifying the set up in order to measure the temperature in the beginning and the end of the
experiment, can help to estimate the total amount of energy that passed through the adsorption system and potentially what can be recycled and reused in the process. However, the exact measures for heat and energy loss was not a part of this study and the setup was not equipped with the proper compartments for process energy behaviour investigation.

5.2.3 Change in reactor design

One of the conditions set for the experiments was to operate the system as a fixed bed reactor. This was mainly due to the simplicity of operation and analysis of the system performance; the hydrodynamics of the fluidization process will strongly influence the adsorption process. However, implementing a fluidized bed reactor can be an effective way of efficiency increase, due to its appropriate mixing, temperature control and small pressure drop. Moreover, the mass transfer coefficient can be increased and diffusion limitations can be eliminated (Khajeh et al., 2014). This would need further study and experimental support for the specific process.

5.2.4 Change in scale

Although laboratory scale experiments are a very important part of new process investigation, every process needs a pilot-scale test in order to confront the scale up problems, and be able to solve them. It also allows one to optimize the process and grow it into an industrial scale process. This scale-up model can also later be connected to the pilot-scale struvite thermal decomposition unit, and work with the actual flow rates and temperatures from this unit’s outlet.
References


doi:10.1017/CBO9781107415324.004


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Sommer, S. ., & Hutchings, N. . (2001). Ammonia emission from field applied manure and its


Appendices

Appendix A
A.1 The XRD test results
Figure A-1 XRD analysis of adsorbent form 2LPM - 10g run in 1st stage setup
Figure A-2 XDR analysis of adsorbent form 4LPM - 50g run in 1st stage setup
Figure A-3 XRD analysis of adsorbent form 4LPM - 20g run in 1st stage setup
Figure A-4 XRD results for oxalic acid dihydrate capacity test
Figure A-5 XRD results for anhydrous oxalic acid capacity test
Figure A-6 XRD results for pure potassium tetraoxalate dihydrate
Total organic carbon is one of the measures that are commonly used in the water and wastewater industry. This test can indicate the total amount of organic carbon in the sample. In many cases for a specific source of water relationships can be developed between TOC, BOD and COD of that source and due to the cost and time limitations with performing a single test more that one characteristics of that source can be monitored. TOC, unlike BOD and COD is independent of the oxidation state of the organic matter existing in the sample solution. Another advantage of TOC test is its specific target for carbon, as it does not measure either other organically bound elements such as nitrogen and hydrogen or inorganics that can contribute to the oxygen demand in BOD and COD measures.
In this test in order to determine the quantity of the organically bound carbons they should be first broken down to single molecules. There are different paths for breaking down these bonds. One is through the application of high temperature, catalyst and oxygen. The other one is by using the energy of ultraviolet irradiation or chemical oxidants in lower temperatures. Table A-1 presents the results obtained for the capacity tests in the third stage setup.

Table A-1 TOC results for capacity tests

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>TOC (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxalic acid dihydrate</td>
<td>201.05</td>
</tr>
<tr>
<td></td>
<td>198.53</td>
</tr>
<tr>
<td>Anhydrous oxalic acid</td>
<td>226.58</td>
</tr>
<tr>
<td></td>
<td>225.55</td>
</tr>
<tr>
<td>Potassium tetraoxalate dihydrate</td>
<td>192.74</td>
</tr>
<tr>
<td></td>
<td>195.39</td>
</tr>
<tr>
<td>Potassium tetraoxalate dihydrate</td>
<td>187.84</td>
</tr>
<tr>
<td></td>
<td>188.48</td>
</tr>
</tbody>
</table>

Appendix B

B.1 Data for producing phase diagram

For producing the phase diagram in 75°C the existing literature data in 30°C and 45°C was used with basic extrapolation and assumption. The diagram is most sensitive to temperature in the lower parts were the equilibrium between solid and liquid is being investigated. However, for our application the solid phase equilibrium points were of interest. The data for obtaining the phase diagrams in 30°C and 45°C is presented in the Table B-1.
Table B-1 Data for ammonium oxalate - oxalic acid - water ternary system (Stephen & Stephen, 1964)

<table>
<thead>
<tr>
<th>Ammonium oxalate</th>
<th>Oxalic acid</th>
<th>Water</th>
<th>t, °C</th>
<th>Composition of solid phase</th>
</tr>
</thead>
<tbody>
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B.2 Calculating sulfuric acid solution heat capacity

Having the heat capacity and heat content for a solution the thermodynamic properties of the solution can be calculated for a wide range of concentrations and temperatures. In the table below the values of specific heat obtained from Biron’s experiments are reported. This work was originally done in 20°C. However, the change in heat capacity with temperature is small and the data can be used satisfactorily to a temperature of 25°C. Moreover, it was calculated that for concentrations of less than 40% the difference did not exceed 0.005 calorie per gram degree for a 20°C interval.

The following equation can be used for calculating the heat capacity for the sulfuric acid solution. In this equation, \( C_p \) is the heat capacity of 1g of solution and \( C_p^\circ \) is the heat capacity of 1g of water. \( \Phi_c \) is the heat content that is depended on the molar ratio of sulfuric acid to water in the solution (Craig & Vinal, 1940).

\[
\Phi_c = \frac{1000}{m} \left( C_p - C_p^\circ \right) + 98.076 C_p.
\]
Table B-2 Heat capacity of sulfuric acid solution (Craig & Vinal, 1940)

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<th>Molar mass of H₃SO₄</th>
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<th>Smoothed values</th>
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