Biological Treatment and Reclamation of Industrial Wastewater from Post-Combustion Carbon Capture

A Thesis
Submitted to Faculty of Graduate Studies and Research
in Partial Fulfillment of the Requirements
for the Degree of
Master of Applied Science
in
Environmental Systems Engineering
University of Regina

By
Joeffrey Bautista Domingo
Regina, Saskatchewan
March, 2020

Copyright 2020: J. Domingo
Joeffrey Bautista Domingo, candidate for the degree of Master of Applied Science in Environmental Systems Engineering, has presented a thesis titled, \textit{Biological Treatment and Reclamation of Industrial Wastewater From Post-Combustion Carbon Capture}, in an oral examination held on March 6, 2020. The following committee members have found the thesis acceptable in form and content, and that the candidate demonstrated satisfactory knowledge of the subject material.

External Examiner: Dr. Adisorn Aroonwilas, Industrial Systems Engineering

Supervisor: Dr. Stephanie Young, Environmental Systems Engineering

Committee Member: Dr. Jinkai Xue, Environmental Systems Engineering

Chair of Defense: Dr. Martin Hewson, Dept of Political Science & International Studies
Carbon capture and storage (CCS) system is a technology that has been developed to reduce the carbon emission in carbon-intensive industries. Although CCS is a sustainable option for power plants, it still produces contaminants in the form of its wastewater stream. The CCS wastewater contains several contaminants that could affect both environmental and human health. This study will focus on the biological treatment of two contaminants: amines and sulfates.

The main objective of this study is to design and develop an effective biological system to treat CCS wastewater to a quality that can be recycled back to the CCS process economically. The two biological treatment systems used were the Sequencing Batch Reactor (SBR) and the Sulfate Reduction, Autotrophic Denitrification, and Nitrification Integrated (SANI) system. These systems were further modified with the addition of another bioreactor containing *Bacillus benzoevorans*.

The influent and effluent water quality was evaluated in terms of the chemical oxygen demand (COD), total nitrogen (TN), total Kjeldahl nitrogen (TKN), ammonia, and sulfate.

From the first experiment, the following removal efficiency for COD, TN, TKN, ammonia, and sulfate were achieved: 95%, 62%, 88%, > 99%, and 11%, and 96%, 38%, 47%, 89%, > 99%, and 18% for SBR and SANI, respectively at low substrate
concentration; 95%, 88%, 88%, > 99%, and 10%, and 97%, 79%, 85% > 99%, and 16% for SBR and SANI, respectively at high substrate concentration. Both SBR and SANI exhibited equivalent removal efficiency for COD removal. The SBR at both low and high substrate concentration exhibited greater removal efficiency in TN, TKN, and ammonia. In contrast, the SANI at both low and high substrate concentration exhibited better sulfate removal efficiency.

The removal efficiency of COD, TN, TKN, ammonia, and sulfate through the addition of the *B. benzoivorans* resulted in 96%, 89%, 88%, > 99%, and 39%, and 97%, 81%, 94%, > 99%, and 25% in SBR and SANI, respectively. The modification of the systems shows that SBR has greater or equivalent removal efficiency for all contaminants. The addition of the *B. benzoivorans* also exhibited an improvement in sulfate removal for both systems.
ACKNOWLEDGEMENTS

I would like to extend my most sincere gratitude to my supervisor and mentor, Dr. Stephanie Young, for all her exceptional support, encouragement, and discipline during my undergraduate and graduate studies at the University of Regina. I would like to recognize and appreciate her former graduate student, Dr. Matthew Palmarin, for his assistance, training, and mentorship. I would like to acknowledge the University of Regina, the Faculty of Graduate Studies and Research, the Faculty of Engineering and Applied Science, and the Clean Energy Fund from SaskPower for their financial assistance in the completion of this program. Above all, I would like to thank the Almighty God for wisdom and knowledge, and for allowing me to experience and finish my MASc program.
DEDICATION

To my beloved parents, Enrique and Pricila, my brothers, Jayson and John, and Erika for all their unconditional love, continuous support, prayers, and encouragement.
TABLE OF CONTENTS

ABSTRACT .....................................................................................................................i

ACKNOWLEDGEMENTS ............................................................................................... iii

DEDICATION ................................................................................................................... iv

TABLE OF CONTENTS ................................................................................................. v

LIST OF FIGURES ......................................................................................................... x

LIST OF TABLES ............................................................................................................ xi

LIST OF ABBREVIATIONS ............................................................................................. xii

1 INTRODUCTION ........................................................................................................ 1

1.1 Problem statement................................................................................................... 2

1.2 Objectives .............................................................................................................. 4

1.3 Significance of research ......................................................................................... 5

2 LITERATURE REVIEW ............................................................................................ 6

2.1 Carbon capture and storage ................................................................................... 6

2.1.1 Capture ............................................................................................................. 7

2.1.2 Transport .......................................................................................................... 7

2.1.3 Storage ............................................................................................................. 8

2.2 Types of carbon capture technologies ................................................................... 8

2.2.1 Pre-combustion ............................................................................................... 12
2.2.2 Post-combustion

2.2.3 Oxy-fuel combustion

2.3 Post-carbon capture separation technologies

2.3.1 Absorption separation

2.3.2 Adsorption separation

2.3.3 Membrane separation

2.4 CCS wastewater

2.4.1 Amine-based solvents and degradation

2.4.1.1 Thermal degradation

2.4.1.2 Oxidative degradation

2.4.1.3 Gas reaction degradation

2.4.2 Composition

2.4.3 Major contaminants and sustainability impacts

2.4.3.1 Amines

2.4.3.2 Sulfates

2.4.4 Review on technologies for amine and sulfate removal

2.4.4.1 Physicochemical treatment processes

2.4.4.1.1 Amine removal

2.4.4.1.1.1 Air stripping
2.4.4.1.2  Ozonation ................................................................. 28
2.4.4.1.3  Membrane filtration .................................................. 29
2.4.4.1.2  Sulfate removal .......................................................... 31
  2.4.4.1.2.1  Precipitation ...................................................... 31
  2.4.4.1.2.2  Adsorption ....................................................... 32
  2.4.4.1.2.3  Ion exchange ..................................................... 33
2.4.4.2  Biological treatment processes ....................................... 33
  2.4.4.2.1  CAS ................................................................ 34
  2.4.4.2.2  SBR ................................................................. 39
  2.4.4.2.3  SANI ............................................................. 43
3  MATERIALS AND METHODS ......................................................... 46
  3.1  Apparatus and experimental set-up ....................................... 46
    3.1.1  Sludge acquisition .................................................... 46
    3.1.2  Preparation of synthetic CCS wastewater ......................... 47
    3.1.3  Equipment ................................................................ 50
  3.2  Methodology ................................................................. 52
    3.2.1  Sludge acclimation .................................................... 52
    3.2.2  Data collection ......................................................... 52
    3.2.3  MLSS/MLVSS analysis ............................................. 53
3.2.4 Wastewater quality analysis .......................................................... 53
3.2.5 Amine and sulfate removal analysis ........................................... 54
3.2.6 Bioreactor operation .................................................................. 54
  3.2.6.1 SBR .............................................................................. 56
  3.2.6.2 SANI ........................................................................... 56

4 RESULTS AND DISCUSSION .................................................................. 58

4.1 Comparison of conventional biological treatment at high and low substrate concentration .............................................................................. 58
  4.1.1 Introduction ........................................................................... 58
  4.1.2 Methodology .......................................................................... 58
  4.1.3 Results and discussion ............................................................ 60
    4.1.3.1 Organics removal ............................................................ 60
    4.1.3.2 Amine removal ............................................................... 62
    4.1.3.3 Sulfate removal ............................................................... 64
  4.1.4 Conclusions ........................................................................... 65

4.2 Comparison of conventional and modified treatment ....................... 66
  4.2.1 Introduction ........................................................................... 66
  4.2.2 Methodology .......................................................................... 69
  4.2.3 Results and discussion ............................................................ 70
4.2.3.1 Organics removal ................................................................. 70
4.2.3.2 Amine removal ................................................................. 72
4.2.3.3 Sulfate removal ............................................................... 74
4.2.4 Conclusions ........................................................................ 75
4.3 Limitations of the research ...................................................... 76
5 CONCLUSIONS ........................................................................ 77
6 RECOMMENDATIONS ............................................................... 79
8 REFERENCES ............................................................................ 80
LIST OF FIGURES

Figure 1. Schematic diagram of the three capture technologies.................................9
Figure 2. Schematic diagram of a typical activated sludge process. .........................36
Figure 3. Schematic diagram of (a) pre-anoxic and (b) post-anoxic denitrification ........36
Figure 4. Schematic diagram of the SBR process.....................................................38
Figure 5. Schematic diagram of the integrated processes and cycles used in SANI.......42
Figure 6. Schematic diagram of a SANI process from a pilot plant..........................45
Figure 7. Equipment used in conducting the experiment: (a) 2 L HDPE bottle, (b) aerator, (c) heating/stirring plate, (d) tubing, (e) one-way air valve, and (f) air stone.....51
Figure 8. Schematic diagram of the conventional (a) SBR and (b) SANI processes ......59
Figure 9. (a) SBR and (b) SANI systems ...............................................................59
Figure 10. Comparison between SBR and SANI at (a) low substrate concentration and (b) high substrate concentration .................................................................61
Figure 11. Comparison between low and high substrate concentration in (a) SBR and (b) SANI ..................................................................................................................61
Figure 12. Schematic diagram of the modified (a) SBR and (b) SANI processes .......68
Figure 13. Parameter analyses and comparison in conventional and modified SBR ....71
Figure 14. Parameter analyses and comparison in conventional and modified SANI ....73
LIST OF TABLES

Table 1. Advantage and disadvantage of the three capture technologies..................10
Table 2. Composition of a real CCS wastewater from a coal-fired power plant.........24
Table 3. Type and application of various membrane processes (Metcalf & Eddy Inc.,
2014)..........................................................................................................................30
Table 4. Composition and characteristics of the synthetic CCS wastewater..........49
Table 5. SBR operation. ............................................................................................55
**LIST OF ABBREVIATIONS**

**ANAMMOX** Anaerobic ammonium oxidation

**AOB** Ammonia-oxidizing bacteria

**BOD** Biochemical oxygen demand

**CAS** Conventional activated sludge

**CCS** Carbon capture and storage

**COD** Chemical oxygen demand

**GHG** Greenhouse gas

**HDPE** High-density polyethylene

**IPCC** Intergovernmental panel on climate change

**MEA** Monoethanolamine

**NOB** Nitrite-oxidizing bacteria

**PCC** Post-combustion capture

**SANI** Sulfate reduction, autotrophic denitrification, and nitrification integrated

**SBR** Sequencing batch reactor

**SOB** Sulfide-oxidizing bacteria

**SPOB** Syntrophic propionate-oxidizing bacteria

**SRB** Sulfate-reducing bacteria

**SRUSB** Sulfate-reducing upflow sludge bed

**TKN** Total Kjeldahl nitrogen

**TN** Total nitrogen

**TPES** Total primary energy supply

**WWTP** Wastewater treatment plant
1 INTRODUCTION

Climate change due to global warming is an important global issue that is related to the sustainable development of every country. The inaction to prevent the emission of global greenhouse gasses (GHG) could lead to a global temperature rise that will exceed 2°C above the pre-industrialized levels (Zheng et al., 2019). According to the Intergovernmental Panel on Climate Change (IPCC) (2014), the vast majority of current GHG emissions are related to anthropogenic sources such as energy, industrial processes and product use, agriculture, waste, and land use (Environment and Climate Change Canada, 2019; Wang et al., 2017). The fossil fuel carbon dioxide (CO₂) contributes the majority of global GHG emissions with an overall increase of 50% from 1990 to 2015 (Crippa et al., 2019).

The worldwide energy supply is still dependent on fossil fuels, as compared to other energy sources such as renewables and nuclear (International Energy Agency, 2019). The world’s total primary energy supply (TPES) consists of 81% fossil fuel, 14% renewables, and 5% nuclear sources. Of the 81% fossil fuel supply, 31% comes from oil, 27% from coal, and 22% from natural gas. Canada’s TPES is made up of 76% fossil fuel, 17.3% renewables, and 6.7% nuclear. Comparatively, the province of Saskatchewan’s TPES consists of 82.3% fossil fuel and 17.7% renewables. From the 82.3% fossil fuel supply, 46.6% is from coal, and 35.7% is from natural gas (Natural Resources Canada, 2019). Approximately 47% of the energy produced in the province of Saskatchewan is generated from coal. The GHG emission of Saskatchewan in 2017 is at
78 Mt CO$_2$ eq, which is approximately 11% of the total GHG emission of Canada (Environment and Climate Change Canada, 2019). High emissions of GHG would lead to the acceleration of global warming, which would cause human, economic, and environmental health issues such as seawater acidification, rising of global sea level, eutrophication, severe weather conditions, increased frequency of heatwaves, economic losses, impacts to human health, and loss of human lives (Dutcher et al., 2015; Ontoria et al., 2019; Woo et al., 2019; Yu et al., 2018).

In the Paris Agreement, Canada has committed to several strategies to reduce GHG emissions to limit the rise of global temperature to 1.5-2°C (Government of Canada, 2016). The federal government has been investing in the research and development of seven technology categories: energy efficiency, fossil fuels, renewable energy sources, nuclear, hydrogen and fuel cells, other power and storage technologies, and other crosscutting technologies and research (Jordaan et al., 2017). The majority of the investment in the fossil fuel category is dedicated to carbon capture and storage (CCS) systems. The CCS system has been designed to be implemented in carbon-intensive industries to limit carbon emission.

1.1 Problem statement

Although CCS is proven to reduce carbon emission in carbon-intensive industries, several drawbacks still exist, considering the three pillars of sustainability. In the economic aspect, CCS is claimed to be both energy-intensive and cost-ineffective. The application of CCS in existing powerplants will reduce the powerplant efficiency by 35%
(Smit et al., 2014). The capital and operating expenditures of implementing CCS also create an economic downside. The capital and operating costs ranges from 870 – 1980 USD kW⁻¹, with electricity cost ranging from 0.075 – 0.080 USD kW⁻¹ (Cuellar-France & Azapagic, 2015; Pettinau et al., 2013; Surampalli Rao et al., 2015; Theo et al., 2016). Another economic issue is the future carbon prices and the future CCS cost. If carbon price is low, then it is more economical to pay CO₂ emission taxes as opposed to the installation of CCS (Araujo & DeMedeiros, 2017).

In the social aspect, the public acceptance of CCS plays an integral role. Although it has already been established that the world is at risk for climate change, some of the lay public does not regard it as a serious problem, thus rejecting the idea for the need for CCS (Surampalli Rao et al., 2015). The CCS also often lacks public acceptance regarding transportation and storage of CO₂, as pipeline corrosion and leakage create an issue (D’Amore et al., 2018; Lee et al., 2017; Surampalli Rao et al., 2015; Viskovic et al., 2014). Furthermore, human health is at risk due to the emission of ethylene oxide to air and water during monoethanolamine (MEA) production (Koornneef et al., 2008).

In the environmental aspect, the capture process produces industrial wastewater that is heavily contaminated by amines, amine derivatives and sulfates resulting from various degradation processes within the absorber and reclaimer units (Gouedard et al., 2012). The amine wastes can pose threats to the surrounding ecosystem including freshwater aquatic ecotoxicity, marine aquatic ecotoxicity, plant growth, acidification, and eutrophication (Botheju et al., 2011; Eide-Haugmo et al., 2009; Ghayur et al., 2019;
Liuzinas et al., 2007; Thitakamol et al., 2007). The gas emissions created by CCS could also cause ozone layer depletion, health and environmental risks, and carcinogenic effects from the nitrosamines (Badr et al., 2017; Gjernes et al., 2013; Karl et al., 2011). Another indirect environmental effect of CCS implementation is the abiotic depletion due to the extraction of materials from nature for construction and operation (Koornneef et al., 2008).

1.2 Objectives

From the three pillars of sustainability, this research will focus on the environmental problem created by CCS, more specifically pertaining to industrial wastewater. The goal of this paper is to design and develop an effective biological system to treat CCS wastewater to a quality that can be recycled back to the CCS process economically. The study focused on three objectives: (1) to investigate the treatment performance of two biological systems – Sequencing Batch Reactor (SBR) and the Sulfate Reduction, Autotrophic Denitrification, and Nitrification Integrated (SANI) system; (2) to investigate the treatment performance of these two biological systems with increasing substrate; and (3) to compare the treatment performance of the conventional and modified biological systems with the addition of Bacillus benzoevorans.

The investigation of the two biological systems used in this study resulted from the lack of research and treatment options concerning the industrial wastewater produced from the CCS. From a variety of biological treatment systems, the study will focus on SBR and SANI system. The biological systems were chosen because of their effectiveness and
were further modified to increase their treatment efficiency. This research will determine the feasibility and practicality of reclaiming the industrial wastewater produced by CCS.

1.3 Significance of research

The principle of wastewater reclamation is to conserve the use of freshwater resources and to preserve the surrounding ecosystem from possible contamination by introducing effective technologies that can treat and recycle wastewater. The CCS wastewater reclamation could provide a solution to the risks posed by wastewater contaminants, especially in the surrounding environment. In addition, the reclamation of industrial wastewater can cause positive economic, social, and environmental benefits that can compensate some of the issues brought upon by the CCS.

The application of the results from this research may be used as a foundation for the further improvement of CCS wastewater reclamation.
2 LITERATURE REVIEW

2.1 Carbon capture and storage

Carbon capture and storage system is a concept that was introduced in 1977 and was further developed to capture carbon emissions at industrial facilities to comply with environmental laws and policies (Raza et al., 2017). A carbon capture and storage system is a technology that steers toward sustainable energy production by the continuous use of fossil fuels while reducing CO$_2$ emissions. The CCS is an integrated process where the CO$_2$ is (1) captured, (2) transported, and (3) stored (Kumar et al., 2019; L'Orange et al., 2014; Oh, 2010; Raza et al., 2019). It is usually implemented in facilities that are carbon-intensive such as fossil power plants and cement plants. It is reported to be capable of reducing 17% of global carbon emissions by 2050 (Raza et al., 2019; Tevetkov et al., 2019).

According to the Global Carbon Capture and Storage Institute (2016), there are a total of 37 large-scale CCS projects. The three largest CCS projects in the thermal sector are the Boundary Dam Carbon CCS Project in Saskatchewan, the Petra Nova Carbon Capture Project in Texas, and the Sinopec Shenli Power Plant CCS Project in Shangdong Province. In the industrial sector, the CSS projects include the Sleipner CO$_2$ Storage Project in Norway, Abu Dhabi CCS Project in the United Arab Emirates, and the Great Plains Synfuel Plant and Weyburn-Midale Project in Canada (Koytsoumpa et al., 2018). From literature, the industries seem to lean towards the implementation of CCS technology in both new or existing plants.
2.1.1 Capture

Capture is the first process of the CCS system. The carbon is captured from different sources in the powerplant according to various parameters like partial pressure, operating conditions, and composition of the gas mixture. There are three main carbon capture options studied in literature, pre-combustion, post-combustion, and oxy-fuel combustion carbon capture (Cuellar-France & Azapagic, 2015; Koytsoumpa et al., 2018). Since the research is focused on the wastewater produced during the capture process, this topic will be further discussed in the succeeding chapters of this research.

2.1.2 Transport

The second process of the CCS technology is the transport of CO₂ from the capture point to the storage or utilization sites. The transport is initially accomplished by converting CO₂ gas into a liquid or supercritical state (Araujo & DeMedeiros, 2017; Raza et al., 2019). This form is preferred to optimize the mass to volume ratio of CO₂ (Leung et al., 2014). The CO₂ could be transported using pipelines, ships, or tanker trucks depending on the volume transferred, and the distance travelled (Leung et al., 2014; Tan et al., 2016). Tank trucks are used for short-distance transport, while ships and pipelines are utilized for long-distance transport. However, pipelines are the preferred method of transport as it could transport large quantities of CO₂. Compared to the other transport methods, pipeline transport is also the most viable and cost-efficient (Araujo & DeMedeiros, 2017; Leung et al., 2014; Raza et al., 2019; Tan et al., 2016).
2.1.3 Storage

After the capture and transport of CO$_2$, the last process is CO$_2$ storage. The storage can be classified as geological storage, ocean storage, or carbon mineralization. The geological storage is the injection of CO$_2$ into a rock formation under the earth’s surface, such as oil and gas reservoirs, deep saline aquifers, and coal bed formations. The ocean storage is the injection of CO$_2$ into the ocean bed. The carbon mineralization is a storage process wherein stable carbonates are formed through the reaction of CO$_2$ with magnesium and calcium oxides. From the three CO$_2$ storage options, the geological storage is considered to be the most viable and effective (Cuellar-France & Azapagic, 2015; Leung et al., 2014; Tan et al., 2016).

2.2 Types of carbon capture technologies

There are three types of carbon capture technologies that are currently being studied in literature, (1) pre-combustion capture, (2) post-combustion capture, and (3) oxy-fuel capture. Figure 1 shows a diagram of the three capture technologies. A summary of the advantages and disadvantages of each capture technology is also presented in Table 1. These technologies are further discussed in the following sections.
Figure 1. Schematic diagram of the three capture technologies.
Table 1. Advantage and disadvantage of the three capture technologies.

<table>
<thead>
<tr>
<th>Technology</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-combustion</td>
<td>• high CO$_2$ concentration enhance capture efficiency</td>
<td>• only applicable to new plants</td>
</tr>
<tr>
<td></td>
<td>• increased driving force for CO$_2$ separation</td>
<td>• commercial availability is limited</td>
</tr>
<tr>
<td></td>
<td>• more technologies available for separation</td>
<td>• high capital and operating costs</td>
</tr>
<tr>
<td></td>
<td>• potential for reduction in compression costs and loads</td>
<td>• high power requirement for sorbent regeneration</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• temperature associated heat transfer problem and efficiency decay issues</td>
</tr>
<tr>
<td></td>
<td></td>
<td>associated to the use of gas turbine fuel</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• inadequate maturity compared to other alternatives</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• fuel processing is needed</td>
</tr>
<tr>
<td>Post-combustion</td>
<td>• retrofit technology to existing plants</td>
<td>• dilute CO$_2$ concentration affects capture efficiency</td>
</tr>
<tr>
<td></td>
<td>• extensive literature about efficiency and cost penalties for</td>
<td>• higher performance or circulation volume is required for high capture levels</td>
</tr>
<tr>
<td></td>
<td>coal-fired power plants with conventional MEA scrubbing</td>
<td></td>
</tr>
</tbody>
</table>

| Oxy-fuel combustion | • more mature technology compared to other alternatives  
|                     | • significant cost savings are possible  
|                     | • very high CO₂ concentration that enhances absorption efficiency  
|                     | • retrofit technology option  
|                     | • reduced volume of gas to be treated  
|                     | • smaller boiler and equipment  
|                     | • large O₂ production is expensive  
|                     | • corrosion problems  
|                     | • high efficiency drop and energy penalty  |
2.2.1 Pre-combustion

Pre-combustion capture is a carbon capture that is typically applied to coal-gasification plants. It is a process where the fuel is initially treated in a gasifier under a low oxygen level to form a synthetic gas (syngas) consisting of CO and H₂. The syngas will pass through a catalytic reactor where the CO reacts with steam to form CO₂ and more H₂. The high CO₂ concentration in the gas mixture allows the separation of CO₂, while the H₂ is burned to produce N₂ and water vapor (Leung et al., 2014; Olajire, 2010).

In comparison to post-combustion capture, the CO₂ concentration in pre-combustion is higher, allowing smaller equipment to be used. The energy penalty in the application of pre-combustion is lower compared to post-combustion capture. Furthermore, the produced hydrogen from gasification and water gas shift reactor can be used as fuel for gas boilers, turbines, fuel cells, and other technologies (Olajire, 2010). Since there are advantages of pre-combustion capture, several pre-combustion capture techniques are also researched and developed such as the integrated gasification combined cycle, physical solvent processes, membranes, and reaction with pre-combustion solvents (Rahman et al., 2017).

2.2.2 Post-combustion

Post-combustion capture (PCC) is a carbon capture process where CO₂ is captured after the coal is combusted for energy generation. This capture type uses different kinds of systems like absorbent-based, adsorbent-based, and membrane-based technology (Dutcher et al., 2015; Figueroa et al., 2008). This capture technology is usually applied
in both coal and gas powerplants and is preferred for retrofitting since it could easily be added to the existing plants. However, this type would increase the cost of electricity production by 70%, and capture efficiency is affected by low CO₂ concentrations (Leung et al., 2014). Of all the three types of CCS, post-combustion carbon capture is mostly used in the industry, as it is more mature and more suitable for retrofitting as opposed to pre-combustion and oxyfuel combustion carbon captures (Lockwood, 2017). Thus, making this capture technology the best near-term solution in reducing GHG emission.

A significant amount of research and development is done on PCC, which introduced the proposal and design of different types of PCC technologies, such as chemical absorption, sorbent adsorption, and membrane separation. However, most of these technologies are still commercially inapplicable, especially with regards to coal-fired power plants. According to Wang et al. (2017), two major issues retard the successful application and operation of these technologies. First, the low partial pressure of CO₂ in the flue gas contributes to the low driving force of CO₂ separation. Second, the flow rate of flue gas is significantly higher compared to the usual streams that are treated by such technologies.

### 2.2.3 Oxy-fuel combustion

The oxy-fuel combustion is a capture process that can be applied to both coal and gas powerplants. It uses pure oxygen instead of air for combustion. With the use of pure oxygen, the composition of the flue gas would be CO₂, water, particulates, and SO₂. The particulates and SO₂ can be subsequently removed using electrostatic precipitator and
flue gas desulphurization methods, yielding a high concentration of CO$_2$ (Figueroa et al., 2008). This capture process consumes a large amount of oxygen from an air separation unit that is very energy-intensive, resulting in higher cost and energy penalty compared to non-CCS powerplants. There are currently no full-scale oxy-fuel carbon capture combustion projects; however, several sub-scale projects are being developed worldwide (Leung et al., 2014).

2.3 Post-carbon capture separation technologies

The post-combustion carbon capture is the capture technology that is most mature and is being commercially implemented in several coal-fired powerplants. Because of this, research and development are being done in its separation technologies to reduce parasitic load and cost. The following sections will discuss the three separation technologies applicable to PCC: absorption, adsorption, membrane.

2.3.1 Absorption separation

The absorption separation in PCC is the most commonly used capture technology in the industry due to its maturity, ease of retrofit, and opportunities for improvement (Subramanian et al., 2017). This separation is a solvent-based PCC and is the conventional CO$_2$ capture technology. It is considered expensive because of its high parasitic energy load, high capital costs, and insufficient commercial-scale application (Nelson et al., 2017). The typical solvent used in this type of PCC is different mixtures of amines, with MEA as one of the primary compounds, because of its fast rate of reaction with CO$_2$ (Aroonwilas & Veawab, 2004). Furthermore, the solvent containing
30% MEA has been successfully tested in a PCC for coal-fired power plants (Aaron & Tsouris, 2005).

The process integration of absorption separation starts after the cooling of the flue gas. The flue gas is brought to the absorber to be in contact with the chemical absorbent through a water wash at temperatures between 40 and 60 °C. The chemical absorbent binds the CO$_2$, and the rest of the vapour leaves the absorber. The rich chemical absorbent solution is collected and pumped to the top of the stripper. The regeneration of the chemical sorbent is done in the stripper at temperatures between 100 to 140 °C and pressures between 1 and 2 bar. Because of the temperature and pressure, the chemically bounded CO$_2$ is collected as a product gas, and the lean chemical absorbent is recycled back to the process (Feron, 2009).

Out of all the three technologies, absorption separation PCC is the most commercially-ready technology for the reduction of carbon emission in carbon-intensive industries. According to Oko et al. (2017), there are at least 17 projects from 2008 to 2014, who have used the solvent-based carbon capture, such as Sleipner CCS, In Salah CCS, Snøhvit CCS, Gorgon CCS, and Quest CCS. The absorption-based carbon separation is also implemented for power plants on a commercial scale. Currently, the coal-fired power plants that use solvent-based carbon capture are the Boundary Dam Unit 3 power plant near Estevan, Saskatchewan, and the Petra Nova facility near Houston, Texas.
Absorption separation is the most significantly studied technology of PCC. However, there are still other developments that can be implemented to increase the efficacy of the technology – process intensification, new solvents, or the combination of the two. The process intensification would allow the considerable reduction of the absorber and the stripper. Some studies show that the conventional packed beds can be replaced by rotating packed beds, which would reduce the packing volume by 7 to 12 times. Other designs include the spinning disc and microwave technology for solvent regeneration (Oko et al., 2017). On the other hand, new solvent mixtures with higher CO₂ loading capacity and lower regeneration energy could decrease both the capital and operating costs of PCC. Some notable research is being conducted at the University of Regina regarding the development of new solvents. The combination of the process intensification and new solvents could also be further studied as this combination may have a synergistic relationship to increase the cost-efficiency of the absorption-based PCC.

Once these designs have been further tested and observed in different scales, it could be implemented in the commercial-scale carbon capture. However, from the three future developments, the new solvents would be more applicable for retrofit to existing carbon capture facilities, as compared to the process intensification and the combination of the two, which can be implemented to future absorption-based PCC projects.
2.3.2 Adsorption separation

The second type of CO₂ separation technology is a sorbent-based PCC which utilizes adsorption, as opposed to absorption. This type of PCC technology separates and recovers CO₂ through a cyclic, thermal swing, sorption-desorption process (Nelson et al., 2014; Nelson et al., 2017). According to Wang et al., (2011), solid sorbents are promising due to its high CO₂ loadings, low heat capacities, low corrosivity, and toxicity/volatility prevention as compared to the solvent-based PCC.

The flue gas initially enters a precooler before being compressed by an exhaust gas fan. The gas then goes through a re-cooler to lower the temperature to 40 °C, where the excess water is removed. After the re-cooler, the flue gas enters the bottom of the adsorption tower in counter-current flow contact with the fluidized sorbent. In this tower, 90% of the CO₂ is adsorbed through an exothermic reaction. The cleaned flue gas leaves from the top of the adsorption tower, while the rich sorbent is transferred to the desorption tower. The desorption reaction in the tower regenerates the lean low-temperature sorbent through a regenerating steam that is extracted from the low-pressure turbine. After the regeneration, the lean sorbent is returned to the adsorption tower, while the extracted CO₂ stream is compressed and prepared for transport and storage (Subramanian et al., 2017).

Currently, solid sorbents are used in air drying and separation. According to Lockwood (2017), most of the research is focused on the temperature swing process of sorbent carbon capture. The studies are geared towards the use of materials, such as amines, and
various designs that provide rapid heat transfer for flue gas flow rates. In addition to research, RTI International has also developed a solid sorbent capture technology for flue gases from different industrial sources such as coal-fired power plants, Natural gas combined cycle power plants, and cement plants. Two notable adsorption-based capture prototypes of RTI are being tested at RTI’s test facility and Nocrcem’s cement plant in Brevik, Norway (Nelson et al., 2017). Another project for sorbent-based capture is being done by Inventys. The novel concept for this capture uses a structured carbon sorbent that would continuously rotate between the flows of flue gas, regenerating stream, and cooling air (Lockwood, 2017).

For future research and improvement, adsorption carbon separation can be developed in two ways: sorbent and bed configuration. The modification of different sorbents would improve performance in terms of working capacity, cycle time, and multicycle durability. Different bed configurations such as fluidized bed, circulating bed, transport bed, and other innovative configurations can also be further studied to eliminate the drawbacks of the fixed bed that is currently used for sorbent-based capture technology (Samanta et al., 2012). The development of these two aspects could increase the economic viability of sorbent-based technology with regards to CO₂ capture from flue gas.

2.3.3 Membrane separation

The third type of carbon separation is the membrane-based carbon separation that uses different types of membranes to separate CO₂ from the flue gas. Varying opinions about
the efficacy of membrane-based capture are spread throughout literature. According to Wang et al. (2017), membrane-based separation can compete with conventional absorption separation. The main advantages of membrane separation include compactness, modularity, ease of retrofit, flexibility, and lower costs (Khalilpour et al., 2015). However, in the same study, Wang et al. (2017) state that it is only advantageous at lower CO₂ capture degrees (< 90%) since the capture is highly restricted by the membrane materials.

The process of membrane-based separation starts with the cooling of the flue gas stream, which is fed to the membrane that is selective to CO₂. The partial pressure difference of CO₂ between the feed stream and permeate stream is the driving force of CO₂ separation. The permeate stream, which has a higher concentration of CO₂, is separated and collected, while the flue gas is brought to the retentate (Khalilpour et al., 2015; Subramanian et al., 2017).

The membrane-based separation is commercially available for natural gas sweetening, where CO₂ and hydrogen sulfide (H₂S) in high-pressure natural gas are lowered. However, this does not translate into the separation of CO₂ in flue gas because of several differences in the applications, product requirements, and molecular characteristics. The IPCC has reported that membrane-based separation has not yet been tested in industrial-scale systems, and their reliability and cost-effectiveness has not been thoroughly evaluated (Khalilpour et al., 2015). However, current research indicates that the
developments in materials and process designs could significantly improve the separation of CO$_2$ in flue gas using membranes.

The development of membrane-based separation can also be categorized in the improvement of the membrane material and the design of the system. The material of the membrane should have the desirable permeance and selectivity to CO$_2$, on top of the stability of the structure. On the other hand, the design of the system should cater to optimal configurations to lower the costs (Khalilpour et al., 2015). Furthermore, Khalilpour et al. (2015) have also considered the development of technical and operational concerns, especially with regards to the impacts of the minor gas components, such as water vapor, SO$_x$, NO$_x$, and NH$_3$.

2.4 CCS wastewater

Although CCS is an effective sustainability technology in reducing intensive carbon emissions, it still produces contaminants that could affect the environment. One of which is the CCS industrial wastewater from the capture process. The wastewater can be mainly found in the washwater, condenser, and amine reclaimer units of the capture technology (Dong et al., 2019).

2.4.1 Amine-based solvents and degradation

Post-combustion using absorbent separation technology is the most viable carbon capture and separation technology for commercial-scale powerplants. The use of absorbent separation technology requires solvents to separate CO$_2$ from the flue gas. The most
developed solvents are amine-based, which were originally used for natural gas sweetening process (Liang et al., 2015; Sharma & Azzi, 2014). The most commonly used amine solvent blends consist of one or more of the following: primary amines (MEA, 2-amino-2-methyl-1-propanol (AMP)), secondary amines (diethanolamine (DEA), 3-amino-1-methylaminopropane (MAPA)), tertiary amines (methyl diethanolamine (MDEA), triethanolamine (TEA), 2-diethylaminoethanol (DEEA)), and cyclic diamines (piperazine (PZ)) (Mazari et al., 2015; Nwahoha et al., 2017; Sharma & Azzi, 2014).

However, the amine solvent blends degrade over time due to several reasons such as high temperature, increased oxygen levels, and impurities in the flue gas (Dutcher et al., 2015). The degradation of amine solvents reduces the ability of the amine solution to capture CO$_2$ (Wang et al., 2015). Furthermore, the degradation leads to operational problems such as viscosity, corrosion of equipment, fouling and foaming that causes the increase of operational cost and environmental concerns through the release of pollutants and toxic degradation by-products (Dong et al., 2019; Mazari et al., 2015; Saeed et al., 2018). There are three main reaction pathways in which amine solvents degrade: (1) thermal degradation, (2) oxidative degradation, (3) gas reaction degradation.

### 2.4.1.1 Thermal degradation

Thermal degradation, also known as carbamate polymerization, often takes place at high temperatures. Therefore, it primarily occurs at the stripper packing, stripper sump, reboiler, solvent reclaimer, and piping leading to the heat exchanger (Saeed et al., 2018;
SEPA, 2015). The most prevalent thermal degradation product is 1-(2-hydroxyethyl)-2-imidazolidone (HEIA), with N-(2-hydroxyethyl)-2-ethylenediamine (HEEDA) and 2-oxazolidone existing in smaller concentrations (Dutcher et al., 2015). This type of degradation accounts for the 20 – 30% of total amine losses in absorption-based PCC (Dong et al., 2019).

2.4.1.2 Oxidative degradation

Oxidative degradation is the main and fastest degradation pathway of amines in absorption-based PCC (Reynolds et al., 2015; Saeed et al., 2018). This degradation is caused by temperature, the reactivity of amines, and high oxygen and metal content in the flue gas (Dickinson et al., 2016; Mazari et al., 2015). This type of degradation occurs in the absorber sump, absorber packing, solvent pipes, and heat exchanger (SEPA, 2015). The main products of oxidative degradation are organic acids such as formate, acetate, and oxalate (Dong et al., 2019; Dutcher et al., 2015; Morken et al., 2019).

2.4.1.3 Gas reaction degradation

Amine solvent degradation is also possible through the reaction of amines with NO\textsubscript{x} and SO\textsubscript{x}. When amines react with NO\textsubscript{x}, it generates ammonia, nitramines and nitrosamines. According to Dong et al. (2019), all amines are potential nitrosamine precursors. Furthermore, when amines react with SO\textsubscript{x}, it produces heat-stable corrosive salts (SEPA, 2015).
2.4.2 Composition

The composition of the CCS wastewater is variable depending on the actual amine solvent blend and the composition of the flue gas. However, the general composition of CCS wastewater will contain water, amine, ammonia, other degradation products, heat stable salts, flue gas impurities, and corrosion products (Henry, 2016). Table 2 shows an overview of the characterized CCS wastewater from a coal-fired powerplant.

2.4.3 Major contaminants and sustainability impacts

From Table 2, the major contaminants of interest found in CCS wastewater from coal-fired power plants are amines, in the form of total nitrogen, and sulfates, in the form of both sulfite and sulfate.

2.4.3.1 Amines

The presence of amines in the CCS wastewater is primarily from the amine blends used as solvents. Amines are organic compounds with N atoms that selectively and reversibly react with CO₂ (Botheju et al., 2011). All amines used to capture CO₂ react to form nitrosamines, which have carcinogenic effects as tested by researchers (Badr et al., 2017; Gjernes et al., 2013). Furthermore, the solubility of most amines in water is relatively high; thus, it will dissolve in rain and fog droplets that could eventually end up in surface water, rivers, and lakes (Gjernes et al., 2013).
Table 2. Composition of a real CCS wastewater from a coal-fired power plant.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Concentration (mg L⁻¹)</th>
<th>Parameter</th>
<th>Concentration (mg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluoride</td>
<td>18</td>
<td>Nitrate</td>
<td>47</td>
</tr>
<tr>
<td>Glycolate</td>
<td>7</td>
<td>Sodium</td>
<td>3765</td>
</tr>
<tr>
<td>Sulfamate</td>
<td>224</td>
<td>Potassium</td>
<td>7</td>
</tr>
<tr>
<td>Chloride</td>
<td>38</td>
<td>Calcium</td>
<td>18</td>
</tr>
<tr>
<td>Sulfite</td>
<td>15774</td>
<td>Magnesium</td>
<td>12</td>
</tr>
<tr>
<td>Sulfate</td>
<td>7591</td>
<td>TN</td>
<td>189</td>
</tr>
<tr>
<td>Oxalate</td>
<td>59</td>
<td>TOC</td>
<td>564</td>
</tr>
</tbody>
</table>
Since MEA is one of the primary compounds in amine blends, the study will consider its degradation and impacts. According to Ndegwa et al. (2004), MEA dissociates to acetaldehyde and ammonium in the presence of water. When the wastewater is released to the receiving water system, the effects of MEA degradation products could cause toxicity in plants, increased pulmonary inflammation, acute toxicity to vertebrate aquatic organisms that may lead to convulsions, coma, and death (Badr et al., 2017; Liuzinas et al., 2007; Poste et al., 2014; Randall & Tsui, 2002). Furthermore, the excess nitrogen concentration in the water will increase biological productivity, resulting in low dissolved oxygen, acidification, and eutrophication (Constable et al., 2003). Humans are also at risk as the presence of amines and amine derivatives in the environment could contaminate drinking water, posing health concerns, including cancer (Karl et al., 2011; Nawrocki & Andrzejewski, 2011; Zhang et al., 2014). The Canadian government effluent quality standards enforce a wastewater regulation with a maximum ammonia level of 1.25 mg L\(^{-1}\) (Canadian Water Network, 2018; Government of Canada, 2016).

2.4.3.2 Sulfates

Another major contaminant found in the CCS wastewater from coal-fired power plants is sulfate. Sulfite could be readily oxidized to sulfate in the presence of oxygen. Sulfates could interact with other compounds present in the wastewater that will cause pipe scaling, resulting in pipe clogging and corrosion (Amjad, 1988; McNeill & Edwards, 2001; Yang et al., 2014). Clogging and corrosion would decrease the efficiency of the carbon capture as the flow of solvents, water, and wastewater would be progressively inhibited in different areas of the process. Once released in the environment, an elevated
level of sulfate consumption can cause osmoregulatory stress in freshwater species (Soucek & Kennedy, 2005) and other health impacts, such as diarrhea, dehydration, catharsis, and changes in methaemoglobin and sulfhemoglobin levels in both humans and animals (Cochetto & Levy, 1981; Morris & Levy, 1983; Runtti et al., 2018).

Sulfate is naturally occurring in the environment, sulfate levels in Canadian lakes range from 3 to 30 mg L\(^{-1}\), while sulfate level in rivers ranges from 1 to 3040 mg L\(^{-1}\), with the average of 580 mg L\(^{-1}\). The objective for sulfate level in drinking water is \(\leq 500\) mg L\(^{-1}\) (Government of Canada, 1994). In other countries, the discharge limit of sulfate ranges from 250 to 4000 mg L\(^{-1}\) (Runtti et al., 2018).

### 2.4.4 Review on technologies for amine and sulfate removal

The following sections will review the current technologies that are used in the lab and commercial scale to remove the major contaminants found in the CCS wastewater. These technologies are divided into two categories: physicochemical and biological processes.

#### 2.4.4.1 Physicochemical treatment processes

Simultaneous removal of the contaminants of concern is the preferred type of treatment for the CCS wastewater to be more cost-effective. However, literature does not exemplify a lot of research or practices regarding a simultaneous physicochemical removal of amines and sulfates. It is to be noted that using most physicochemical treatment results in two streams – permeate and retentate. The permeate is the treated water free of contaminants, while the retentate is the concentrated waste stream left after
treatment. Thus, physicochemical wastewater treatment can be regarded as a separation technique rather than a treatment process. The following are physicochemical technology used in the industry to remove amines and sulfates independently.

2.4.4.1.1 Amine removal

2.4.4.1.1.1 Air stripping

Air stripping has been widely used in the industry for the recovery of ammonia. It is a technique that uses a simple desorption process to treat wastewater streams (Adam et al., 2019). The process occurs in the stripping tower, where ammonia reacts with water to form ammonium hydroxide. The temperature and pH of the wastewater are adjusted to convert ammonium hydroxide to free ammonia gas. The ammonia gas is then stripped from the falling water droplets and is discharged into the atmosphere (Adam et al., 2019; Eskicioglu et al., 2018).

There are three approaches in which air stripping is used: acid stripping, steam stripping, and thermal stripping. Acid stripping is the combination of air stripping and absorption that can be used to remove and recover ammonia. A full-scale acid stripping process is in operation in Oslo since 1996, with approximately 88% ammonia removal. Steam stripping is a process where ammonia is stripped through the use of high-temperature carrier liquid or air steam. Bench- and pilot-scale research and study of ammonia steam stripping has been done by New York City, which yielded a 90% removal. The final approach to air stripping is thermal stripping, which is usually used in conjunction with acid adsorption. This process uses a heated solution to distill the ammonia, which is then
scrubbed by sulfuric acid and ammonium sulfate to form ammonium sulfate crystals (Eskicioglu et al., 2018).

Some advantages of the air stripping process are the use of simple equipment, insensitivity to toxic substances, and is a common approach to wastewater pre-treatment. However, there are still some drawbacks due to large reactor volume, high time and energy consumption, fouling and scaling, and high operational costs (Adam et al., 2019; Jiao et al., 2017).

### 2.4.4.1.2 Ozonation

Ozonation is a common process that uses ozone ($O_3$) to treat water and wastewater from contaminants (Mansas et al., 2020). Ozone is an unstable triatomic molecule gas that is characterized by a penetrating odour and is partially soluble in water (Khan et al., 2020). It is a powerful oxidizing agent that is very reactive to compounds incorporating conjugated double bonds. It can be used for the degradation of organic pollutants in water, such as amines and aldehydes (Agustina et al., 2005; Shah et al., 2013). According to Shah et al. (2013), ozone achieved 90% amine removal in washwaters. There are two pathways in which ozone oxidizes organics: direct oxidation and indirect oxidation. Direct oxidation is a low-rate and selective reaction that targets specific organics to react. In contrast, the indirect oxidation is processed by OH radicals, which are generated from the decomposition of $O_3$ (Jiao et al., 2017; Wang & Chen, 2020).
Ozonation has several disadvantages, such as low efficiency of ozone utilization and low efficiency of mineralization for organic pollutants. The disadvantages are managed by coupling ozonation with other techniques, thus resulting in advanced oxidation processes. Some of these processes are OH/O, O/HO, UV/O, and UV/biological processes (Jiao, 2017; Wang & Chen, 2020).

2.4.4.1.3 Membrane filtration

The application of membrane technology in wastewater treatment has been reported since the 1970s (Abasi et al., 2010). Membrane technology has become the modern choice of separation due to its ability to minimize additional costs and lack of disposal issues relative to other technologies. The membrane filtration process is a physical separation technique that uses a semi-permeable membrane that effectively rejects solids and dissolved components in the water or wastewater. Typically, one membrane process is followed by another to produce water of increasing purity and quantity for various purposes (Borhan & Johari, 2014). The membrane filtration process can be divided according to its pore size: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) (Hube et al., 2020; Karri et al., 2018). A summary of the constituents removed by each process is provided in Table 3.
Table 3. Type and application of various membrane processes (Metcalf & Eddy Inc., 2014).

<table>
<thead>
<tr>
<th>Membrane Process</th>
<th>Typical Operating Range (µm)</th>
<th>Constituents Removed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microfiltration</td>
<td>0.07 - 2.0</td>
<td>Suspended solids, protozoan oocysts and cysts, some bacteria, and viruses</td>
</tr>
<tr>
<td>Ultrafiltration</td>
<td>0.008 - 0.2</td>
<td>Macromolecules, colloids, most bacteria, some viruses, and proteins</td>
</tr>
<tr>
<td>Nanofiltration</td>
<td>0.0009 - 0.01</td>
<td>Small molecules, viruses, and some hardness</td>
</tr>
<tr>
<td>Reverse Osmosis</td>
<td>0.0001 - 0.002</td>
<td>Very small molecules, colour, hardness, sulfates, nitrates, sodium, and other ions</td>
</tr>
</tbody>
</table>
Besides the conventional membrane filtration, other advanced membrane filtration systems are widely used and studied in literature. Such advanced membrane systems are forward osmosis, membrane distillation, microporous hollow fiber membrane contactor, and electrodialysis (Ansari et al., 2017; Eskicioglu et al., 2018). Membrane filtration is one of the most used treatment technologies because of its selectivity, efficiency, compactness, and wide range of availability and applications (Adam et al., 2019). One major drawback of this treatment system is membrane fouling, especially when coupled with biological processes. Fouling would require high investment in membrane replacement costs (Hube et al., 2020; Mook et al., 2012; Yenkie, 2019).

### 2.4.4.1.2 Sulfate removal

#### 2.4.4.1.2.1 Precipitation

A popular method for removing sulfate on an industrial scale is precipitation due to its cost and simplicity (Fernando et al., 2018). The process of precipitation includes neutralization, heavy metal removal, coagulation, and clarification (Yan et al., 2019). Several precipitation methods are found in literature, such as lime, ettringite, jarosite, and barite. Of all these methods, lime precipitation is most well-known (Nariyan et al., 2018; Runtti et al., 2018).

Lime precipitation is the addition of lime in wastewater to raise the pH to 9.5. With the lime addition, a reaction between lime and aqueous sulfate form gypsum, which can be used as an alternative calcium source (Runtti et al., 2018). This method is dependent on the pH level and the low solubility of metal hydroxides in the wastewater (Fernando et
Some of the advantages of this method are: cost, metal precipitates as hydroxides, and insensitivity to temperature changes. The drawbacks of this process are: large volume of sludge formation, high maintenance, high saturation of gypsum in solution, scaling of equipment and pipelines, and can only decrease sulfate concentration by $1200 - 1800 \text{ mg L}^{-1}$ (Fernando et al., 2018; Nariyan et al., 2018; Runtti et al., 2018).

### 2.4.4.1.2.2 Adsorption

Adsorption is generally preferred in sulfate removal due to its rapid and high selectivity and cost-effectiveness (Cao et al., 2011). The mechanism of sulfate adsorption in wastewater starts with the formation of an oxi-hydroxide layer on the surface of adsorbents that changes the surface charge from negative to positive. The change in surface charge allows the sulfate to bind with the adsorbent and form stable complexes (Runtti et al., 2016). The efficiency of the treatment is affected by pH, temperature, concentration, flow rate, the dose of adsorbent, and ionic strength. However, one factor that affects the technical and economic feasibility of adsorption in industrial applications is adsorbent capacity. Currently, there are many studies regarding the efficiency of various adsorbents; among these are the activated carbon, fly ash, modified geopolymers, modified rice straw, soil, iron sand, and pulp and paper wastes (Runtti et al., 2018).

Other advantages of the adsorption process are the usefulness of waste, high removal efficiency, the novelty of approach, cost, and regeneration. The major drawback of this technology is its immaturity in research, development, and application, as it is still a growing area of research (Fernando et al., 2018).
2.4.4.1.2.3  Ion exchange

Ion exchange is one of the most effective and economical technology in removing contaminants in wastewater (De Los Santos et al., 2015). In the ion exchange process, equivalent counter ions on the exchanger resin surface displace the impurity ions found in the wastewater (Runtti et al., 2018). An ion exchange treatment plant is composed of resin loading, regeneration, and loading (Fernando et al., 2018). The sulfate can be removed using an anionic resin (R-OH) that is represented in Equation 1, where R is the ion exchange radical, $k_1$ is the forward reaction rate, and $k_2$ is the backward reaction rate constant (Haghsheno et al., 2009).

\[ 2R - \text{OH} + \text{SO}_4^{2-} \xrightleftharpoons[k_1,k_2]{k_1,k_2} R_2\text{SO}_4 + 2\text{OH}^- \]  

(1)

There are four major rate-limiting steps in the removal of contaminants using this process: (1) mass transfer of solute to boundary film, (2) mass transfer of ions from boundary film, (3) sorption reaction, and (4) internal diffusion (Haghsheno et al., 2009). The advantages of using this technology are its reversible process, high removal efficiency, fast kinetics, and the ability to treat residual sulfate. On the other hand, the disadvantages are its limited capacity, necessary resin regeneration, and cost of resin (Fernando et al., 2018).

2.4.4.2  Biological treatment processes

As compared to the physicochemical treatment of amines and sulfate, a wide scope of research, development, and application is being done with regards to biological
wastewater treatment. Furthermore, studies about the simultaneous biological removal of amines and sulfates are available. The biological wastewater treatment process converts organics and contaminants to carbon dioxide, water, and bacterial cells (Liu, 2003). The process is dependent on various microorganisms to remove contaminants of concern. Because of this, all biological treatment processes share similar attributes. Unlike the physicochemical treatment, biological treatment does not produce a retentate stream because the microorganisms assimilate the contaminants. Due to the extensive number of conventional, advanced, and novel treatments, the following sections will only discuss three biological treatment systems: conventional activated sludge (CAS), SBR, and SANI.

2.4.4.2.1 CAS

The CAS process is a widely used treatment system to remove organic matter and nutrients in municipal and industrial wastewater (Guo et al., 2013; Ren, 2004). This process was first developed around 1913 by Clark and Gage, and by Ardern and Lockett in 1914 (Metcalf & Eddy Inc., 2014). Currently, it is the main biological process in wastewater treatment plants. The system is mainly composed of two tanks: an aeration tank and a clarifier. The conversion of organic matter, ammonia, and other nutrients to biomass, carbon dioxide, and nitrogen gas through the use of aerobic microorganisms happen in the aeration tank. These microorganisms form floculent particles that are then separated using a clarifier through settling. The settled biomass, called the activated sludge, is either wasted or returned to the process (Ansari et al., 2017; Hreiz et al., 2015;
The typical CAS process is presented in Figure 2.

Since the activated sludge process became the core process in biological treatment, there exist many different types. Some of the processes are: completely mixed, contact stabilization, extended aeration, high purity oxygen, membrane bioreactor, selector, and step feed. Although a wide variety of activated sludge processes are available, there are four factors that are common to all these processes: (1) mixed liquor suspended solids (MLSS) is used to remove the contaminants from the influent; (2) a separation of liquid and solid is done to produce a treated effluent; (3) the activated sludge is recycled back to the process; and (4) excess sludge are wasted (Grady Jr. et al., 2011).

Some of the advantages of the activated sludge process are its simplicity, cost, and the degradation of organic matter into gas, water, and other end products. Some of the drawbacks of this process are the maintenance of microbial activity, poor decolorization, sludge bulking and foaming, and sludge settling ability (Mesquita et al., 2013; Yenkie, 2019).
Figure 2. Schematic diagram of a typical activated sludge process.

Figure 3. Schematic diagram of (a) pre-anoxic and (b) post-anoxic denitrification.
In relation to this research, using the CAS process would not be able to treat amines and sulfates simultaneously. Therefore, a combination of different activated sludge tanks in sequence can be used. One of the widely used combinations is called enhanced nitrogen removal. The enhanced nitrogen removal is a two-step nitrification-denitrification process. Nitrification is a process where ammonia is oxidized to nitrate and then to nitrite, with the help of ammonia-oxidizing bacteria (AOB) under aerobic conditions. Denitrification is the reduction process of nitrite to nitrogen gas, with the help of the nitrite-oxidizing bacteria (NOB) anoxic conditions (Hreiz et al., 2015). There are two common configurations of the enhanced nitrogen removal, the pre-anoxic denitrification and the post-anoxic denitrification shown in Figure 3.

A pre-anoxic denitrification configuration positions the anoxic tank before the aerobic tank. This configuration will then recirculate the nitrate feed from the aerobic tank to the anoxic tank for denitrification to occur. The NOB in the anoxic tank consumes the influent biochemical oxygen demand (BOD) and reduce the nitrate to nitrogen gas. In the post-anoxic denitrification, the ammonia is first oxidized to nitrate/nitrite by the AOB in the aerobic tank. The nitrate/nitrite is then subsequently reduced to nitrogen gas in the anoxic tank. Using the post-anoxic configuration may require exogenous carbon sources to achieve efficient denitrification (Hreiz et al., 2015; Metcalf & Eddy Inc., 2014). However, even with the use of enhanced nitrogen removal, sulfates are still present in the effluent wastewater. Removal of sulfates will entail the addition of another activated sludge process at the end of the treatment train, which will be further discussed in the next sections.
Figure 4. Schematic diagram of the SBR process.
2.4.4.2.2 SBR

A sequencing batch reactor technology is typically a treatment process accomplished over a series of time steps in a single bioreactor compared to a flow-through activated sludge system. This technology uses a single bioreactor as opposed to two or more and does not require a return activated sludge system (Metcalf & Eddy Inc., 2014). The SBR process consists of a series of treatment cycles that are implemented in a timed sequence. The process includes fill, react, settle, decant and idle (Figure 4). In the initial fill stage, wastewater fills the tank, where it is combined with the mixed liquor. The next step, called the react, is where the microorganisms remove the contaminants. Because SBR utilizes a single bioreactor, the aerobic and anaerobic stages are timed instead of the wastewater being transferred to a separate reactor. The timing of the aerobic and anaerobic phases can be achieved using an aerator. Once the reaction is done, the mixing and aeration are suspended to allow for solids to settle. Once the suspended solids have settled, the supernatant liquid is decanted out of the bioreactor. At the final stage of the SBR process, the bioreactor is left to idle in preparation for the reception of the influent wastewater from primary treatment.

There have been several studies on the removal of MEA in wastewater using SBR (Dong et al., 2019; Mannina et al., 2016; Suarez-Garcia et al., 2019). From the experiment conducted by Kim et al. (2010), MEA removal efficiency of 92% could be reached. Since the CCS wastewater contains both amine and sulfate, the microorganism dominant in the bioreactor should be able to degrade both contaminants. Therefore, this reactor would include four types of microorganisms: AOB, NOB, sulfate-reducing bacteria
(SRB), and sulfide-oxidizing bacteria (SOB) (Liu et al., 2012). These four types of microorganism will be able to degrade ammonia to nitrogen gas and sulfate to elemental sulfur by manipulating the conditions of the environment and creating two phases— aerobic and anaerobic—in the single bioreactor.

When the aerator is turned on, the process of nitrification and sulfide oxidation occurs. Nitrification is a two-step process, where ammonia is oxidized to nitrate and then to nitrite, with the help of AOB. During the aerobic phase, the SOB will also oxidize the sulfide to sulfur (Liu et al., 2012; Xu et al., 2013). When the aerator is turned off, the bioreactor will transition from an aerobic environment to an anaerobic environment. During the anaerobic phase, the process of denitrification and sulfate reduction occurs. Denitrification is the reduction process of nitrite to nitrogen gas, with the help of the NOB. Sulfate reduction is the biological conversion of sulfate to sulfide with the help of the SRB. Ultimately, the bioreactor would convert both ammonia and sulfate to nitrogen gas and sulfur (Liu et al., 2012; Xu et al., 2013). With the addition of oxygen as a factor, it should be noted that the timing of the aerator should always be accounted for.

The use of the four microorganisms to reduce both ammonia and sulfate has been utilized in pilot-scale research in the Netherlands (Liu et al., 2012). However, the wastewater was treated in separate tanks rather than combined in a single bioreactor. It was found that placing SRB and SOB in one bioreactor would cause low sulfur conversion (Xu et al., 2013). To further develop the feasibility of simultaneous ammonia and sulfate removal, researchers have studied simultaneous denitrification and
desulfurization (Cai et al., 2008; Liu et al., 2012; Show et al., 2013; Wang et al., 2005).

Wang et al. (2005) presented the reduction of nitrate and sulfide using a facultative anaerobe, *Thiobacillus denitrificans*, as shown below in Equations 2 and 3.

\[
\begin{align*}
12H^+ + 2NO_3^- + 5S^{2-} &\rightarrow N_2 + 5S + 6H_2O \tag{2} \\
5S + 6NO_3^- + 8H_2O &\rightarrow 5H_2SO_4 + 6OH^- + 3N_2 \tag{3}
\end{align*}
\]

For this to be effective, the second reaction should be inhibited to prevent the conversion of sulfur to sulfuric acid. The inhibition can be achieved by controlling the pH level and the S/N ratio (Wang et al., 2005). However, this would only solve part of the problem since nitrate is still required for denitrification to occur; thus, an aerobic phase should still be present. Using the SBR technology, AOB, SRB and *T. denitrificans* may be placed in a single bioreactor as operational phases will be able to provide both aerobic and anaerobic environments. During the aerobic period, nitrification occurs as AOB reduces ammonia to nitrate and nitrite. During the anaerobic phase, three reactions will occur: sulfate reduction, sulfide reduction, and denitrification. The SRB allows the reduction of sulfate to sulfide. With the presence of both sulfide and nitrite in the bioreactor, the *T. denitrificans* reduce the sulfide to sulfur using nitrite as an electron acceptor, which would, in return, reduce nitrite to nitrogen gas (Wang et al., 2005).
Figure 5. Schematic diagram of the integrated processes and cycles used in SANI.
2.4.4.2.3 SANI

According to Liu et al., (2012), sulfide-dependent denitrification could be adopted into a three-stage process rather than using the technology to remove ammonia and sulfate simultaneously in a single tank. This idea has been realized using the SANI process that originated from the treatment of saline wastewater found in Hong Kong sewage. The water supply shortage allowed Hong Kong to develop a technology that uses seawater for toilet flushing. Because of this, there is an abundance of saline sewage present in Hong Kong that is characterized by a high sulfate concentration (Lu et al., 2012; Winkler & Straka, 2019).

The process of SANI can be divided into three categories: sulfate reduction, autotrophic denitrification, and nitrification. Moreover, the method integrates three cycles—carbon, sulfur, and nitrogen cycles, into the technology for treatment (Figure 5).

As seen in Figure 5, three bioreactors are necessary for the SANI process. The first bioreactor would be an anaerobic environment that involves SRB to reduce sulfate to sulfide. Furthermore, carbon will be oxidized to carbon dioxide. The first bioreactor is usually a sulfate-reducing upflow sludge bed (SRUSB) (Hao et al., 2015). This bioreactor will not contain SRB but rather Lactococcus species (Jiang et al., 2013). The second tank would be an anoxic bioreactor that would include SOB. In this bioreactor, the process of autotrophic denitrification occurs, where nitrate is reduced to nitrogen gas and sulfide is converted back to sulfate (Yang et al., 2016; Wu et al., 2016). The final bioreactor is an aerobic tank that uses autotrophic nitrifiers to convert amines to nitrite.
and nitrate. A recycle flow from the final bioreactor is necessary to provide nitrite to the second bioreactor. Figure 6 shows the schematic diagram of a simple SANI process from the pilot plant studied by Lu et al. (2012).

However, using the SANI process does not entail sulfate treatment as it is being used only as an intermediate to treat amines (Wu et al., 2016). A modification in the arrangement of bioreactors could be made to ensure the theoretical feasibility of the SANI process. Instead of the initial SRUSB treatment, sulfate treatment could be placed after the aerobic bioreactor. This configuration would be able to treat amines in the first two bioreactors and treat sulfate at the last bioreactor. The first anoxic bioreactor would contain denitrifiers that will convert nitrite to nitrogen gas. The second bioreactor would be in an aerobic phase that will nitrify ammonia to nitrate and nitrite. A part of the effluent from the second bioreactor should be recycled to provide nitrate and nitrite to the first bioreactor. The other portion of the effluent from the second bioreactor will be sent to the third bioreactor, where sulfate reduction occurs. The sulfate will be reduced to sulfide and react with water to produce H₂S.
Figure 6. Schematic diagram of a SANI process from a pilot plant.
3 MATERIALS AND METHODS

All the apparatus, experimental set-ups, and procedures discussed in this section will apply to all chapters. Specific materials and methods relating to an experiment will be provided under its designated section.

3.1 Apparatus and experimental set-up

3.1.1 Sludge acquisition

Biological treatment system requires specific microbial ecology to function specifically for the required treatment. The activated sludge is necessary for both biological treatment systems utilized in the research project. Two types of domestic activated sludge from Regina Wastewater Treatment Plant (WWTP) were used: aerobic heterotrophic and anaerobic sludge.

The aerobic heterotrophic sludge came from the bioreactor aerobic and anoxic zones of the Regina WWTP. This sludge was primarily used for both aerobic and anoxic bioreactors as it contains AOBs and NOBs that helps in the nitrification and denitrification processes. According to studies, the microbial communities commonly found in a municipal WWTP that are capable of nitrification belong to the genera of *Nitrosomonas*, *Nitrospira*, and *Nitrosooccus*. Additionally, the microbes capable of denitrification in a municipal WWTP are in the genera of *Alcaligenes*, *Pseudomonas*, *Methylobacteria*, *Bacillus*, *Paracoccus*, and *Hyphomicrobium* (Ferrera & Sanchez, 2016; Wagner et al., 2002). With these microorganisms present in the sludge acquired, the process of converting ammonia to nitrogen gas will be achieved.
The anaerobic sludge came from the anaerobic biodigester of the Regina WWTP. This sludge was used for the possible reduction of sulfate to sulfur due to the presence of syntrophic propionate-oxidizing bacteria (SPOB) (Van Kuijk & Stams, 1995). The SPOBs mainly oxidize propionate; however, it is known that these bacteria perform sulfate reduction as well. As such, the anaerobic sludge from the Regina WWTP was utilized to perform treatment in the anaerobic bioreactor.

### 3.1.2 Preparation of synthetic CCS wastewater

The real CCS wastewater exhibits a wide range of characteristics. Therefore, the use of synthetic CCS wastewater would provide consistent influent characteristics during the experimental procedures under varying conditions. The preparation of synthetic wastewater was based on the characteristic of the wastewater obtained from a coal-fired carbon capture system. Since the wastewater from carbon capture contains impurities, only four main parameters have been considered: carbon, nitrogen, sulfate, and phosphorus. The average concentration of the carbon, nitrogen, sulfate, and phosphorus in the real wastewater are 700 mg L$^{-1}$, 150 mg L$^{-1}$, 13,000 mg L$^{-1}$, and 0 mg L$^{-1}$, respectively.

Alternative sources have been considered for the creation of synthetic wastewater. As for the carbon source, sucrose has been used mainly due to its low cost as compared to other carbon sources. Furthermore, Hamlin et al. (2008) show that most nitrite/nitrate has been removed after five days of laboratory trial using sucrose as a substrate. Greben et al.
(2000) also found out that sucrose is a suitable carbon source for microbes that perform sulfate reduction.

The influent inorganic nutrient feed for synthetic wastewater are MEA, magnesium sulfate (MgSO₄), and sodium phosphate (NaPO₄). The nitrogen source for the synthetic wastewater is MEA. Although different blends of amines are used in carbon capture, MEA is typically present in the common blends as it is widely studied and used in coal-fired power plants (Aaron & Tsouris, 2005; Aroonwilas & Veawab, 2004; Dutcher et al., 2015; Knudsen et al., 2009; Leung et al., 2014). Using MEA as a source of nitrogen would increase the similarity of the synthetic wastewater to the real CCS wastewater sample. Magnesium sulfate is the sulfate source of the synthetic wastewater. Magnesium sulfate readily dissociates into magnesium and sulfate when dissolved in water. The last inorganic nutrient is taken from the addition of sodium phosphate into the synthetic wastewater to obtain phosphorus. The addition of phosphorus would increase the viability of biological treatment. It is one of the primary nutrients needed for bacterial growth and a requirement to obtain the minimum COD:N:P ratio (Miettinen et al., 1997). Both magnesium sulfate and sodium phosphate are the compounds commonly used to create synthetic wastewater in literature (Ghosh & LaPara, 2004; Harper & Jenkins, 2005; Klatt & LaPara, 2003; Rezakazemi et al., 2018; Zitomer & Shrout, 2000).
Table 4. Composition and characteristics of the synthetic CCS wastewater.

<table>
<thead>
<tr>
<th>Wastewater Description</th>
<th>Composition</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Chemical</td>
<td>Molecular Formula</td>
</tr>
<tr>
<td><strong>Initial Synthetic Wastewater (per 1 L of Tap Water)</strong></td>
<td>Sucrose</td>
<td>C₁₂H₂₂O₁₁</td>
</tr>
<tr>
<td>COD:N:P = 155:5:1</td>
<td>MEA</td>
<td>C₇H₇NO</td>
</tr>
<tr>
<td></td>
<td>Magnesium sulfate</td>
<td>MgSO₄</td>
</tr>
<tr>
<td></td>
<td>Sodium phosphate</td>
<td>NaPO₄</td>
</tr>
<tr>
<td><strong>Modified Synthetic Wastewater (per 1 L of Tap Water)</strong></td>
<td>Sucrose</td>
<td>C₁₂H₂₂O₁₁</td>
</tr>
<tr>
<td>COD:N:P = 180:5:1</td>
<td>MEA</td>
<td>C₇H₇NO</td>
</tr>
<tr>
<td></td>
<td>Magnesium sulfate</td>
<td>MgSO₄</td>
</tr>
<tr>
<td></td>
<td>Sodium phosphate</td>
<td>NaPO₄</td>
</tr>
</tbody>
</table>
Most components of the synthetic wastewater, with the exemption of MEA, were considered due to their low cost. The composition and characteristics of the synthetic wastewater are provided in Table 4. The initial synthetic CCS wastewater is below the optimum COD:N:P ratio to mimic the real CCS wastewater. In contrast, the modified synthetic CCS wastewater composition results in the optimum COD:N:P ratio needed for bacterial growth, which will be discussed in the succeeding sections. Synthetic wastewater is prepared directly into the influent tank. Fresh synthetic wastewater solutions were prepared every week to prevent the biodegradation of the components. The pH level of the synthetic wastewater was maintained at a range of 7-8.

3.1.3 Equipment

Since the research is done using a bench-scale model, the equipment used in the experiments was downsized. Figure 7 shows the main equipment used throughout the study. A 2 L Nalgene wide-mouth high-density polyethylene (HDPE) bottle was used as the main body of the bioreactor. The specific bottle was utilized for translucency, ease of influent transfer, and temperature and acid resistance. It was situated atop of a heating/stirring plate to allow for temperature adjustment and mixing. The aerobic bioreactors were installed with an air stone attached to an aerator using plastic tubing. The anoxic and anaerobic bioreactors were installed with a one-way air valve to prohibit the entry of oxygen from the surroundings. In total, there were six bioreactors used for the completion of the experiment. One bioreactor for SBR, three for SANI, and additional two for the *Bacillus benzoevorans*. 
Figure 7. Equipment used in conducting the experiment: (a) 2 L HDPE bottle, (b) aerator, (c) heating/stirring plate, (d) tubing, (e) one-way air valve, and (f) air stone.
3.2 Methodology

3.2.1 Sludge acclimation

The bioreactors for both the SBR and SANI processes were seeded with activated sludge samples from the Regina WWTP. The SBR bioreactor and the SANI aerobic and anoxic bioreactors were all seeded with the aerobic heterotrophic sludge, while the SANI anaerobic bioreactor was seeded with the anaerobic sludge. These bioreactors were acclimated for 14 days using synthetic wastewater as the influent.

One important attribute that should be observed in the following biological treatment process is the minimum BOD:N:P ratio of 100:5:1 (Lewis et al., 2011; Sapari, 1996) for the acclimation of sludge. This ratio is critical because it is a requirement for biomass growth. Most biological treatment operating under the minimum BOD:N:P ratio will observe minimum contaminant removal. However, in this experiment, chemical oxygen demand (COD) is used in place of BOD. From the conducted experiment, the derived COD/BOD ratio is 1.7, which is supported by literature (Grady Jr. et al., 2011). Therefore, the minimum COD:N:P ratio is 170:5:1.

3.2.2 Data collection

The experiment can be divided into three parts: (1) use of initial synthetic wastewater, (2) use of the modified synthetic wastewater, and (3) addition of the *Bacillus benzoevorans*. For each experimental procedure at least five data points were collected. The tests were done for two to three weeks depending on the completion of the data...
collection. With the inclusion of the acclimation of the bioreactors for each procedure, the experimental phase lasted for at least four months.

3.2.3 MLSS/MLVSS analysis

The mixed liquor suspended solids (MLSS) concentration, and the mixed liquor volatile suspended solids (MLVSS) concentration were determined using the procedure found in the Standard Methods for the examination of Water and Wastewater (APHA, 2005). The analysis of this parameter is essential to ensure a sufficient amount of biomass is present in the bioreactor to consume the contaminants. The MLSS and MLVSS concentration analyses were performed using one Thermo Scientific 0V601G precision standard oven, one Thermo Scientific FD1535M furnace, and one Ohaus Pioneer PA114 Analytical Balance. The MLSS and MLVSS concentration were maintained to be in the range of approximately 2700 - 3000 mg L\(^{-1}\) and 1500 - 1700 mg L\(^{-1}\), respectively.

3.2.4 Wastewater quality analysis

For each bioreactor, six parameters were analyzed to determine the efficiency of the system: COD concentration, total nitrogen (TN) concentration, nitrate (NO\(_3\)) concentration, ammonia (NH\(_3\)) concentration, nitrite (NO\(_2\)) concentration, and sulfate (SO\(_4^{2-}\)) concentration. The wastewater quality analysis was performed using one Hach DR 2800 spectrophotometer and two Hach DRB 200 ovens. Hach test kits were extensively used for the analyses of COD (TNT 821LR), TN (TNT 826 LR and TNT 827 HR), NO\(_3\) (TNT 835 LR), NH\(_3\) (TNT 832 HR), NO\(_2\) (TNT 839 LR), and SO\(_4^{2-}\) (TNT 865 LR).
HR. The collection of each parameter is done for every bioreactor daily and were analyzed in duplicates to ensure the viability of the data.

3.2.5 Amine and sulfate removal analysis

Since amines dissociate to ammonium and acetaldehyde, the research project accounted for the concentration of amines using TN, total Kjeldahl nitrogen (TKN), and ammonia concentration. The total amine removal from the system is determined by subtracting the concentration of TN, TKN, or ammonia from the final phase or bioreactor to the initial phase or bioreactor. The concentration of TN and ammonia is determined using the procedure described in parameter analysis. The TKN was calculated using Equation 4.

\[
TKN = TN - (NO_2^- + NO_3^-)
\]

(4)

The total sulfate removal from the system is determined by subtracting the concentration of sulfate from the final phase or bioreactor to the initial phase or bioreactor. The concentration of sulfate in each bioreactor is determined using the procedure described in parameter analysis.

3.2.6 Bioreactor operation

All the bioreactors are operated in their optimum conditions in both processes, with the consideration of pH level, temperature, and oxygen levels. The optimization would enable the fair comparison between the two processes.
Table 5. SBR operation.

<table>
<thead>
<tr>
<th>Step</th>
<th>Time</th>
<th>Environment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fill</td>
<td>5 minutes</td>
<td>Aerobic</td>
</tr>
<tr>
<td>React</td>
<td>24 hours</td>
<td>Aerobic</td>
</tr>
<tr>
<td>Settle</td>
<td>24 hours</td>
<td>Anoxic</td>
</tr>
<tr>
<td>Decant</td>
<td>5 minutes</td>
<td>Anoxic</td>
</tr>
<tr>
<td>Idle</td>
<td>5 minutes</td>
<td>Anoxic</td>
</tr>
</tbody>
</table>
3.2.6.1 SBR

The SBR bioreactor was filled to 1.5 L of mixed liquor at a proportion of 1 L of activated sludge and 0.5 L of CCS wastewater. The remaining unfilled 0.5 L volume will allow for oxygen exchange. The temperature has been maintained to be in the range of 30 – 35 °C and the pH level at a range of 7 – 8 (Bioscience, Inc., 2014; Foglar et al., 2005; Moestedt et al., 2013; Sarti & Zaiat, 2011). The pH was adjusted by adding hydrochloric acid (HCl) or sodium bicarbonate (NaHCO₃) accordingly. A timed aerator was installed to operate and provide oxygen to the bioreactor every other day for at least 24 hours. The flow rate of the influent is 0.5 L every two days to allow for a 24 hours hydraulic retention time (HRT) for both the aerobic and anaerobic phases of the SBR. Table 5 provides the operation of the SBR used in the experiment.

3.2.6.2 SANI

The reactors under this process were operated in a batch flow mode. The aerobic bioreactor was filled to 1.5 L of mixed liquor at a proportion of 1 L of activated sludge and 0.5 L of CCS wastewater. The remaining unfilled 0.5 L volume will allow for oxygen exchange. An aerator was installed and operated for 24-hours to provide oxygen to the bioreactor every day. The anoxic and anaerobic bioreactors were filled to 2 L of mixed liquor at a proportion of 1 L of activated sludge and 1 L of CCS wastewater. Both bioreactors were installed with a one-way air valve to prohibit the entry of oxygen from the surroundings. The three bioreactors were set at a temperature that has been maintained to be in the range of 30 – 35 °C and a pH level at a range of 7 – 8 (Bioscience, Inc., 2014; Foglar et al., 2005; Moestedt et al., 2013; Sarti & Zaiat, 2011).
The pH level was adjusted by adding HCl or NaHCO₃ accordingly. The flow rate of the influent for each bioreactor is 0.5 L per day.
4 RESULTS AND DISCUSSION

4.1 Comparison of conventional biological treatment at high and low substrate concentration

4.1.1 Introduction

Two experiments have been designed and conducted for the research project. The initial experiment is the comparison of the efficiency of amine and sulfate removal of two biological treatment systems, the conventional SBR and the conventional SANI, with a distinct configuration, as discussed in the literature review section. This section of the research project will demonstrate the potential treatment of synthetic CCS wastewater using elementary SBR and SANI treatment trains. Furthermore, both high and low substrate concentration will be introduced to the systems to examine its effects.

4.1.2 Methodology

The sludge acclimation, analyses, and operation of the bioreactors used in this experiment have been described in the general methodology section. The diagram of both systems used in this experiment is seen in Figure 8. On the other hand, Figure 9 shows the actual system used in the experiment.
Figure 8. Schematic diagram of the conventional (a) SBR and (b) SANI processes.

Figure 9. (a) SBR and (b) SANI systems.
4.1.3 Results and discussion

The comparison between SBR and SANI removal efficiencies at low and high substrate concentration is shown in Figure 10 and the comparison of removal efficiencies between low and high substrate concentration in both processes is shown in Figure 11. The removal efficiencies of each parameter are discussed in detail in the following sections.

4.1.3.1 Organics removal

The removal of organic pollutants was measured using COD. The two processes exhibited equivalent removal of COD with 95% and 96% for SBR and SANI at low substrate concentration, respectively. Initially, the COD concentration of the real CCS wastewater composition is relatively low. The experiment added a substantial amount of COD using sucrose to achieve a COD:N:P ratio of 180:5:1 for bacterial metabolic process. Despite the exogenous addition of COD to obtain a higher substrate concentration, both SBR and SANI were still capable of removing a significant amount of COD from the influent at 95% and 97% removal. In literature, several researchers have also reported a COD removal ranging from 85 – 99% using SBR (Chen et al., 2015; Maranon et al., 2008; Moussavi et al., 2010; Val del Rio et al., 2012), and 80 – 97% using SANI (Jiang et al., 2013; Lu et al., 2009; Qian et al., 2015). The literature is in agreement with the current findings of the experiment. The average COD residuals were 112 ± 22 mg COD L\(^{-1}\) and 101 ± 41 mg COD L\(^{-1}\) for low substrate concentration in SBR and SANI. The average COD residuals for high substrate concentration were 75 ± 8 mg COD L\(^{-1}\) and 50 ± 5 mg COD L\(^{-1}\) in SBR and SANI.
Figure 10. Comparison between SBR and SANI at (a) low substrate concentration and (b) high substrate concentration.

Figure 11. Comparison between low and high substrate concentration in (a) SBR and (b) SANI.
4.1.3.2 Amine removal

The removal of amines was measured in terms of TN, TKN, and ammonia since MEA readily dissociates to acetaldehyde and ammonium (Ndewga et al., 2004). The average removal efficiency of TN, TKN, and ammonia is 62%, 88%, and 98% for SBR and 38%, 47%, and 89% for SANI at low substrate concentration. Using a low substrate concentration, SBR is more efficient in removing amines as opposed to SANI. The substrate concentration was increased, and the average removal efficiency of TN, TKN, and ammonia resulted in 88%, 88%, > 99% for the SBR, and 79%, 85%, and > 99% for the SANI. There was no significant difference in the removal of TKN and ammonia between the two systems. However, a significant difference (p < 0.05) in TN removal was found, where SBR is capable of removing more TN compared to SANI.

The difference in amine removal efficiencies between the two systems is more apparent at lower substrate concentration. At low substrate concentration, TN, TKN, and ammonia removal were 24%, 41%, and 9%, higher than SANI. The number of bioreactors for the SANI system may have affected the substrate present for each bioreactor, decreasing the viability of microbes to perform amine removal. Since SBR only has one bioreactor, the substrate concentration of the bioreactor remained relatively high as only a particular microbial population utilizes the substrate. The SANI system has a series of three bioreactors that have a decreasing substrate concentration. Thus, the final bioreactor in the SANI system would have the least substrate concentration, providing a low amount of substrate for the microbes in the bioreactor.
A significant difference was observed in terms of TN and TKN removal with increasing COD/N ratio, which was also found by other researchers (Huang et al., 2019; Pelaz et al., 2018). The COD/N ratio of the influent was 34.8 and 38.6 at low and high substrate concentration. In SBR, a high COD/N ratio increased the removal of TN by 26% from a low COD/N ratio, while TKN and ammonia removal remained relatively equivalent. An increase in TN removal without the change of TKN and ammonia removal indicates an increase in denitrification rate, where more nitrate is reduced to nitrogen gas. The average residual concentration of ammonia, nitrite, and nitrate are 0.12 ± 0.07 mg NH$_3$-N L$^{-1}$, 8.8 ± 0.8 mg NO$_2$-N L$^{-1}$, and 4.7 ± 0.8 mg NO$_3$-N L$^{-1}$ at low substrate concentration, and 0.012 ± 0.004 mg NH$_3$-N L$^{-1}$, 0.009 mg NO$_2$-N L$^{-1}$, and 0.17 ± 0.03 mg NO$_3$-N L$^{-1}$ at high substrate concentration.

In SANI, a high COD/N ratio increased the total amine removal by increasing TN, TKN, and ammonia removal. From a low COD/N ratio, the TN, TKN, and ammonia removal increased by 41%, 38%, and 10%. The increase of amine removal could be shown by the increased nitrification and denitrification rates, where ammonia is reduced to nitrate/nitrite and nitrate to nitrogen gas. The average residual concentration of ammonia, nitrite, and nitrate are 12.7 ± 3 mg NH$_3$-N L$^{-1}$, 0.04 ± 0.02 mg NO$_2$-N L$^{-1}$, and 6.4 ± 1.4 mg NO$_3$-N L$^{-1}$ at low substrate concentration, and 0.032 ± 0.02 mg NH$_3$-N L$^{-1}$, 0.13 ± 0.05 mg NO$_2$-N L$^{-1}$, and 3.6 ± 1.4 mg NO$_3$-N L$^{-1}$ at high substrate concentration.
The average TN residuals for SBR and SANI were 25.0 ± 7.4 mg N L\(^{-1}\) and 35.6 ± 6.3 mg N L\(^{-1}\) at low substrate concentration, and 5.1 ± 1.2 mg N L\(^{-1}\) and 7.7 ± 0.7 mg N L\(^{-1}\) at high substrate concentration.

### 4.1.3.3 Sulfate removal

The removal of sulfates was directly measured by the amount of sulfate concentration present in the effluent. There is little removal of sulfates observed in both processes as they only exhibited 11% and 18% removal for SBR and SANI at low substrate concentration and 10% and 16% at high substrate concentration. An increase of substrate concentration does not significantly affect the removal of sulfates in both systems.

Sulfate removal in SBR was not likely because SBR undergoes an aerobic phase, which is detrimental to SRB that is anaerobic (Wang et al., 2009; Wu et al., 2016; Xu et al., 2013). However, the low sulfate reduction in SANI was unexpected as it has a final bioreactor operating in an anaerobic condition, seeded with anaerobic sludge to perform heterotrophic sulfate reduction. Although SANI uses sulfate reduction and sulfur oxidation (Wu, et al., 2016) as an electron intermediary, a higher sulfate removal efficiency should still be expected in SANI, unless the influent entering the anaerobic bioreactor does not contain enough organic carbon to donate electrons from sulfate or insufficient nitrate that accepts electrons to sulfur. Another probable consideration of the low sulfate removal in SANI is the absence of any SRBs in the anaerobic sludge.
The average sulfate residuals for SBR and SANI were $8443 \pm 900 \text{ mg SO}_4^{2-} \text{ L}^{-1}$ and $7679 \pm 750 \text{ mg SO}_4^{2-} \text{ L}^{-1}$ at low substrate concentration, and $7858 \pm 328 \text{ mg SO}_4^{2-} \text{ L}^{-1}$ and $7714 \pm 880 \text{ mg SO}_4^{2-} \text{ L}^{-1}$ at high substrate concentration.

### 4.1.4 Conclusions

This research is set out to examine the efficiency of SBR and SANI in treating synthetics CCS wastewater, including the effects of increasing substrate concentration done in the lab. From these experiments, the following conclusions were found:

1. Both SBR and SANI can remove > 90% of organic nutrients and almost > 40% of amines present in the synthetic CCS wastewater at low substrate concentration. It is evident that at low substrate concentration, SBR is more effective as it could remove 24% more TN, 41% more TKN, and 9% more ammonia compared to SANI. The SBR is capable of removing more amines due to a high TN removal at low substrate concentration.

2. Both SBR and SANI can remove > 90% of organic nutrients and almost > 80% of amines present in the synthetic CSS wastewater at high substrate concentration. A significant difference between the two systems can be seen in the TN removal, as SBR can remove 9% more than SANI. The SBR is capable of removing more inorganic nitrogen at high substrate concentration.
3. Both SBR and SANI can only remove < 20% of sulfates in low or high substrate concentration. However, SANI showed a promising result in sulfate removal in both low and high substrate concentration as compared to SBR.

These findings suggest that SBR and SANI process systems can effectively treat wastewater that is high in organic nutrients and amines. However, the systems require improvement to treat highly contaminated synthetic CCS wastewater with low organic nutrients, high amines, and high sulfate concentration.

4.2 Comparison of conventional and modified treatment

4.2.1 Introduction

The study of simultaneous removal of amines and sulfates using SBR is limited in literature. However, several SBR improvements could be made, such as the addition of upflow anaerobic sludge blanket (UASB) (Li et al., 2011) bioreactor or the use of anaerobic ammonium oxidation (ANAMMOX)-dependent microorganism. ANAMMOX is an anaerobic biochemical reaction that uses ammonium and nitrite as electron donor and acceptor to produce nitrogen (Cai et al., 2010). Two ANAMMOX processes could be considered in the simultaneous removal of amines and sulfate: sulfate-dependent ANAMMOX and sulfide-dependent ANAMMOX. Sulfate-dependent ANAMMOX is an autotrophic process that uses sulfate and organics as the electron acceptors. Some microbial strains that are capable of such a process are the *Bacillus benzoivorans* and the *Plantomycete anammoxoglobus*. On the other hand, sulfide-dependent ANAMMOX uses nitrate and nitrite as electron acceptors to oxidize sulfide and produce energy. Since the
CCS wastewater is rich in sulfate as opposed to sulfide, the system should accommodate for the reduction of sulfate to sulfide, if sulfide-dependent ANAMMOX is to be considered. Some microbial strains that are capable of such a process are the *Thiobacillus denitrificans* and the *Bacillus pseudofirmus* (Liu et al., 2012).

This research will focus on the use of SBR with the integration of the sulfate-dependent ANAMMOX process using *B. benzoevorans* to treat amines and sulfates simultaneously. The biochemical reaction of the sulfate-dependent ANAMMOX process that will be applied in the experiments is shown in Equation 5.

\[
SO_4^{2-} + 2NH_4^+ \rightarrow S + N_2 + 4H_2O
\]  

This section will focus on the effects of an additional bioreactor on the SBR process. Thus, a comparison between conventional SBR and the modified SBR will be done. Because of the presence of the sulfate-dependent ANAMMOX bacteria, an increase in sulfate removal efficiency should be observed. The substrate concentration between the two systems will remain constant.
Figure 12. Schematic diagram of the modified (a) SBR and (b) SANI processes.
4.2.2 Methodology

An additional bioreactor containing *B. benzoivorans* was introduced at the end of the conventional SBR treatment process. The *B. benzoivorans* was ordered at Cedarlane lab in a 0.4 mL freeze-dried format with a strain designation of B3 [CCM 3366] (ATCC 49006). The bacteria were cultured using the ATCC Broth Medium #3 (ATCC, 2019) for 14 days at a temperature of 30 °C. The additional bioreactor was filled with 1.5 L of synthetic CCS wastewater and inoculated with 0.5 L of the combined broth and bacillus culture. Additional 14 days were required for the acclimation of the bacillus to the synthetic CCS wastewater. A one-way air valve was installed to prohibit the entry of oxygen from the surroundings. The bioreactor was set at a temperature that has been maintained to be in the range of 30 – 35 °C and a pH level at a range of 8 – 8.5 (Liu et al., 2012), which is adjusted by adding HCl or NaHCO₃ accordingly. The flow rate of the influent for the bioreactor is 0.5 L per day. Similar wastewater quality analyses were conduct to observe the treatment of amine and sulfate. The diagram of the systems used in this experiment is seen in Figure 12.
4.2.3 Results and discussion

The removal efficiencies of each conventional and modified SBR process are shown in Figure 13. The removal efficiencies of each parameter are discussed in detail in the following sections.

4.2.3.1 Organics removal

The removal of organic pollutants was measured using COD. The two systems exhibited equivalent removal of COD with 95% and 96% for conventional and modified SBR (cSBR, mSBR), respectively. The average COD residuals were 75 ± 9 mg COD L⁻¹ for cSBR and 56 ± 14 mg COD L⁻¹ for mSBR, which have no significant difference (p = 0.066 at α = 0.05). The addition of another bioreactor containing B. benzoevorans did not significantly affect the COD removal efficiencies of the treatment process as it only increased the average removal efficiency by 1%. Several researchers reported a COD removal ranging from 85 – 99% using SBR (Chen et al., 2015; Maranon et al., 2008; Moussavi et al., 2010; Val del Rio et al., 2012) which is in agreement with the current findings.
Figure 13. Parameter analyses and comparison in conventional and modified SBR.
4.2.3.2 Amine removal

The removal of amines was measured in terms of TN, TKN, and ammonia since MEA easily dissociates to acetaldehyde and ammonium (Ndegwa et al., 2004). The average removal efficiency of TN, TKN, and ammonia is 88%, 87%, and > 99% for cSBR. The addition of another bioreactor for the mSBR did not affect the TN, TKN, and ammonia removal efficiency (89%, 88%, and > 99%). A high TN, TKN, and ammonia removal indicate that nitrification and denitrification occur, where ammonia is oxidized to nitrite/nitrate, and nitrate is reduced to nitrogen gas. The average ammonia, nitrite, and nitrate residuals were 0.012 ± 0.004 mg NH₃-N L⁻¹, 0.009 ± 0.001 mg NO₂-N L⁻¹, and 0.17 ± 0.03 mg NO₃-N L⁻¹ for cSBR, and 0.048 ± 0.012 mg NH₃-N L⁻¹, 0.03 ± 0.04 NO₂-N L⁻¹, and 0.18 ± 0.13 mg NO₃-N L⁻¹ for mSBR. The residuals indicate that most amines have been reduced to nitrate due to the higher nitrate concentration in comparison with the ammonia and nitrite. However, since the TN removal is at 88% and 89%, most of the nitrate present in the influent has been reduced to nitrogen gas. The average TN residuals were 5.1 ± 1.2 mg N L⁻¹ for cSBR and 6.2 ± 0.6 mg N L⁻¹ for mSBR. The residuals of TN, nitrate, and nitrite between both systems do not show significant differences at p < 0.05. However, even at low residual concentrations, there is a significant difference (p = 0.002 at α = 0.05) in ammonia residuals, where the cSBR shows better results compared to mSBR.
Figure 14. Parameter analyses and comparison in conventional and modified SANI.
4.2.3.3 Sulfate removal

The removal of sulfates was directly measured by the amount of sulfate concentration present in the effluent. There is no significant removal of sulfates in cSBR, as it only exhibited 9% removal. Sulfate removal in cSBR was not likely because cSBR undergoes an aerobic phase, which is detrimental to SRB that is anaerobic (Wang et al., 2009; Wu et al., 2016; Xu et al., 2013). The addition of another bioreactor at the end of the treatment process significantly increased the sulfate removal efficiency of the system to 39%. The increase could be attributed to the presence of *B. benzoevorans* in the bioreactor, which is capable of sulfate-dependent ANAMMOX process. The bacteria can reduce sulfate to sulfur. The slight increase of the TN and TKN removal of the modified SBR could also be attributed to the additional bioreactor as *B. benzoevorans* can convert ammonia to nitrogen gas.

The same bioreactor was added to a SANI lab-scale system under the same operating conditions, which resulted in 25% sulfate removal; this supports the claim of sulfate removal by the addition of *B. benzoevorans*. Figure 14 shows the removal efficiencies of conventional and modified SANI (cSANI, mSANI). An almost equivalent removal efficiencies can be observed in both COD and TN of cSANI and mSANI. However, the addition of *B. benzoevorans* in the mSANI caused a 9% increase in TKN removal and 15% increase in sulfate removal. The findings in this experiment is in agreement with the results seen in the mSBR.
A < 50% of sulfate removal efficiency may be attributed to the pure cultured bacteria inoculated in the additional bioreactor that is not part of a microbial community. An extended acclimation period of the B. benzoevorans to the synthetic CCS wastewater may be required to observed increased sulfate removal efficiency (Cai et al., 2010).

The average sulfate residuals were 7858 ± 328 mg SO$_4^{2-}$ L$^{-1}$ and 7714 ± 880 mg SO$_4^{2-}$ L$^{-1}$ for conventional SBR and SANI, while the average sulfate residuals for modified SBR and SANI were 4500 ± 736 mg SO$_4^{2-}$ L$^{-1}$ and 4871 ± 1774 mg SO$_4^{2-}$ L$^{-1}$.

### 4.2.4 Conclusions

This research is set out to examine the efficiency of conventional and modified SBR in treating synthetic CCS wastewater. The modified SBR includes an additional bioreactor containing B. benzoevorans. Furthermore, to support the results, the same experiment was done using the SANI process. From these experiments, the following conclusions were found:

1. Conventional and modified SBR can remove > 90% of organic nutrients and almost > 80% of amines present in the synthetic CCS wastewater. The SBR modification did not affect the removal of organics pollutants and inorganic nitrogen.

2. The addition of a bioreactor containing B. benzoevorans could significantly increase sulfate removal efficiency to an average of 39% in mSBR. The same pattern is noticed in
the modification of SANI through the addition of a bioreactor containing *B. benzoevorans*. The mSANI exhibited a 15% increase in sulfate removal efficiency.

These findings suggest that the addition of a bioreactor containing *B. benzoevorans* in any system could effectively treat a highly contaminated synthetic CCS wastewater. The improvement in the systems is attributed to the sulfate-dependent ANAMMOX ability of the bacteria.

### 4.3 Limitations of the research

Although the research provided a possible way of removing the contaminants present in the CCS wastewater, there are still limitations of the research that should be taken into consideration.

1. The real CCS wastewater exhibits a low concentration of carbon that is insufficient for biological treatment. Therefore, this research added exogenous substrate in the form of sucrose to meet the optimum COD:N:P ratio for the biological treatment.

2. The research used a bench-scale SBR. To be implemented in the industry, a minimum of two SBR reactors need to be operated simultaneously, but at different stages, to maintain a continuous wastewater flow rate.
The study identified two major contaminants present in the CCS wastewater – amines and sulfate, which could affect both environmental and human health. The main objective of this study is to design and develop an effective biological system to treat CCS wastewater to a quality that can be recycled back to the process economically. Furthermore, it focused on the goals of investigating and comparing two conventional biological treatment systems and modifications done throughout the study: Sequencing batch reactor and the Sulfate reduction, autotrophic denitrification, and nitrification integrated system.

Using the conventional treatment of SBR and SANI, it was observed that SBR is more effective in removing organic and amine pollutants in both low and high substrate concentration compared to SANI. The removal efficiency of COD, TN, TKN, and ammonia in SBR are 95%, 62%, 88%, and 98%, in low substrate concentration; and 95%, 88%, 88%, and > 99%, in high substrate concentration. However, SANI showed greater sulfate removal compared to SBR in both low and high substrate concentration at 18% and 16%. The modification of the biological systems was the addition of another bioreactor containing sulfate-dependent anaerobic ammonium oxidation-capable bacterium – *Bacillus benzoevorans*. With this modification, both the SBR and SANI exhibited higher sulfate removal efficiency at 39% and 25%, respectively.
It could be observed that the ammonia and sulfate residuals in modified SBR are at 0.048 ± 0.012 mg NH$_3$-N L$^{-1}$ and 4500 ± 736 mg SO$_4^{2-}$ L$^{-1}$. These residuals were compared to the discharge limit and guidelines. The ammonia residual is below the maximum ammonia level required of 1.25 mg L$^{-1}$; however, sulfate residual is above the maximum sulfate limit of 4000 mg L$^{-1}$. Therefore, improvements in these systems are still required in order to treat and reclaim CCS wastewater effectively.
The conventional and modified SBR and SANI has been tested using synthetic CCS wastewater, in which both systems show promising results. Besides SBR and SANI, other biological treatment systems are available for testing the synthetic wastewater. The contaminant removal efficiency of these treatment systems can be compared to SBR and SANI to choose the most cost-effective system.

Furthermore, other microbial strains capable of nitrification, denitrification, and sulfate reduction should be studied. Since ANAMMOX process was used in the research, other microbial strains capable of the process can also be used in place or on top of *Bacillus benzoevorans*. 

ATCC. (2019). *ATCC Medium: 3 nutrient agar/broth*. Retrieved from ATCC credible leads to incredible:
https://www.atcc.org/~/media/E6FA2163B72E4DCD880719A2612F2C92.ashx

ATCC 49006. (n.d.). Bacillus benzoevorans Pichinoty et al. ATCC.


Intergovernmental Panel on Climate Change (IPCC). (2014). *Summary for policy-makers. Contribution of working group III to the fifth assessment report of the intergovernmental panel on climate change.*


