A Comparative Study of Greenhouse Gases Produced by Membrane Bioreactors, Submerged Membrane Electro Bioreactors and Lagoons During Wastewater Treatment Process

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Abstract

A comparative study of greenhouse gases produced by membrane bioreactors, submerged membrane electro bioreactors and lagoons during wastewater treatment process

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Climate change is without a doubt the most important environmental issues of our age. Numerous studies have indicated the climate change and its effects are attributed to anthropogenic activities emitting CO_2, CH_4, N_2O and other greenhouse gases. Wastewater treatment plants and their discharge account for 7.6% of the total emissions. The main objective of this study was to investigate greenhouse gases generated by two advanced wastewater treatment methods: conventional membrane bioreactor (MBR) and novel submerged membrane electro bioreactor (SMEBR). Subsequently, outcomes from both systems in lab scale were compared to the most popular wastewater treatment method, the lagoon systems, which account for 80% in Canada. This study comprises four phases. In phase 1, the 7 L MBR system was set up and run based on synthetic wastewater, simulating discharge to lagoons in in a municipality in Quebec. Subsequently, gas emissions were collected and analyzed. In phase 2, a submerged membrane electro-bioreactor, with identical technological parameters as MBR in phase 1, was submitted to investigations, where its emitted gases were also analyzed. In phase 3, a larger MBR was exposed to biogas measurements. Then, it was transformed to SMEBR while gas measurements continued. In phase 4, gas emissions from lagoons were estimated and compared to the outcomes from phases 1, 2 and 3. Results showed that the MBR produced around 22 g of CO_2 equivalent per litre of wastewater per day, while the SMEBR generated around 12 g CO_2 eq/L per day. In phase 3, the MBR transformation to SMEBR permitted to decrease the gas production while improving the ammonia removal efficiency. Phase 4 showed that the SMEBR reactor generated less N_2O when compared to other investigated systems. It was concluded that the SMEBR system produced the lowest amounts of N_2O per litre of wastewater, while showing superiority in nutrient removal. It is an important information from the point of view of sustainability and climate change prevention.

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Dedication

To thinking

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CH_4	Methane
CO_2	Carbon dioxide
COD	Chemical oxygen demand
DO	Dissolved oxygen
EFF	Effluent
GHG	Greenhouse gas
HRT	Hydraulic retention time
INF	Influent
MBR	Membrane bioreactor
MLSS	Mixed liquor suspended solids
NO_2	Nitrous oxide
SMEBR	Submerged membrane electro bioreactor
SRT	Solids retention time
TN	Total nitrogen

Chapter 1: Introduction

Climate change is considered as one of the most important environmental issues of our age. There is a strong body of evidence to prove this phenomenon. Climate change can happen by both natural causes and human activities. However, it is believed that human influence on this is not negligible. Intergovernmental Panel on Climate Change (IPCC) reports that greenhouse gas (GHG) emissions from human activities are the highest in history (IPCC Team 2014).

Climate change is a long-term shift in average weather pattern over a certain region (IPCC Team 2014). Weather refers to the atmosphere condition at a specific location over a short period. While climate is a 30-year average weather pattern for a given region (Environment Canada 2016).

A wide range of indicators attributed the recent warming to human activity by emitting carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O) and other GHGs to the atmosphere. Natural and anthropogenic sources of GHGs increase the concentration of these gases in the atmosphere. According to IPCC 2001, this increase is linked to climate change (Sahely, et al. 2006).

There has been a serious increase in atmospheric concentration of GHGs since pre-industrial times (IPCC Team 2014). World Meteorological Organization (WMO) reports the increase of CO_2 by 142%, CH_4 by 253% and N20 by 121% in the atmosphere since pre-industrial times, 1750. (World Meteorological Organization 2017). IPCC 2013 accounts the use of fossil fuel for energy, land use and land use changes responsible for this change.

IPCC reports the unequivocal warming of the climate system, highlighting the warming of atmosphere and oceans, diminishing amounts of snow and ice, rising sea levels, and increasing concentration of GHGs (IPCC Team 2014). Environmental Canada considers extreme weather events, freshwater resources reduction, increased risk and severity of forest fires and pest infestation, Arctic ice reduction and glacial melting acceleration as symptoms of climate change in the region. They reported annual temperature of above normal in Canada since 1993 and recorded a warming trend of 1.6°C over the last 66 years (Environment Canada 2016).

The year 2019 ends with a decade of exceptional global heat, caused by greenhouse gases from human activities (WMO 2019). Concentrations of carbon dioxide in the atmosphere hit 407.8 parts per million in 2018 and continued to rise in 2019, which is a new record. Based on WMO reports, climate change and extreme weather events such as floods, drought, etc. are among the causes of rise in global hunger and severe crises (WMO 2019). Urgent climate action is needed.

Absorbing around 30% of emitted anthropogenic CO_2, the ocean is facing acidification. The energy uptake of the climate system is caused by positive total radiative force, and the largest contributor to this is the increase of CO_2 concentration in the atmosphere since 1750 (IPCC Team 2014).

The amount of emissions of GHGs from anthropogenic sources have gone over the amount of natural absorption mechanisms. This caused the increase in the concentration of GHGs in the atmosphere (Sahely, et al. 2006). Concentration of CO_2, CH_4, and N_2O have reached levels unprecedented in the last 800,000 years.

IPCC (2014) highlights that continued emissions of GHGs will lead to further changes in all components of the climate system. In order to limit this change, it is required to substantially reduce GHG emissions (IPCC Team 2014).

Many international agreements have been developed to control the production of GHGs by different activities and industries (Ashrafi 2012). Governments have decided to act on climate change. The international treaty of United Nations Framework Convention on Climate Change (UNFCCC) was established to stabilize GHG concentrations in the atmosphere. The goal of this treaty is to stop the dangerous interferences of human activities with the climate system (Environment Canada 2016). Canada signed this treaty in December 2019. UNFCCC asks several commitments to reach its objective. One of these principles requires every country to provide their national inventories of anthropogenic emissions, their sources and sinks. Canada provides its National GHG Inventory every year in compliance with UNFCCC guidelines. GHGs in this report are CO_2, CH_4, N_2O, perfluorocarbons (PFCs), hydrofluorocarbons (HFCs), sulphur hexafluoride (SF6) and nitrogen trifluoride (NF_3). This inventory provides the emissions from five major economy sectors: Energy; Industrial Processes and Product Use; Agriculture; Land Use, Land-Use Change and Forestry; and Waste. Wastewater treatment is included in the waste sector. This report is prepared following the guidelines provided by the IPCC.

In 2015, Canada planned to reduce its greenhouse gas (GHG) emissions by 30% less than 2005 levels by 2030. In 2017, Canada reported 716 mega tonnes of CO_2 equivalent (Mt CO_2 eq), which is a 2.0% decrease from 2005.

IPCC (2014) also reported about 0.77479 Gt CO_2 eq/year of direct emissions from wastewater treatment industry, counting for 7.6% of total direct emissions in 2010. This is an important number considering that this value was 0.5822 Gt CO_2 eq/year in 1990. However, IPCC only considers CH_4 and N_2O emissions from wastewater treatment plants, 666.75 Mt CO_2 eq and 108.04 Mt CO_2 eq, respectively (IPCC Team 2014). Unfortunately, emission of CO_2 produced by biological treatment processes has not been counted.

Nevertheless, United States Environmental Protection Agency (EPA) considers wastewater treatment plants as one of the larger minor GHG emission sources, producing CO_2, CH_4, and N_2O during the treatment process (Doorn, et al. 1997).

Canada National Inventory Report in 2013 considers wastewater treatment as a stable minor source of CH_4 and N_2O emissions. In 2013, Canada reported 1100 kilo tons (kt) of CO_2 eq GHG emissions from wastewater treatment and discharge; Quebec contributed 260 kt CO_2 eq, around 24% of total. This consists of 16 kt CH_4 (390 kt CO_2 eq) and 2 kt N_2O (700 kt CO_2 eq). Still CO_2 emissions from wastewater handling are not measured in this report. It should be noted that since 1990, CH_4 emissions have fluctuated between 14 - 16 kt, while N_2O emissions stayed the same (Environment Canada 2016).

Overall, Canada produces three trillion litres of wastewater per year (CCME, Canadian Council of Ministers of the Environment 2006). This wastewater contains several types of pollutants which could affect the environment. Therefore, the wastewater is treated by various methods before discharging to the environment. In Quebec, 80% of the municipalities use aerated or non-aerated lagoons for their wastewater treatment. This is also an average number across Canada. Lagoons are not able to remove nutrients such as phosphorous and nitrogen well enough. Therefore, the effluent poses a risk to the receiving water body and environment. There has been a need for upgrading the existing lagoons and use advanced treatment methods, while sustainability and prevention measures against climate change are considered either.

GHGs emitted from wastewater treatment systems consist of a wide range of compounds. Intergovernmental Panel on Climate Change Protocol (IPCCP) accounts CH_4 and N_2O in this list only and considers biochemical oxygen demand (BOD) and flow as contributing factors (Monteith, et al. 2005).

The characteristics of the wastewater, such as biochemical (BOD) and chemical oxygen demand (COD) as well as suspended solid concentration (SS) of organic origin would lead to a higher GHG production per volume treated (IPCC Team 2014). The amount of each one of GHGs produced depends on the characteristics of influent, required level of treatment, and processes applied for wastewater treatment.

Variations in wastewater quality may affect the performance of conventional treatment methods. Wastewater produced in different regions in the world may have different characteristics which leads to higher sludge production. In such cases, an appropriate treatment method can be considered for a sustainable solution for wastewater management (IPCC Team 2014).

IPCC 2014 reports the use of centralized wastewater treatment plants by most of developed countries, while around half of the wastewater from domestic and manufacturing sectors is left untreated. It has been indicated that CH_4 and N_2O emissions in developed countries are typically smaller because of centralized wastewater treatment infrastructure and gas collection systems. However, in developing countries, high CH_4 and N_2O production increases due to rapid population growth in the absence of wastewater infrastructure development (IPCC 2018).

Centralized wastewater treatment plants require high capital investments, while not providing flexibility to growing demands of expanding cities or mostly megacities. Hence, decentralized wastewater treatment infrastructure seems to be more favorable. Membrane bioreactor (MBR) is one of the advanced treatment technologies, which can be used for decentralized facilities while potentially decreasing GHG emissions (IPCC 2015). However, it still deals with ammonia nitrogen removal (nitrification) while building additional facilities is required for nitrate nitrogen elimination (denitrification). This deficiency is eliminated by more advanced novel system - submerged membrane electro-bioreactor (SMEBR). This unique system is able to conduct nitrification and denitrification in a sole vessel due to application of an adequate current density into bioreactor. Such sustainable system has even more advantages to be applied to decentralized wastewater treatment facilities since it removes carbon, nitrogen and phosphorous simultaneously in a compacted small fingerprint system (Elektorowicz, Bani-Melhem and Oleszkiewicz 2009)

It is predicted that CH_4 emissions from wastewater handling will rise more than 45% from 1990 to 2020, mostly in developing countries. The current emissions of N_2O from wastewater are comparatively low to total global anthropogenic N_2O emissions. However, it is believed that N_2O emission predictions from wastewater in Asia, Africa, South America and the Caribbean are underestimated due to insufficient data (IPCC 2015).

To upgrade the wastewater treatment plants (WWTPs), different aspects from available options are considered such as nutrient removal efficiency, installation cost, operating cost, etc. However, the GHGs produced by the method is not of concern. Municipalities are not required to report emissions from WWTPs. This is since Canada uses a per capita estimation, where the emissions from wastewater treatment and discharge do not rely on the treatment method. So, the emissions presented in National Inventory Reports (NIRs) do not take the method of treatment into account. Population and protein consumption per capita are the main components of this estimation method.

Canada uses this method for estimations because of the lack of data in this field. Since there are not enough information on the amount of GHGs produced by each method, Canada follows the guidelines provided by IPCC to estimate the emissions from this sector.

This study aimed to provide more data on the amount of GHGs produced by two advanced wastewater treatment methods, namely, membrane bioreactor (MBR) and submerged membrane electro bioreactor (SMEBR). Thus, the main objective of this research was to investigate the emissions generated by these both systems in various configurations. Detailed objectives were:

- Running lab scale MBR system for assessment its GHG emissions
- Running SMEBR system for assessment of its GHG emissions.
- Estimation the gas emissions from conventional lagoons
- Providing a comprehensive comparison of emissions generated by MBR, SMEBR and lagoons.

Achievement of these objectives permits the following contributions:

- First assessment of GHG emissions by SMEBR
- Assessing GHG production by an existing lagoon system in the city of L'Assomption (Quebec)
- First comparative data for GHGs generated by MBR, SMEBR and lagoons
- Updating the knowledge on GHG emissions by WWTPs.

Chapter 2: Literature review

2.1 Carbon Cycle

The carbon cycle refers to large carbon flows and reservoirs, in which the carbon dioxide (CO_2) is removed and produced by various sources. It is consisted of the connections between human activities, greenhouse gas emissions, changing of climate system components, radiative balance changes, and the climate reaction (Kheshgi and Jain 2003). The removal of CO_2 can be done by water absorption and plant's photosynthesis whereas its production is by plant and animal respiration, decay of plant and soil organic matter, and water surfaces outgas. Hengeveld et al. (2005) acknowledges anthropogenic sources of CO_2 as a small contributor to this cycle, accounting for 1/20 of the total flow of carbon (Hengeveld, Whitewood and Fergusson 2005). However, this small change has shown significant impacts on this natural balance (Environment Canada 2016). The carbon flows and reservoirs are summarized in Figure 1 (Post, et al. 1990).

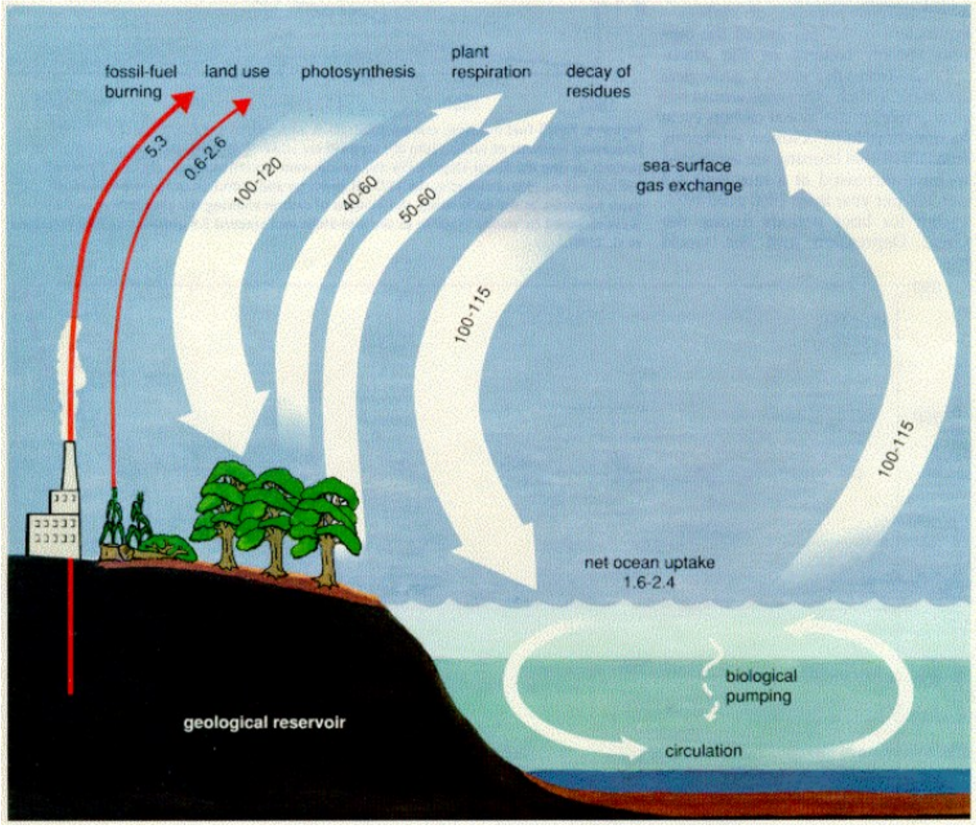


Figure 1: Carbon flows and reservoirs in the environment (Post, et al. 1990)

2.2 Global warming potential

Global warming is the increase in the combined surface air and sea surface temperatures, averaged all over the earth and over a 30-year period (IPCC 2018). A higher global average in various regions and seasons has been experienced and reported. Greenhouse gas's potential to contribute to global warming is based on atmospheric lifetime and heat-trapping potential of the gas. The amount of heat-trapping potential is referred to as radiative forcing and quantifies the global warming potential. Direct radiative forcing comes from the GHGs themselves. On the contrary, indirect radiative forcing comes when a gas chemically transforms to one or multiple GHGs or affects the atmospheric lifetimes of other gases (Environment Canada 2016).

Global warming potential (GWP) is defined as the change in radiative forcing over a certain period of time following the instantaneous release of 1 kg of a substance. This value is considering this effect by release of 1 kg of CO_2 as a reference. GWP considers the instant radiative forcing by the concentration increase as well as the substance lifetime (Environment Canada 2016). For instance, the 110-year GWP of NO_2 is reported as 298; hence an emission of 100 tonnes of NO_2 is equivalent to 298 x 100 tonnes = 29,800 t = 29.8 kilotons (kt) CO_2 eq.

This developed concept allows a better comparison of the effect of each GHG on climate change (IPCC Team 2014, Eggleston, et al. 2006). It allows us to have a better understanding of the warming effect of GHGs by calculating how much CO_2 would make a similar warming effect over a certain period. It is done by multiplying the amount of the substance by its GWP. This also allows us to measure the total emissions shown as CO_2 eq (Environment Canada 2016).

The IPCC oversees the development and update of GWPs. These values are based on existing conditions and therefore need to be updated as the GHG concentrations and climate change.

IPCC Global Warming Potentials (GWPs)	GHG Formula	20-year GWP (kg CO2/kg gas)
Carbon Dioxide	CO_2	1
Methane	CH_4	62
Nitrous Oxide	N_2O	275

Table 1: IPCC global warming potential equivalents for carbon dioxide, methane and nitrous oxide (Eggleston, et al. 2006)

2.3 Carbon-based greenhouse emissions

2.3.1 Carbon dioxide

Carbon dioxide (CO_2) is a natural odourless colourless incombustible gas. It can be produced by respiration, fossil fuel and biomass combustion, burning of solid waste, trees and wood products, building heating and cooling, transportation, land-use changes, certain chemical reactions and other industrial processes (EPA 2016). It can be constantly removed or released by the carbon cycle which was mentioned before.

In wastewater treatment, CO_2 can be produced as a product of chemical reactions, when microorganisms oxidize organic material to generate energy and reproduce. Zhan et al. (2015) simplifies this in equation [1] (Zhan, Hu and Wu 2015).

$$\text{Organic Matter} + O_2 + \text{Nutrients} \rightarrow \text{New Cells} + CO_2 + H_2O \qquad [1]$$

The carbon in the influent can be used to form biomass. This carbon in the biomass is then converted to CO_2 under aerobic conditions through endogenous respiration. Biomass is characterized as $C_5H_7O_2N$ (McCarty 2001), and the equation for this reaction is as follows:

$$C_5H_7O_2N + 5O_2 \rightarrow 5CO_2 + 2H_2O + NH_3 \qquad [2]$$

The carbon in the incoming wastewater can also be converted to CO_2 directly under aerobic conditions. If the soluble BOD is assumed as $C_{10}H_{19}O_3N$, (McCarty 2001), the oxidation of BOD is the equation that reflects this conversion, which is:

$$2C_{10}H_{19}O_3N + 25O_2 \rightarrow 20CO_2 + 16H_2O + 2NH_3 \qquad [3]$$

IPCC guidelines do not cover CO_2 emissions from wastewater treatment plants. The reason being that the CO_2 is coming from a biogenic origin and hence not considered in national total emissions reports.

2.3.2 Methane

Methane (CH_4) is a colourless, odourless, flammable GHG. It is the simplest hydrocarbon. It can be produced naturally by animal digestion and animal waste decomposition, and by industrial processes such as petroleum and natural gas production and distribution, coal production, anaerobic waste decomposition and incomplete combustion of fossil fuel. It is used as feedstock in chemical industry, and as fuel for many purposes (Environment Canada 2016). Its concentration in the atmosphere is increased by 0.6% per year (EPA 2016).

CH_4 is produced by methanogenic microorganisms under anaerobic conditions. These conditions may be provided intentionally or unintentionally. CH_4 production and release to the environment depend on the process producing it and the mechanism capturing it. CH_4's 100-year global warming potential of 23 shows that the effect of one kilogram of it on global warming is equivalent to that of 23 kg of CO_2 (Monteith 2005).

CH_4 can be removed by natural processes in soil, and chemical reactions in the atmosphere. It can enter the atmosphere from industry, agriculture, and waste management activities. Although it has a shorter lifetime that CO_2 in the atmosphere, its impact is 25 times larger than that of CO_2 over a 100-year period (EPA 2016).

It has been demonstrated that anaerobic sludge digestion with a proper CH_4 recovery system will not only reduce its emissions of this gas, but also be able to treat high strength organic wastewater (Intergovernmental Panel on Climate Change 2015).

2.4 Noncarbon-based greenhouse gas emissions

2.4.1 Nitrous oxide

Nitrous oxide (N_2O) is a colourless, non-flammable GHG. It can be used as an anesthetic in dentistry and surgery, and as a propellant in aerosol cans. It is created naturally in the atmosphere from oceans, bacteria in soils, and animal waste. Human activities can also be responsible for its production through nylon and nitric acid manufacturing, fossil fuels and biomass combustion, soil cultivation practises, as well as using fertilizers. (Environment Canada 2016).

Currently, N_2O sources are not fully known, and there is still a debate over it in the literature. The amount of its emissions is quite variable and depends on several factors, which include operating and environmental conditions (Kampschreur 2009).

N_2O, with 100-year global-warming potential of 296, can be produced during the biological secondary treatment of wastewater, while the denitrification process is incomplete. Many works have shown that N_2O can be produced in wastewater treatment plants during nitrogen removal processes. Both nitrification and denitrification can cause N_2O production. A complete nitrification and denitrification process will limit the N_2O generation (Davis and Cornwell 1998).

In the nitrification process, N_2O can be found as a product of ammonium oxidizing bacteria (AOB), although it is not an intermediate product in the main pathway. On the other hand, N_2O is an intermediate product of denitrification. So, an incomplete process can leave N_2O in the solution. Anammox denitrification is not expected to produce N_2O, by reducing nitrite with ammonia oxidation directly to nitrogen gas (Kampschreur 2009).

Linking N_2O emission to its sources, A. Castellano-Hinojosa (2018) studies have shown that AOB plays a major role in N_2O generation in an activated sludge system. N_2O accumulation and lower temperatures can contribute to higher amounts of AOB in the system (Castellano-Hinojosa, et al. 208).

2.4.2 Fluorinated gases

Fluorinated gases are a group of synthetic gases coming from various industries. They have a high GWP compared to natural GHGs. Thus, even small amounts of these gases in the atmosphere can greatly impact the global temperature. They also have long atmospheric lifetimes and are therefore scattered in the atmosphere evenly. Their removal is only made possible by sunlight in the far upper atmosphere. These gases are considered the most powerful and the longest lasting GHGs made by human activities (EPA 2016).

Four main fluorinated gases are hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), sulfur hexafluoride (SF_6), and nitrogen trifluoride (NF_3).

2.4.3 Hydrofluorocarbons (HFCs)

HFCs are a group of synthetic powerful GHGs. They are composed of fluorine, carbon and hydrogen. Since they do not deplete the ozone layer, they are used as alternatives for chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs) and halons. These gases are used in the refrigeration, fire extinguishing and semiconductor industries. Their global warming potential varies from 140 to 11700.

2.4.4 Perfluorocarbons (PFCs)

PFCs are a powerful class of man-made GHGs. They contain carbon and fluorine. They are used in semiconductors, in the electronic industry, and in some refrigeration systems. They are also a by-product of aluminum industry (Environment Canada 2016). This group of gases have a global warming potential of 6500 to 9200.

2.4.5 Sulfur hexafluoride (SF_6)

SF_6 is a human-made colourless odourless GHG. It is commonly used in electricity and magnesium industries (Environment Canada 2016). Its global warming potential is 23900.

2.4.6 Nitrogen Trifluoride (NF_3)

NF_3 is a colourless non-flammable gas. It is usually used in electronics, semiconductors, liquid crystal display (LCD) panels and photovoltaics industries. This gas 100-year period global warming potential is 17200.

2.4.7 Wastewater Treatment and Discharge

Wastewater can be a source of methane (CH_4) and nitrous oxide (N_2O). Carbon dioxide (CO_2) emissions are not included in the national inventory reports due to their biogenic origin. Wastewater can come from domestic, commercial and industrial sources. It can be treated on-site, sent to centralized wastewater treatment plants (WWTPs) via sewage systems or disposed, untreated, in nearby water bodies. Treatment and discharge systems vary between countries, between rural and urban areas, and between low-income and high-income users (Eggleston, et al. 2006).

The sewage systems may also vary between the previously stated conditions. Open sewage systems can include open canals, gutters and ditches. Closed sewage systems may consist of networks of sewers underground. Used mostly in developed countries and high-income urban areas, this type of system does not contribute to CH_4 emissions. However, it is believed that open sewage systems are prone to exposure to sun heat and low flow rates, leading to anaerobic conditions and therefore CH_4 production (Doorn, et al. 1997).

In developed countries, centralized aerobic WWTPs and lagoons are the most common wastewater treatment method (Eggleston, et al. 2006). In Quebec, aerobic WWTPs and lagoons take 84% of the total 811 WWTPs (Moreira and Boudreault 2011). According to IPCC data, decentralized WWTPs are somehow common in developed countries. Due to regulations, some industries may need to have on-site pretreatment before releasing their wastewater into the sewage network. Another common decentralized treatment method is septic tanks for domestic wastewater. Despite all the regulations and these methods, untreated wastewater is still disposed into near water bodies in some developed countries. This can be summarized in Figure 2: Wastewater treatment and discharge (Eggleston, et al. 2006).

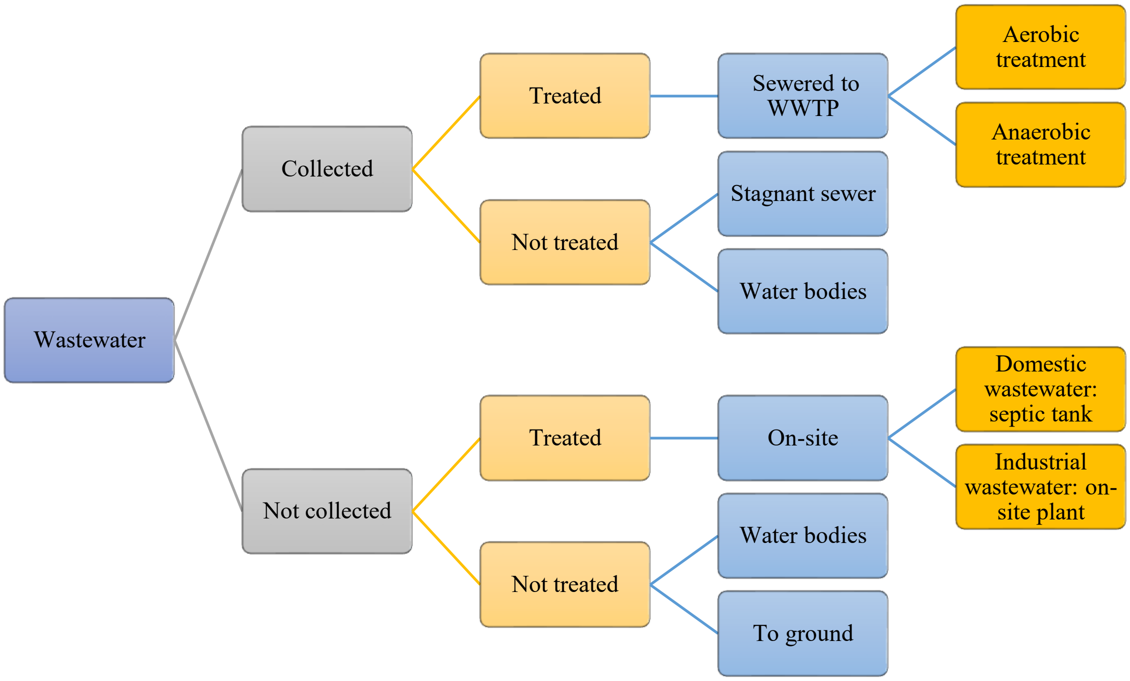


Figure 2: Wastewater treatment and discharge pathways (Eggleston, et al. 2006)

Centralized WWTPs may consist of primary, secondary and tertiary treatment. Primary treatment removes large suspended solids by physical barriers, and secondary treatment biodegrades the organic material by microorganisms available in biological processes. This can be done by various methods such as activated sludge systems, lagoons, membrane bioreactors (MBRs), anaerobic reactors, etc. Tertiary treatment removes pathogens, contaminants and nutrients. This may be done by many methods like advance filtration, ozonation, etc.

In all these three treatments, sludge is a by-product. It is the result of biological activities as well as large and small particles in the influent. This sludge needs to be treated and disposed of. It can be done by various methods including centrifugation, aerobic and anaerobic digestion, composting, etc. GHG emissions from sludge are not considered in this work.

The IPCC considers emissions estimations from sludge separately. There are different guidelines for estimating emissions from sludge applied to agriculture soils, incinerated, and deposited in solid waste disposal.

2.5 Biological Wastewater Treatment

Microorganisms can be controlled and engineered to remove organic matter and nutrients from wastewater. These microorganisms can oxidize pollutants such as chemical oxygen demand or COD, Fe^{2+} and NH_3. These pollutants act as electron donors, and will be reduced to oxygen (O_2), nitrate (NO_3), sulfate (SO_4) or CO_2 (McCarty and Rittmann 2001).

Reactors are used to provide suitable conditions for the microorganisms to function and grow. There are different types of reactors currently used in WWTPs. To choose the type of reactor, a few factors need to be taken into consideration: influent physical and chemical characteristics, pollutants type and concentration, required treatment level, operating climatic conditions, and construction and operation cost and expertise (McCarty and Rittmann 2001).

2.5.1 Activated sludge

Activated sludge is the most commonly used biological process in municipal and industrial WWTPs. It consists of an aeration tank, a settling tank, sludge recycle and sludge removal. It is a biological treatment method with suspended growth of microorganisms (McCarty and Rittmann 2001).

In this process, microorganisms, as biological sludge, are mixed with wastewater, agitated and aerated, and suspend in this liquid mixture which leads to a suspended growth process. In the end, these microorganisms are extracted from the effluent and returned to the system. This mixture, including air and organic compounds in the wastewater, provides a desirable condition for microorganisms' growth, which leads to their flocculation and forming an active mass of microbes known as activated sludge (Davis 1998).

This mixture, also known as mixed liquor, then goes to a secondary settling tank, where the flocks settle out (Flemming and Wingender 2001). This settled sludge mostly returns to the aeration tank to make the biological degradation possible or exit the system to go through a sludge handling procedure, which takes care of sludge treatment and disposal (Davis and Cornwell 1998).

Bacteria are held together by extracellular polymeric substances (EPS) and form floc particles. These flocs settle by gravity, leaving a supernatant which can be clarified and disposed to the receiver body. The particles settled form sludge splits into waste activated sludge or return activated sludge. Waste activated sludge goes through a sludge treatment process and then is either disposed of or is used as a fertilizer. The return activated sludge goes back to the aeration tank to provide an acceptable level of treatment for the incoming fresh wastewater (McCarty and Rittmann 2001).

The flocs consist of a wide variety of bacteria and protozoa which oxidize the organic matter present in the wastewater and convert them into water, CO_2 and new cells. Temperature, sludge return rate, amount of oxygen and organic material available, pH and other factors can define the efficiency of this process (McCarty and Rittmann 2001).

In an activated sludge process, different types of conversions might occur, depending on the type of microorganisms and boundary conditions. Aerobic oxidation happens in the presence of oxygen and organic matter, and solid retention time of a few days when the oxygen acts as the electron acceptor and the organic matter as an electron donor, making this type of conversion easy to achieve (McCarty and Rittmann 2001).

The amount of sludge leaving the system, also known as waste activated sludge, controls the entire process. A proper wasting ratio must be kept to achieve an efficient treatment. The balance between growth and production of new microorganisms and waste activate sludge in the mixed liquor is required for this process. The average amount of time that microorganisms are in the system is known as sludge age, solid retention time (SRT), or mean cell residence time (θc) (Davis 1998).

In the field, wastewater and activated sludge is mixed in the aeration tank continuously with the help of aerators. Aerators also provide the required oxygen for microorganisms to degrade the organic compounds present in the influent.

In a conventional activated sludge system, aeration tanks are long rectangular basins, where aeration is done for 6 to 8 hours, providing around 8 m^3 of air for each cubic metre of influent wastewater. Usually, around 20 to 30% of the settled sludge returns to the basin and the rest leaves the system (Davis 1998).

Many modifications and justifications of the conventional activated sludge process, including the aeration, basins and influent flow system, have been done to provide a reliable treatment for different wastewater characteristics and different problems (Davis 1998).

2.5.2 Lagoon

Lagoons can be an alternative to activated sludge. They manage to achieve equal removal efficiency to activated sludge. They are simpler in design and operation and do not require complex machinery. However, they require more surface area than the compact activated sludge process (McCarty and Rittmann 2001). They also cause high suspended solid concentration in the effluent (Fortin 2000).

Lagoons are commonly used in rural communities. Some industries opt for this method as their wastewater treatment if they can provide large land areas (McCarty and Rittmann 2001).

Two main types of lagoons are aerated lagoons and stabilization lagoons. The major difference is in how they provide oxygen to microorganisms. Aerated lagoons use pumps and mechanical devices for aeration whereas stabilization lagoons use the natural oxygenation by sunlight (McCarty and Rittmann 2001).

Aerated lagoons are basins where biological processes provide the wastewater treatment. Surface or submerged aerators differentiate this type of lagoon. This aeration provides dissolved oxygen for suspended heterogeneous microbial cultures to consume biodegradable organic material in the wastewater. Low capital and operating costs and minimal maintenance requirements make the aerated lagoon an easy and affordable choice for municipal wastewater treatment. However, they fail to achieve effluent limits of CBOD =25 mg/L, posed by Environment Canada, while treating industrial wastewater (Environment Canada 2019).

This treatment method is also common in the province of Quebec. Availability of large land areas in the province and minimal maintenance required make this method a good choice for Quebec municipalities. In Quebec, 540 aerated lagoons are currently in use (Fortin 2000).

Stabilization lagoons are a cheap solution to domestic and industrial wastewater treatment. These ponds, also known as oxidation lagoons, need low capital and operation cost and expertise, but require large land areas. They are designed to contain a mixture of phototrophic and heterotrophic bacteria. Relying solely on solar-driven oxygenation, they reach their best performance in moderate temperature and sunlight. They also are not as powerful as aerobic methods to remove organic matter. Another downside is their smell when reached anoxic or anaerobic conditions, hence not suitable for locations close to population centres (McCarty and Rittmann 2001).

In any lagoon, three types of reactions occur: oxidation, synthesis and endogenous respiration. In aerated lagoons, oxidation happens aerobically. These reactions can be simplified as (Pfafflin and Ziegler 2006):

Organic matter oxidation: $C_xH_yO_z + O_2 \rightarrow CO_2 + H_2O$ + energy + other products [4]

Inorganic matter oxidation: $NH_4+ + 2O_2 \rightarrow CO_2 + H_2O$ + energy + other products [5]

Cell growth: $C_xH_yO_z + NH_3 + O_2$ + energy $\rightarrow C_5H_7NO_2 + H_2O$ [6]
$C_xH_yO_z + H^+ + NO_3^-$ + energy $\rightarrow C_5H_7NO_2 + CO_2 + H_2O$

Cell material oxidation: $C_5H_7NO_2 + 5O_2 \rightarrow 5CO_2 + 2H_2O + NH_3$ + energy [7]

Lagoons without aeration and mixing can also be a source of CH_4 depending on their depth. Shallow lagoons not deeper than 1 m usually provides enough oxygen to reach aerobic conditions, hence no CH_4 generation. However, lagoons with more than 2-3 metres in depth cause anaerobic conditions which lead to greater CH_4 generation (Eggleston, et al. 2006).

2.5.3 Membrane Bioreactor

A membrane bioreactor (MBR) consists of an activated sludge treatment followed by micro/ultra-filtration to separate the suspended solids and mixed liquor. As a result, the effluent quality is high, and it can be used in agricultural fields. Due to the presence of a nitrification process, a sufficient dissolved oxygen level must be maintained. A major challenge for this process is fouling, which is the result of the presence of organic colloids and extra polymer substances (Hosseini 2016).

In the field, membrane bioreactors provide biological degradation and solid/liquid separation in one reactor. Membranes can be either internal or external. Internal membranes are submerged in the reactor, while external membranes are side stream (Lobos, et al. 2008). Submerged membranes provide a low liquid pumping cost (28% of total cost) (Gender et al, 2000), lower energy consumption (Côté, et al. 1997) and a lower operating cost. Meanwhile, membrane fouling, and high capital and aeration costs are the main disadvantages (Hassan 2011).

Membranes are often used to improve the efficiency of an activated sludge system. They allow more suspended solids in the reactor, reduce the reactor size and make it easier to control the solid retention time (McCarty and Rittmann 2001).

2.5.4 Submerged Membrane Electro Bioreactor

Submerged membrane electro bioreactors (SMEBR) are compact hybrid systems that couple the MBR system with electrokinetic phenomena (Bani Melhem and Elektorowicz 2010). This system consists of a membrane module, an aluminum anode, a stainless-steel cathode, and air diffusers (Ibeid, Elektorowicz and Oleszkiewicz, Novel electrokinetic approach reduces membrane fouling 2013). They are connected to a direct current (DC) power supply, coupled with a timer. This timer controls the exposure time of microorganisms to the electric field (Bani-Melhem and Elektorowicz 2011). Air diffusers provide fine air bubbles for bacteria (Hassan 2011).

Electrical current was applied to a membrane bioreactor to improve nutrient removal and decrease membrane fouling . In a single reactor, electrodes are designed around a membrane, producing aluminum hydroxide by the dissolution of the anode (Hosseini 2016).

Applied current passes through the electrodes and oxidizes the metal. The metal (M) oxidizes to its cation (Mn+). For example, the electro oxidation of sacrificial aluminum anode produces monomeric species such as Al^{3+}, $Al(OH)^{2}$+, $Al(OH)_3$, $Al_n(OH)_3$n and $Al(OH)^{2+}$. The composition of the products depends on the pH of the medium (Hasan 2014).

Applied DC field causes the oxidation of water around the electrodes; hydrogen (H^+) and oxygen gas (O_2) are produced at the anode, while hydrogen gas (H_2) and hydrogen oxide (OH^-) are produced at the cathode. The oxidation of water also produces hydroxyl radicals (-OH) which are strong oxidizing agents, reacting with organic matter and forming dehydrogenated or hydroxylated derivatives.

The anode dissolves into cations due to the applied DC field into cations. Then, they are entered into the solution and hydrolyzed to hydrated ions (Mollah, et al. 2004). Hydrogen gas is the by-product of these reactions from cathode (Wei 2016). The electro-chemical reactions in electrocoagulation can be described as follows (Brillas, et al. 2017):

Anode: $Al^0 \rightarrow Al^{3+} + 3e^-$ [8]

Cathode: $2H_2O + 2e^- \rightarrow 2OH^- + H_2$ (gas) [9]

2.5.5 Nitrogen control

Nitrogen in all soluble forms except nitrogen gas, including NH_3, NH_4^+, NO_2^-, and NO_3^-, is considered a nutrient for algal growth. Furthermore, if ammonia-nitrogen applies, toxicity rises, and oxygen demand increases. It needs to be removed from the wastewater before being disposed to the receiving body. Nitrification and denitrification, which are biological processes to remove nitrogen, can be achieved by providing the preferable criteria (Davis and Cornwell 1998).

Nitrification is biological oxidation of NH_4^+ by nitrifies to NO_2^- and subsequently to NO_3^-, shown in equations [10] and [11]. Nitrification might occur in an activated sludge by providing enough cell detention time (θc), depending on the climate and nitrifying bacteria. This process can be expressed as follows (Davis and Cornwell 1998):

$2\ NH_4^+ + 3\ O_2 \rightarrow 2\ NO_2^- + 4\ H^+ + 2\ H_2O$ [10]

$2\ NO_2^- + O_2 \rightarrow 2\ NO_3^-$ [11]

Being obligate aerobes, nitrifiers need oxygen for respiration. This process happens in two steps: NH_4^+ oxidizes to NO_2^-, then oxidizes NO_3^- (McCarty and Rittmann 2001).

Denitrification is biochemical reduction of NO_2^- or NO_3^- to nitrogen gas (N_2). This happens in advance wastewater treatment methods, where nitrite and nitrate levels are too high to meet the regulations. To have denitrification occurring in the system, NO_2^- and NO_3^- needs to be available. This requirement has made the nitrification and denitrification essential processes (equations [10][11]) in WWTPs with high nitrogen loads (McCarty and Rittmann 2001).

In this process, nitrate is reduced to nitrite, nitric acid (NO), nitrous oxide (N_2O) and N_2 gas. Dissolved oxygen (DO) plays an important role in this sequence. It is noticed that denitrification can happen with a DO above zero. Low concentration of electron donors or high DO can lead to the production of intermediate by-products such as N_2O gas.

Denitrification might occur after nitrification if Anammox denitrifying bacteria are present, and organic matter available to act as an energy source for the bacteria. This process can be shown as follows:

$NO_3^- + 2\ e^- + 2H^+ \rightarrow NO_2^- + H_2O$ [12]

$NO_2^- + e^- + 2H^+ \rightarrow NO + H_2O$ [13]

$2NO + 2\ e^- + 2H^+ \rightarrow N_2O + H_2O$ [14]

$N_2O + 2\ e^- + 2H^+ \rightarrow N_2\ (gas) + H_2O$ [15]

This process can also have a direct CO_2 emission, depending on the electron donor used; if the incoming biological oxygen demand is used, an external carbon-based electron donor, or a non-carbon-based electron donor (Davis and Cornwell 1998):

$2NO_3 + \text{organic matter} \rightarrow N_2 + CO_2 + H_2O$][16]

Nitrification and denitrification are basically nitrogen compound oxidation. This could happen by various enzymes, leading to multiple intermediate products. N_2O may be an intermediate product in these processes, mostly denitrification (McCarty and Rittmann 2001).

Anammox bacteria can have a significant impact on the amount of carbon-based GHG emissions by directly oxidizing ammonia to nitrogen gas, using nitrite as an electron acceptor. High rates of ammonia and removal with minimal aeration and no need of external organic carbon (ethanol) made this method a suitable alternative to conventional biological nutrient removal methods. This process can be expressed with chemical reactions as follows:

$NO_2^- \rightarrow NO + NH_4 \rightarrow \text{hydrazine oxidoreductase enzymes (HZO)} \rightarrow N_2H_4 \rightarrow N_2$ [17]

2.6 Methane Generation

Wastewater and sludge may be sources of methane (CH_4) as a product of anaerobic digestion. The amount of influent organic matter, temperature and treatment method play the main role in the quantity of CH_4 production. Temperature is an important factor particularly in warm regions that utilize uncontrolled methods such as lagoons. As the temperature goes above 15°C, lagoons become a source of CH_4. In general, the amount of degradable organic matter in the influent acts as the main factor, determining the extent of CH_4 production, i.e., CH_4 generation potential (Eggleston, et al. 2006).

Canada considers anaerobic digestion system as the only source of CH_4 emissions from wastewater treatment sector (Environment Canada 2016). Generally, methanogenesis can be defined as follows:

$$\text{Organic matter} + H_2O + \text{nutrients} \rightarrow \text{new cells} + \text{resistant organic matter} + CO_2 + CH_4 + NH_3 + H_2S + \text{heat} \quad [18]$$

It has been demonstrated that anaerobic sludge digestion with a proper CH_4 recovery system will reduce methane emissions, while being able to treat high-strange organic wastewater (IPCC Team 2014).

2.7 Nitrous Oxide Generation

Nitrous oxide (N_2O) comes from various nitrogen components in the wastewater. Nitrogen in domestic wastewater comes from shower drains, sink drains, etc., which contain urea, protein and human sewage. WWTPs may be equipped with various methods to remove nitrogen components before disposing to water bodies. However, N_2O may be emitted in the plant or the water body by nitrification and denitrification processes (Eggleston, et al. 2006).

N_2O emissions can be direct or indirect. Direct emissions come from nitrification and denitrification, happening in WWTPs. Indirect emissions can occur after effluent disposal. The IPCC considers N_2O direct emissions as a minor source, being much lower than indirect emissions. However, it is mentioned that this may vary for developed countries using advanced WWTPs (Eggleston, et al. 2006).

Kowal et al (2017) performed multiple patch tests with different dissolved oxygen set points and two compositions of synthetic wastewater. They noticed that reducing dissolved oxygen from 1 mg/L to 0.4 mg/L can double the N_2O production when the only source of nitrogen is ammonia. They also posited that the wastewater containing both nitrite and ammonia as nitrogen sources can cause a higher rate of N_2O production, regardless of the dissolved oxygen concentration. They claim that hydroxylamine oxidation is the dominant pathway to N_2O production (Kowal and Mąkinia 2017).

2.8 CH_4 and N_2O Generation Potential

No matter if the wastewater is collected or not, each pathway may produce CH_4 and N_2O. Treatment or discharge methods that involve anaerobic conditions usually lead to CH_4 production. On the other hand, methods that provide nutrient removal are generally a source of N_2O. IPCC guidelines have provided all the possible pathways to CH_4 and N_2O generation, summarized in the table (Eggleston, et al. 2006).

Table 2: CH_4 and N_2O generation potential by possible pathways (Eggleston, et al. 2006)

Treatment and disposal method				CH_4 **and** N_2O **emission potentials**	**Cause**
Collected	Untreated	River discharge		May allow anaerobic condition to produce CH_4.	Stagnant, ocean-deficient rivers and lakes
				Likely source of N_2O.	
		Closed sewers		Not a source of CH_4/N_2O.	
		Open sewers		Significant source of CH_4.	Being Stagnant and overloaded
	Treated	Aerobic treatment	Centralized aerobic WWTPs	Likely source of CH_4.	Anaerobic pockets, poor design or management
			Sludge anaerobic treatment in aerobic WWTP	Sludge may be a significant source of CH_4.	If not recovered and flared
			Aerobic shallow ponds	Unlikely source of CH_4	
		Anaerobic treatment	Anaerobic lagoons	Likely source of CH_4.	Anaerobic condition
				Not a source of N_2O.	
			Anaerobic reactors	May be a significant source of CH_4.	If not recovered or flared
Uncollected	Septic tanks			Likely source of CH_4.	Solids
	Open pits			Likely source of CH_4.	Temperature and retention time allowing anaerobic condition
	River discharge			See above.	

2.9 International and national emission estimation guidelines

Various international agreements were signed to decrease GHG emissions and by signing the international agreements, various countries agreed on reporting their GHG emission to the environment, called national inventory report. Canada provides a detailed report by pointing out the emissions from each economic sector.

The IPCC developed a comprehensive guideline for estimating CH_4 and N_2O emissions coming from wastewater. These guidelines consider the amount of organic waste generated per person and an emission factor as the main parameters in estimating CH_4 and N_2O emissions. These parameters are based on available dates, country developmental state, treatment or discharge method and income groups.

Canada implements its own modifications to this suggested guideline. To calculate the amount of CH_4 and N_2O emitted from wastewater treatment industry, Canada has used a country-specific method to calculate an emission factor based on available data. Where actual measured facility data were available, they were taken into consideration (Environment Canada 2016).

For municipal wastewater, CH_4 emission estimation is based on the amount of organic matter generated per person, conversion of organic matter to CH_4, and fractions of wastewater treated anaerobically. CH_4 emissions from industrial wastewater treatment facilities are based on the available date gained from facility surveys conducted by Environment Canada. In the absence of actual measured facility data, estimations are based on design specifications.

N_2O emissions are calculated based on annual per capita protein consumption, protein nitrogen content, N_2O-N produced by sewage and N_2O/N_2O-N conversion factor.

The IPCC provides guidelines on how to measure uncertainties. Canada national inventory report estimated the overall uncertainty of wastewater treatment and discharge emissions to be from -40% to +55% (Environment Canada 2016).

These methods estimate gas emissions relied solely on mass balances, converting all the biodegradable carbon of the influent to gases. One challenge with this estimation is the distribution of gases, which may lead to inaccurate estimation of global warming potential. Another challenge with this simple estimation is revealed when the GHGs produced are captured and used. For example, CH_4 can be combusted for heating and electricity, to be used at the same facility, while polyhydroxyalkanoates is recovered to produce plastics. These cases would change the emissions of the system and would affect the global warming potential estimation. (Monteith 2005).

2.10 Greenhouse Gas Emissions from Wastewater Treatment Plants

Many works have been done to estimate or measure the amount of CO_2, CH_4 and N_2O generated by WWTPs. The IPCC has provided a detailed guideline to estimate the amount of each GHG emitted by wastewater treatment industry. However, some believe that this approach can be improved.

Works have been done to improve the estimation of GHG emissions. Monteith et al. present a rational procedure for estimating GHG emissions, based on the common treatment methods in North America. They evaluated this procedure with data from 16 full-scale WWTPs in Canada and applied it to all Canadian provinces. It is estimated that the main GHG emitted from Canadian municipal WWTPs is CO_2 and with very little CH_4 (Monteith, et al. 2005).

Ashrafi also came up with a suggestion for estimating GHG emissions from pulp and paper industry wastewater treatment. A dynamic model was used to develop mass and energy balances. Reactor temperature and SRT were the main operating conditions affecting GHG emissions (Ashrafi 2012).

Ashrafi et al. (2014) estimated the emissions from a treatment system consisting of aerobic, anaerobic and hybrid biological processes using a mathematical model. It was estimated that the hybrid biological process produced more GHGs than two other processes. A series of changes in the working parameters were then suggested to decrease the total emissions (Haghighat, Ashrafi and Yerushalmi 2014).

Cakir et al. (2005) analyzed GHG emissions from aerobic and anaerobic treatments. It is claimed that anaerobic treatment is favourable in the presence of a system collecting CH_4. However, aerobic treatment works better with a lower BOD (Cakir and Stenstrom 2005).

These works (Monteith 2005, Ashrafi 2012) also provided an estimation for indirect GHG emissions. Electricity for the operation of WWTP, fuel for reactor heating or transport, and such activities in the lifecycle of wastewater treatment is included in indirect GHG emission.

There are works done to measure the amount of each GHG from wastewater treatment. Daelman et al. (2013) measured all the emissions of municipal WWTP continuously for more than a year. Using two activated sludge systems, this plant generated more N_2O than the other two GHGs combined. Seasonal fluctuations in N_2O emissions were noticed. Total CH_4 and N_2O emissions were higher than indirect emissions. It is claimed that using fixed emission factors do not provide best results in estimating GHG emissions (Daelman, et al. 2013).

Wunderlin et al. (2011) measured N_2O emissions in a lab-scale batch test. They found that under aerobic conditions, N_2O generation is at its highest in the beginning, when nitrite or ammonia is the highest. It is mentioned that under anoxic condition, N_2O production is at its lowest, when there is no oxygen input and enough organic carbon in the system (Wunderlin, et al. 2012).

Park et al. (2000) also measured N_2O emissions in two lab-scale reactors. It is shown that nitrate nitrogen (NO_3^-) is the main contributor in N_2O generation (Park 2000, Tallec 2006). It is shown that in the mentioned DO range, ammonium oxidizing bacteria (AOB) transforms to nitrifier denitrification. Becoming the electron acceptor, nitrite transforms to N_2O gas (Foley, et al. 2010).

Tallec et al. (2006) performed a lab scale batch test, using urban activated sludge. It is found that the highest N_2O generation happens when dissolved oxygen (DO) is between 0.1 mg/L to 2 mg/L. It is claimed that this happens due to autotrophic nitrifier denitrification and heterotrophic denitrification. Nitrifier denitrification is mentioned to be the main source of N_2O emission (Tallec, et al. 2006).

Many works have measured CH_4 emissions from WWTPs (Daelman, et al. 2012). In developed countries, the CH_4 generated is captured and used for electricity or heating. In the absence of an advanced collection system, CH_4 emissions could be harmful for the environment and dangerous.

2.11 Conclusions Drawn from Literature Review

As shown in this section, many works have been done to estimate or measure the amount of GHGs generated by different methods used in WWTPs. Various pathways have been mentioned that cause N_2O and CH_4 emissions, yet no work has been done to measure the GHGs emitted from the SMEBR system.

It could be summarized that climate change is still a major concern and that GHG emission reduction is in the agenda of almost all the developed countries in the world. To reduce these emissions, the amount of GHG generation by each pathway must firstly be measured and only then can the best alternatives be found and used.

There is an obvious lack of data related to GHG production by WWTPs. There is no work done to measure GHGs generated by SMEBR. There is a need for updating the knowledge on GHGs generated by treatment methods.

This study focused on the measurement of GHGs from a lagoon treating municipal wastewater in the city of L'Assomption, a lab-scale MBR, and a lab-scale SMEBR. The following chapter explained the methodology used to reach these objectives.

Chapter 3: Methodology

To better understand the GHG emissions from wastewater treatment, different treatment processes were exposed to investigations. As it was mentioned in literature review, biological carbon and nutrient removal produce several by-products including gaseous forms. The type of process has a crucial impact on biogas production, due to different microbial communities involved in the process. The most abandon methods of wastewater treatment in Canada (80%) are aerated and non-aerated ponds (lagoons) which generate GHG and have problems with nutrient removal. Thus, a comparison of the biological treatment impact of the processes, starting from the most common (lagoons) to the most advanced (membrane electro-bioreactor), was conducted with respect to GHG emissions.

Therefore, it was crucial to simulate target processes in lab scale to proceed with biogas capture. Since simulation of lagoons cannot be performed adequately in a small scale, experimental work focused on the common membrane bioreactor (MBR) and the most advanced – submerged membrane electro-bioreactor (SMEBR). As it was defined in chapter 2 (2.5.4), the SMEBR modifies properties of the sludge and permits on coexistence of various microbial cultures responsible for ammonia and nitrate removal in a sole reactor. Contrary, MBR's microbial community is unable to remove nitrates. Then, it was expected that gas production in MBR and SMEBR will vary, as well as lagoons.

Subsequently, this project was done in four phases shown in Figure 3. In phase 1, the objective was to install and run lab scale MBR to collect and measure its gas production. In phase 2, the SMEBR system was installed and run. When it produced gases. samples were collected for further analyses. The third phase was conducted in the system where MBR, after reaching equilibrium was transformed into SMEBR; then, a collection of gas samples from MBR and SMEBR systems were conducted for further analyses. The fourth phase was dedicated to comparison study of all systems and commonly used lagoons.

In each phase, there were four main stages. The first stage was designing the system and its working parameters. The second stage was the acclimatization of the microbial community to the new conditions. The third stage was the closure of the system, accumulation of the gases and sample collection. The last stage was measuring the gas samples using gas chromatography.

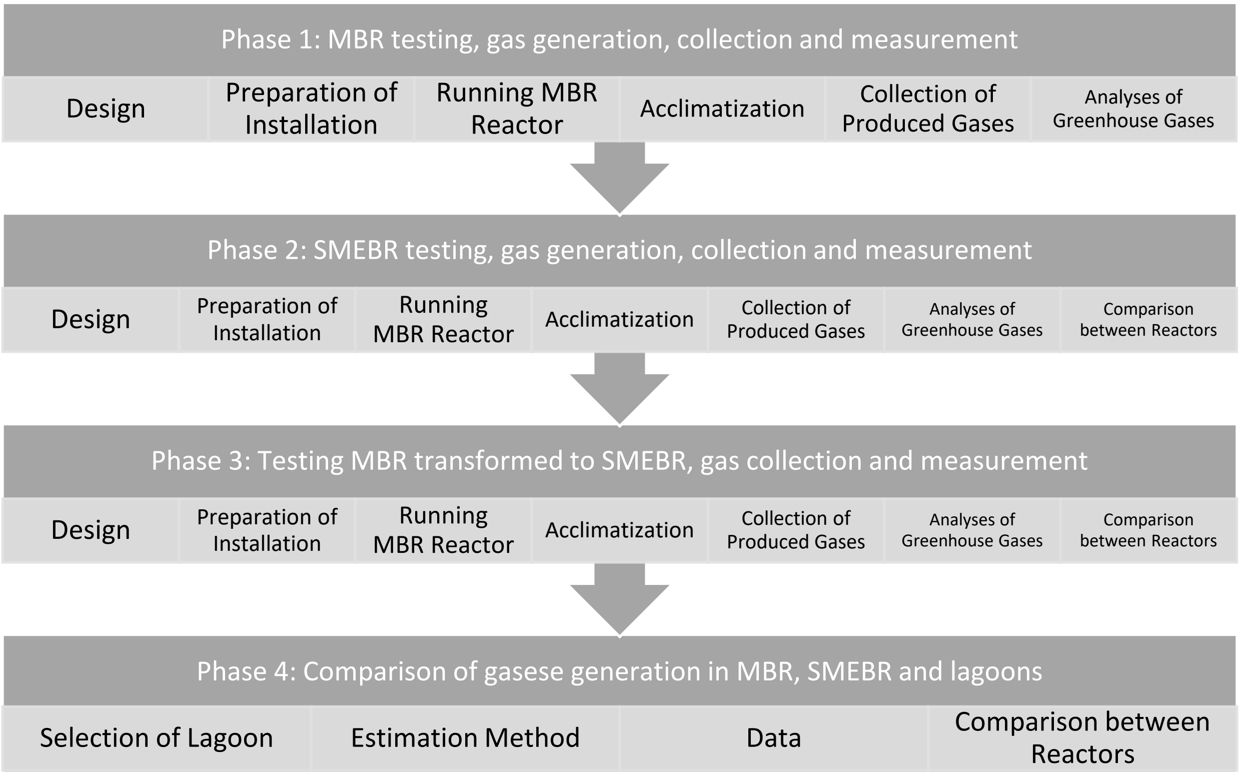


Figure 3: Summary of this study

Every phase started with designing the system. Various aspects needed to be considered, from different equipment and parts to parameters in working condition. Equipment included the structure of the reactor and the cap, pumps, pump heads, tubes, stirrer, aerators, air diffusers, membrane, electrodes, power supply and timer. Working conditions included HRT, SRT, DO, wastewater composition, air flow rate, mixing speed, current density and on/off time. Then, this design needed to be prepared and installed. Parts and equipment had to be acquired and set in place. Parameters in different equipment had to be adjusted.

After setting up the system and verifying every aspect, the system had to function continuously until reaching a steady state with efficient removal efficiency. This included preparing the synthetic wastewater, controlling different working conditions such as DO, providing enough mixing, sampling the effluent every day and doing different measurements such as COD, NH_3, total nitrogen, TKN, total and reactive phosphorous, nitrite and nitrate. These measurements were done to analyze the performance trend and achieve acceptable removal efficiency by adjusting the working conditions. Once the microorganisms were fully acclimatized, the collection of gases produced could be performed.

Collection of gases required the system closure which made different changes to working conditions. Safety measures also needed to be taken into consideration to prevent the reactor from breaking and explosions. During the gas sampling period, a non-stop monitoring of the system was needed. This could prevent incidents causing spills. It was also necessary to monitor different aspects of the system to make sure everything is going as planned.

Collection of gas samples had to be done carefully to reduce measurement errors. Gas samples were taken using a special syringe and vials. The vials were then kept in a cool and dry place until the measurement. Gas measurement was done by gas chromatography.

3.1 Phase 1: Collection and Measurement of Gases Emitted from Lab-Scale MBR

The objective of this phase was to find out the amount of N_2O, CH_4 and CO_2 generated by a lab-scale MBR. This would help in estimating the amount of GHGs produced by this method in WWTPs. To design this system, different parameters had to be considered.

3.1.1 Stage 1: Design

3.1.1.1 Influent Characteristics and Composition

To have the emissions closer to reality, and to have a better comparison of results to the actual WWTPs, the synthetic wastewater composition was based on the influent of the city of L’Assomption WWTP. Located in southwestern Quebec on the L’Assomption River, this off-island suburb of Montreal has a population of 22,430. The city’s WWTP was first designed and built in 1986. It used four lagoons with big-bubble diffusers as the only method of treatment. The plant was then upgraded in 2006 by adding a pretreatment that was built to remove the particles prior to entering the lagoons. Air diffusers were also upgraded to linear fine bubbles. The 10,000 m^3/day influent consists of 90% residential and 10% industrial wastewater. Regulations require industries in this region to have their own WWTP in place. City officials estimated 4000 tonnes of CO_2 eq/year emissions from this plant.

Figure 4: Four lagoons in the City of L'Assomption WWTP

Figure 5: Aeration in one of the lagoons

Municipality reports for four consecutive years were considered. These reports included physical and chemical characteristics of the influent, such as BOD, TKN, total phosphorus and total suspended solids. The highest amounts of COD and NH_4 were selected and would represent the worst-case scenario. Considering the diluted average influent, this selection would also allow the lab-scale reactor to maintain biological activity and growth. Choosing the average influent would also make the collection and measurement of gas emissions more difficult. Having a diluted influent, the lab-scale reactor would have emitted low amounts of gas, making it harder to detect.

The composition of synthetic wastewater was then selected to be glucose (173.1 mg/L), ammonium sulfate ($(NH_4)_2SO_4$, 96.2 mg/L) and mono potassium phosphate (KH_2PO_4, 5 mg/L). Based on the literature and previous researches conducted in the environmental lab, these compounds were found to provide the closest conditions to reality, while allowing the microorganisms in a lab-scale reactor to grow. Using this composition, the synthetic wastewater characteristics were as follows:

Table 3: Synthetic wastewater composition for all phases

Compound	Concentration (mg/L)
Ammonium Sulfate	96.15
Dextrose	173.08
Potassium Phosphate	4.62

3.1.1.2 Microbial Community

The first step for this biological reactor was to provide the microorganisms. Adding the sludge from a municipal WWTP could help to achieve the target microbial community faster and avoid having unwanted microorganisms. The sludge was brought from the city of Saint-Catherine WWTP (Figure 6).

Located in southwestern Quebec, this off-island suburb of Montreal is on the St. Lawrence River with a population of 16,762. Treating between 65,000 m^3/day in summer and 200,000 m^3/day in winter, this plant uses four aerated activated sludge systems. Around half of the influent comes from the municipality, while the other half is treated industrial wastewater. The SRT of 3 days and HRT of 1 day, this plant removes around 30% of its sludge as waste.

Figure 6: Activated sludge reactor in the City of Saint-Catherine WWTP, where the sludge was brought from

3.1.1.3 Reactor Design

The reactor active volume was set to 7 L. This was based on various parameters. The total volume of the reactor was 19 L (Figure 7). Based on the height of the membrane, 7 L was required for the membrane to be submerged (Figure 8). It was predicted that the closure of the system would affect the reactor activity by stopping the flow of fresh air with oxygen to microorganisms. Having half the volume filled could provide an oxygen buffer for biological activity. Having the system closed, this could provide a little more air for the microorganism to continue their activity as before. This would also help with the accumulation of the gases over days in that free space, replacing the oxygen.

Figure 7: Bucket used for reactors

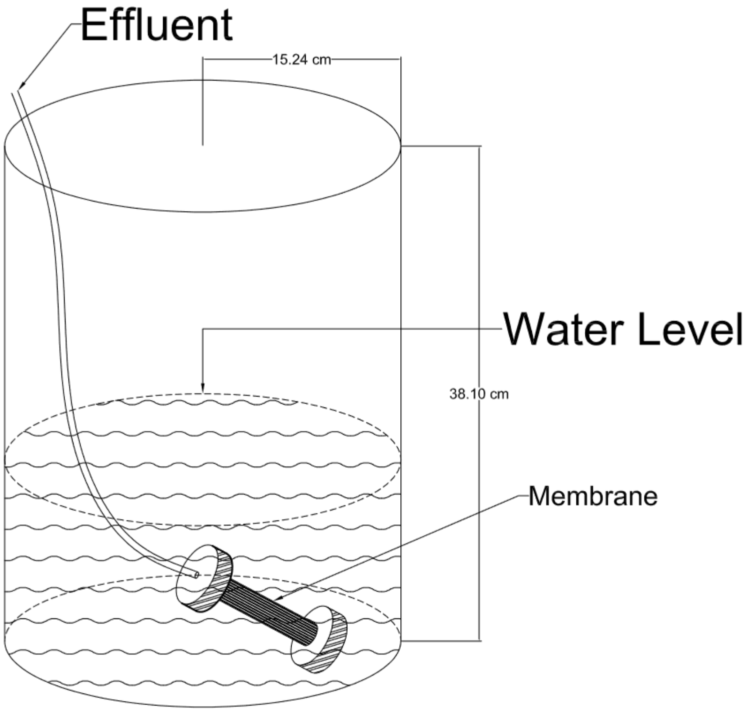


Figure 8: Design of the bucket and the membrane

The reactor was put on a magnetic stirrer to provide mixing. The speed was set to 60 rpm which was high enough to provide a homogeneous liquor inside the reactor, but not too high as to hinder biological activities (Figure 17: The design of flat electrodes and the membrane in the reactor).

The first design did not include the magnetic stirrer and relied solely on aeration for mixing. However, some zones in the reactor were noticed to have accumulated sludge. Therefore, manual mixing was needed once every day. Due to the closure of the system for days, the magnetic stirrer was put below the bucket to improve mixing, when inside the reactor was not accessible.

A valve was designed and put at the bottom of the reactor. It was used to remove liquor from the reactor to control solid retention time (SRT). A safety valve was also designed and added to the top side of the reactor. This would prevent the overflow of the reactor due to malfunctions affecting the effluent (Figure 11: PVC cap, with designed holes). This was designed after spills overflowing the reactor had occurred from the malfunctioning of the effluent pump or membrane fouling.

3.1.1.4 Reactor Working Parameters

Based on the literature (Hassan 2011) and the city of L'Assomption municipality reports, the mixed liquor suspended solids (MLSS) was set to 5500 mg/L. The hydraulic retention time (HRT) was set to 1 day and the flow rate would then be 7 L/day. The solid retention time (SRT) was set to 14 days in the beginning, reduced to 7 days as microorganisms' activity increased. These parameters have been worked with before in the environmental lab, and proven to provide favourable conditions to microorganisms.

The DO in the system was decided based on the literature (Gao 2014). The amount of oxygen in the reactor was decided based on the carbon to nitrogen ratio of the synthetic wastewater. Gao shows that in the carbon to nitrogen ratio of 3:1, the highest removal in a lab-scale MBR system happens in DO of 2-4 mg/L.

3.1.2 Stage 2: Preparation of Installation

The bucket was put on the stirrer, and the magnet was set in place. Around 4 L of tap water was added to the reactor. Air diffusers were connected to an air flow divider and to the air inlet. The airflow divider helped the flow of air to be evenly distributed between the diffusers. Then, they were put towards the reactor wall, away from each other. The flow was controlled by the airflow inlet. These air diffusers provided a minimum aeration until the microorganisms were fully revitalized. The aeration also helped the mixing.

The sludge brought from the WWTP was kept in the refrigerator to preserve its characteristics. Before adding to the reactor, the sludge had to be revitalized. It was poured in a beaker mixed with the synthetic wastewater and high aeration until DO reach 1 mg/L and the colour was changed from black to brown. This could take between 24 and 48 hours. Then, it was poured slowly to the reactor. Tap water was added until the active reactor volume is 7 L.

The influent and effluent was set to 7 L/day. The flow was provided using Cole-Parmer Masterflex L/S pumps, Cole-Parmer Masterflex Easy-Load pump heads and Masterflex tubes. Double-tube heads were selected to have the exact influent and effluent flow in the system. It also helped to prevent spills in case of an issue with pumps.

Two barrels were put below the pumps to provide adequate space for synthetic wastewater and effluent.

The air flow rate was adjusted by DO. DO was measured often by Orion™ RDO™ Dissolved Oxygen Probe and Thermo Scientific™ Orion Star™ A223 Dissolved Oxygen Portable Meter. It was controlled by the airflow inlet valve to reach a DO of 2-4 mg/L in the reactor.

3.1.3 Stage 3: Running MBR Reactor

The objective to reach an acceptable level of nutrient removal was not only to represent the reality in WWTPs, but also to be able to collect and measure GHGs. If the microorganisms had not been removing the nutrients, no emissions would have taken place.

In each phase, microorganisms were given enough time to get used to the new working conditions. Microorganisms with favourable conditions could grow and reproduce and become the dominant microbial community in the reactor.

Synthetic wastewater was made every four days to provide a fresh influent to the system. The ingredients were first weighed and mixed in a 1 L beaker using a magnetic stirrer. Then, it was poured into the barrel with tap water. Fifty-two liters of synthetic wastewater was created every time. The synthetic wastewater barrel needed to be properly cleaned to prevent the accumulation of unwanted bacterial communities. Influent and effluent tubes had to be cleaned every week to prevent bacteria forming inside them.

The membrane had to be taken out of the system and cleaned every couple of days to prevent fouling. With microorganism growing, sludge covered the membrane. It had to be washed often with water.

To achieve the target TSS, mixed liquor was taken out to maintain SRT. Liquor was removed every couple of days from the bottom valve of the reactor.

Measurement including COD, NH_3, PO_4, NO_2, NO_3, TKN, TN and DO were performed often to see the activity trend. DO was measured using the DO probe. If needed, air flow rate was adjusted accordingly. Other measurements were done using HACH vials, TNT series. These measurements showed the status of the reactor, which reactions were happening, and provided a trend. This trend could then show if the reactor has reached its steady state.

3.1.4 Stage 4: Acclimatization

After 70 days, the removal of nutrients reached an acceptable level. The results are summarized in the Table 4.

Table 4: DO measurement in MBR, phase 1

Date	Dissolved Oxygen (mg/L)
4/6/2019	0.91
4/7/2019	4.58
4/9/2019	1.35
4/14/2019	0.16
5/1/2019	3.5
5/7/2019	4.33
5/10/2019	4.23
5/15/2019	4.07
5/16/2019	0.33
5/19/2019	1.52
5/25/2019	5.11

Table 5: Concentrations of COD and NH_3 in the MBR effluent, phase 1

Date	NH_3-N (mg/L)	COD (mg/L)
3/30/2019	20.6	44.8
4/6/2019	24.3	74.4
4/14/2019	18.1	42.3
4/16/2019	26.2	17.4
4/17/2019	27.7	50.1
4/18/2019	28.4	72
5/1/2019	24.9	35.1
5/7/2019	25.1	23.8
5/10/2019	17.4	18.5
5/19/2019	9.56	90.7
5/25/2019	8.84	60.3

Table 6: Concentrations of TKN, total nitrogen, NO_3 and NO_2 in the MBR effluent, phase 1

Date	TKN (mg/L)	Total Nitrogen (mg/L)	NO_3-N + NO_2-N (mg/L)
3/30/2019	23.3	23.3	0.088
4/6/2019	26	26.2	0.15
4/14/2019	20	20.6	0.512
4/16/2019	26.4	26.8	0.368
4/17/2019	29	30.8	1.886
4/18/2019	29.4	29.6	0.286
5/19/2019	15.3	17	1.68

During this period, synthetic wastewater was prepared. Tubes had to be cleaned every week to remove the bacteria forming inside them. The membrane often needed to be cleaned to prevent fouling. A sample of the mixed liquor was taken out of the reactor and was replaced by water to achieve the target SRT.

3.1.5 Stage 5: Collection of Produced Gases

To measure the gases generated by the reactor, the system was closed and sealed. Influent and effluent flow was continued. However, the aeration was stopped, and aerators were removed from the system. Having the aeration in the sealed system could have resulted in not only cracks and explosion but also dilution of the accumulated gas in the reactor. This would have made emission measurements impossible.

Having the reactor sealed with no aeration for microorganisms except the limited air in the system could result in reduced removal efficiency. To compensate for the loss of air and less mixing by air diffusers, a recycle flow was designed. It took the air from the top and inserted it at the bottom of the reactor (Figure 9). While this design could not provide enough air for microorganisms, it helped with the mixing and with dissolving the available air.

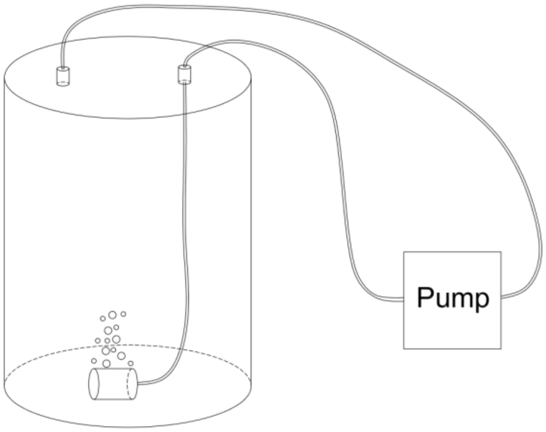


Figure 9: Design of air recycle system

Another pathway to increase the DO inside the reactor was through the influent. The synthetic wastewater, once made, had a dissolved oxygen of 9-10 mg/L. This could compensate for the lack of dissolved oxygen in the liquor. Therefore, the synthetic wastewater was made fresh every day to be rich in DO when entering the reactor.

An airlock was designed as a safety measure. It prevented cracking in the reactor from high or low air pressure. It was also used to monitor the rate of air generation or consumption. A narrow long tube was inserted through the top seal of the reactor. Then, a few millilitres of water were added to the tube to work as a blocker. The tube was then hung by the side of the reactor, making the water work as a meter to the air pressure. This airlock was then used to verify the reactor’s air seal. Having a complete air seal, the water level in the lock would change by pushing the reactor in.

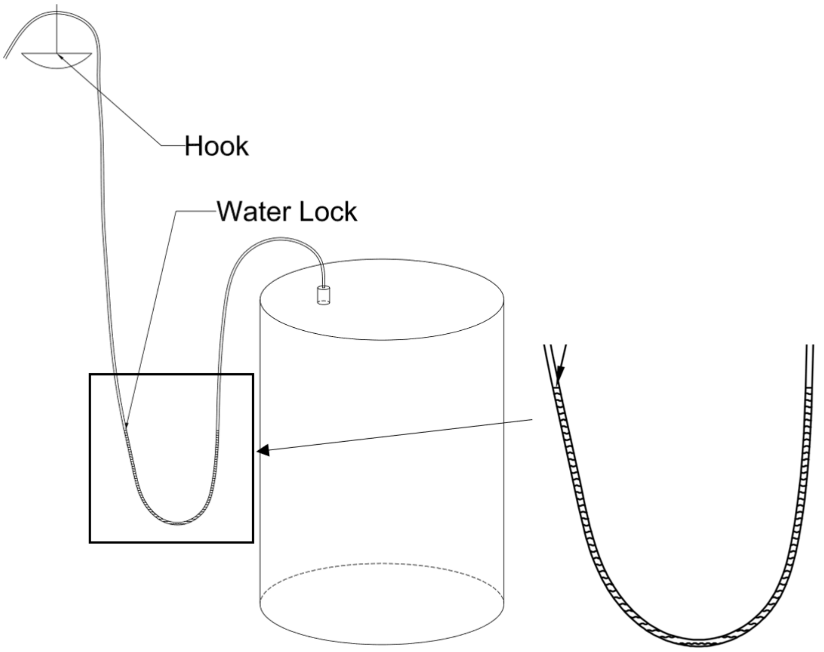


Figure 10: The design of the air-lock system

The top seal consisted of a PVC cap with holes for tubes to provide air or water flow. This cap was designed thick enough to withstand the pressure. It was then screwed to a metal ring wrapped around the reactor. A ring was used to make the seal complete between the bucket and the cap. Four tubes were passed through the cap: influent, effluent, air recycle and airlock. Rest of the holes and valves were sealed by silicone.

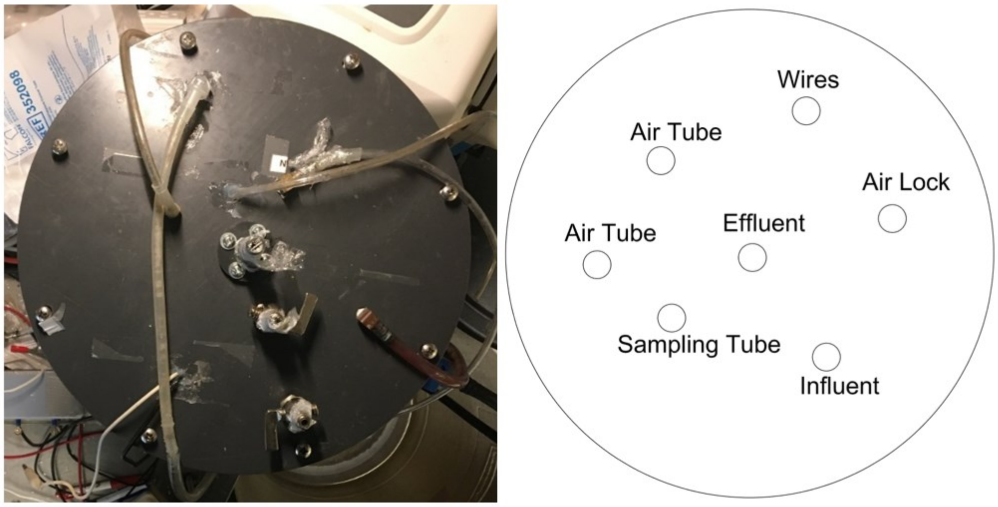


Figure 11: PVC cap, with designed holes

The collection of samples was done in four consecutive days. The first day was for the gases to accumulate. Then, one sample was taken every day for three days. Collection of gas samples should have been done in a few days. Closing the reactor would affect the biological activity due to the lack of oxygen, causing nutrient removal to decrease. However, to have reliable results, at least three samples per phase were required.

The samples were taken with a syringe and inserted into vacuumed vials made especially for gas chromatography (GC). One sample and one duplicate sample were taken every day. Labco Exetainer® 12ml vials, flat bottom, evacuated and with DW cap vials were used. These samples were then kept in a cool and dry place, in room temperature until performing GC. The temperature and air pressure inside the reactor were recorded at sampling for further analyses.

Figure 12: Vials used for gas sampling

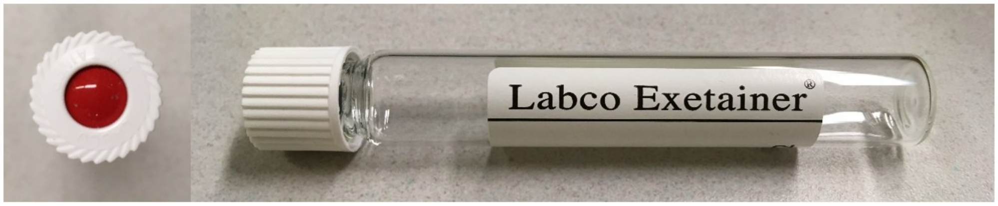


Figure 13: Vials and special caps used for gas sampling

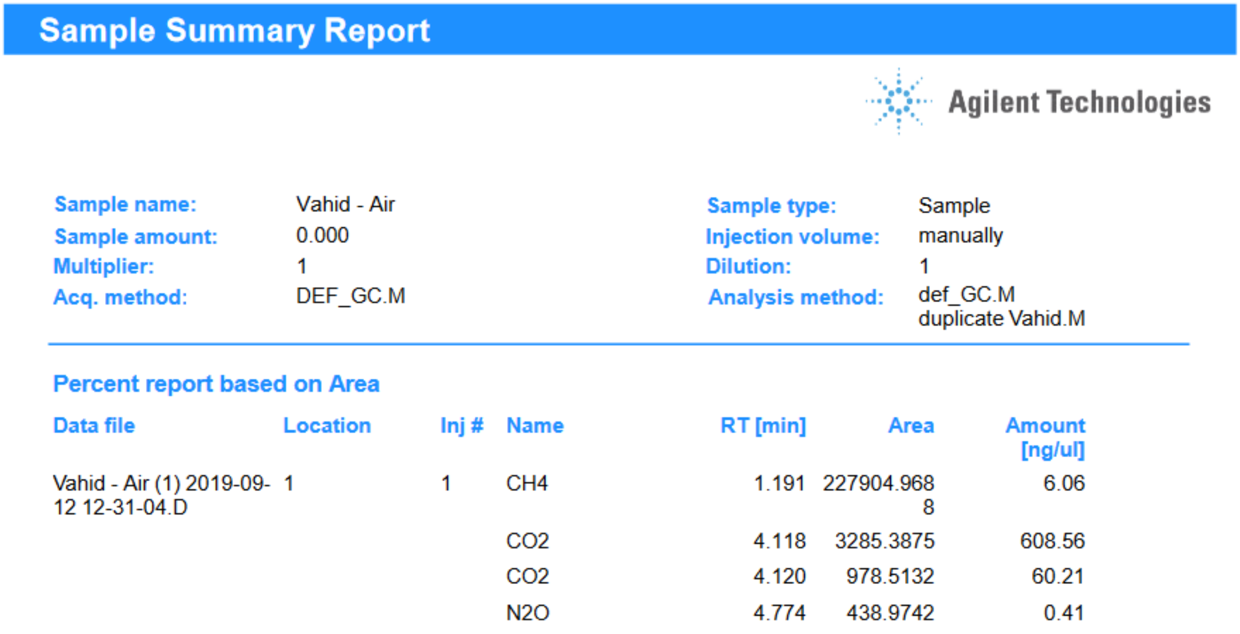
3.1.6 Stage 6: Analyses of Greenhouse Gases

The samples were then analyzed by gas chromatography. Agilent Technologies 7890B GC system was used. It uses Retention Time Locking to maintains exact retention times, Capillary Flow Technology to provide unique instrument capabilities, Single filament TCD, and auto-ranging FID to detect and quantitate from parts per billion to parts per thousand in a single injection. This device was adjusted by the manufacturer to measure three main GHGs; CO_2, N_2O and CH_4. A special standard gas cylinder was also provided by the manufacturer to use as blank samples during measurements.

The machine was run by a method created by the manufacturer tailored to measure GHGs. This method includes all the parameters and calibration techniques. The chromatograph used a software to communicate with the connected computer. This software notifies the chromatograph about the sample's characteristics such as samples sequence or dilution. It also identifies the blank and standard samples and runs the calibration.

The sample's details such as name, date and dilution were entered in the software that runs the gas chromatography. Then, the samples were injected using a special syringe through an airtight inlet. This metal syringe with a glass container uses a valve in the top of the needle to control the air flow. The gas was inserted until air bubbles were seen coming out of the gas outlet. This showed that the amount of the gas inserted into the equipment was enough for the measurements. However, as a rule of thumb and based on the training given by the manufacturer technician, 30 mL of gas was inserted for each measurement.

Each run took around eight minutes. The machine then generated the results including calibration curves, standard deviation, retention time, area and correlation coefficient. Figure 14 shows the sample summary report of the gas chromatography. These results show the retention time, area and amount of each gas based on calibration curves and calculations shown in Figure 15. These results show the details of gas chromatography results such as columns used for each gas and exponential retention time.



Sample Summary Report

Agilent Technologies

Sample name:	Vahid - Air	**Sample type:**	Sample
Sample amount:	0.000	**Injection volume:**	manually
Multiplier:	1	**Dilution:**	1
Acq. method:	DEF_GC.M	**Analysis method:**	def_GC.M duplicate Vahid.M

Percent report based on Area

Data file	Location	Inj #	Name	RT [min]	Area	Amount [ng/ul]
Vahid - Air (1) 2019-09-12 12-31-04.D	1	1	CH4	1.191	227904.9688	6.06
			CO2	4.118	3285.3875	608.56
			CO2	4.120	978.5132	60.21
			N2O	4.774	438.9742	0.41

Figure 14: Sample report created by gas chromatography

Compound: CH4
Signal: TCD3C
Exp. RT: 1.219
Corr. Coeff.: 1.000000
Residual: 0.00000
RF RSD%:
Formula: y = ax + b
a: 37607.94688
b: 0.00000
c: 0.00000
d: 0.00000

Compound: CO2
Signal: ECD2B
Exp. RT: 4.121
Corr. Coeff.: 1.000000
Residual: 0.00000
RF RSD%:
Formula: y = ax + b
a: 16.25257
b: 0.00000
c: 0.00000
d: 0.00000

Compound: N2O
Signal: ECD2B
Exp. RT: 4.738
Corr. Coeff.: 1.000000
Residual: 0.00000
RF RSD%:
Formula: y = ax + b
a: 1079.33118
b: 0.00000
c: 0.00000
d: 0.00000

Figure 15: Sample calibration by gas chromatography

3.2 Phase 2: Collection and Measurement of Gases Emitted from Lab-Scale SMEBR

The objective of this phase was to find the amount of N_2O, CH_4 and CO_2 generated by a lab-scale SMEBR. This could help the estimation of the GHG emissions from WWTPs using this method. To design a SMEBR system, a few more parameters compared to MBR had to be considered.

3.2.1 Stage 1: Design

Various parameters in designing and operating this system were as it was from the MBR system. This reactor was set up in the same space. Same pumps, membrane, magnetic stirrer and air diffusers were used. Physical parameters including reactor active volume, HRT and stirrer speed stayed the same. The chemical parameters such as the composition of synthetic wastewater, SRT, DO and temperature were kept the same.

Having most of the parameters be the same as the MBR system, the comparison of the gases generated in each method would provide more insight. This could reveal the amount of GHG produced by these two methods under the same working conditions. However, a few parameters had to be considered.

3.2.1.1 Electrodes

First, electrodes needed to be designed. Based on the literature and previous studies done in this research group, it was found that perforated aluminum and perforated stainless steel are the best options to use as the anode and cathode respectively.

The shape and size of the membranes needed to be decided. Previous works have been done with both circular and flat electrodes. Depending on the reactor shape, each type of electrodes can provide a better removal efficiency. Circular electrodes work better in circular electrodes due to their coverage of the whole reactor. Whereas flat reactors have proven to work better in square reactors. They also work better if coupling multiple electrodes are required. Another advantage of the flat electrodes would be the simultaneous replace time. Due to the different size of the electrodes in the circular type, they need to be replaced once the smaller electrode closer to the centre of the reactor is corroded.

Circular type of electrodes was first considered. They provided a good removal efficiency. However, they left a small space for the membrane in the centre of the reactor. This would have been the best option if the air diffusers could have provided enough mixing. Because of the presence of the magnetic stirrer at the centre of the reactor, the membrane could not be placed there. Realizing the need to use a magnetic stirrer, flat electrodes were chosen.

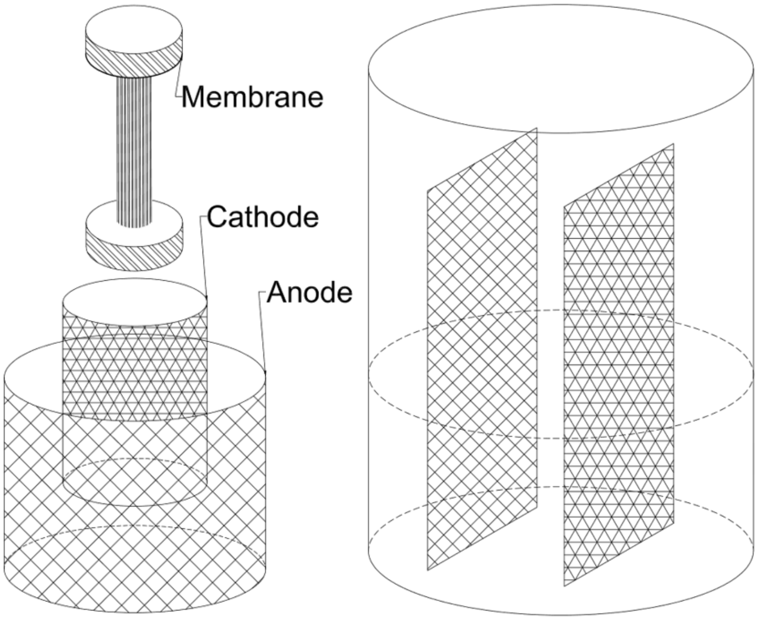


Figure 16: Design of circular and flat electrodes

3.2.1.2 Current

Based on the previous works done (Hassan 2011), (Ibeid 2011), current density of 15 A/m^2 was selected. This amount of current density has proven to provide the best removal efficiency in lab-scale biological reactors, while being safe for microorganisms. Then, the current density had to be calculated based on the surface area of the electrodes. Due to the electrode's perforation, the actual surface area had to be reduced based on the holes' size. The height of the liquid in the reactor had to be chosen as the height of the surface area of the electrode. The calculation of the current is as follows:

Area: 15 cm width x 11 cm height = 165 cm^2
165 cm^2 x 40% non-perforated = 66 cm^2
66 cm^2 x 15 Amp/m^2 x 1 m^2 / 10,000 cm^2 = 0.099 Amp ≈ 0.1 Amp

A timer was necessary to provide an intermittent current. The electrical timer is an essential part of the SMEBR system. Microorganisms cannot operate and will die if there is a constant exposure to the current. The interval of 5 minutes ON and 20 minutes OFF was selected based on previous research (Ibeid 2011).

The power supplies GWINSTEK GPR-11H300 and BK PRECISION 1902 were used. Constant current density was selected

Stage 2: Preparation of Installation

In addition to the parts and equipment in place from the MBR system, items were needed for the electrical system. Electrodes were cut and put in the reactor. To keep the distance between them at 5 cm, wooden sticks were used. The membrane was put behind the electrical zone, so that it stays intact from the current. The power supply had to be set up and adjusted to provide the target constant current. The timer was connected to the current to provide the on and off time.

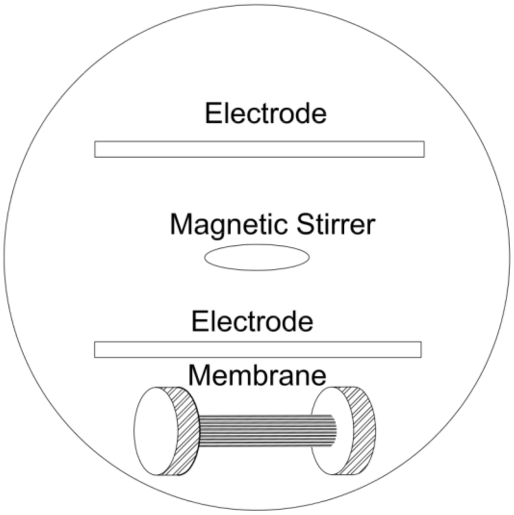


Figure 17: The design of flat electrodes and the membrane in the reactor

3.2.2 Stage 3: Running the SMEBR Reactor

Like the process of MBR, acclimatization of microorganisms to new conditions was required. This time was necessary for microorganisms to get used to the electrical current in the reactor. With the presence of the current, new microorganisms had the chance to take over the dominant ones in the MBR system.

Same measures were taken to place to achieve the steady state. Synthetic wastewater was created every four days. Cleaning of barrels, tubes and the membrane continued. However, membrane cleaning was needed less often due to the presence of electrical current and its impact on fouling reduction. Also, electrodes were required to be cleaned every few days to prevent bacteria and oxides forming on them.

The power supply needed to be checked often. With sludge moving always and constant current, the voltage would change all the time. Every week, the voltage needed to be adjusted, so the current density stayed the same.

Measurements were done to see the trend of the different elements in the reactor. It helped to adjust different parameters and monitor the system. Mixed liquor was replaced with tap water to achieve the objective SRT. Measurements were done until the reactor reached a steady state.

3.2.3 Stage 4: Acclimatization

After running the system with these conditions for 35 days, the nutrient removal efficiency reached the acceptable levels. The results are presented in Table 7.

Table 7: Concentration of NH_3 and COD in the SMEBR effluent, phase 2

Date	NH_3-N (mg/L)	COD (mg/L)
7/15/2019	14.7	25.1
7/25/2019	18.4	76.1
7/31/2019	9.27	56.2
8/5/2019	9.09	24.2

3.2.4 Stage 5: Collection of Produced Gases

The system was closed and sealed similar to the MBR system. Same steps were taken for this stage. In addition to available flows in the cap, the current had to pass with wires. The hole was then sealed with silicone, and it was tested by the airlock.

The reactor was closed and sealed for four days. The first day was for the accumulation of the gases, and three samples were taken every day. Samples were kept in a cool and dry place, in room temperature, until further analyzes.

3.2.5 Stage 6: Analyses of Greenhouse Gases

The measurement of the samples was done by the same method and equipment.

3.3 Phase 3: Collection and Measurement of Gases Emitted from Lab-Scale MBR and SMEBR

The MBR and SMEBR lab-scale reactors were both analyzed separately. Both systems were given enough time, so that the microbial communities could get used to the new conditions. In this phase, the objective was to find out how the microbial community present in the MBR system would perform after changing the conditions to SMEBR, without enough time to acclimatize.

This process could show how a stable MBR system would perform after a sudden introduction of the current. It would reveal the effects of an electrical current on the performance of acclimatized microorganisms. These results could be used to predict the performance of an existing WWTP, upgrading their MBR systems to SMEBR.

It could also show the difference between the amounts of gas produced from the same microbial community under different conditions. In phase 1 and phase 2, microbial communities were given enough time to adapt to the new conditions. Then, microorganisms with more compatibility to those conditions would grow and reproduce, leaving the less compatible organisms dead. The microbial community and the conditions would match. Therefore, a comparison could be discussed considering the difference of microorganisms. But this phase would make a direct comparison of the amount of gases possible.

3.3.1 Stage 1: Design

Another objective of this phase was to see how the results would change by doubling the active reactor volume. Having the active volume of 7 L, these two small lab-scale reactors were vulnerable by minor changes in the working conditions. When the systems were closed to collect gas samples, they could not continue the removal due to the lack of oxygen. After the system closures, COD and NH4 removal efficiencies decreased in both systems. So, the emissions for three consecutive days were not consistent and could not reflect the reality. However, a reactor with more active volume could withstand these changes better, continuing the removal process.

Having a larger active volume, there could be less space for the gases to accumulate. Therefore, the safety of the system was of concern. After discussing with the technician who made this reactor, he confirmed that this system could withstand high pressure and expansion, but compressions could cause cracks. Also, the airlock would show the increase in the pressure and prevent the explosion. The tube of the airlock was changed with a longer tube to provide more space before the water in the airlock would overflow.

3.3.2 Stage 2: Preparation of Installation

The parts and equipment from the previous methods stayed in place. The same sludge was used in this reactor. However, with reactor active volume at 14 L, the flow rate was changed to 14 L/day. This needed the synthetic wastewater to be prepared every three days. Same cleaning and maintenance were needed for barrels, tubes, the membrane and electrodes.

The electrodes and electrical system stayed in place. This was because the transformation from MBR to SMEBR was supposed to happen when the system was closed.

3.3.3 Stage 3: Running the MBR & SMEBR Reactor

Like previous phases, acclimatization of microorganisms to new working conditions was necessary. HRT and SRT stayed the same. However, reactor active volume was doubled. This also required a higher airflow. The microbial community needed time to get used to these new conditions. Mixed liquor was removed to reach the target SRT.

Same measurements were done to help analyzing the reactor. These measurements showed the current status of the reactor, and dominant microbial communities removing the pollutants. To know the present microorganisms better, the LIVE/DEAD™ BacLight™ Bacterial Viability Kit test was used. The standard procedure for this test was used. The main objective of this test is to see if the bacteria are alive and active. Its results proved the presence of active organisms in the reactor. Because this test was not an objective of this work, and it was solely to analyze the organisms in the reactor, its results are provided in Figure 18.

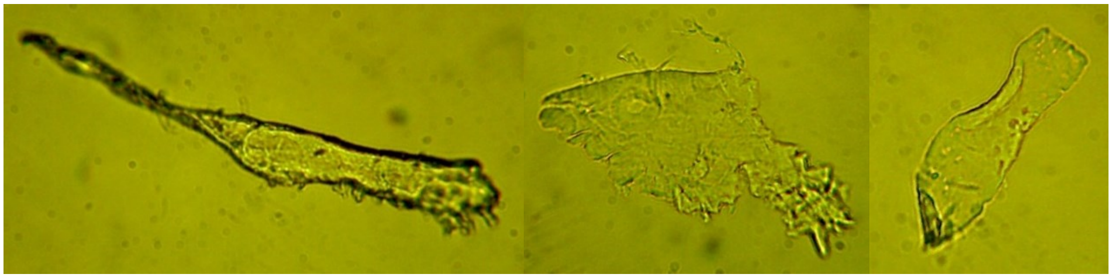


Figure 18: Three results from BacLight test

3.3.4 Stage 4: Acclimatization

Like the previous phases, acclimatization of microorganisms to new conditions was required. In this stage, microorganisms matching the MBR conditions were forming. After running the system with these conditions for 120 days, the nutrient removal efficiency reached the acceptable levels. The results are presented in Table 7.

Table 8: Concentration of NH3 and COD in the MBR and SMEBR effluent, phase 3

Date	NH_3-N (mg/L)	COD (mg/L)
9/10/2018	36.2	70.4
9/18/2018	31.3	62.8
9/25/2018	22.4	40.7
11/7/2018	39.1	51.2
11/14/2018	18.8	22.3
1/10/2019	22.7	27.8

3.3.5 Stage 5: Gas Collection and Sampling

Like previous phases, the system was closed and sealed. The electrodes were placed inside the reactors with wires connected, but without a current. The gas sampling process was decided to be three days of accumulation by the MBR system, followed by three days of sampling. On day seven, the electrical current was connected. After one day of gas accumulation, three samples were taken for three days. A constant monitoring of the system was necessary to prevent any incident and control the procedure. Samples were taken at the end of each day and kept in a dry place and room temperature.

3.3.6 Stage 6: Analyses of Greenhouse Gases

Same method and equipment were used to measure the gas samples.

3.4 Phase 4: Comparison of All Phases Treatment Methods with Lagoons

In this phase, a study was done to compare the results of GHGs produced by lab scale reactors and GHGs estimated from a lagoon. This comparison could shed light on gaseous-form by-products of wastewater treatment activities.

3.4.1 Stage 1: Selection of Lagoon

The lagoons in the city of L’Assomption WWTP were selected. Four aerated lagoons are the main treatment method in this plant. Since the composition of wastewater for three other phases was based on this plant annual reports, and the data was available, this plant was used. This selection would benefit the comparison of results.

3.4.2 Stage 2: Estimation Method

To estimate the GHG emissions from this plant, the method was selected from IPCC guidelines. This method is also used by Environment Canada to prepare national inventory reports. In this study, IPCC 2006 and 1996 guidelines were followed. These guidelines are used by most of the countries in the Paris agreement to estimate their national inventory reports. They are prepared by the committee in the IPCC to provide a solid estimation method. They are based on various parameters, depending on the availability of data. In this study, the method used by Environment Canada was selected. It is based on the level of organic in the influent.

As mentioned in the literature review, CO_2 emissions are excluded from these estimations due to their biogenic source.

3.4.3 Stage 3: Data

To find the organic levels in the wastewater, this method uses a per capita basis. Therefore, most of the parameters in this estimation was obtained from Statistics Canada. The rest of the parameters such as different factors were selected from Canada National Inventory Report 2016.

Chapter 4: Results and Discussion

In this chapter, the results of each phase are presented. For phases 1, 2 and 3, the performance of each reactor is discussed first. Then, the results of gas analyses are presented. Then, the results of phases are compared. Phase 3 results are compared from stage 1 to stage 2, and they compared to phase 1 and 2. In phase 4, greenhouse gas (GHG) emissions from the city of L'Assomption wastewater treatment plant (WWTP) is estimated. Then, the results from each phase are compared to have a better understanding of the impact of these methods on the environment.

4.1 Phase 1: Analyses of Greenhouse Gases in MBR Reactor

The objective of phase 1 was to investigate the GHGs produced by the MBR reactor. After the installation of the system, the MBR reactor was run to reach its steady state. The acclimatization of microorganisms and achieving the steady state was the first step in GHG investigations. The concentrations of carbon and ammonia in effluent were measured systematically over the period of entire investigations until the period of gas collection.

Table 9: Concentrations of COD and NH3 in the MBR effluent, phase 1

Date	**COD (mg/L)**	NH_3**-N (mg/L)**
Influent	191.8	30.7
3/30/2019	44.8	20.6
4/6/2019	74.4	24.3
4/14/2019	42.3	18.1
4/16/2019	17.4	26.2
4/17/2019	50.1	27.7
4/18/2019	72	28.4
5/1/2019	35.1	24.9
5/7/2019	23.8	25.1
5/10/2019	18.5	17.4
5/19/2019	90.7	9.56
5/25/2019	60.3	8.84

The COD concentration in the influent was set at 200 mg/L, and NH_3 was set to 30 mg/L. The COD concentrations fluctuated based on the amount of aeration in the system. DO being set to 1-2 mg/L, The COD concentration stabilized after two months of running. The NH_3 concentration also fluctuated, but the reactor reached 71.4% removal after two months.

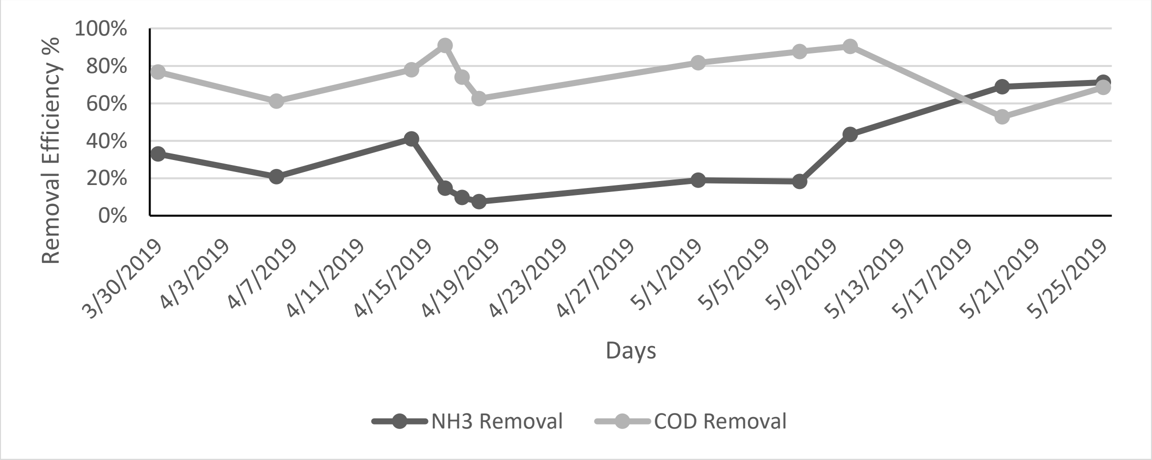


Figure 19: COD and NH_3 removal efficiency in the MBR, phase 1

The system was then closed to capture the gases generated by this method. The samples collected were measured by gas chromatography. As mentioned in methodology, day 1 was for only for the accumulation of the gases. The collection of gases continued for additional three days. In each day, three samples were taken for measurements and mean of such measurements was reported (Table 10).

The standard error of the mean for each day of sampling was calculated and provided in this table. The standard error is the standard deviation of the sampling distribution. It equals to standard deviation divided by the square root of the sample size.

4.1.1 Results of Gas Chromatography Analyses

Gas chromatography provided the concentration of CH_4, CO_2 and N_2O in each of the samples in mg/L. In these results, day 2, 3 and 4 are the first, second and third day of measurement.

Table 10: Gas chromatography results in the MBR, phase 1

Phase 1	**Day 2 Sample**	**Day 2 Duplicate 1**	**Day 2 Duplicate 2**	**Day 2 Mean**	**Day 2 Standard Error**
CH_4 (mg/L)	5.6	5.83	5.84	5.76	0.08
CO_2 (mg/L)	21698.45	21041.03	17817.90	20185.79	1199.06
N_2O (mg/L)	40.84	11.79	15.28	22.64	9.16

Phase 1	**Day 3 Sample**	**Day 3 Duplicate 1**	**Day 3 Duplicate 2**	**Day 3 Mean**	**Day 3 Standard Error**
CH_4 (mg/L)	5.71	5.77	5.77	5.75	0.02
CO_2 (mg/L)	43139.69	37269.1	33086.07	37831.62	2915.83
N_2O (mg/L)	8.06	3.02	5.04	5.37	1.46

Phase 1	**Day 4 Sample**	**Day 4 Duplicate 1**	**Day 4 Duplicate 2**	**Day 4 Mean**	**Day 4 Standard Error**
CH_4 (mg/L)	5.65	5.7	5.72	5.69	0.021
CO_2 (mg/L)	54543.94	47966.34	44291.24	48933.84	2998.97
N_2O (mg/L)	3.4	1.21	2.55	2.39	0.64

As seen in Table 10, the concentration of CH_4 stayed the same decreasing from 5.76 mg/L to 5.69 mg/L. Howeve, the concentration of CO_2 increased drastically. It was at 20,185.79 mg/L in day 1, and it increased to 48,933.84 mg/L. The concentration of N_2O was high in the beginning, at 22.64 mg/L. But it decreased sharply at the end of the experiment to 2.39 mg/L

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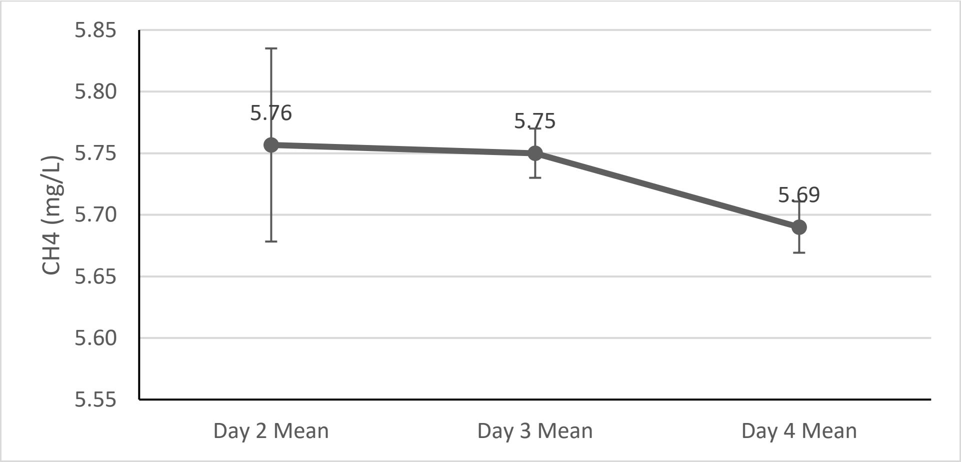

Figure 20: CH_4 concentration in the MBR, phase 1

The concentration of CH_4 stayed the same. This can show that the MBR system does not produce CH_4 gas. However, the concentration of CO_2 increased by 151% from day 2 to day 4. On average, the concentration of CO_2 increased 63% every day. On the other hand, the concentration of N_2O decreased by -91% from day 2 to day 4, averaging by -69% per day show in Figure 22.

The average increase or decrease in the concentration is calculated by:
(Concentration in day 4 - concentration in day 2) / (4 – 2)

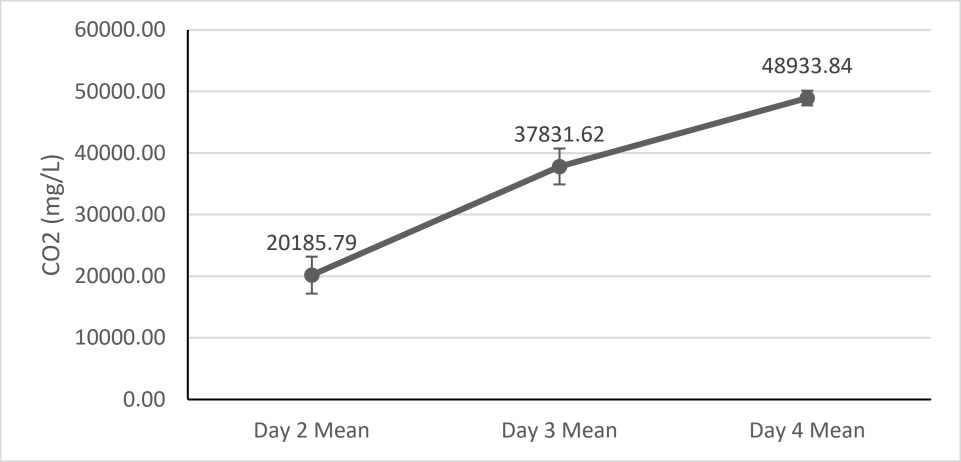

Figure 21: CO_2 concentration in the MBR, phase 1

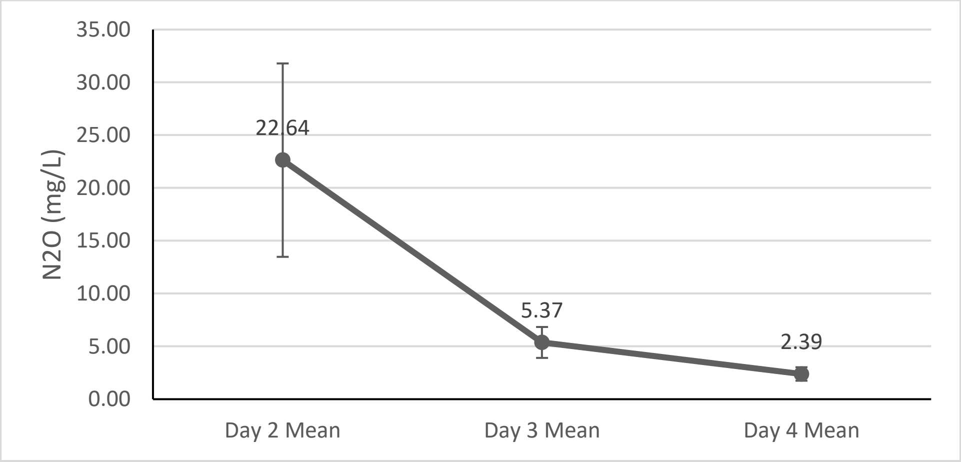

Figure 22: N_2O concentration in the MBR, phase 1

In order to have a better understanding of the results, COD and NH_3 in the effluent need to be considered. This can help better understand not only the removal efficiency of the reactor, but also the reason behind the amount of gas produced by the reactor. For example, if a reactor does not provide an efficient NH_3 removal, N_2O production will not be expected.

Table 11: NH_3 and COD concentration in the MBR effluent, phase 1

Measurement	Influent	Day 1	Day 2	Day 3	Day 4
COD (mg/L)	176	20.7	18	16.2	17.4
NH_3 (mg/L)	30.7	9.26	10	12.3	14.1

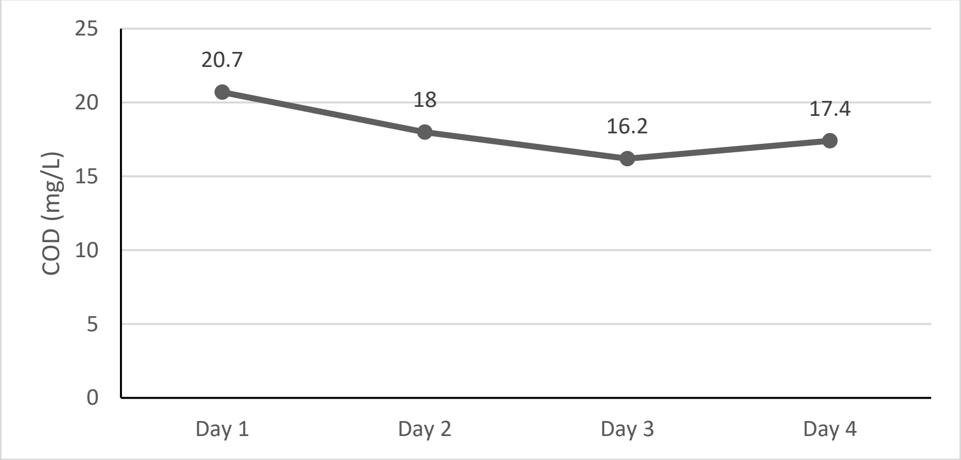

Figure 23: COD concentration in the MBR effluent, phase 1

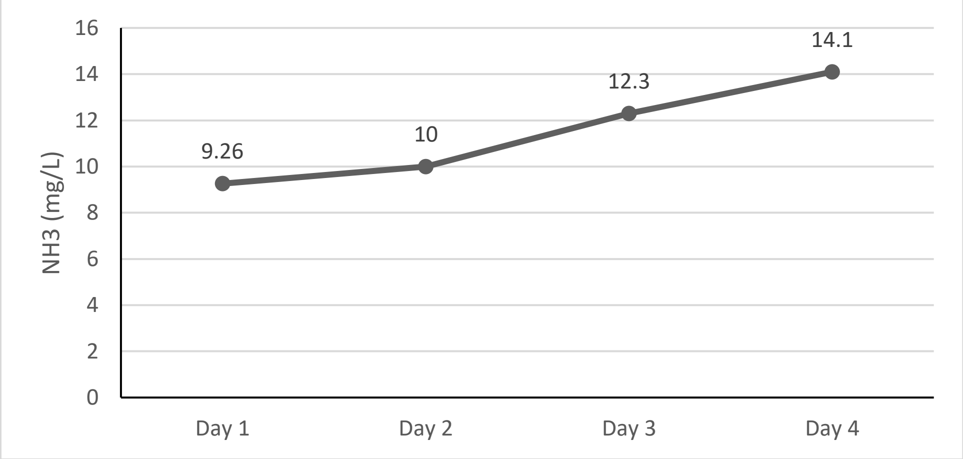

Figure 24: NH_3 concentration in the MBR effluent, phase 1

COD removal stayed consistent from day 1 to day 4. This shows that the reactor has reached its steady state in COD removal. Also, this could also mean that the bacterial community removing COD was not affected by the system closure and lack of dissolved oxygen. This constant trend of COD removal shows the reason behind the constant increase in CO_2 production.

As mentioned in the literature review, COD removal can impact the amount of CO_2 generated by the biological reactor. The equation can be simplified as (Zhan, Hu and Wu 2015):

$$\text{Organic Matter} + O_2 + \text{Nutrients} \rightarrow \text{New Cells} + CO_2 + H_2O \qquad [19]$$

NH_3 removal decreased from 70% to 54%. This could explain why N_2O generation decreased. It might be due to the decrease of nitrifying bacteria activity, because of the lack of dissolved oxygen. While nitrifying bacteria were inactive, denitrifying bacteria had an opportunity to use the remaining nitrite and nitrate in the system. Therefore, N_2O generation decreased due to the denitrification process. Below are the reactions taking place during nitrification and denitrification processes.

$$1/6\ NH_4^+ + 1/4\ O_2 \text{ -> } 1/6\ NO_2^- + 1/3\ H^+ + 1/6\ H_2O \qquad [20]$$

$$1/2\ NO_2^- + 1/4\ O_2 \text{ -> } 1/2\ NO_3^- \qquad [21]$$

$$NO_3^- + 2\ e^- + 2H^+ \text{ -> } NO_2^- + H_2O \qquad [22]$$

$$NO_2^- + e^- + 2H^+ \text{ -> } NO + H_2O \qquad [23]$$

$$2NO + 2\ e^- + 2H^+ \text{ -> } N_2O + H_2O \qquad [24]$$

$$N_2O + 2\ e^- + 2H^+ \text{ -> } N_2\ (\text{gas}) + H_2O \qquad [25]$$

4.1.2 Amount of Gas Produced

In the previous section, gas chromatography results provided the concentration of each gas in the samples. While the concentrations can show a trend, they do not provide the amount of gas produced per day. However, the amount of gases produced in each day can be obtained. Considering the volume of gas accumulated in the reactor, the amount of each gas can be calculated based on the gas concentration. In phase 1, with the active volume of 7 L, and the total reactor volume was 19 L. Therefore, the volume of gas accumulated in the reactor was 19 L – 7 L = 12 L. The results were then calculated to represent the CO_2 equivalent based on their global warming potential. According to IPCC guidelines, CO_2 emissions from wastewater treatment industry are not considered in the national inventory report due to their biogenic source. However, for the sake of comparison, these results include CO_2 amounts.

In this calculation, an error of measurement needs to be included. Since the air pressure in the reactor was not measured. However, during the collection of gas samples, no change in the airlock level was noticed. Therefore, no change in the pressure was assumed.

Table 12: Amounts of gases produced in MBR, phase 1

Phase 1	**Day 2 Sample**	**Day 2 Duplicate 1**	**Day 2 Duplicate 2**	**Day 2 Mean**	**Day 2 Standard Error**
CH_4 g	0.0672	0.0700	0.0701	0.0691	0.0009
CO_2 g	260.38	252.49	213.81	242.23	14.39
N_2O g	0.4901	0.1415	0.1834	0.2716	0.1099
Total CO_2 eq	408.11	296.40	270.21	324.91	42.28

Phase 1	**Day 3 Sample**	**Day 3 Duplicate 1**	**Day 3 Duplicate 2**	**Day 3 Mean**	**Day 3 Standard Error**
CH_4 g	0.0685	0.0692	0.0692	0.0690	0.0002
CO_2 g	517.68	447.23	397.03	453.98	34.99
N_2O g	0.0967	0.0362	0.0605	0.0645	0.0176
Total CO_2 eq	548.21	459.76	416.79	474.92	38.69

Phase 1	**Day 4 Sample**	**Day 4 Duplicate 1**	**Day 4 Duplicate 2**	**Day 4 Mean**	**Day 4 Standard Error**
CH_4 g	0.0678	0.0684	0.0686	0.0683	0.0002
CO_2 g	654.53	575.60	531.49	587.21	35.99
N_2O g	0.0408	0.0145	0.0306	0.0286	0.0076
Total CO_2 eq	668.38	581.63	542.33	597.45	37.24

The trend of each gas amount followed the same path as its concentration. The amount of CH_4 stayed the same, the amount of CO_2 increased constantly while the amount of N_2O decreased. However, total CO_2 eq increased constantly, going up 146.74 ± 8.24 g/day.

The first day of measurement demonstrated the production of N_2O (Figure 27) and simultaneous removal of ammonia (Figure 24), which showed that during the nitrification (and low denitrification) process, the generation of N_2O was prevalent.

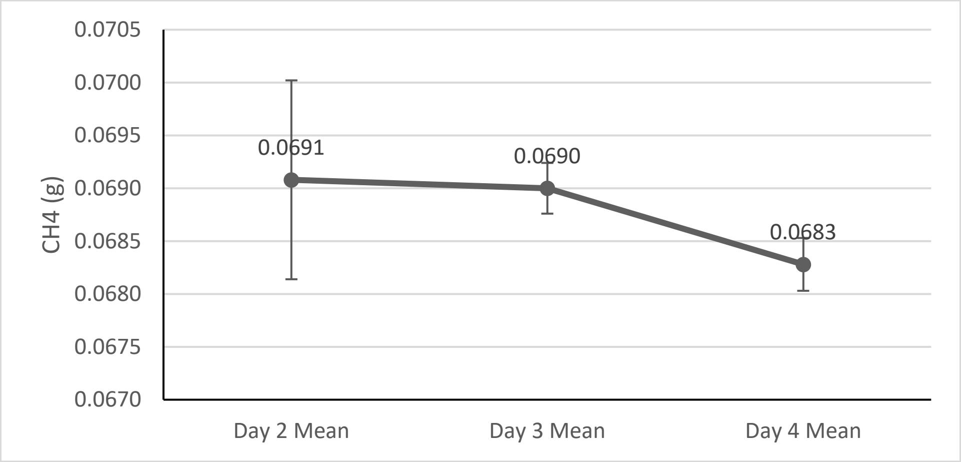

Figure 25: Amount of CH_4 produced in MBR, phase 1

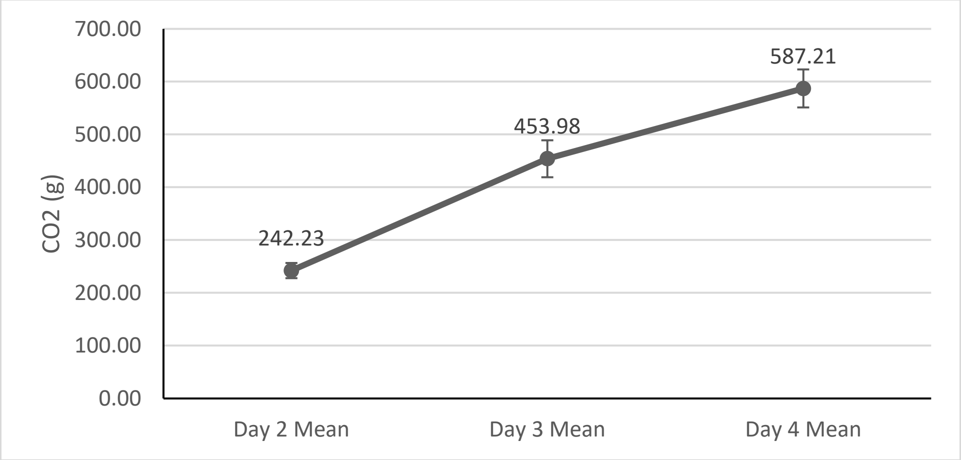

Figure 26: Amount of CO_2 produced in MBR, phase 1

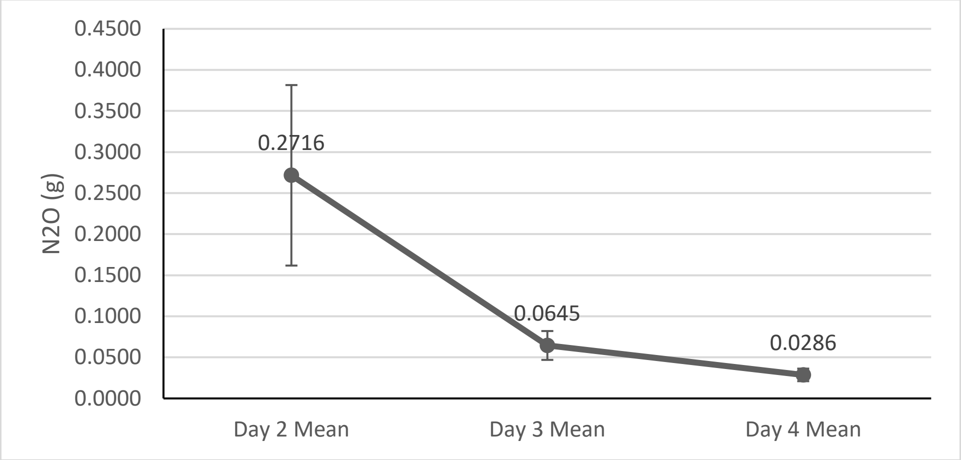

Figure 27: Amount of N_2O produced in MBR, phase 1

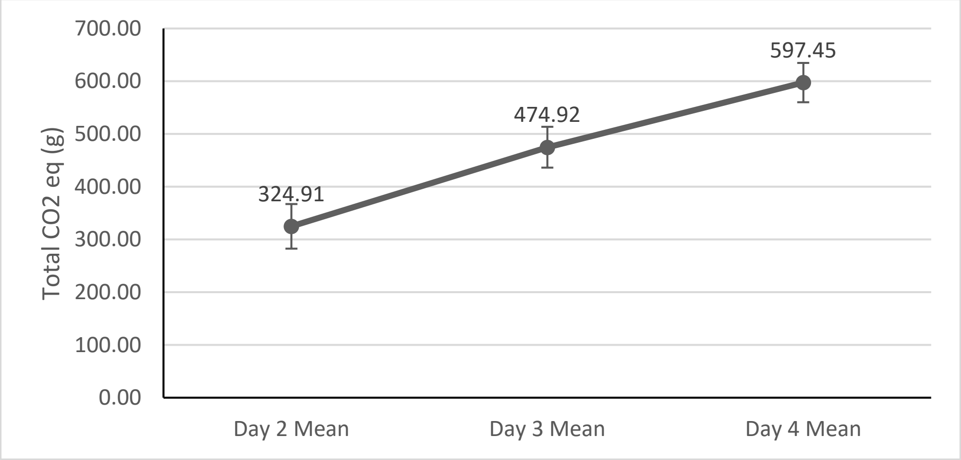

Figure 28: Amount of total CO_2 eq produced in MBR, phase 1

Considering the inflow rate of 7 L/day, the results can be shown as the amount of gas produced per litre of wastewater. On average, 20.96 ± 1.18 g of total CO_2 eq per L of wastewater was produced, provided in Table 13 and Figure 29.

Considering the first two days of system closure, the amount of N_2O and CO_2 per the amount of NH_3 and COD removed from the effluent can be calculated respectively. On average, 681.19 g of CO_2 per g of COD removed, and 6.33 g of N_2O per g of NH_3 removed is produced.

Table 13: Amount of total CO_2 eq produced per volume of wastewater in MBR, phase 1

Gas per Wastewater	Day 2 Mean	Day 3 Mean	Day 4 Mean
Total CO_2 eq	46.42	67.85	85.35

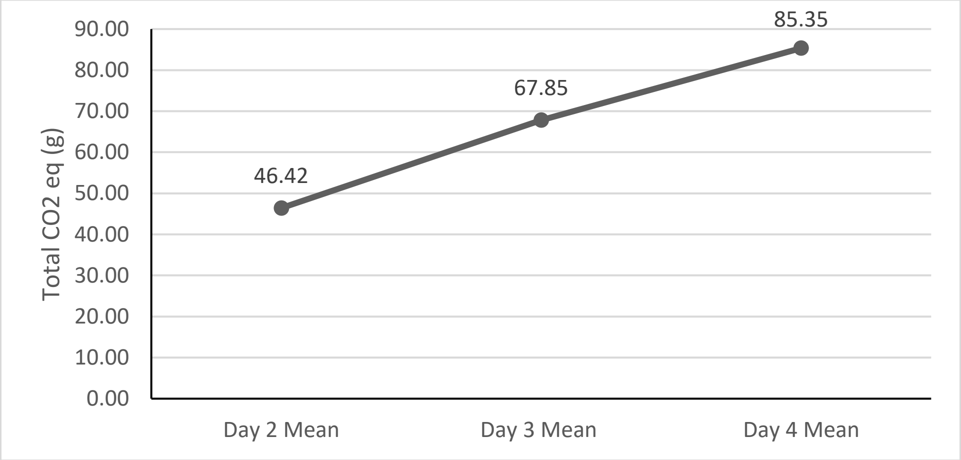

Figure 29: Amount of total CO_2 eq produced per volume of wastewater in MBR, phase 1

4.2 Phase 2: Analyses of Greenhouse Gases in SMEBR Reactor

The objective of phase 2 was to investigate the gases generated by the SMEBR reactor. After the installation of the system, microorganisms needed to be acclimatized to the electrical current, even though the timer provided only 5 minutes of live current every 25 minutes.

The electrical system also needed to be monitored in additional to what was necessary for the MBR reactor. Power supply needed to be checked often to make sure the constant current density is set. Electrodes also needed to be cleaned often to clean the accumulated precipitates on the anode. This unfavourable precipitation is due to the chemical reactions in the SMEBR reactor. It stops the metal below to continue electro-chemical reactions (Wei 2016).

Before starting the as collection and sampling, the system had to reach its steady state. Therefore, it was run while measurements were taking place often. A summary of the measurements are presented in

Table 14.

Table 14: Concentration of COD and NH_3-N in the SMEBR effluent, phase 2

Date	NH3-N (mg/L)	COD (mg/L)
Influent	35.2	196.1
7/15/2019	14.7	25.1
7/25/2019	18.4	76.1
7/31/2019	9.27	56.2
8/5/2019	9.09	24.2

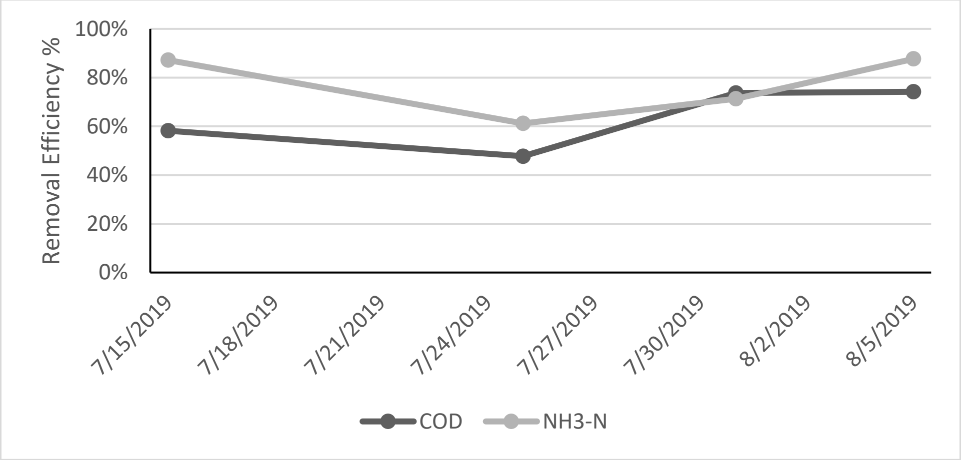

Figure 30: COD and NH_3-N removal efficiency in the SMEBR, phase 2

The reactor reached its steady state after 35 days. The acclimatization took less time than the MBR reactor, since the bacterial community was already used to similar working conditions such as HRT, SRT, reactor active volume, and DO. In this phase, microorganisms needed to get used to the electrical current in the system only. Then, the same procedure was conducted to measure the GHGs generated by SMEBR the reactor.

4.2.1 Results of Gas Chromatography Analyses

The concentration of each gas in the samples are presented in Table 15 in mg/L. In these results, day 2, 3 and 4 are the first, second and third day of measurement.

Table 15: Gas chromatography results in SMEBR, phase 2

Phase 2	**Day 2 Sample**	**Day 2 Duplicate 1**	**Day 2 Duplicate 2**	**Day 2 Mean**	**Day 2 Standard Error**
CH_4 (mg/L)	5.75	5.8	5.8	5.78	0.016
CO_2 (mg/L)	25848	24708.6	23694.52	24750.37	622.01
N_2O (mg/L)	2.59	0.96	2.05	1.87	0.4794

Phase 2	**Day 3 Sample**	**Day 3 Duplicate 1**	**Day 3 Duplicate 2**	**Day 3 Mean**	**Day 3 Standard Error**
CH_4 (mg/L)	5.72	5.8	5.8	5.77	0.0267
CO_2 (mg/L)	27134.83	23017.23	22329.79	24160.62	1500.29
N_2O (mg/L)	1.58	1.05	1.89	1.51	0.25

Phase 2	**Day 4 Sample**	**Day 4 Duplicate 1**	**Day 4 Duplicate 2**	**Day 4 Mean**	**Day 4 Standard Error**
CH_4 (mg/L)	5.72	5.77	5.78	5.76	0.018
CO_2 (mg/L)	26741.23	28846.33	27485.46	27691.01	616.32
N_2O (mg/L)	2.66	1.25	1.89	1.93	0.4076

In this phase, the results for CH_4, CO_2 and N_2O generations were constant. The concentrations of CH_4 and N_2O stayed about the same. The concentration of CH_4 went from 5.78 mg/L to 5.76 mg/L. The concentration of N_2O was at 1.87 in day 2, increased to 1.93 in day 4. The concentration of CO_2 stayed around the same, with 12% increase from day 2 to day 3. It was 24750.37 mg/L on day 2, went up to 27691.01 mg/L on day 4.

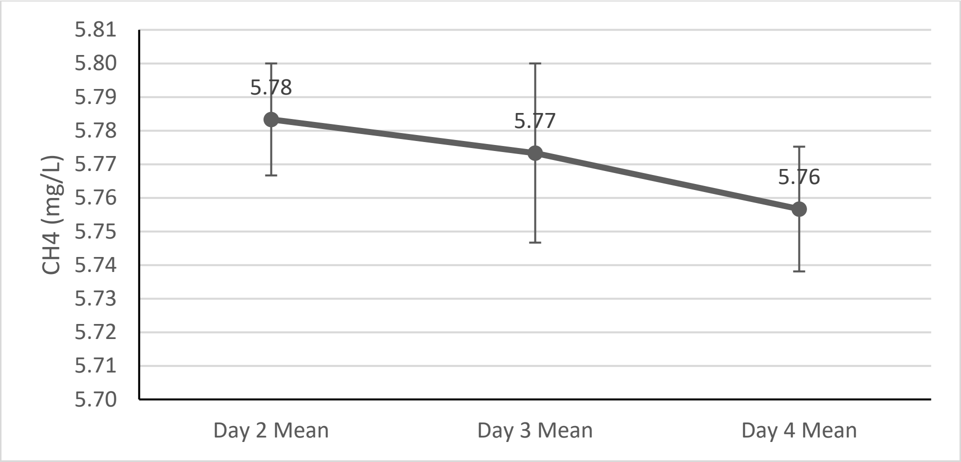

Figure 31: Concentration of CH_4 in SMEBR, phase 2

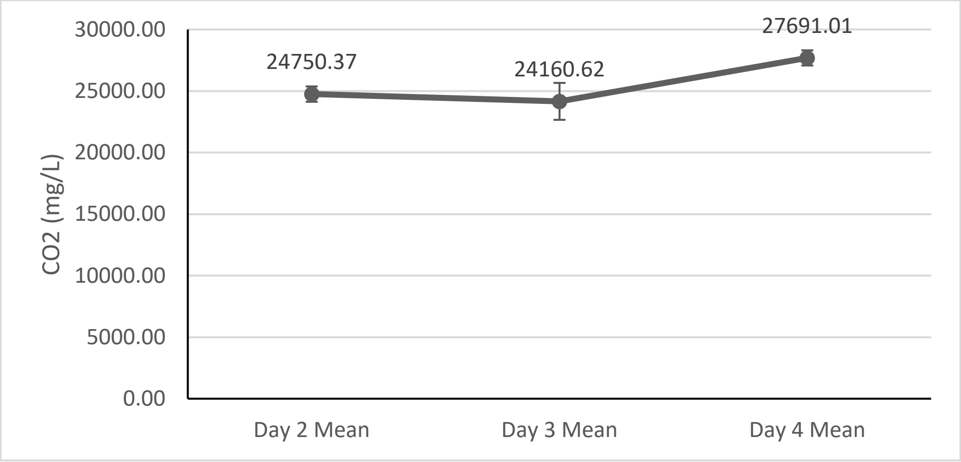

Figure 32: Concentration of CO_2 in SMEBR, phase 2

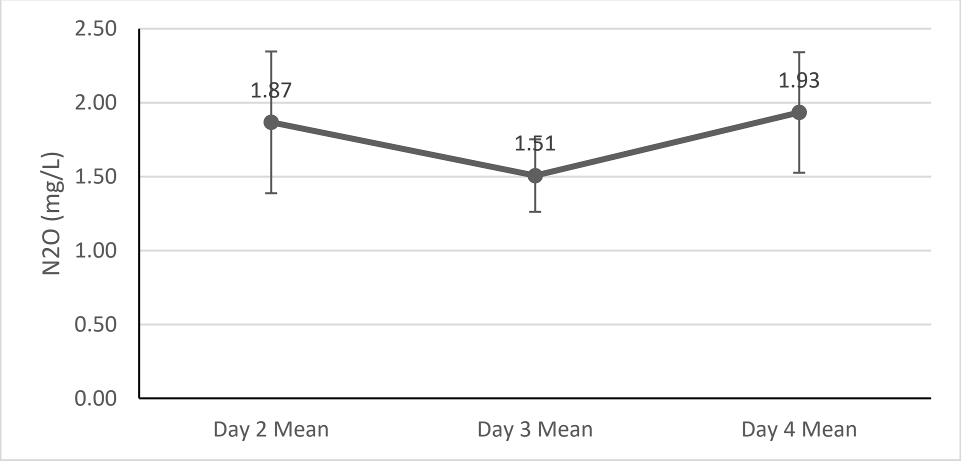

Figure 33: Concentration of N_2O in SMEBR, phase 2

To have a better understanding of these results, we can consider COD and NH_3 concentration in the effluent, while samples were being taken.

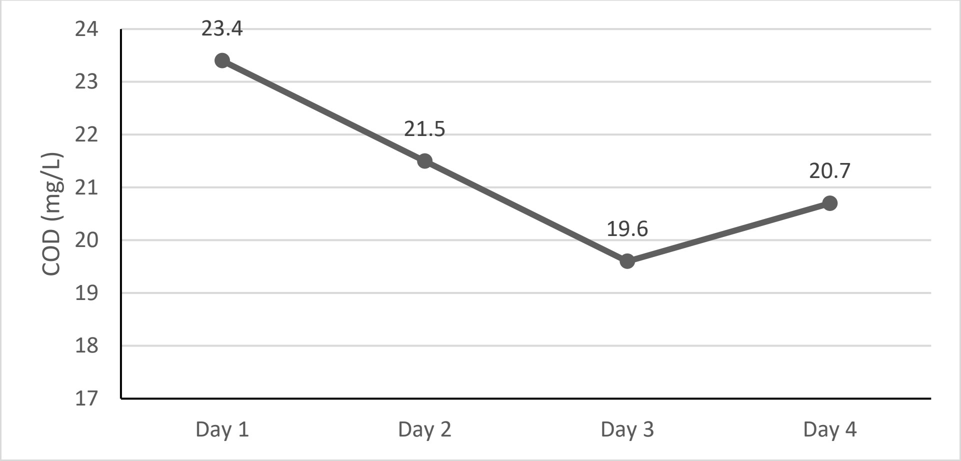

Figure 34: Concentration of COD in the SMEBR effluent, phase 2

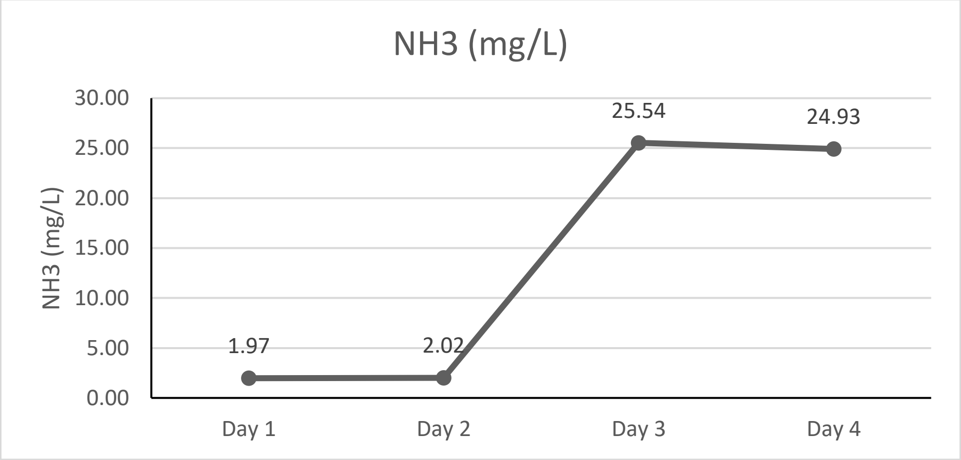

Figure 35: Concentration of NH_3 in the SMEBR effluent, phase 2

The COD removal slightly increased in these 4 days. The concentration of COD was at 23.4 mg/L in day 1, and decreased to 20.7 mg/L. This can show that COD removal continued after the system was closed, and lack of DO does not affect the bacteria removing COD. This can explain the constant increase in the concentration of CO_2.

However, NH_3 removal decreased sharply from day 2. The concentration of NH_3 in day 1 and two were 1.971 and 2.016 respectively. This is around 94% removal efficiency. On day 3, its concentration in the effluent increased to 25.54 mg/l, with removal efficiency at 27%.

In the first two days of gas collection with 94% NH_3 removal, no N_2O production was seen. This can prove the presence of nitrification and denitrification in this reactor. As mentioned before in the previous section (2.5.5), removing NH_3 by nitrification will produce N_2O gas as a by-product. This can be prevented only if denitrification comes into action after nitrification. Therefore, no increase in the concentration of N_2O in gas samples means shows the present of nitrifying and denitrifying bacteria in the SMEBR reactor.

The sudden increase in the concentration of NH_3 in the effluent can show that the decrease of DO in the system after system closure hindered the biological activities removing nitrogen. However, no sudden change was noticed in the concentration of N_2O. Considering N_2O gas as a by-product of nitrification, this could prove that denitrification process continued well after the system closure, and was not impacted by the lack of DO in the reactor. While nitrification activities decreased and NH_3 removal efficiency went down.

4.2.2 Amount of Gases Produced

The results of gas chromatography provided the concentrations of CH_4, CO_2, and N_2O in mg/L. The volume of gas in the reactor at 12 L, similar to phase 1, the amounts of gases per gram can be calculated. Then, the results were multiplied by the global warming potential to show the total CO_2 eq. These total CO_2 eq includes the amounts of CO_2.

Table 16: Amounts of gases produced in SMEBR, phase 2

Phase 2	**Day 2 Sample**	**Day 2 Duplicate 1**	**Day 2 Duplicate 2**	**Day 2 Mean**	**Day 2 Standard Error**
CH_4 g	0.0690	0.0696	0.0696	0.0694	0.0002
CO_2 g	310.18	296.50	284.33	297.00	7.46
N_2O g	0.0311	0.0115	0.0246	0.0224	0.0058
Total CO_2 eq	321.16	301.68	293.40	305.41	8.23

Phase 2	Day 3 Sample	Day 3 Duplicate 1	Day 3 Duplicate 2	Day 3 Mean	Day 3 Standard Error
CH_4 g	0.0686	0.0696	0.0696	0.0693	0.0003
CO_2 g	325.62	276.21	267.96	289.93	18.00
N_2O g	0.0190	0.0126	0.0227	0.0181	0.0029
Total CO_2 eq	332.98	281.70	276.46	297.05	18.03

Phase 2	Day 4 Sample	Day 4 Duplicate 1	Day 4 Duplicate 2	Day 4 Mean	Day 4 Standard Error
CH_4 g	0.0686	0.0692	0.0694	0.0691	0.0002
CO_2 g	320.89	346.16	329.83	332.29	7.40
N_2O g	0.0319	0.0150	0.0227	0.0232	0.0049
Total CO_2 eq	332.12	352.36	338.32	340.93	5.99

The results in Table 16 show the same trend as concentration in Table 15. The amount of all three gases in the three days of sampling stayed about the same. As seen in Figure 36, the amount of CH_4 on day 2 was 0.0694 g, went down to 0.0691 g. The amount CO_2 increased slightly, from 297.00 g on day 2 to 332.29 g on day 4. This may be due to increase in COD removal efficiency. Regardless of NH_3 removal, N_2O production stayed low, from 0.0224 g on day 2 to 0.0232 g on day 4. This revealed a good denitrification in this system. Also, this shows that denitrifying bacteria were present and active in the reactor. Independent of NH_3, they turned nitrite and nitrate available in the reactor to N_2O gas. Considering the amount of COD and NH_3 removed from the influent, 834.18 g of CO_2 per g of COD removed, and only 0.26 g of N_2O per g of NH_3 removed is produced.

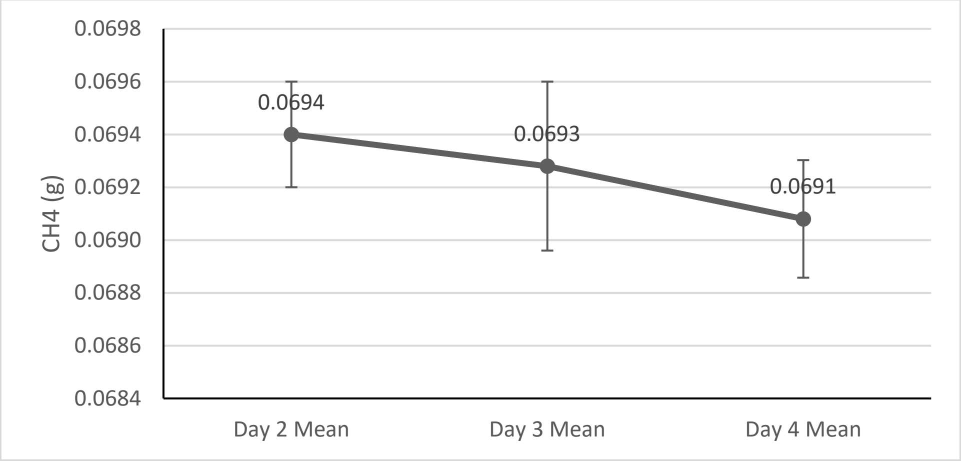

Figure 36: Amount of CH_4 produced in SMEBR, phase 2

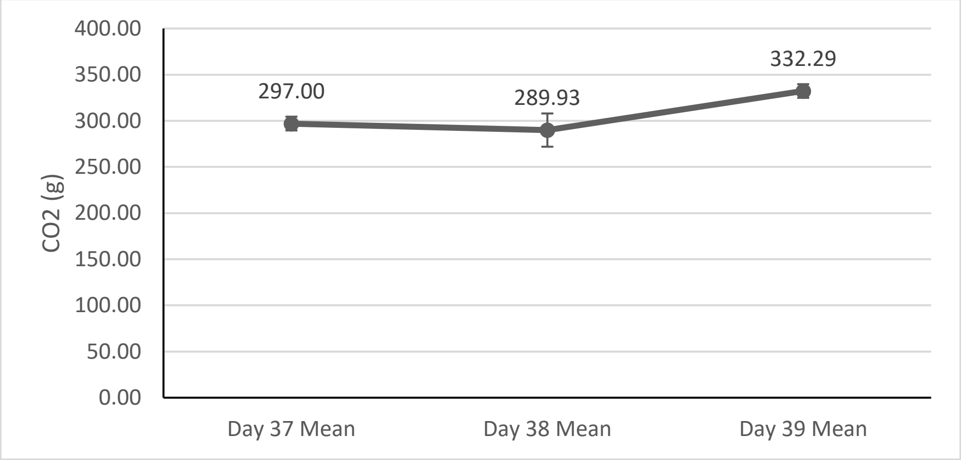

Figure 37: Amount of CO_2 produced in SMEBR, phase 2

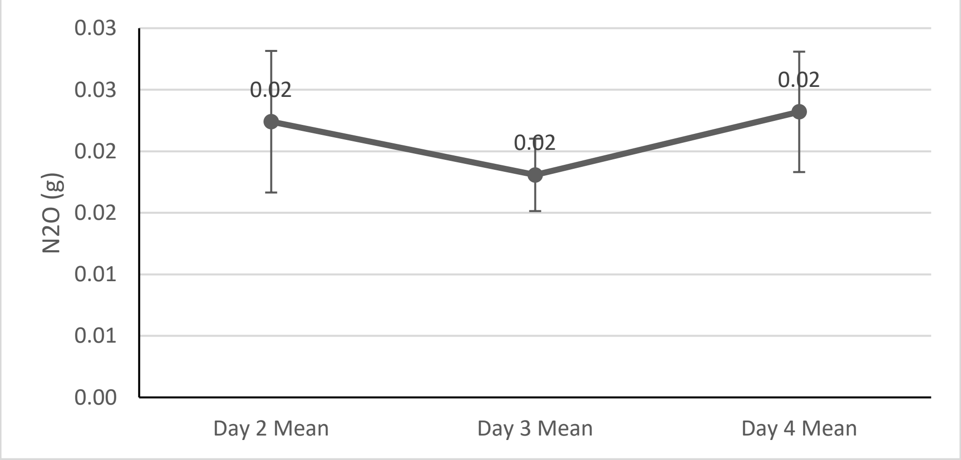

Figure 38: Amount of N_2O produced in SMEBR, phase 2

If the inflow rate is taken into account, the results of Table 16 can be calculated to show GHG production per litre of wastewater. This shows that on average, 11.80 ± 5.56 g CO_2 eq / L of wastewater is produced.

Table 17: Amount of total CO_2 eq produced per litre of wastewater in SMEBR, phase 2

Gas per Wastewater	Day 2 Mean	Day 3 Mean	Day 4 Mean
Total CO_2 eq	43.63	42.44	48.70

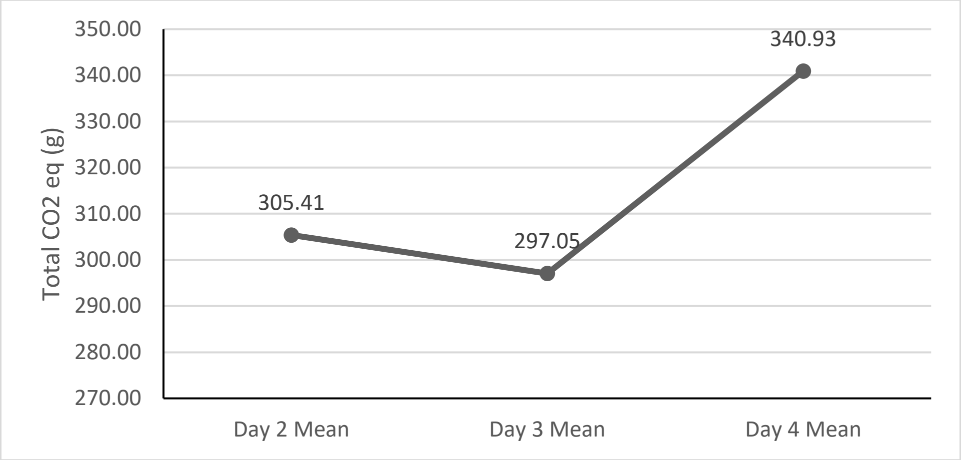

Figure 39: Amount of total CO_2 eq per litre of wastewater in SMEBR, phase 2

4.2.3 Comparison of results generated in Phases 1 and 2

Phases 1 and 2 results can be compared to analyze the performance of MBR and SMEBR. These systems had the same working conditions such as active volume, DO, HRT, SRT, temperature and mixing. A synthetic wastewater had the same composition in both reactors, discussed on stage 1 in phase 1 (3.1.1). The same sampling procedure, mentioned in stage 5 of phase 1(3.1.5), was conducted for these systems. The amounts of total CO_2 eq (g) are compared in Table 18.

Table 18: Phase 1 and 2, MBR and SMEBR, total CO_2 eq comparison

Total CO_2 eq (g)	Day 2 Sample	Day 2 Duplicate 1	Day 2 Duplicate 2	Day 2 Mean	Day 2 Standard Error
MBR	408.11	296.40	270.21	324.91	42.28
SMEBR	321.16	301.68	293.41	305.41	8.23

Total CO_2 eq (g)	Day 3 Sample	Day 3 Duplicate 1	Day 3 Duplicate 2	Day 3 Mean	Day 3 Standard Error
MBR	548.21	459.76	416.79	474.92	38.69
SMEBR	332.98	281.70	276.46	297.05	18.03

Total CO_2 eq (g)	Day 4 Sample	Day 4 Duplicate 1	Day 4 Duplicate 2	Day 4 Mean	Day 4 Standard Error
MBR	668.38	581.63	542.33	597.45	37.24
SMEBR	332.12	352.36	338.32	340.93	5.99

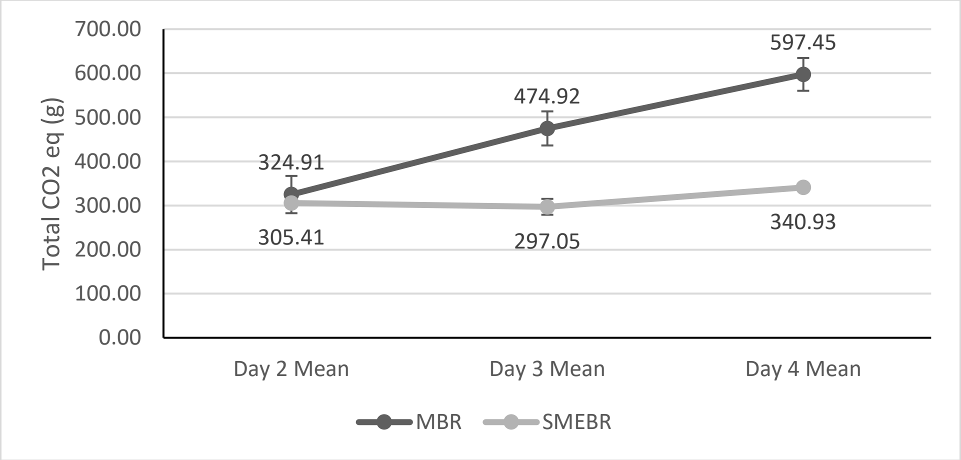

Figure 40: Phase 1 and 2, MBR and SMEBR, total CO_2 eq comparison

The results in Figure 40 show that the total CO_2 eq produced in the MBR system are on average 151.29 ± 69.70 g more than that of SMEBR. Considering the 7 L of influent, the amount of gases generated per litre of wastewater follows the same trend as the amount of gases per day. As seen in Figure 41, the MBR reactor produced more total CO_2 eq per litre of wastewater. On average, the MBR reactor produced 21.61 ± 9.96 g total CO_2 eq per litre of wastewater per day; the SMEBR reactor produced 11.80 ± 5.56 g total CO_2 eq.

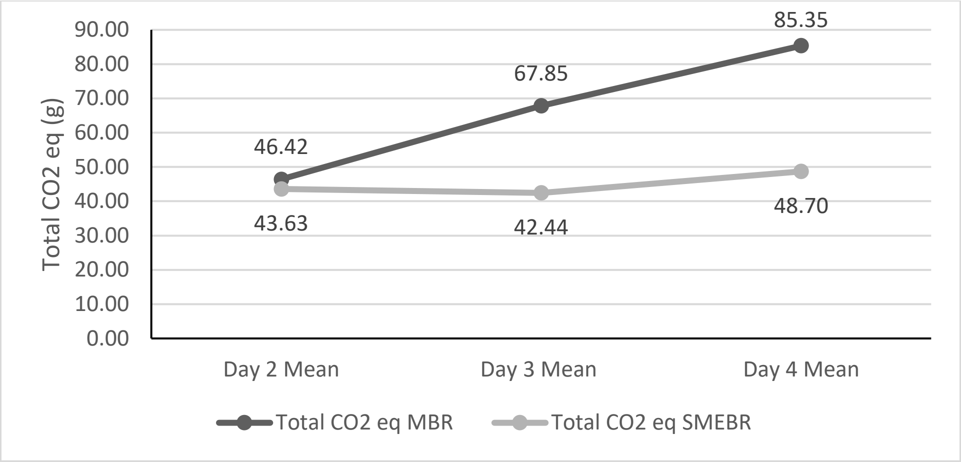

Figure 41: Phases 1 and 2, MBR and SMEBR, total CO_2 eq per litre of wastewater comparison

If CO_2 emissions are ignored due to their biogenic source, and the results of the first day of measurement are considered only, the emissions of MBR are 12 times higher of that of SMEBR.

System closure and gas sampling was done in three days to have reliable results of the amount of gases produced each day. With three days of sampling, GHG generation per day could be calculated with standard errors. However, due to nature of biological activity, closing the system while having the same removal efficiency was impossible. By decreasing of air supply during closing the system, changed the reactor conditions and a deficiency of oxygen influenced microbial activity. Thus, measurement of gases in the second day were used for comparison only.

Comparing the removal efficiency of these reactors, COD removal in SMEBR reactor was slightly higher than of the MBR reactor. Effluent NH_3 in the SMEBR reactor was considerably low in the beginning, going up in the last two days of sampling. However, the concentration of NH_3 in the effluent increased steadily. NH_3 removal decreased in the MBR reactor from 70% to 54%. The difference in the trends of the concentration in the effluent might be due to a rapid depletion of DO in the SMEBR reactor compared to the MBR reactor. Due to electrical current present in the SMEBR reactor, bacterial communities are more active, compared to the MBR reactor (Hassan 2011). Therefore, in SMEBR method, DO is consumed faster than MBR method.

Also, in the MBR and SMEBR systems, 681.19 and 834.18 g of CO_2 per g of COD removed is generated respectively. This shows that MBR system generated around 18% more CO_2 per the amount of COD removed. However, MBR and SMEBR systems produced 6.33 and 0.26 g of N_2O per g of NH_3 removed from the influent. This shows that SMEBR produced around 24 times less N_2O per NH_3 treated from the influent.

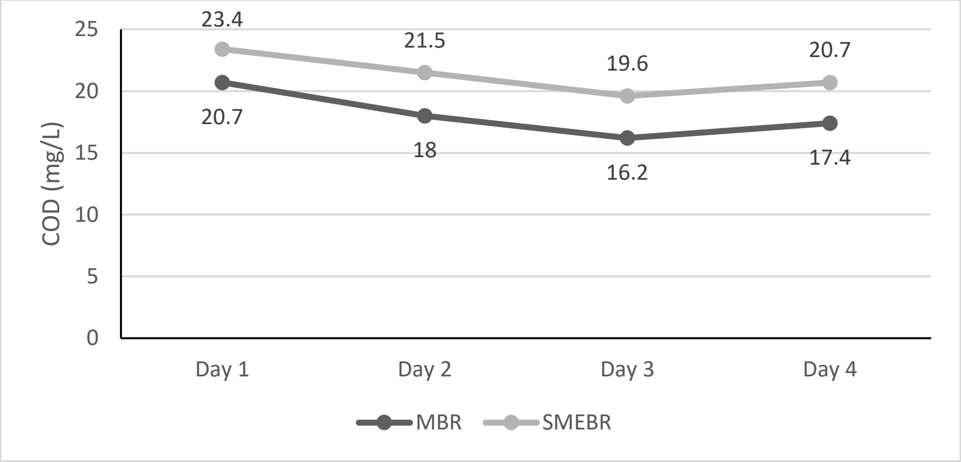

Figure 42: Phases 1 and 2, MBR and SMEBR, comparison of COD in the effluent

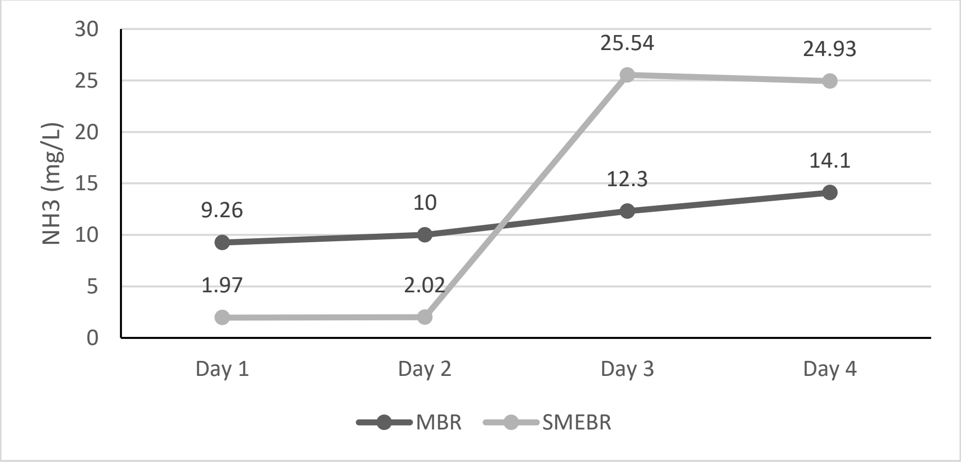

Figure 43: Phases 1 and 2, MBR and SMEBR, comparison of NH_3 in the effluent

4.3 Phase 3: Analyses of Greenhouse Gases in MBR transformed into SMEBR

In this phase, the gas production of the MBR system transformed to SMEBR is presented. The gas sampling period totalized over 10 days. Three first days were dedicated to gas accumulation in the MBR reactor. Subsequently, the sampling of biogas was conducted on days 4, 5 and 6 in MBR. On day 7, the system was transformed to SMEBR, when DC was supplied to the submerged electrodes. One day was dedicated to accumulation of gases, followed by three days of sampling on days 8, 9 and 10.

In this phase, as mentioned in section 3 of chapter 2, some of working conditions were changed, such as reactor volume, flow rate, etc. Due to this change, the microbial community needed enough time to reach the steady state. There was no change in the installation other than increasing the reactor active volume. For the first part of this phase, the electrical current was not live. However, the electrodes, wires and equipment were left there, so that the system can be transformed to SMEBR during gas collection.

Same tasks to maintain the reactor were necessary, such as wastewater preparation and the membrane and tubes cleaning. Measurements were needed to show the trend of the reactor and its steady state. The results of the measurements can be seen in Table 21.

Table 19: Concentration of NH_3 and COD in MBR effluent, phase 3

Date	NH_3 **(mg/L)**	**COD (mg/L)**
Influent	40.2	176
9/10/2018	36.2	70.4
9/18/2018	31.3	62.8
9/25/2018	22.4	40.7
11/7/2018	39.1	51.2
11/14/2018	18.8	22.3
1/10/2019	22.7	27.8

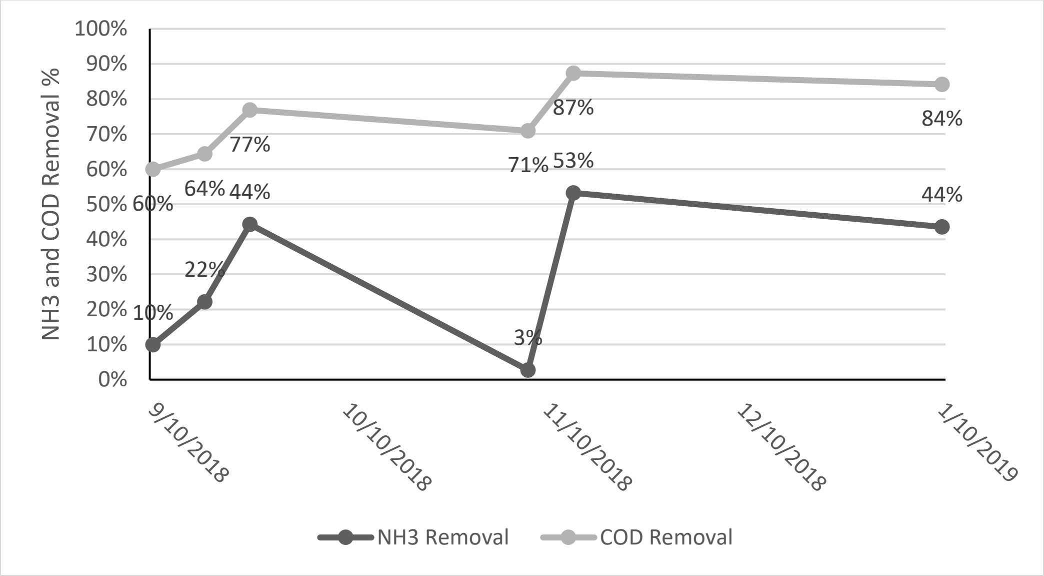

Figure 44: NH_3 and COD removal of the MBR reactor, phase 3

These results fluctuated due to the necessary changes made to the system to achieve the best removal efficiency of COD and NH3 at the same time. The development and acclimatization of the microbial community required the reactor to operate for a while.

4.3.1 Results of Gas Chromatography Analyses

The concentration of CH_4, CO_2 and N_2O sampled in MBR from day 4 to 6 are presented in Table 20. Gases sampled in SMEBR from 8 to 10 are shown in Table 21. In these results, day 4, 5 and 6 are the first, second and third day of measurement. Then, day 8, 9 and 10 are the 4th, 5th and 6th day of measurement.

Table 20: Gas chromatography results in MBR, phase 3

Phase 3	**Day 4 Sample**	**Day 4 Duplicate 1**	**Day 4 Duplicate 2**	**Day 4 Mean**	**Day 4 Standard Error**
CH_4 (mg/L)	5.21	5.88	5.88	5.66	0.22
CO_2 (mg/L)	18140.51	17161.76	14888.09	16730.12	963.38
N_2O (mg/L)	27.11	26.25	24.58	25.98	0.74

Phase 3	Day 5 Sample	Day 5 Duplicate 1	Day 5 Duplicate 2	Day 5 Mean	Day 5 Standard Error
CH_4 (mg/L)	5.24	5.89	5.89	5.67	0.22
CO_2 (mg/L)	20529.99	12678.16	10167.77	14458.64	3120.98
N_2O (mg/L)	42.73	25.67	23.89	30.76	6.01

Phase 3	Day 6 Sample	Day 6 Duplicate 1	Day 6 Duplicate 2	Day 6 Mean	Day 6 Standard Error
CH_4 (mg/L)	5.31	5.85	5.84	5.67	0.18
CO_2 (mg/L)	22030.60	20444.76	18084.34	20186.57	1146.48
N_2O (mg/L)	342.59	303.18	290.31	312.03	15.73

Table 21: Gas chromatography results in SMEBR, phase 3

Phase 3	Day 8 Sample	Day 8 Duplicate 1	Day 8 Duplicate 2	Day 8 Mean	Day 8 Standard Error
CH_4 (mg/L)	5.35	5.84	5.84	5.68	0.16
CO_2 (mg/L)	22207.20	21247.08	18815.39	20756.56	1009.38
N_2O (mg/L)	908.62	812.60	773.65	831.62	40.11

Phase 3	Day 9 Sample	Day 9 Duplicate 1	Day 9 Duplicate 2	Day 9 Mean	Day 9 Standard Error
CH_4 (mg/L)	5.42	5.84	5.84	5.70	0.14
CO_2 (mg/L)	21492.12	19771.93	17627.53	19630.53	1117.85
N_2O (mg/L)	1058.69	919.36	876.67	951.57	54.96

Phase 3	**Day 10 Sample**	**Day 10 Duplicate 1**	**Day 10 Duplicate 2**	**Day 10 Mean**	**Day 10 Standard Error**
CH_4 (mg/L)	5.51	5.83	5.83	5.72	0.11
CO_2 (mg/L)	20514.38	21168.56	19055.10	20246.01	624.68
N_2O (mg/L)	1227.97	1242.23	1186.67	1218.96	16.66

The results in Figure 45 show that the concentration of CH_4 increased insignificantly. It started from 5.66 mg/L on day 4 and increased to 5.72 mg/L on day 10. The concentration of CO_2 increased in the first three days of sampling and stayed about the same for the rest of time. On day 4, the concentration of CO_2 was 16730.12 mg/L and went down to 14458.64 mg/L on day 5. It increased on day 6 and stayed about the same, with the concentration at 20246.01 on day 10.

The concentration of N_2O increased sharply after day 5 and continued to increase slowly after day 8. On day 4, the concentration of N_2O was 25.98 mg/L. Then it increased rapidly to 831.62 mg/L on day 8. It continued to increase, going up to 1218.96 mg/L on day 10.

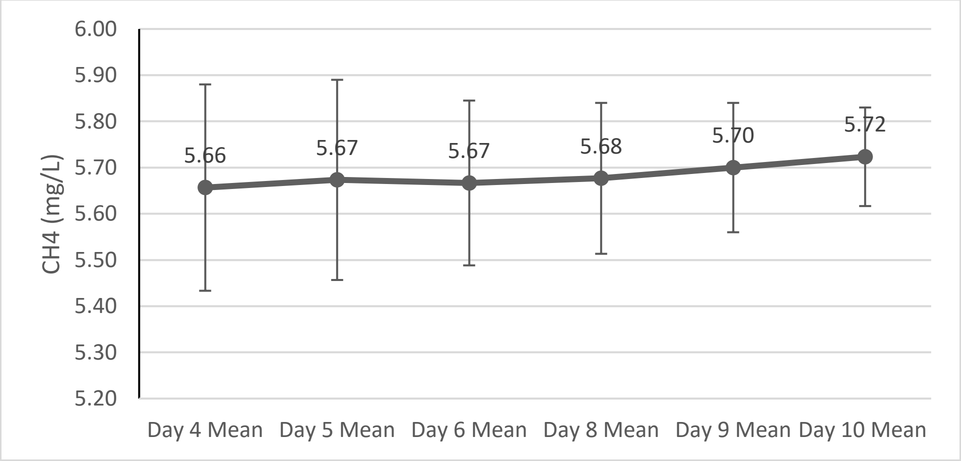

Figure 45: Concentration of CH_4 in the MBR and SMEBR reactor, phase 3

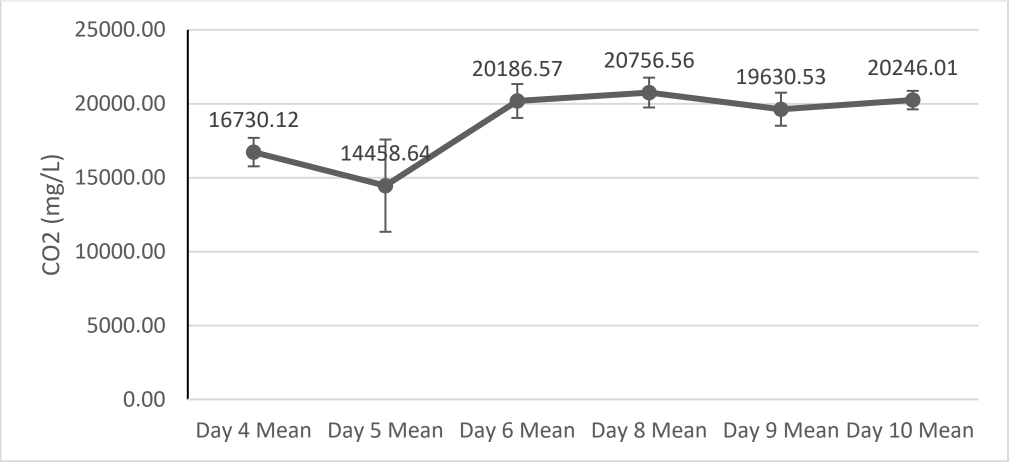

Figure 46: Concentration of CO_2 in the MBR and SMEBR reactor, phase 3

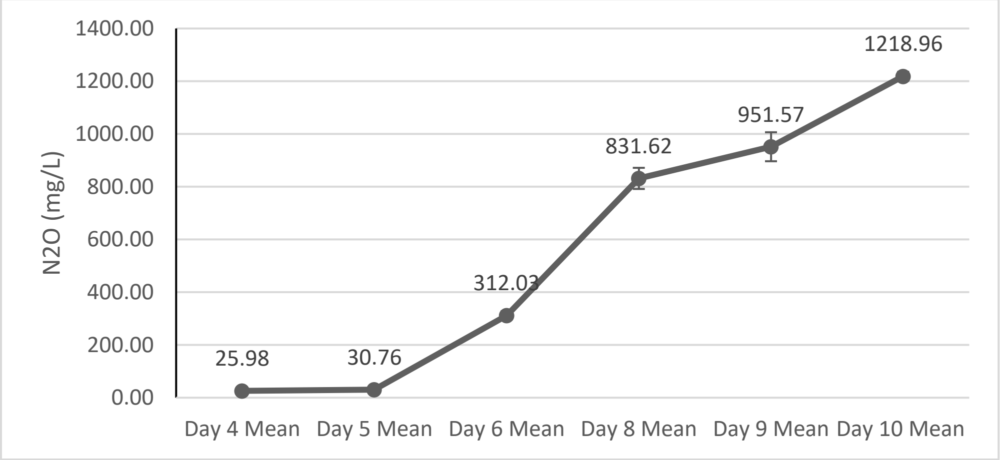

Figure 47: Concentration of N_2O in the MBR and SMEBR reactor, phase 3

As discussed in the chapter of literature review, two types of processes happen in the MBR and SMEBR methods; organic and nitrogen removal. The organic removal process can remove the COD from the wastewater by creating CO_2 as a by-product, summarized in 2.3.1. The nitrogen removal process can remove NH_3, NO_2, NO_3 and other nitrogen compounds. It consists of nitrification and denitrification, summarized in 2.5.5.

In the SMEBR reactor, two different reactions occur in aluminum anode and iron cathode (Wei 2016):

Anode: $Al_0(S) \rightarrow Al_3+ + 3e-$ [26]

Cathode: $2H_2O+2e- \rightarrow 2OH- + H_2(g)$ [27]

Measurements of COD and NH_3 were conducted during the entire phase 3 and help better understand processes in the reactors and subsequently biogas production.

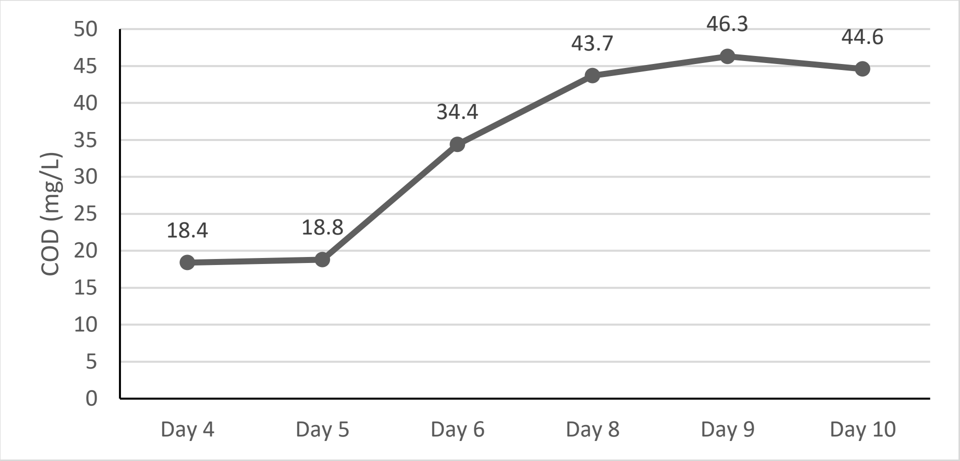

Figure 48: Concentration of COD in MBR and SMEBR effluent, Phase 3

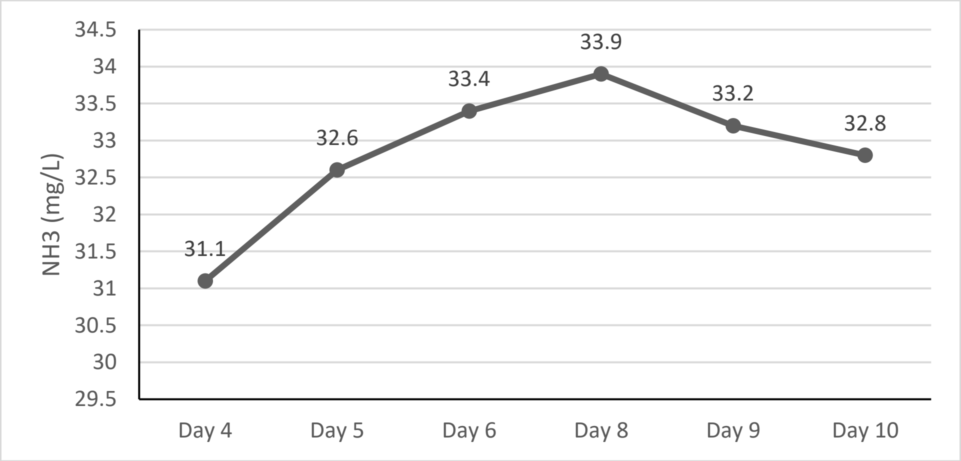

Figure 49: Concentration of NH3 in MBR and SMEBR effluent, Phase 3

The MBR reactor was able to decrease the COD concentration from average 176 mg/L to 25.05 mg/L in adequate aerobic conditions. The concentration of COD in the effluent increased sharply after day 5. While its concentration stayed between 14 and 18 mg/L in the first five days after the system closure. This shows that microorganisms continued their activity with the available oxygen in the system until oxygen was depleted on day 5. Then, the COD removal decreased to reach a stable level of the concentration. It seems then some bacteria activity was preserved maybe due to oxygen production on the anode in SMEBR. This can explain the fate of COD in MBR transformed to SMEBR system.

The NH_3 concentration in the effluent also went up until day 8 and decreased slowly after. While NH_3 removal went down, N_2O concentration increased. This shows that until day 8, nitrification was the main nitrogen removal activity. However, after day 8, NH_3 concentration decreased and N_2O concentration increase slowed down. Since denitrification is the main sink of NO2, this decrease of N_2O in the results shows that after day 8, denitrification started to increase. Day 8 was the second day after the current was live.

4.3.2 Amount of Gases Produced

Considering the volume of air in the reactor, the amount of gas in each day was calculated. These results were then multiplied by the appropriate global warming potentials to show the total CO_2 eq. These results include CO_2.

Table 22: Amount of gases produced in MBR, phase 3

Phase 3	**Day 4 Sample**	**Day 4 Duplicate 1**	**Day 4 Duplicate 2**	**Day 4 Mean**	**Day 4 Standard Error**
CH_4 g	0.0261	0.0294	0.0294	0.0283	0.0011
CO_2 g	90.70	85.81	74.44	83.65	4.82
N_2O g	0.14	0.13	0.12	0.13	0.0037
Total CO_2 eq	131.75	125.66	111.80	123.07	5.90

Phase 3	**Day 5 Sample**	**Day 5 Duplicate 1**	**Day 5 Duplicate 2**	**Day 5 Mean**	**Day 5 Standard Error**
CH_4 g	0.0262	0.0295	0.0295	0.0284	0.0011
CO_2 g	102.65	63.39	50.83	72.29	15.60
N_2O g	0.2137	0.1284	0.1195	0.1538	0.0300
Total CO_2 eq	166.97	102.37	87.17	118.84	24.46

Phase 3	Day 6 Sample	Day 6 Duplicate 1	Day 6 Duplicate 2	Day 6 Mean	Day 6 Standard Error
CH_4 g	0.0266	0.0293	0.0292	0.0283	0.0009
CO_2 g	110.15	102.22	90.42	100.93	5.73
N_2O g	1.7130	1.5159	1.4516	1.5601	0.0786
Total CO_2 eq	621.28	554.69	523.71	566.56	28.78

Table 23: Amount of gases produced in SMEBR, phase 3

Phase 3	Day 8 Sample	Day 8 Duplicate 1	Day 8 Duplicate 2	Day 8 Mean	Day 8 Standard Error
CH_4 g	0.0268	0.0292	0.0292	0.0284	0.0008
CO_2 g	111.04	106.24	94.08	103.78	5.05
N_2O g	4.5431	4.0630	3.8683	4.1581	0.2005
Total CO_2 eq	1465.55	1317.74	1247.55	1343.61	64.25

Phase 3	Day 9 Sample	Day 9 Duplicate 1	Day 9 Duplicate 2	Day 9 Mean	Day 9 Standard Error
CH_4 g	0.0271	0.0292	0.0292	0.0285	0.0007
CO_2 g	107.46	98.86	88.14	98.15	5.59
N_2O g	5.2935	4.5968	4.3834	4.7579	0.2748
Total CO_2 eq	1685.59	1469.44	1395.11	1516.71	87.12

Phase 3	Day 10 Sample	Day 10 Duplicate 1	Day 10 Duplicate 2	Day 10 Mean	Day 10 Standard Error
CH_4 g	0.0276	0.0292	0.0292	0.0286	0.0005
CO_2 g	102.57	105.84	95.28	101.23	3.12
N_2O g	6.1399	6.2112	5.9334	6.0948	0.0833
Total CO_2 eq	1932.94	1957.49	1864.14	1918.19	27.94

These results showed a similar trend as the concentration of gases in Table 21. An amount of CH_4 stayed about the same over 10 days of sampling. The CO_2 amount also stayed the same after day 6 of sampling, while N_2O amounts increased constantly. The total CO_2 eq showed the same trend as N_2O. It increased sharply until day 8 and slowed down afterwards.

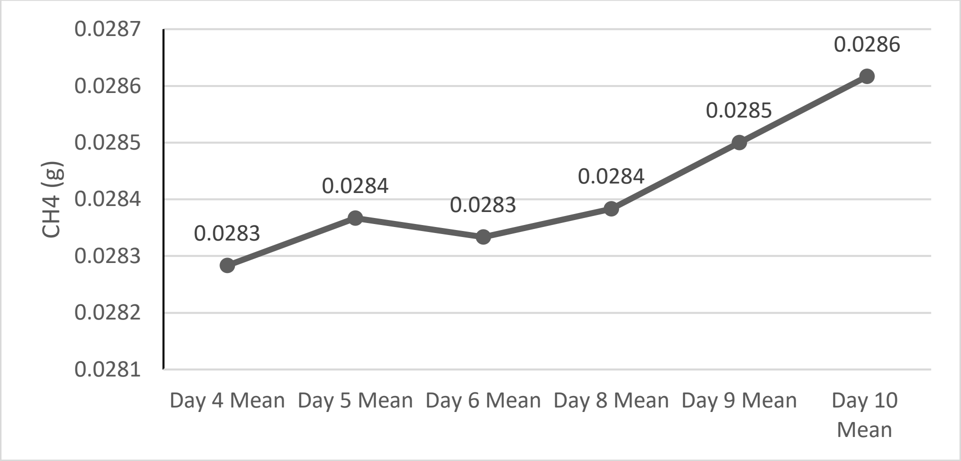

Figure 50: Amount of CH_4 produced in MBR and SMEBR, phase 3

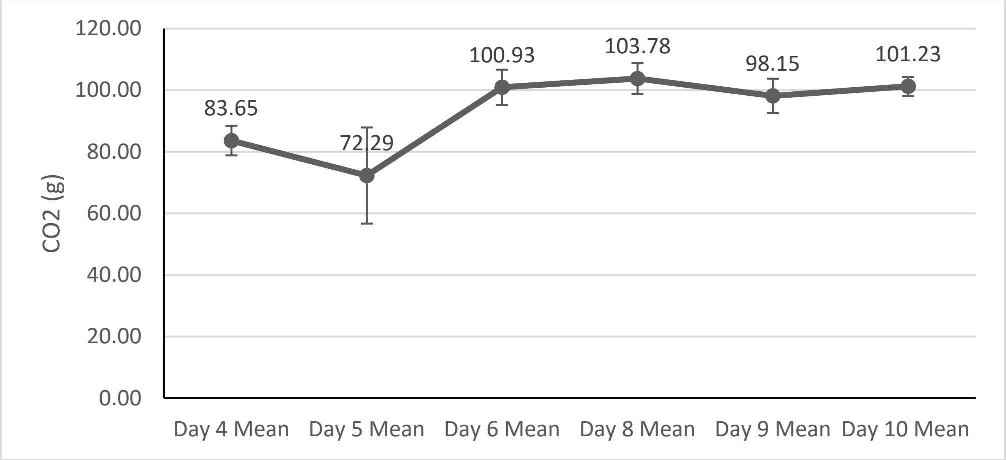

Figure 51: Amount of CO_2 produced in MBR and SMEBR, phase 3

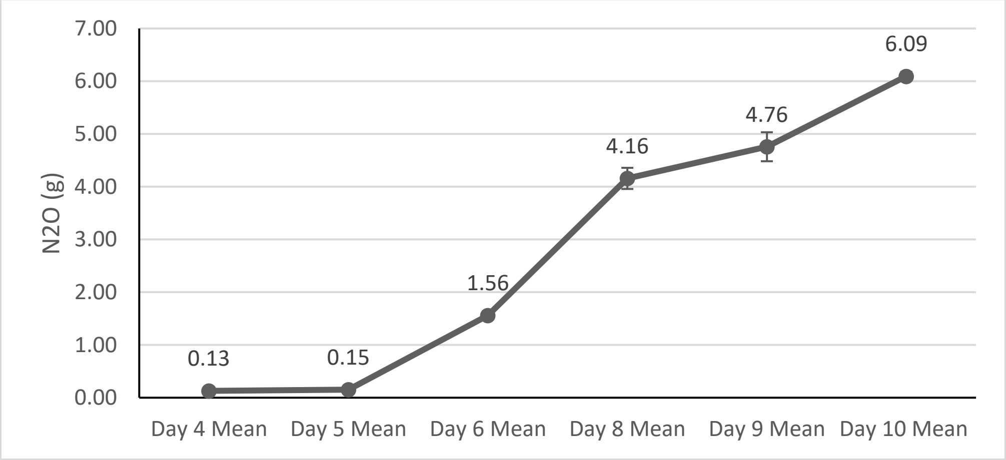

Figure 52: Amount of N_2O produced in MBR and SMEBR, phase 3

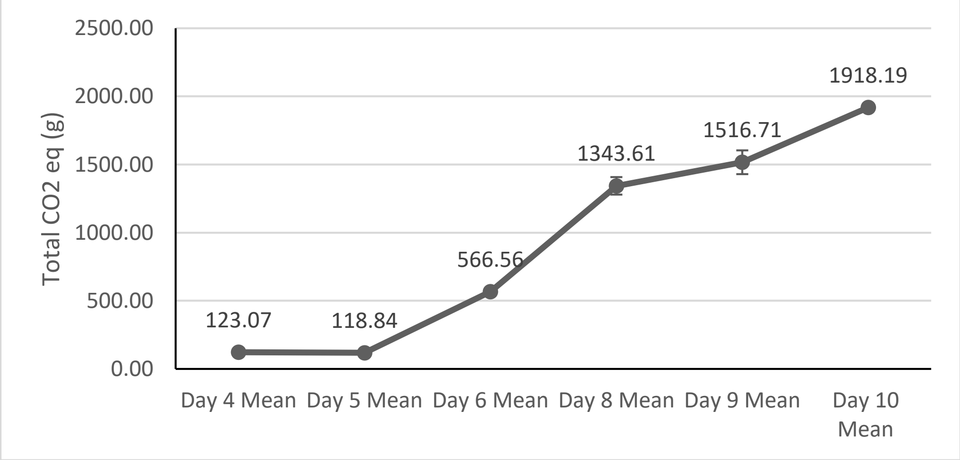

Figure 53: Amount of total CO_2 eq produced in MBR and SMEBR, phase 4

Considering the inflow rate of 14 L/day, the amount of CO_2 eq produced per litre of wastewater can be calculated.

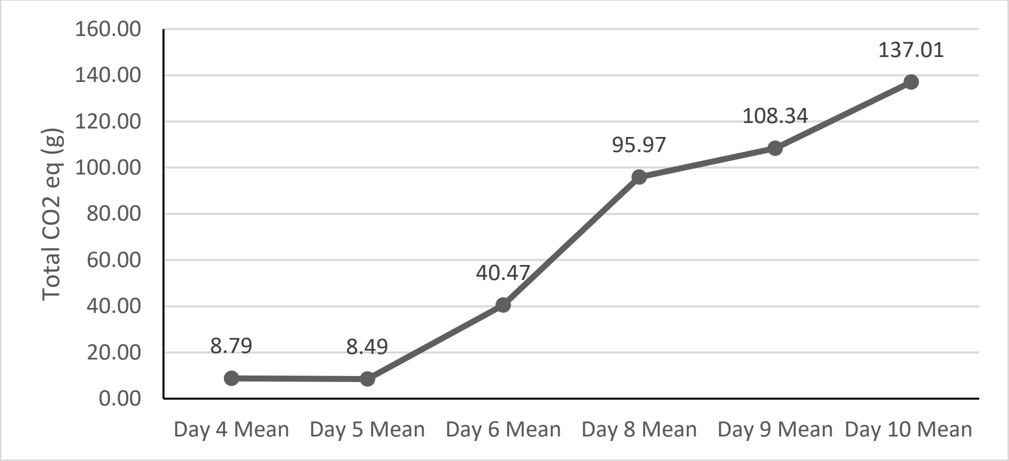

Figure 54: Phase 3 amount of total CO_2 eq produced per litre of wastewater

On average, the MBR reactor produced 13.38 ± 9.63, and the SMEBR reactor produced 24.14 ± 3.93. Compared to the results of chapters 1 and 2 in Figure 40, these results show the opposite. In phases 1 and 2, the amount of total CO_2 eq per litre of wastewater in MBR reactor was twice of that of SMEBR reactor. This might be due to the accumulation of gases from the first part of this phase, the MBR process. However, the sharp increase in the amount of total CO_2 eq started to slow down after day 8. SMEBR transformation also slowed down the sharp increase of total CO_2 eq from day 8.

4.3.3 Comparison of Phase 1, 2 and 3

To have a better understanding of the results, the performance of all three phases was compared. The Table 24 shows comparison of total CO_2 eq generated per litre of wastewater in phases 1,2 and 3. As mentioned in phases 1 and 2, these results are calculated by dividing the amount of gases by the volume of wastewater coming into the reactor per day.

Table 24: Phase 1, 2 and 3 the amount of total CO_2 eq per litre of wastewater

Gas per Wastewater	Sampling Day 1	Sampling Day 2	Sampling Day 3	Sampling Day 4	Sampling Day 5	Sampling Day 6
Total CO2 eq MBR	46.42	67.85	85.35			
Total CO2 eq SMEBR	43.63	42.44	48.70			
Total CO2 eq MBR & SMEBR	8.79	8.49	40.47	95.97	108.34	137.01

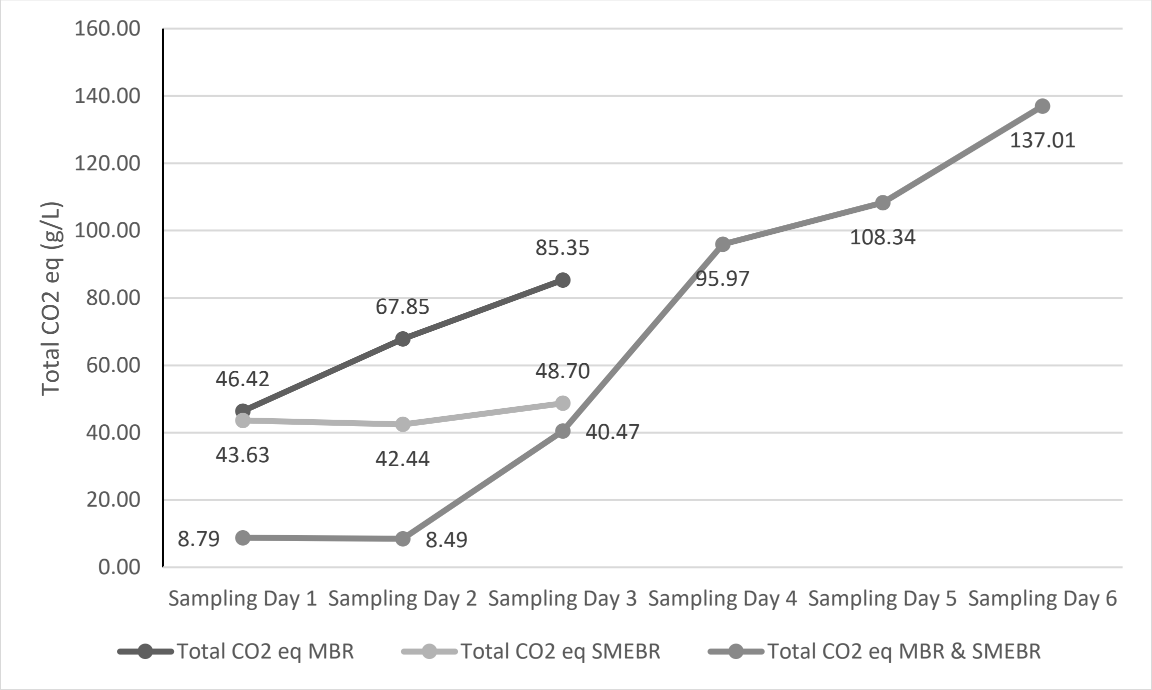

Figure 55: Phase 1, 2 and 3 the amount of total CO_2 eq per litre of wastewater

The results show that in a smaller scale, MBR and SMEBR produced more gases than the first three days of MBR reactor. In the smaller scale, the MBR reactor produced total 20.96 ± 1.18 g CO_2 eq/L . At the bigger scale production by MBR decreased to average 13.38 ± 9.63 g CO_2 eq /L. This shows that the reactor with 7 L of active volume produced 56.8% more GHGs per litre of wastewater. This might be since in both phases 1 and 2, the COD and NH_3 removal efficiency was higher than that of phase 3. Therefore, the concentration of COD and NH_3 in the effluent of these reactors is considered as well. On average, the MBR process produced 27.65 g CO_2 eq per litre of wastewater.

On the other hand, the smaller scale SMEBR reactor generated 11.80 ± 5.56 g CO_2 eq per litre of wastewater, with bigger scale SMEBR producing 24.14 ± 3.93 g CO_2/L. On the contrary to MBR reactors, the smaller scale produced 51% less amounts of gases than bigger scale. This may be due to the smaller space in the top of the reactor and bigger active volume in phase 3. Therefore, dilution of gases in the mixed liquor may have played a role in these results.

On average, the SMEBR method produced 17.97 g CO_2 eq per litre of wastewater. If we compare the averages, the SMEBR reactor generated 54% less GHGs.

4.4 Phase 4: Comparison of All Phases Treatment Methods with Lagoons

In this phase, estimated gas emissions from a plant treating water using aerated lagoons is compared with the MBR and SMEBR systems as tested in phases 1, 2 and 3. This comparison was done to analyze three different methods in wastewater treatment: a common method (Lagoon), a comparatively new and conventional method (MBR) and a new advanced method (SMEBR). The results could shed a light on the impacts of a WWTP gas by-products from different perspectives.

The synthetic wastewater in this work was prepared to mimic the sewage influent characteristics in the City of L'Assomption, after pre-treatment. Therefore, an estimation was done to measure this plant's GHG emissions due to biological processes in lagoons. This estimation was calculated based on the IPCC and Environment Canada guidelines (Eggleston, et al. 2006).

4.4.1 L'Assomption Gas Emissions by Aerated Lagoons

Canada follows the 2006 IPCC and 1996 IPCC guidelines to estimate CH_4 and N_2O emissions from municipal wastewater treatment plants. As mentioned in the literature review, CO_2 emissions are excluded from national inventory report due to their biogenic origin (Environment Canada 2016).

The estimates provided in guidelines are based on per capita values. Thus, the estimation of CH_4 emissions is conducted based on organic per capita load to wastewater. Canada considers anaerobic treatment processes such as facultative lagoons and septic systems as the sole pathway to CH_4 generations. Having four aerated lagoons as the main method of treatment in L'Assomption WWTP, CH_4 emissions were not considered in the Canadian guidelines (Environment Canada 2016).

4.4.2 Input Data

Because the guidelines only consider anaerobic methods accountable for CH_4 generation, it is not included in this estimation. In the national inventory reports, the generation of CH_4 is not reported from aerobic biological methods. Also, CH_4 production in the reactors were not noticed, since there is no change in its concentration.

To estimate N_2O emissions, per capita protein consumption was considered, followed by calculating nitrogen loading to wastewater. The emission factor for N_2O emissions from domestic wastewater was set to 0.005 kg N_2O-N/kg N was used, based on IPCC guidelines. The following equation was used to estimate N_2O emissions (Environment Canada 2016):

$$N_2O = \text{EFF } N_2O\text{-N x N Effluent x } 44/28 \tag{28}$$

Where:

-N_2O is the N_2O emissions, kg N_2O/year.
- EFF N_2O-N is the emission factor for N_2O emissions from discharged to wastewater. This factor is set to 0.005 kg N_2O-N/kg N.
- N Effluent is the amount of nitrogen in the effluent discharged to aquatic environments in kg N/year.
- 44/28 is the stoichiometric factor to convert nitrogen gas to N_2O.

The amount if nitrogen in the influent (N Effluent) was based on protein consumption per capita and a factor for industrial input, using the following equation:

$$\text{N Effluent} = (\text{Protein Consumption x Population x Fraction N-Protein x Factor Non-Consumed Protein x Factor Industrial Protein}) - \text{N Sludge} \tag{29}$$

Where:

- N Effluent is the amount nitrogen in the effluent in kg N/year.
- Protein Consumption is the annual per capita protein consumption in kg/capita per year (based on Statistics Canada, 67.74 g/capita per day), kg/person/yr.
- Fraction N-Protein is the fraction of nitrogen in protein (0.16 kg N/kg protein).
- Factor Non-Consumed Protein is the factor for non-consumed protein added to the wastewater (IPCC default value of 1.1).
- Factor Industrial Protein is the factor for industrial and commercial co-discharged protein into the sewer system (IPCC 2006 default value of 1.25).
- N Sludge is the nitrogen removed with sludge (IPCC 2006 default value of 0 due to limited data), kg N/yr.

Based on the present population of the city of L'Assomption, N_2O emissions from wastewater treatment and discharge are as follows:

N Effluent = 67.74 g/capita per day x 22,429 x 0.16 x 1.1 x 1.25 = 334,254.9 g/day = 334.25 kg/day [30]

N_2O = 0.005 kg N_2O-N/kg N x 335.25 kg N/day x 44/28 = 2.63 kg N_2O/day [31]

If we consider the 10,000 m^3/day of influent to the plant, we can have the estimation per cubic metre of wastewater:

2.63 kg N_2O/day x 0.001 day/m^3 = 2.63 g/m^3 = 0.00263 g/L of wastewater [32]
where average nitrogen concentration is 67.74 g/capita per day.

4.4.3 Comparison of biogas emissions

Having the amount GHGs generated per litre of wastewater, the results of each phase can be compared. IPCC and Environment Canada guidelines consider N_2O as the sole gas emitted by wastewater treatment plants in the national inventory reports. Therefore, only N_2O emissions from each phase is considered. Because of the difference in the amounts of phase 3, the results are shown are separate graphs. These results in Figure 56 and Figure 57 are the accumulative amounts of N_2O produced per day.

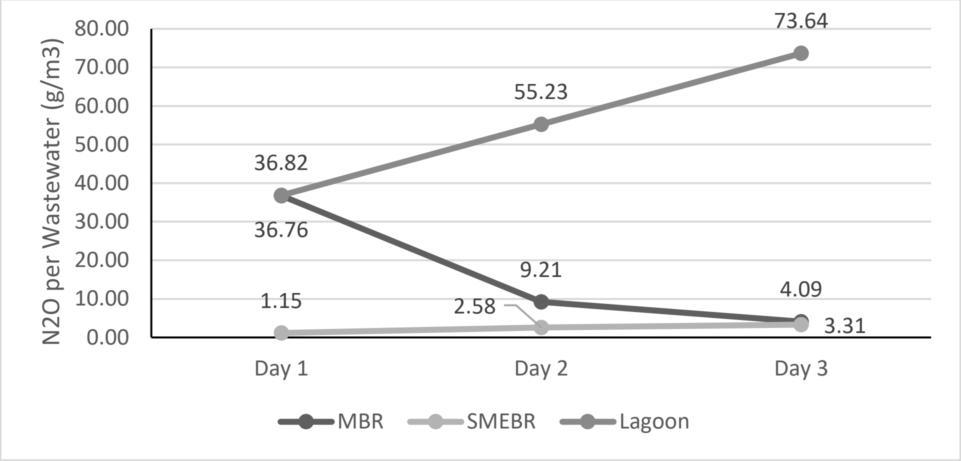

Figure 56: Comparison of phase 1, 2 and 4 with respect to N_2O produced per litre of wastewater

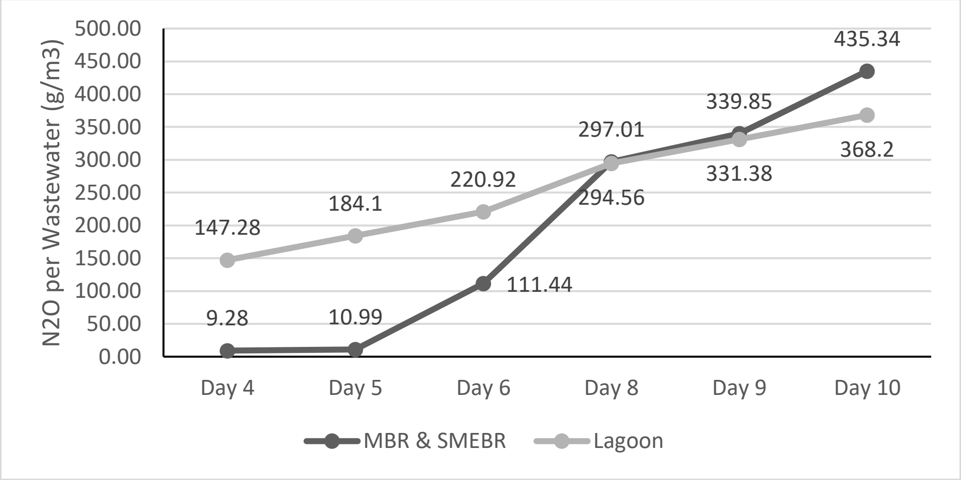

Figure 57:Comparison of phases 3 and 4 with respect to amounts of N_2O produced per litre of wastewater

Considering the effects of system closure on microbial activity, it would be better to compare the results of the first day of measurement. N_2O production estimation from the lagoons is around the same as the MBR reactor, and around 32 times more than SMEBR (Figure 56). Both lagoon and MBR methods produce around 36 g/m^3 of N_2O, while SMEBR method generated only 1.15 g/m^3. This shows the great potential of SMEBR method in wastewater treatment, providing close to zero N_2O production with 93% NH_3 removal efficiencies (Figure 35). This nitrogen removal with no N_2O production is due the capability of SMEBR method to have nitrification and denitrification in one single reactor.

Comparing the results of phase 3 and lagoon estimation in Figure 57, the MBR reactor produced on average around 150 g/m^3 less N_2O . However, an average NH_3 removal by MBR in three days of sampling was 7.5%. So, low N_2O production by the MBR part of phase 3 might be due to low NH_3 removal. Even in the reactor with DO being close to zero, SMEBR reactor produced N_2O close to the estimated value for lagoons, 2.63 mg/L of wastewater. It might be related to reactions on electrodes. Nevertheless, in the last three days of sampling, NH_3 concentration in the effluent started to decrease. This shows that SMEBR reactor started to improve NH_3 removal while slowing down the N_2O production.

Chapter 5: Conclusion, Contribution, Future Work

Conclusion

In this work, investigation of GHG emissions by municipal wastewater treatment facilities were studied. The study consisted of experimental stage in lab scale and estimating stage for full-scale
5.1 lagoon facilities. The experimental stage consisted of 3 phases when a conventional MBR and an advance SMEBR systems were run for comparison purpose. Such two different methods of treatment were studied, using two reactors active volumes. First, the reactors were run to achieve their steady state. Then, they were closed, and gas samples were collected. Then, samples were analyzed using gas chromatography to assess the concentration of CO_2, CH_4 and N_2O. The results were then presented with respect to various parameters. Finally, the results from each phase were compared to provide insight on the impact of by-products of such wastewater treatment methods on the environment.

The MBR reactor in phase 1 produced 21.61 g total CO_2 eq per litre of wastewater per day, while the SMEBR reactor in phase 2 generated 11.80 g total CO_2 eq. In phase 3, the MBR reactor produced 13.38 g total CO_2 eq, and the SMEBR reactor generated 24.14 g total CO_2 eq. Both these results showed a higher N_2O production in MBR reactors compared to SMEBR reactors. In phase 1, the MBR reactor produced 36.76 g N_2O per m^3 of wastewater. However, the SMEBR reactor in phase 2 generated only 1.15 g per m^3 of wastewater.

These results showed that under the same operating conditions and same wastewater composition, the SMEBR system produced less GHGs as by-products while providing higher quality of effluent. This can prove the existence of nitrification and denitrification in this reactor, providing a complete nitrogen removal from the influent. These reactors produced about the same amount of CO_2 per the amount of COD removed from the influent. However, SMEBR produced around 24 times less N_2O per NH_3 treated.

Furthermore, an estimation, using IPCC guidelines, was conducted for the emission of N_2O from lagoons for a comparison purpose.

The comparison between the results of reactors and estimations in Figure 56 showed that the MBR reactor and lagoon estimation both produced around 36 g per m^3 of wastewater, with

SMEBR reactor generating only 1.15 g per m^3 of wastewater. This shows a big difference on the amount of N_2O produced by these methods.

Overall, the SMEBR reactor results showed the lowest amounts of N_2O per litre of wastewater production (Figure 56), while providing the best NH_3 removal efficiency. The SMEBR system proved to perform simultaneously nitrification and denitrification in one reactor. On the other hand, lagoons estimation showed the highest values of N_2O production compared to other two methods, i.e. MBR, SMEBR.

The results also showed the impact of sudden transformation from the MBR to the SMEBR reactor, improving the removal efficiency of NH_3, while slowing down the increasing trend of GHG production. The N_2O produced by the MBR reactor was in average 1.0075 g per day. After the transformation, it went down to 0.97 g per day (Figure 52). Considering the concentration of NH_3 in the effluent, the SMEBR reactor also improved the removal efficiency (Figure 49). Without much time for acclimatization, the SMEBR reactor enhanced the MBR reactor performance.

The gases generated by MBR and SMBER systems could be collected and separated by special membranes. Then, the separated gases could be transformed and utilized for other purposes.

Considering the need to upgrade the existing lagoons in the province of Quebec and Canada, this work can provide insight for decision makers. To choose the method for the upgrade, decision makers can consider not only the effluent quality, but also the GHGs produced as by-products. This study updated the knowledge on GHG production by three methods, which can be used by decision makers.

Considering the small footprint of MBR and SMEBR comparing to lagoons, decision makers could also consider that advanced methods use around a quarter of the size needed for lagoons. Therefore, the cost of land would decrease. Furthermore, lower land use permits to provide the possibility of creating a healthy habitat for bird communities around the WWTP. There are usually birds living in the lagoon area; however, lagoons do not provide a health habitat. Upgrading lagoons by MBR or SMEBR could provide an opportunity for municipalities to create healthy habitats for aquatic organisms.

This study also showed the amount of CO_2 produced by MBR and SMEBR systems. This could suggest that policy makers need to include CO_2 emissions from wastewater treatment in the national inventory reports. Although the CO_2 emissions are from a biogenic source, they are produced as a result of human activities and are contributing to greenhouse effects and climate change. Including CO_2 in the national inventory reports can positively affect the regulations and policies; thus, they would not only consider the effluent quality, but also the emissions by WWTPs. These regulations could urge the municipalities and decision makers to choose the methods of treatment considering preventive measures to climate change.

5.2 Research Contribution

The most important contribution to the knowledge in this field was the measurement of GHGs emitted from a SMEBR reactor, which had never been done before. Furthermore, the measurement of GHGs from two lab-scale MBR reactors represented a major contribution to the current body of knowledge.

Regarding methodology, this study provided the necessary steps to collect gases produced by different wastewater treatment methods, including safety measures and strategies to overcome challenges.

5.3 Recommendations for Future Work

The measurement of GHGs produced in a pilot scale SMEBR system with a flowrate of 100 m^3/day could be the next step. A wider study could be done to also include the energy used in each reactor versus total CO_2 eq. A bigger scale could help to have more reliable results, avoiding significant gas measurement errors.

Regarding the methodology, continuous measurement of GHGs using available instruments, coupled with continuous measurement of the NH_3 and COD concentration, where biological processes and biogas production at the same time would be generated.

It would be recommended for a lager scale sampling to close the system for two days and collect only one sample for multiple times, which could provide more reliable results.

FISH, or PCR methods could be used to better understand the microorganisms’ involvement in production of GHG in each reactor.

References

Ashrafi, Omid. 2012. *Estimation of Greenhouse Gas Emissions in Wastewater Treatment Plant of Pulp & Paper Industry.* PhD Thesis, Montreal, Canada: Concordia University.

Bani Melhem, Khalid, and Maria Elektorowicz. 2010. "Development of a novel submerged membrane electro-bioreactor (SMEBR): performance for fouling reduction." *Environ. Sci. Technol. no. 44* 3298-3304.

Bani-Melhem, Khalid, and Maria Elektorowicz. 2011. "Performance of the submerged membrane electro-bioreactor (SMEBR) with iron electrodes for wastewater treatment and fouling reduction." *Journal of Membrane Science 379, no. 1-2* 434-439.

Brillas, Enric, Miguel Angel Banos, Marcel Skoumal, Pere Lluís Cabot, José Antonio Garrido, and and Rosa María Rodríguez. 2017. "Degradation of the herbicide 2, 4-DP by anodic oxidation, electro-Fenton and photoelectro-Fenton using platinum and boron-doped diamond anodes." *Chemosphere 68, no. 2* 199-209.

Cakir, F. Y., and M. K. Stenstrom. 2005. "Greenhouse gas production: a comparison between aerobic and anaerobic wastewater treatment technology." *Water research 39, no. 17* 4197-4203.

CCME, Canadian Council of Ministers of the Environment. 2006. *Municipal wastewater effluent development.* Report, Canadian Council of Ministers of the Environment.

Côté, Pierre, Hervé Buisson, Charles Pound, and Greg Arakaki. 1997. "Immersed membrane activated sludge for the reuse of municipal wastewater." *Desalination 113, no. 2-3* 189-196.

Daelman, M. R. J., Ellen M. van Voorthuizen, L. G. J. M. Van Dongen, E. I. P. Volcke, and M. C. M. Van Loosdrecht. 2013. "Methane and nitrous oxide emissions from municipal wastewater treatment–results from a long-term study." *Water Science and Technology 67, no. 10* 2350-2355.

Daelman, Matthijs RJ, Ellen M van Voorthuizen, Udo GJM van Dongen, Eveline IP Volcke, and Mark CM van Loosdrecht. 2012. "Methane emission during municipal wastewater treatment." *Water research 46, no. 11* 3657-3670.

Davis, Mackenzie Leo, and David A. Cornwell. 1998. *Introduction to environmental engineering.* McGraw-Hill Education.

Doorn, M. R. J., R. P. Strait, W. R. Barnard, and B. Eklund. 1997. *Estimates of global greenhouse gas emissions from industrial and domestic wastewater treatment.* Final report, Pechan (EH) and Associates, Inc.

Eggleston, Simon, Leandro Buendia, Kyoko Miwa, Todd Ngara, and eds Kiyoto Tanabe. 2006. *2006 IPCC guidelines for national greenhouse gas inventories. Vol. 5.* Hayama, Japan: Institute for Global Environmental Strategies.

Elektorowicz, Maria, Bani-Melhem, and Jan Oleszkiewicz. 2009. Submerged Membrane Electro-Bioreactor (SMEBR). United States of America Patent 12553,680.

Environment Canada, Greenhouse Gas Division. 2016. *National inventory report : greenhouse gas sources and sinks in Canada.* Report, Ottawa: Environment Canada.

EPA. 2016. *Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990–2014.* Report, EPA.

Fechner, Harold Hemond Elizabeth. 2014. *Chemical Fate and Transport in the Environment.*

Flemming, H-C., and J. Wingender. 2001. "Relevance of microbial extracellular polymeric substances (EPSs)-Part I: Structural and ecological aspects." *Water science and technology 43, no. 6* 1-8.

Foley, Jeffrey, David De Haas, Zhiguo Yuan, and Paul Lant. 2010. "Nitrous oxide generation in full-scale biological nutrient removal wastewater treatment plants." *Water research 44, no. 3* 831-844.

Fortin, Isabelle. 2000. *Study of municipal aerated lagoon system in Ste-Julie, Quebec.* Master Thesis, Montreal: McGill University.

Gao, Yuan. 2014. *Enhancement of wastewater treatment under low carbon/nitrogen ratio by using submerged membrane electro-bioreactor (SMEBR).* Master's Thesis, Montreal: Concordia University.

Haghighat, Fariborz, Omid Ashrafi, and Laleh Yerushalmi. 2014. "Greenhouse gas emission and energy consumption in wastewater treatment plants: impact of operating parameters." *CLEAN–Soil, Air, Water 42, no. 3* 207-220.

Hasan, Shadi W., Maria Elektorowicz, and Jan A. Oleszkiewicz. 2014. "Start-up period investigation of pilot-scale submerged membrane electro-bioreactor (SMEBR) treating raw municipal wastewater." *Chemosphere 97* 71-77.

Hassan, Shadi. 2011. *Design and Performance of a Pilot Submerged Membrane Electro-Bioreactor (SMEBR) for Wastewater Treatment.* PhD Thesis, Montreal: Concordia University.

Hengeveld, H., Whitewood, and A. Fergusson. 2005. *An introduction to climate change : a Canadian perspective.* Report, Canada: Environment Canada.

Hosseini, Seyedehfatemeh. 2016. *Novel submerged membrane electro-bioreactor-anaerobic/anoxic ammonia oxidation (SMEBR-Anammox).* Master's Thesis, Montreal, Canada: Concordia University.

Ibeid, Sharif. 2011. *Enhancement of the submerged membrane electro-bioreactor (SMEBR) for nutrient removal and membrane fouling control.* PhD Thesis, Montreal: Concordia University.

Ibeid, Sharif, Maria Elektorowicz, and Jan A. Oleszkiewicz. 2013. "Novel electrokinetic approach reduces membrane fouling." *Water research 47, no. 16* 6358-6366.

IPCC Team. 2014. *Climate change 2014: synthesis report. Contribution of Working Groups I, II and III to the Fifth Assessment Report of the intergovernmental panel on Climate Change.* Report, Geneva, Switzerland: IPCC, 151.

IPCC. 2018. *Warming of 1.5°C. An IPCC Special Report on the impacts of global warming of 1.5°C above pre-industrial levels and related global greenhouse gas emission pathways, in the context of strengthening the global response to the threat of climate change, sustai.* Report, In Press.

Kampschreur, Marlies J., Hardy Temmink, Robbert Kleerebezem, Mike SM Jetten, and Mark CM van Loosdrecht. 2009. "Nitrous oxide emission during wastewater treatment." *Water research 43, no. 17* 4093-4103.

Kheshgi, Haroon S., and Atul K. Jain. 2003. "Projecting future climate change: implications of carbon cycle model intercomparisons." *Global Biogeochemical Cycles* 17, no. 2.

Kowal, Przemysław, and Jacek Mąkinia. 2017. "The Relationship Between Gene Activity and Nitrous Oxide Production During Nitrification in Activated Sludge Systems." *Frontiers International Conference on Wastewater Treatment and Modelling.* Cham: Springer. 470-475.

Kuokkanen, A., A. Mikola, and M. Heinonen. 2017. "Seasonal and Diurnal Variations of GHG Emissions Measured Continuously at the Viikinmäki Underground WWTP." *Frontiers*

International Conference on Wastewater Treatment and Modelling,. Cham: Springer. 464-469.

Lobos, Jorge, Christelle Wisniewski, Marc Heran, and Alain Grasmick. 2008. "Sequencing versus continuous membrane bioreactors: effect of substrate to biomass ratio (F/M) on process performance." *Journal of membrane science 317, no. 1-2* 71-77.

McCarty, Perry L., and Bruce E. Rittmann. 2001. "Environmental biotechnology: Principles and applications." *Ed. McGraw Mil. Cap 2* 19-55.

Mollah, Mohammad YA, Saurabh R. Pathak, Prashanth K. Patil, Madhavi Vayuvegula, Tejas S. Agrawal, Jewel AG Gomes, Mehmet Kesmez, and David L. Cocke. 2004. "Treatment of orange II azo-dye by electrocoagulation (EC) technique in a continuous flow cell using sacrificial iron electrodes." *Journal of hazardous materials 109, no. 1-3* 165-171.

Monteith, Hugh D., Halla R. Sahely, Heather L. MacLean, and David M. Bagley. 2005. "A rational procedure for estimation of greenhouse-gas emissions from municipal wastewater treatment plants." *Water Environment Research 77, no. 4* 390-403.

Moreira, J. F. V., and M. C. Boudreault. 2011. *Évaluation de performance des ouvrages municipaux d'assainissement des eaux pour l'année 2011.* Report, Quebec: Ministère des Affaires municipales, des Régions et de l'Occupation du territoire (MAMROT).

Park, Ki Young, Yuhei Inamori, Motoyuki Mizuochi, and Kyu Hong Ahn. 2000. "Emission and control of nitrous oxide from a biological wastewater treatment system with intermittent aeration." *Journal of bioscience and bioengineering 90, no. 3* 247-252.

Pfafflin, James R., and Edward N. Ziegler. 2006. *Encyclopedia of Environmental Science and Engineering, Volumes One and Two.* CRC Press.

Post, Wilfred M., Tsung-Hung Peng, William R. Emanuel, Anthony W. King, Virginia H. Dale, and Donald L. DeAngelis. 1990. "The global carbon cycle." *American scientist 78, no. 4* 310-326.

Sahely, Halla R., Heather L. MacLean, Hugh D. Monteith, and David M. Bagley. 2006. "Comparison of on-site and upstream greenhouse gas emissions from Canadian municipal wastewater treatment facilities." *Journal of Environmental Engineering and Science 5, no. 5* 405-415.

Tallec, Gaelle, Josette Garnier, Gilles Billen, and Michel Gousailles. 2006. "Nitrous oxide emissions from secondary activated sludge in nitrifying conditions of urban wastewater treatment plants: effect of oxygenation level." *Water research 40, no. 15* 2972-2980.

Thompson, Alexander. 2010. *REALTIME MONITORING OF NITROUS OXIDE EMISSIONS FROM WASTEWATERTREATMENT PROCESSES BY MEMBRANE INTRODUCTION MASS SPECTROMETRY.* MASTER OF SCIENCE Thesis, Colwood: ROYAL ROADS UNIVERSITY.

Wei, Chunliang. 2016. *Nutrient Removal and Fouling Reduction in Electrokinetic Membrane Bioreactor at Various Temperatures.* PhD Thesis, Winnipeg: University of Manitoba .

WMO. 2019. *2019 concludes a decade of exceptional global heat and high-impact weather.* December 3. Accessed December 6, 2019. https://public.wmo.int/en/media/press-release/2019-concludes-decade-of-exceptional-global-heat-and-high-impact-weather.

World Meteorological Organization. 2017. *WMO Statement on the State of the Global Climate in 2016.* World Meteorological Organization (WMO).

Wunderlin, Pascal, Joachim Mohn, Adriano Joss, Lukas Emmenegger, and Hansruedi Siegrist. 2012. "Mechanisms of N2O production in biological wastewater treatment under nitrifying and denitrifying conditions." *Water research 46, no. 4* 1027-1037.

Zhan, Xinmin, Zhenhu Hu, and Guangxue Wu. 2015. *Greenhouse Gas Emission and Mitigation in Municipal Wastewater Treatment Plants*. IWA PUBLISHING.