

**Estimation of Greenhouse Gas Emissions from Industrial Wastewater Treatment
Plants**

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ABSTRACT

Estimation of Greenhouse Gas Emissions from Industrial Wastewater Treatment Plants

Maziar Bani Shahabadi

The outcome of Kyoto protocol and other National and International agreements influence the design and operation of wastewater treatment facilities by restricting their greenhouse gas (GHG) emissions. Wastewater treatment plants (WWTPs) are recognized as one of the larger minor sources of GHG emissions that produce CO₂, CH₄, and N₂O during the treatment processes. The overall on-site and off-site greenhouse gas (GHG) emissions by WWTPs of food processing industry were estimated by using an elaborate mathematical model. Three different types of treatment systems were examined in this study which included aerobic, anaerobic, and hybrid anaerobic/aerobic processes. The overall on-site emissions were 1952, 1992, and 2435 kg CO₂e/d while the off-site emissions were 1313, 4631, and 5205 kg CO₂e/d for the aerobic, anaerobic and hybrid treatment systems respectively. The on-site biological processes made the highest contribution to GHG emissions in the aerobic treatment system while the highest emissions in anaerobic and hybrid treatment systems were obtained by off-site GHG emissions due to on-site material usage. Biogas recovery and reuse as fuel were shown to cover the total energy needs of the treatment plants for aeration, heating and electricity for all three types of operations, and considerably reduced GHG emissions by 512, 673, and 988 kg CO₂e/d from a total of 3265, 6623, and 7640 kg CO₂e/d for aerobic, anaerobic, and hybrid treatment systems, respectively. In the end, recommendations were given on feasible approaches to reduce GHG emissions from WWTPs.

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Chapter 1

Introduction

1.1 Nature of Greenhouse Gases (GHGs)

GHGs are gases in the atmosphere that cause the Greenhouse effect. GHGs mainly include water vapor, carbon dioxide, methane, nitrous oxide, and ozone. Without the impact of GHGs, the earth surface average temperature would be -19°C (Baede et al., 2001). Incoming solar radiation hits the surface of the planet; some part of this energy is reflected from the surface in the form of infrared radiation. Clouds and the atmosphere also radiate infrared radiation. The GHGs absorb part of this radiation, which elevates the kinetic energy of their molecules. Elevated concentrations of GHGs induce the elevated atmospheric heat retention and cause GHGs perform as a blanket that keeps solar heat inside the atmosphere. The energy absorbed by GHGs increases the temperature of the earth to the current average temperature of 14°C (Baede et al., 2001).

Since the beginning of the industrial revolution, the concentration of GHGs in the atmosphere has increased. This is mostly due to human activities (anthropogenic sources) like fossil fuel production and combustion, human promoted anaerobic decomposition in landfills, industrial operations, and application of fertilizers (IPCC, 2001a). Table 1.1 presents the concentration of GHGs in 1750 compared to their concentration in 1998. The accumulation of GHGs reduces the amount of energy escaping the atmosphere. This leads to an increase in the average surface temperature of the earth.

Each GHG has a different contribution to the overall greenhouse gas effect. For example, one tonne CH₄ in the atmosphere has 23 times the Global Warming Potential (GWP) of one tonne of CO₂ over a 100-year period. GWP is related to the radiative forcing potential and atmospheric life time of the gas. Methane has a shorter residence time than CO₂ in the atmosphere, so the relative GWP of CH₄ compared to CO₂ decreases from 56 over a 20-year period to 6.5 over a 500-year period (Pickin et al., 2002). The unit of CO₂-equivalent (CO₂e) is used to assess the impact of different GHGs compared to CO₂.

Table 1.1- Relative global warming potential, residence time, and atmospheric concentrations of eight major GHGs in 1750 and 1998 (Ramaswamy et al., 2001)

GHG	Global warming potential over 100-year period	Atmospheric residence time (years)	Atmospheric concentration in 1750 (ppb)	Atmospheric concentration in 1998 (ppb)
CO ₂	1	5-200 ^a	278000	365000
CH ₄	23	12	700	1745
N ₂ O	296	114	270	314
CFC-12*	10600	100	0	0.533
CFC-11*	4600	45	0	0.268
PFC*	6500-9200	2600-50000	0	0.083
HFC*	140-11700	0.3-260	0	0.022
SF ₆ *	23900	3200	0	0.042

*CFC, chlorofluorocarbon; PFC, perfluorocarbon; HFC, Hydrofluorocarbon; SF₆, Sulfur hexafluoride

^aNo single life time can be allocated to CO₂ because of different rate of uptake by different removal processes.

It is recommended by the Intergovernmental Panel on Climate Change (IPCC) to consider the CO₂e over a 100-year time frames for use in GHG inventories. Table 1.1 also gives the GWP and atmospheric residence time of different GHGs.

Global average temperatures have risen by 0.6 ± 0.2 °C over the past century (IPCC, 2001b). According to a report by IPCC “there is new and stronger evidence that most of the warming observed over the last 50 years is attributable to human activities” (IPCC, 2001b). With this evidence in place, there have been increasing international attempts to mitigate the increase of GHG concentrations in the atmosphere.

1.2 Greenhouse gases and the Kyoto Protocol:

Kyoto protocol is an international agreement that resulted from the United Nations Framework Convention on Climate Change (UNFCCC). The goal of the UNFCCC was to attain stabilization of GHG concentrations in the atmosphere at a level that would avoid dangerous anthropogenic intrusion with the climate system. This goal requires serious efforts to reduce the emissions of GHGs. Canada signed the UNFCCC on June 12, 1992, and ratified the treaty on December 4, 1992. The UNFCCC did not allocate specific GHG emission targets for each nation at first. The GHG emissions targets were allocated at the Third Conference of the Parties to the UNFCCC in Kyoto, Japan, from December 1 to 10, 1997, which created the Kyoto Protocol. The Kyoto Protocol demands nations from the UNFCCC to decrease their overall GHG emissions by at least 5% from the national emission levels of 1990, and this must be achieved during the commitment period of 2008–2012 (UNFCCC, 1997). Canada signed the Kyoto

Protocol on April 29, 1998 and ratified the protocol on December 17, 2002 (UNFCCC, 2004). Under the Kyoto protocol commitment, Canada should reduce its GHG emissions to 94% of its GHG emissions in 1990. Canada emitted 608 Mt (megatonnes) CO₂e in 1990 (Olsen et al., 2003) and so Canada must reduce its GHG emission to 571 Mt CO₂e under the Kyoto Protocol commitment. The Canadian government predicts that GHG emissions will reach 809 Mt CO₂e, if no action is taken to reduce the emissions before 2010, which is the middle point of the Kyoto Protocol commitment period. Therefore, according to the Government of Canada's climate change plan, GHG emissions must be reduced by 240 Mt CO₂e for Canada to meet its commitment under the Kyoto Protocol (Government of Canada, 2002). The GHGs covered under the Kyoto Protocol are carbon dioxide, methane, nitrous oxide, hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and sulphur hexafluoride. Kyoto Protocol has three aims. The first is to reduce the GHG emissions; the second is to produce a framework for commoditization of fixed carbon and impose cost for emitted carbon; and the third is to be a driver of renewable energy and carbon sequestration technology development and the technology transfer to developing countries (Greenfield and Batstone, 2005). There has been greater success with the second objective, especially in Europe where carbon credits are traded at 12-13 Euros/tonne (Richter and Talley, 2003).

1.3 The relationship between GHG emissions of waste sector and Wastewater Treatment Plants (WWTPs):

With the ratification of the Kyoto Protocol by Canada, each sector of the economy should determine its emissions and establish reduction strategies. The wastewater

treatment sector is classified as one of the larger minor sources of greenhouse gas emissions (U.S. EPA, 1997). As mentioned before, in reporting the GHG emissions, the Canadian national inventory categorized wastewater treatment sector under the “waste” sector along with solid waste disposal on land and waste incineration. From 1990 to 2005, GHG emissions from waste sector increased about 4.8 Mt, or 20.7%, exceeding the population growth of 16.5% (Environment Canada, 2005). Table 1.2 shows the GHG emission attributed to solid waste disposal, wastewater handling, and waste incineration under the waste sector category from 1990 to 2005. It is clear that the GHG emissions because of wastewater handling increased from 780 Kt CO₂e in 1990 to 930 Kt CO₂e in 2005, indicating a 20% increase in GHG emissions from the treatment processes in the WWTPs. As presented in Table 1.2, in year the 2005, the waste sector accounted for approximately 28000 Kt CO₂e or 3.7% of total Canadian GHG emissions of 747000 Kt CO₂e.

**Table 1.2-Waste sector GHG emission inventory
(Environment Canada, 2005)**

Source Category		1990	2003	2005	2003-2005	1990-2005
		Kt CO ₂ e	Kt CO ₂ e	Kt CO ₂ e	change	change
Total		596000	745000	747000	0.3%	25.3%
Waste		23000	27000	28000	3.2%	20.7%
a.	Solid waste disposal on land	22000	26000	27000	3.2%	21.9%
b.	Wastewater handling	780	910	930	2.4%	20.1%
c.	Waste incineration	400	230	240	4.3%	-41.0%

In the waste sector, solid waste disposal on land accounted for the majority of emissions with 27000 Kt CO₂e, while wastewater handling and waste incineration accounted for 930 and 240 Kt CO₂e respectively. The Canadian climate change inventory calculates the wastewater treatment contribution to the country's total GHG emissions to be 0.12% in year 2005. This estimation considers only on-site emissions resulted from the wastewater treatment process and the emissions originating from the off-site energy generation to operate the wastewater treatment plants are not assigned to the wastewater treatment sector, but remain associated with the energy sector. Therefore, if the upstream emissions are added to the existing values, the fraction of GHG generation from wastewater treatment plants increases considerably.

1.4 Objective of the thesis:

In the near future, WWTPs will be investigating abatement strategies to reduce the generation of GHGs to avoid possible taxes imposed on these operations due to stringent environmental protocols, like Kyoto. In order to achieve this objective, the amount of GHGs generated by the treatment plants and the processes that produce them must be determined. The present research is aimed at the development of a comprehensive methodology for the estimation of GHG emissions from WWTPs and its application in the estimation of emissions from industrial operations, particularly food processing. Literature-cited data of full-scale and pilot-scale WWTPs are used in this study. Mathematical models based on the kinetics of biological processes and mass balance methodologies are developed to estimate the extent of GHG emissions by the diverse

aerobic and anaerobic treatment processes used in WWTPs under various operating conditions. GHG emissions during energy generation processes are estimated by using emission coefficients and Global Warming Potential (GWP) as recommended by the (IPCC, 2001a). Recommendations are made on feasible approaches to reduce GHG emissions from WWTPs.

Chapter 2

Literature review

2.1 The GHGs produced in the wastewater treatment plants:

The GHGs attributed to the wastewater treatment plants are carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O). Wastewater treatment is believed to be a significant source of N₂O emissions. However, accurate quantities of these emissions are not available due to the lack of reliable measurement techniques (Rittmann and McCarty, 2001; Barton and Atwater, 2002). Although N₂O emissions occur during both nitrification and denitrification processes, denitrification has been reported to be a more important source of N₂O (Barton and Atwater, 2002). N₂O generation can be avoided with the implementation of complete nitrification and denitrification. Accordingly, in this study N₂O emissions have not been taken into consideration and only CO₂ and CH₄ are considered as the greenhouse gases emitted from wastewater treatment plants. This study did not consider GHG emissions related to tertiary unit operations such as filtration and disinfection.

2.2 Types of industrial wastewater treatments:

Generally the WWTPs include these unit operations:

- 1- Preliminary treatment, such as comminution, screening, and grit removal processes

- 2- Flow equalization for damping the flow rate variations and to reach a constant flow rate
- 3- Primary treatment, using primary clarification
- 4- Secondary treatment, mainly using biological processes for the oxidation of carbonaceous and nitrogenous organic compounds
- 5- Nitrogen removal, depending on local environmental standards for nitrogen concentration in the effluent
- 6- Solid treatment for thickening the primary and secondary sludge, digestion of solids (either aerobically or anaerobically), dewatering of the digested sludge

The effluent from the secondary treatment is disinfected and released into the natural water course. The digested solid is landfilled if it does not have the appropriate quality for land application or if this process is not economically viable. Figure 2.1 represents a flow diagram of a typical wastewater treatment facility.

The present study focuses on the wastewaters from the food processing industry. Vegetable processing wastewaters are nutrient deficient and need to overcome their nutrient limitation (Xu et al., 2006). Anaerobic processes have been successfully applied for the treatment of several types of food processing wastewaters. Cannery and meat processing can be treated with anaerobic filters (AF) and up-flow anaerobic sludge blanket (UASB) reactors (Oliva et al., 1995). Poultry slaughterhouse wastewaters are successfully treated with a dissolved air-floatation system followed by UASB reactors (Del Nery et al., 2001).

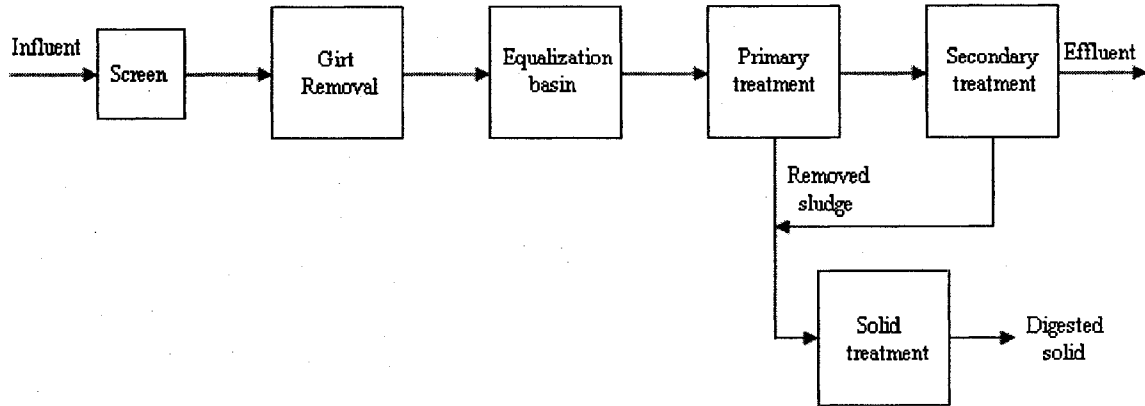


Figure 2.1- A typical wastewater treatment flow diagram

It is reported that meat processing plants, dairies, beer, soft drink and food canning plants extensively use anaerobic technology to treat their wastewater (Del Nery et al., 2007). Anaerobic lagoons have also been used extensively for high strength industrial wastewaters like meat processing (Crites and Tchobanoglous, 1998). Vegetable processing wastewaters are treated with hybrid anaerobic/aerobic technologies (Austermann-Haun et al., 1999). However, anaerobic processes are usually not capable of meeting final discharge requirements (Moody and Raman, 2001) and hybrid anaerobic/aerobic processes are employed to meet the discharge requirements. The schematic diagram of a hybrid anaerobic/aerobic treatment is illustrated in Figure 2.2.

Successful treatment of meat-processing wastewater was demonstrated using UASB reactors followed by rotating biological contactors (RBC) with overall pollutant removal efficiencies of more than 90% (Wahaab and El-Awady, 1999). In such applications, the low soluble nutrient concentration, commonly found in high strength food processing wastewaters, can limit the efficiency of anaerobic treatment. Therefore, solubilization of nutrients by anaerobic hydrolysis can be attempted (Xu and Nakhla, 2007) followed by

aerobic treatment processes such as activated sludge system to polish the wastewater and increase the removal efficiency, thus meeting the discharge standards.

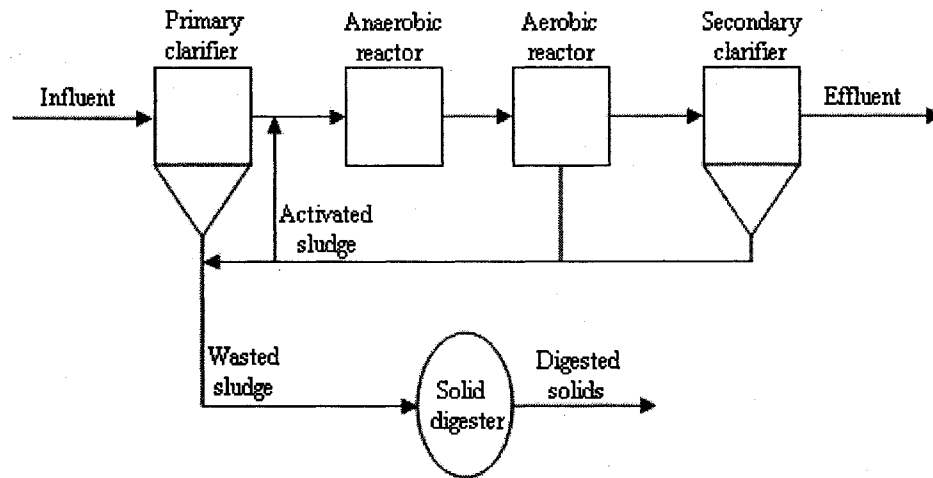


Figure 2.2- Schematic diagram of hybrid anaerobic/aerobic wastewater treatment

Anaerobic Membrane BioReactors have also been used to treat food processing wastewaters (Butcher, 1989; Choate et al., 1983). The presence of membranes increases the retention of microbial biomass and lowers the suspended solids content of the effluent, thus improving its quality. Also the retention of biomass by membranes decouples the solid retention time (SRT) from the hydraulic retention time (HRT) while increasing the concentration of biomass, permitting higher organic loading rates and smaller reactor sizes. This design allows the treatment system to reach the discharge standards without the aerobic post-treatment stage that exists in hybrid anaerobic/aerobic treatments. Membrane technology is used widely as the final polishing process, but the cost of membrane treatment is higher than aerobic treatment while it makes it less favorable for industries. Consequently, treatment plants commonly use hybrid anaerobic/aerobic processes where the anaerobic treatment precedes aerobic treatment.

Treatment of industrial effluents with a high organic matter content has been preferably pursued with anaerobic biological reactors due to the significant economic and technical advantages compared to aerobic treatment. Some of the advantages of using anaerobic treatment compared to aerobic treatment are (Metcalf and Eddy, 2003):

- 1- Less energy required by anaerobic treatment
- 2- Less biological sludge production
- 3- Methane production that can be used as energy source
- 4- Smaller reactor volumes required compared to aerobic treatment processes (that reduces the capital cost of the treatment process)
- 5- Rapid response to substrate addition after long periods without feeding.

A remarkable point in anaerobic treatment is producing a useful energy byproduct-methane gas. The biogas then can be used in boiler to generate heat to warm up the wastewater and elevate temperature because in anaerobic treatment elevated temperature is needed to let the slow growing methanogens grow. The produced biogas also can be combusted in generators for electricity generation. In both cases, the biogas eliminates the need of fossil fuel importation to meet the energy demand of WWTP. This means less GHG production because of the energy need of WWTP. This issue is further discussed.

When nutrient removal is required during the treatment process, conventional activated sludge processes or an activated sludge process along with a membrane treatment process is used instead of anaerobic treatment (Moussa et al., 2004). A schematic diagram of conventional activated sludge system is shown in Figure 2.3.

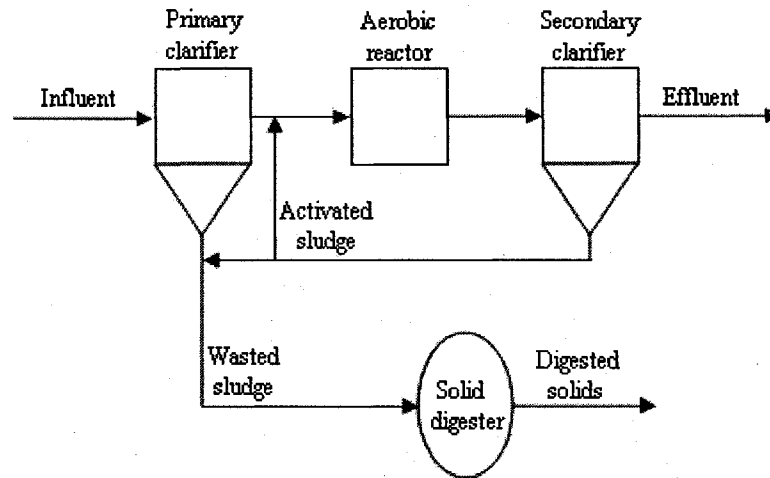


Figure 2.3- Schematic diagram of activated sludge treatment system

Anaerobic treatment systems also have some disadvantages compared to aerobic treatment. They include (Metcalf and Eddy, 2003):

- 1- Need for longer start-up time to develop necessary biomass inventory,
- 2- Slow growth rate of methanogenic organisms that demands a long solid retention time
- 3- Complexity of the system
- 4- Requirement for alkalinity addition
- 5- Requirement for further treatment with an aerobic processes to meet discharge criteria
- 6- Lack of biological nitrogen and phosphorous removal in solely anaerobic treatment
- 7- Sensitivity to adverse effect of lower temperatures on reaction rates
- 8- Susceptibility to upset due to toxic substances

9- Potential for the production of odors and corrosive gases

10- Lower effluent quality.

Wastewaters originating from food processing industries are treated by a variety of processes. Hybrid anaerobic/aerobic treatment, anaerobic treatment, and aerobic treatment are all applied successfully to treat food processing wastewater. The purpose of this study is to develop a method for the estimation of GHG emissions from food processing wastewater treatment plants independent of the applied method of treatment. Therefore, for each type of treatment, an appropriate generic methodology for GHG estimation from WWTP is developed, implying that three different methods of GHG emissions estimation are developed associated with three distinct types of treatment.

2.3 The sources of GHG attributed to the WWTP:

The GHG emissions of WWTP originate from two distinct sources. They are on-site GHG emissions that occur inside the WWTP due to biological processes used for the removal of contaminants, and also combustion of fossil fuels for energy and heat production, and off-site or upstream GHG emission because of off-site production and transmission of fuels and chemicals and off-site generation of electricity.

2.3.1 On-site GHG emissions: A number of processes inside the wastewater treatment plant produce GHG emissions, they include:

- 1- Removal of soluble organic matter aerobically or anaerobically which is measured by BOD (Biochemical Oxygen Demand) in the wastewater
- 2- Endogenous respiration of the microorganisms in charge of BOD removal
- 3- CO₂ production from combustion of biogas resulting from anaerobic solids digestion for energy recovery or gas flares
- 4- Leakage of biogas which mainly consists of CH₄
- 5- CO₂ production from the combustion of fossil fuels such as natural gas or diesel fuel for heating purposes and other energy requirements

The current GHG emissions inventories for Canada and the United States do not consider emissions of CO₂ resulting from the biogas combustion. This is related to the issue of biomass and renewable fuels. According to Intergovernmental Panel on Climate Change (IPCC), emissions of CO₂ resulting from biomass and biomass-based wastes like decomposition of food are not included in national emissions estimates (IPCC, 2000; El-Fadel and Massoud, 2001). This is because of the assumption that over time the re-growth of biomass in the form of crops and forests equals the consumption of biomass and so emissions of processes that generate CO₂ from such wastes are not treated as net GHG emissions. Also the CO₂ produced from the flaring of biogas produced from such wastes degradation is considered as being derived from biomass sources, therefore it is not considered as GHG. Only the CO₂ emissions resulting from treatment and incineration of wastes and wastewaters that are produced from fossil fuel-derived raw material is considered as GHG (e.g. oil, paints, polymers, and textiles). The emissions of other GHGs such as methane or N₂O from nutrient removal operations are considered in

this method. The IPCC concept is accurate under a very strict set of conditions that are rarely met in reality. For example only if the biomass or the renewable fuels are produced without the fossil fuel input then the CO₂ emissions are zero. In addition the fossil fuels produced for consumption in wastewater treatment plants and the emissions resulting from the combustion of these fuels should be counted as GHG. IPCC considers this issue by attributing the fossil fuel input for agriculture (for example to run the tractors) to energy sector and so the corresponding GHG emission because of combustion of this fossil fuel is ascribed to the energy sector. Also the fossil fuel produced for wastewater treatment operations and corresponding emissions of GHGs resulting from the combustion of these fuels on-site are transferred to the energy sector. So the net zero assumption by IPCC can give helpful information just on the national inventory level because national inventories monitor the overall emissions of GHGs. Although the emissions of CO₂ resulting from biomass and biomass-based wastes are not directly attributed to wastewater treatment processes, they are considered somewhere else during national GHG inventories. So the net zero assumption should be used with caution when the life cycle assessment is considered. In the present work, the on-site CO₂ emissions are considered as GHG emissions associated with the wastewater treatment process.

2.3.2 Off-site GHG emissions: The off-site sources of GHG emissions are the production and transmission of fuels for on-site consumption for heat and energy generation, and the off-site production of electricity for WWTP. As described earlier, in national GHG inventory these upstream GHG emissions are attributed to energy sector. For conducting GHG inventory for WWTP, the GHG emissions of fuel and electricity

generation should be allocated to the end user which is the wastewater treatment facility. The GHG emissions attributed to fuel and electricity demand is calculated based on the amount of energy used in plant. This issue will be described further in the methodology chapter.

2.4 Characteristics of food processing wastewater:

Typically, anaerobic digestion has been applied as a stand alone treatment choice to industrial WW with a high biodegradable carbon content (Greenfield and Batstone, 2005). Food processing wastewaters are suitable for treatment by anaerobic processes because they do not contain toxic and inhibitory compounds. Apart from the cleaning of the equipments and floors and walls at the end of the working day by means of chemicals, the other sources of the wastewater from food processing industry include the preparation and processing of raw vegetables or animal meat. The characteristics of the food processing wastewater depend on the nature and type of organic compounds and their concentrations in the raw material, and the upstream processes used. These wastewaters are among the most concentrated wastewaters.

The effluent from the fruit and vegetable industry has a high organic loads and contains cleaning and blanching agents, salt, and suspended solids such as fibers and soil particles. They may also contain pesticide residues washed from the raw materials. The major parts of solid wastes are the organic materials such as discarded fruits and vegetables. The characteristics of wastewater from fruit and vegetable processing plants are shown in Table 2.1. Vegetable processing wastewaters are nutrient deficient which

means that the soluble nutrients are not sufficient to support cell synthesis and the biodegradation processes.

Table 2.1- Data comparison for vegetable and fruit processing wastewater

Wastewater	BOD ₅ mg/l	COD mg/l	FOG mg/l	TSS mg/l	TKN mg/l	Total P mg/l	Reference
Tomato processing	1680-2000	4500-5420		1000-1650	120-140	14-24	[1]
Maize processing		1100-98960		800-72500			[2]
Potato processing	155-3465	389-5899	10-296		88-509	6-51	[3]

Note: FOG: fat, oil and grease; TSS: total suspended solids; TKN: total Kjeldahl nitrogen; NH₄-N: ammonium nitrogen; Total P: total phosphorus.

[1] Xu and Nakhla, 2007

[2] Ross et al., 1992

[3] Austermann-Haun and Seyfried, 1992

Vegetable processing wastewaters are typical of slowly biodegradable high strength wastewaters generated from the food canning industry. They contain high particulate and colloidal fractions that are not only slowly biodegradable but also exhibit very poor settling characteristics (Xu and Nakhla, 2007). Preliminary treatment of these wastewaters includes screening and grit removal, if required. This is followed by pH adjustment and biological treatment of the organic load. These types of wastewater are mostly treated with anaerobic treatment methods or hybrid anaerobic/aerobic method as mentioned before (Austermann-Haun et al., 1999; Del Nery et al., 2007; and Austermann-Haun and Seyfried, 1992).

The meat processing industry is known to produce wastewaters with a high concentration of organic compounds and high organic loads. Table 2.2 shows the

contaminant concentration in wastewaters from slaughterhouse and meat and poultry processing plants.

Table 2.2- Data comparison for meat and poultry processing wastewater

Wastewater	BOD ₅ mg/l	COD mg/l	FOG mg/l	TSS mg/l	TKN mg/l	NH ₄ -N mg/l	Total P mg/l	Reference
Slaughterhouse	490-650	1500-2200	50-100		120-180		12-20	[1]
Slaughterhouse	1600-3000	4200-8500	100-200	1300-3400	114-148	65-87	20-30	[2]
Poultry processing	660-6400		55-3570	40-3700			14-19	[3]
Poultry processing	1116	1177	169			9		[4]
Turkey processing	706	1552	253	281				[5]
Turkey processing	704		93	270				[4]
Turkey processing		2192	156	981	90		21	[6]

Note: FOG: fat, oil and grease; TSS: total suspended solids; TKN: total Kjeldahl nitrogen; NH₄-N: ammonium nitrogen; Total P: total phosphorus.

[1] Sayed et al., 1987

[2] Stebor et al., 1990

[3] Rusten et al., 1998

[4] Ross et al., 1990

[5] Sheldon et al., 1990

[6] U.S. EPA, 2002

Effluent from meat processing facilities has a high fraction of slowly biodegradable organic material. The concentration of this material is not precisely measured by conventional BOD₅ tests. The wastewater from a slaughterhouse can contain blood, manure, hair, fat, feathers, and bones. The wastewater contains high organic material and nitrogen, as well as pathogens and pesticide residues from treatment of animals or their feed. Chloride concentrations from curing and pickling may be very high and up to 77000 mg/L. The wastewater temperature is also considerably higher because of process conditions (Wahaab and El-Awady, 1999). The processes used in the treatment of meat

and poultry processing wastewaters are similar to those used in the treatment of municipal wastewaters (Eremektar et al., 1999). Primary treatment processes such as screens and fat traps and flotation precede secondary biological treatment. Common biological treatment systems such as conventional activated sludge, extended aeration, oxidation ditches, and sequencing batch reactors have been used for meat and poultry processing wastewater. Biological treatment consisting of anaerobic lagoon systems followed by activated sludge process is used for about 25% of the US poultry facilities (U.S. EPA, 2002).

Vegetable and meat processing industries are the major food processing industries, and therefore this study is based on the wastewaters originating from these two industries.

2.5 Unit operations responsible for GHG emission:

The main purpose of this study is the estimation of GHG emission from WWTP. The wastewater treatment study or the applicability of treatment methods for treating specific wastewaters are not addressed in this study. Since the main focus is on the GHG emissions, the study has focused on unit operations which are responsible for GHG emissions in the treatment plant as described below. The unit operations responsible for GHG production are anaerobic and aerobic reactors, and digesters which are then further described below.

2.5.1 Anaerobic Tank: When an oxidation reduction reaction involves electron acceptors other than oxygen, for example like organic compounds, Fe, SO₄, CO₂, the

reaction is considered to be anaerobic. The microorganisms engaged in anaerobic reactions can generate energy by fermentation. They can be divided into two categories: Obligate anaerobes which can live in an environment depleted of oxygen and they do not tolerate any trace of oxygen, and facultative anaerobes which have the ability to grow in either presence or absence of oxygen. Anaerobic processes take place in an anaerobically controlled environment called anaerobic reactors. There are several anaerobic processes used in industrial wastewater treatment. These include completely mixed suspended growth anaerobic digesters, anaerobic contact processes, and anaerobic sequencing batch reactors (ASBR), sludge blanket and attached growth processes, anaerobic lagoons, and membrane separation. In the completely mixed anaerobic digester, the HRT and SRT are equal. The complete mix digester is appropriate for wastewaters with high concentration of solids or high soluble organic concentration where the thickening of solids is difficult to perform (Metcalf and Eddy, 2003). Figure 2.4 illustrates a completely mixed process.

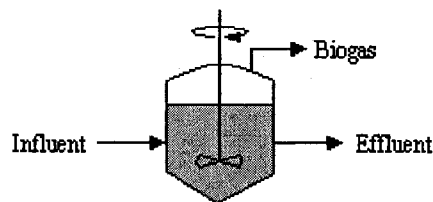


Figure 2.4- Completely mixed suspended growth anaerobic digester

In the anaerobic contact process the disadvantage of completely mixed process is overcome by sludge recycling so that the SRT is longer than HRT (Metcalf and Eddy, 2003). Figure 2.5 shows a typical anaerobic contact process.

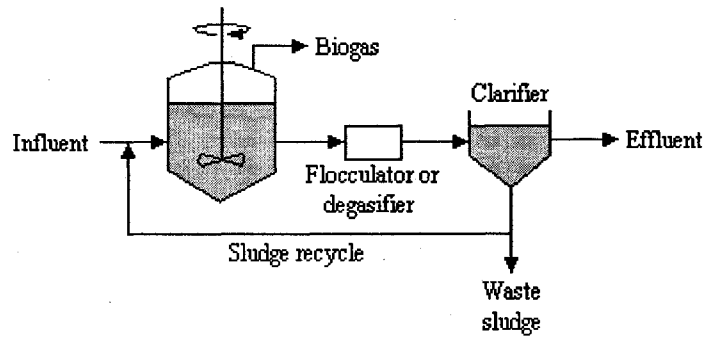


Figure 2.5- Anaerobic contact process

Anaerobic sequencing batch reactor (ASBR) is a suspended growth process where the biological processes and solid-liquid separation occur in the same reactor. The operation of ASBR consists of four steps: 1) feed, 2) react, 3) settle, and 4) decant/effluent withdrawal. The success of this process depends on the formation of good settling granulated sludge (Metcalf and Eddy, 2003). Figure 2.6 demonstrates a typical ASBR.

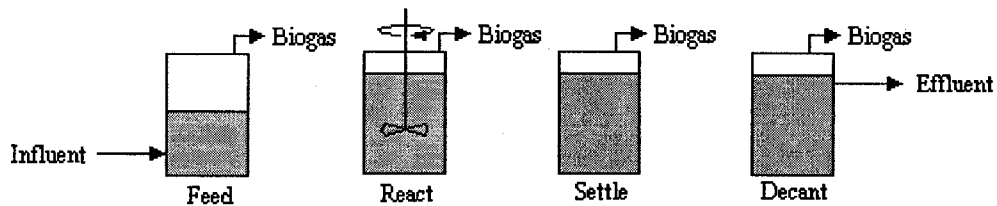


Figure 2.6- Anaerobic sequencing batch reactor (ASBR)

In addition to the aforementioned processes, there is a notable development in anaerobic technology called the sludge blanket process. The major types of sludge blanket processes include 1) the original UASB process and its modification, 2) the anaerobic baffled reactor (ABR), and 3) the anaerobic migrating blanket reactor

(AMBR). Of these processes, the UASB process is commonly used to treat a wide range of industrial wastewaters (Metcalf and Eddy, 2003). In this process the influent wastewater is introduced from the bottom of the reactor and moves in the upflow direction through the sludge blanket. The key feature of the UASB reactor that permits the high volumetric COD loading compared to other anaerobic treatment methods is its dense granulated sludge blanket at the bottom of the reactor. To provide better solid capture in the system, the UASB reactor is often coupled with a settling tank. Figure 2.7 shows a UASB reactor with a sedimentation tank and sludge recycling system.

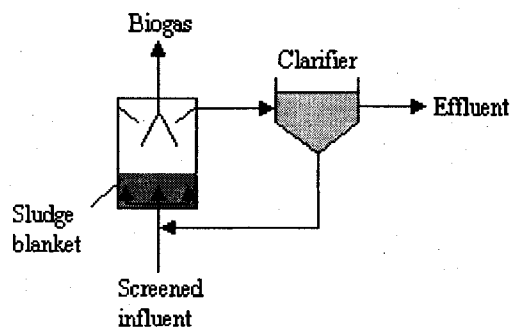


Figure 2.7- UASB reactor with sedimentation tank and sludge recycle

Attached growth anaerobic processes use a variety of packing materials and they are divided with respect to the degree of their bed expansion. There are generally three types of anaerobic attached growth treatment reactors: 1) anaerobic upflow packed-bed reactor, 2) anaerobic expanded bed reactor, 3) anaerobic fluidized bed reactor (Peavy et al., 1985). In these reactors the wastewater is introduced from the bottom of reactor and it flows upward through the spaces between the packing material and biomass. In most

cases, synthetic plastic packing material is used to support the biomass growth. Normally biomass is recycled in order to prevent its washout.

In addition to anaerobic processes mentioned above, there are other anaerobic processes that have been developed such as anaerobic lagoon and membrane separation anaerobic treatment process. Membrane technology was described earlier. The anaerobic lagoons are used for the treatment of various types of industrial wastewaters including food processing (Crites and Tchobanoglous, 1998). A typical anaerobic lagoon is shown in Figure 2.8.

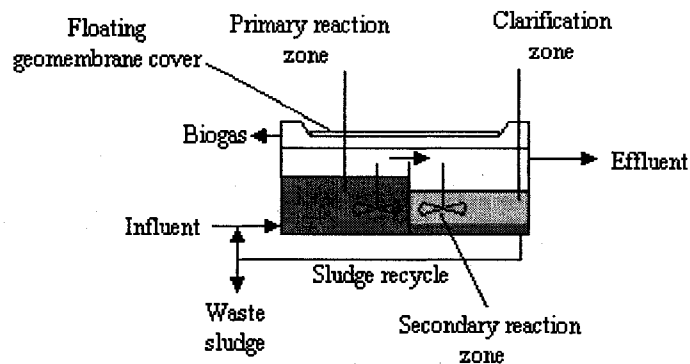


Figure 2.8- Covered anaerobic lagoon

The main advantage of the covered lagoon is its capability of accepting a wide range of wastewaters with different characteristics. Other advantages are simple and economic construction, large volume that causes equalization of loads and a high effluent quality. The principal disadvantage of lagoons is that they require a large area and a geomembrane cover.

In hybrid anaerobic/aerobic reactors the anaerobic reactor is coupled with an aerobic treatment method (mainly activated sludge). A schematic diagram of hybrid

treatment method was presented in Figure 2.2. In hybrid anaerobic/aerobic treatment methods, the microorganisms in anaerobic reactor hydrolyze and solubilize the particulate nutrients and substrate for uptake and biodegradation, and in the next step they utilize the soluble substrate and nutrient and produce biogas. The completion of hydrolysis and biodegradation depends on the HRT and SRT in anaerobic reactor. With long HRT and SRT, most of the substrate will be hydrolyzed and consumed by microorganisms in an anaerobic reactor. In some cases the HRT and SRT are not long enough to let microorganisms consume the soluble substrate and the process only provides time for hydrolysis and fermentation. In this case the anaerobic reactor acts as pre-fermentation reactor and most of biodegradation is carried out in the next reactor which contains aerobic condition. Under these conditions, almost no biogas is produced during the anaerobic process because of the low HRT and SRT employed. So the extent of biodegradation in each reactor depends on the residence time of wastewater in each reactor. In food processing wastewaters, as mentioned before, due to nutrient deficiency and the presence of slowly biodegradable and high strength wastewaters (Xu and Nakhla, 2007), hydrolysis is a necessary step to provide soluble substrate and nutrient for biodegradation. In these treatment systems, an anaerobic reactor is commonly used as the pre-fermentation reactor (Xu and Nakhla, 2007; Xu and Nakhla, 2006; and Xu et al., 2006). The anaerobic pre-fermentation reactor increases the rate of soluble BOD and COD by hydrolysis. The volatile fatty acid content of wastewater increases considerably from the anaerobic reactor's influent to its effluent (Xu and Nakhla, 2006), indicating the effectiveness of anaerobic reactor in hydrolyzing the substrate. Hybrid treatment methods take advantage of positive points of both anaerobic and aerobic treatment methods. In

these systems, anaerobic treatment precedes the aerobic treatment, and the major substrate degradation occurs in anaerobic reactor, yielding biogas that can be recovered for use as fuel, contributing to energy conservation. The subsequent aerobic treatment, contributes to the removal of nutrients which could not be removed by the anaerobic treatment alone. The treated wastewater after aerobic post-treatment achieves the dry-ditch discharge criteria of soluble biochemical oxygen demand (SBOD) <10 mg/L, total suspended solids (TSS) <10 mg/L, ammonia nitrogen <3 mg/L and soluble phosphorus <0.5 mg/L (Xu and Nakhla, 2006). Furthermore, since some biodegradation occurs in the anaerobic reactor, less energy is required for treatment in aerobic stage compared to full aerobic treatment. Normally, biological treatment processes require a BOD:N ratio of 100:5. The solubilization of nutrients in the anaerobic reactor provides soluble nutrients, thus circumventing the limitations imposed by nutrient-limited wastewaters such as those produced in food processing wastewaters, providing technical and economical benefits to the treatment plant. Respirometric studies have shown that the use of an anaerobic pre-fermentation reactor improves biodegradation kinetics. In addition, the readily biodegradable fraction of substrate and the maximum specific growth rate of biomass increase during the anaerobic stage (Xu et al., 2006), indicating that the anaerobic reactor's effluent wastewater is more readily biodegradable than the raw wastewater.

Three basic steps are included in the overall oxidation of wastewaters in an anaerobic reactor: 1) hydrolysis, 2) fermentation (also known as acidogenesis stage), and 3) methanogenesis. During the hydrolysis step, the particulate material is hydrolyzed to soluble compounds and simple monomers that are used by fermentation bacteria. During

the fermentation stage, amino acids, sugars, and some fatty acids are degraded further. During this process organic substances serve as both the electron donors and acceptors. The principal products of the fermentation are acetate, hydrogen, carbon dioxide, propionate and butyrate. The propionate and butyrate are fermented further to produce hydrogen, carbon dioxide, and acetate. So the final products of fermentation are acetate, hydrogen, and CO_2 which are the supporters of methane formation during the methanogenesis stage. During the methanogenesis process, one group of microorganisms transforms acetate into methane and CO_2 and the other group of microorganisms produces methane from the reaction of carbon dioxide and hydrogen by using hydrogen as the electron donor and the CO_2 as the electron acceptor. So the methanogenic organisms serve as hydrogen sink that allows the fermentation reaction to proceed. If the methanogenesis process is upset and the produced hydrogen is not consumed by the methanogenic bacteria at the same rate as its production, then the production of hydrogen gas during the fermentation process will slow down and the volatile fatty acids will accumulate in the anaerobic reactor, resulting in the decrease of liquid pH, thus inhibiting further biodegradation processes. This implies that the anaerobic process proceeds at a higher rate and it is more stable when the concentrations of volatile fatty acids are kept at a minimal level, indicating a high rate of methanogenesis and a minimum accumulation and emission of hydrogen gas. Because of the low free energy changes for anaerobic process, growth yield coefficients and microbial kinetics are remarkably lower than the corresponding values for aerobic treatment.

The rate-limiting steps in anaerobic processes are: 1) hydrolysis, 2) soluble substrate utilization rate for fermentation and methanogenesis. The hydrolysis of particles

does not affect the process operation and stability but it affects the conversion of total solids and their accessibility for biodegradation. During the treatment of wastewaters that contain high concentrations of solids, the hydrolysis process is essential in order to ensure the availability of adequate soluble substrate for microorganisms, enabling them to carry on further biological reactions. In hybrid anaerobic/aerobic treatment systems the pre-fermentation and hydrolysis of substrate is carried out in an anaerobic reactor and this facilitates further biodegradation processes and the removal of remained organic material from the wastewater. The hydrolysis process is especially crucial for the treatment of food processing wastewaters that suffer from nutrient bioavailability, and contain high concentrations of poorly biodegradable substrate. After hydrolysis, the rate limiting step is the conversion of the volatile fatty acids by the methanogenic microorganisms and not the fermentation process. Reactor temperatures of 25-35°C are preferred to support optimal rates of biological reactions and a stable treatment. At lower temperatures, the reaction rates are lower, implying that longer solid retention times, larger reactors, and lower COD loadings are needed (Banik and Dague, 1996). At higher SRTs, the concentration of suspended solids in the effluent may increase up to 100 mg/L or even higher since high solid retention times, especially under anaerobic condition produce less flocculent solids (Metcalf and Eddy, 2003). Thus a method should be used to retain solids in the anaerobic reactor. A longer SRT is also needed when the solid hydrolysis process is the rate-limiting step compared to fermentation or methanogenesis.

During anaerobic biodegradation processes, the produced GHGs are in the form of CO₂ and CH₄. Normally, the biogas produced during anaerobic processes contains 60-70% CH₄ and 30-35% CO₂ on volume basis (Metcalf and Eddy, 2003). As mentioned

before, the anaerobic treatment process is advantageous because of the lower biomass yields and the production of methane that can be recovered from the biological conversion of organic substances and used as fuel. The GHGs are produced in anaerobic biological reactors where a fraction of carbon in the BOD is transformed by anaerobic microorganisms to CO_2 and CH_4 and the rest of BOD is converted to biomass. A fraction of the carbon integrated into biomass is further converted to CO_2 and CH_4 via decay of biomass inside the anaerobic reactor. The rest of the carbon incorporated into the biomass will leave the biological reactor and is separated from the treated liquid in clarifiers. As mentioned above, some solids are returned to the biological reactor to maintain the microorganisms' population in the anaerobic reactor and to ensure adequate treatment efficiency while the rest of solids will be wasted. Carbon in the waste solids is then converted to other forms during the solid treatment processes. Figure 2.9 illustrates the stages and types of GHG produced during anaerobic biological reactors.

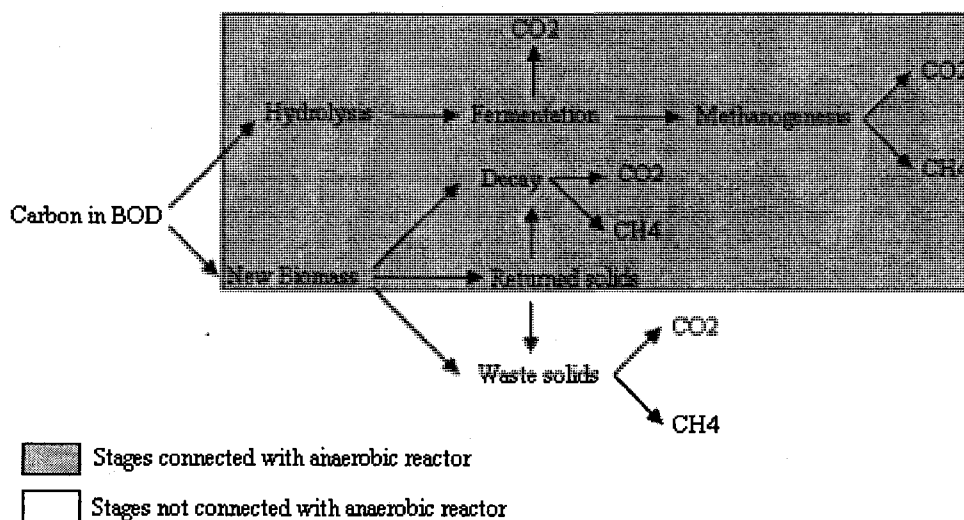


Figure 2.9- Stages and types of GHG produced in an anaerobic reactor

2.5.2 Aerobic Tank: Oxygen is used as the electron acceptor in aerobic processes. Organisms that use oxygen as the terminal electron acceptor and can gain energy via the transfer of electrons to oxygen are called obligate aerobes. There are also some bacteria that can use nitrate/nitrite as electron acceptors when oxygen is not available. These bacteria are called facultative aerobic bacteria. An aeration reactor is a vessel where the biological treatment occurs in the presence of oxygen by means of aerobic bacteria. A fraction of biodegradable carbon, represented by biodegradable chemical oxygen demand (bCOD) or biochemical oxygen demand (BOD) will be oxidized to CO_2 by microorganisms and the rest will be converted to new biomass, known as volatile suspended solids (VSS). In the aerobic biological reactor, contact time is provided for mixing and aerating the influent wastewater with suspended microorganisms. These microorganisms are commonly referred to as mixed liquor suspended solids (MLSS) or more specifically, mixed liquor volatile suspended solids (MLVSS). Mechanical devices are also used to provide mixing and to supply oxygen to the aerobic process. The mixed liquor is then transferred to a clarifier where the microbial suspension is settled and thickened and returned to the process again. The settle biomass is called activated sludge because it contains active microorganisms and it is then returned to the aerobic biological reactor to continue the biodegradation of the influent material. A portion of thickened solid is discarded periodically as the process produces excess biomass that accumulates with the non-biodegradable solids in the influent wastewater. If the excess biomass is not removed, they will find their way to the effluent wastewater and decrease the treatment efficiency. Similar to the anaerobic processes, aerobic processes can also be carried out with suspended-growth or attached-growth microorganisms. Suspended-growth processes

use microorganisms in suspension for the removal of contaminants. In these processes adequate mixing is essential to ensure that microbial biomass is kept in suspension. An example of a suspended growth process is the activated sludge process. Activated sludge process is divided into four main categories. 1) Complete mix process, 2) Plug-flow process, 3) Oxidation ditch, 4) Sequentially operated systems. The complete mix process is the application of continuous flow to a stirred tank reactor. The wastewater and recycled sludge are introduced at several points in the aeration tank. Because of the mixing, the organic load and oxygen concentrations are uniform throughout the tank. The advantage of a complex mixed process is the dilution of shock loads which occurs in the treatment of industrial wastewaters. This process is rather easy to operate but it does not produce a high efficiency at high concentrations of organic substrate. Figure 2.10 presents a completely mixed activated sludge process.

In plug flow reactors, the wastewater and returned sludge enter the front end of the aeration tank and they are mixed by diffused air or mechanical aeration.

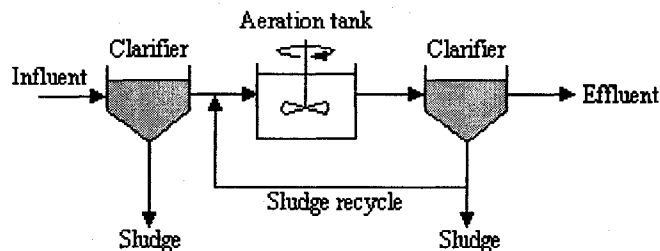


Figure 2.10- Completely mixed activated sludge

Normally, three to five channels are used. In modern designs of the plug flow reactors, the aeration system is designed to match the oxygen demand along the length of tank, by applying higher rates of oxygen in the beginning and lower rates near the end of

the reactor. There are some modification of this type of treatment like high rate aeration and step feed. Figure 2.11 shows the typical conventional plug flow treatment process.

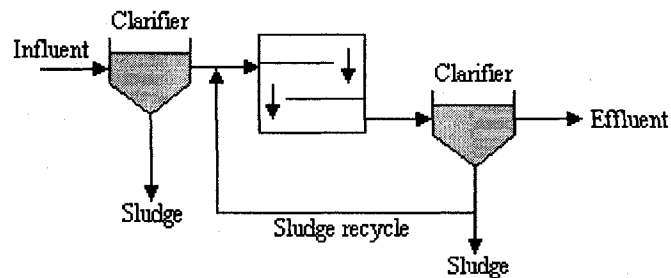


Figure 2.11- Conventional plug flow treatment process

The oxidation ditch consists of a ring or oval shaped channel equipped with mechanical aeration and mixing devices. Screened wastewater enters the channel and is mixed with recycled sludge. The tank configuration, aeration and mixing devices cause unidirectional channel flow. The magnitude of flow causes the dilution of the influent wastewater. The process kinetics are similar to the complete mixing process but there is a plug flow pattern along the channel. Figure 2.12 shows a typical oxidation ditch.

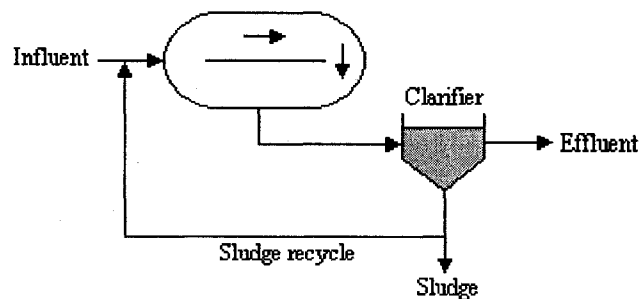


Figure 2.12- Oxidation ditch

The sequencing batch reactors can operate under aerobic or anaerobic conditions. The anaerobic sequencing batch reactor (ASBR) was described before. Under aerobic conditions, aeration is provided during the reaction stage in order to prevent oxygen depletion.

If nutrient removal is required along with the removal of carbonaceous compounds during the treatment of wastewater, the treatment systems will undergo certain modifications in order to incorporate the necessary process conditions required for nutrient removal. These processes will be described later.

In attached growth processes, the microorganisms are attached to a packing material inside the reactor. The organic material and nutrients are removed from the wastewater that flows through the reactor and is in intimate contact with the immobilized microorganisms, also known as biofilm attached on packing material. The most common aerobic attached growth treatment systems are trickling filters and Rotating Biological Contactors (RBC).

As described before, aerobic treatment processes result in the generation of greenhouse gases (GHGs) in the form of CO₂ during the oxidation of the carbonaceous material, represented by BOD or COD. Some CO₂ is also produced during endogenous respiration of microbial biomass that carries a fraction of influent carbon and is formed as a result of anabolic microbial metabolism. An additional source of GHG generation is the treatment of the waste solids that will generate carbon dioxide alone (if treated aerobically), or carbon dioxide and methane (if treated anaerobically). Figure 2.13 shows the stages and types of GHG produced during aerobic biological reactors.

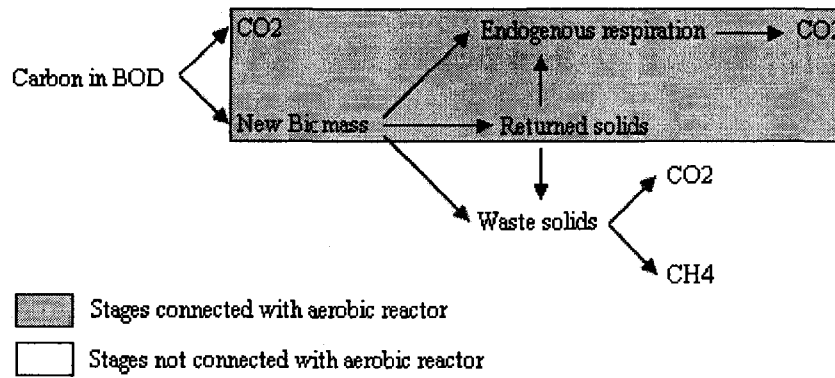


Figure 2.13- Stages and types of GHG produced in aerobic reactor

2.5.2.1 Nutrient removal processes in aerobic tank: In addition to carbon removal, GHGs are also generated during the removal of nutrients, particularly during the nitrogen removal process. Nitrogen removal is commonly carried out in wastewater treatment systems by a two-stage biological process called nitrification and denitrification. Nitrification, the first stage of nitrogen removal, is an aerobic process and is carried out by a two-step process in which ammonia is first oxidized to nitrite (NO_2) followed by the oxidation of nitrite to nitrate (NO_3). During this process there is a large oxygen requirement of 4.2 mg oxygen for the oxidation of 1 mg ammonia nitrogen to nitrate. In denitrification step which is an anoxic process, the produced nitrate is reduced to nitrogen gas. The nitrogen cycle in biological treatment process is shown in Figure 2.14. There is a high demand for energy expenditure during the nitrification process to supply the large volumes of oxygen needed for the oxidation of ammonia. Biological GHGs in the form of nitrous oxide are generated during the nitrification process. This process also contributes to the generation of carbon dioxide and methane since it produces nitrifying bacteria that will undergo endogenous decay or will be treated by solid digestion processes.

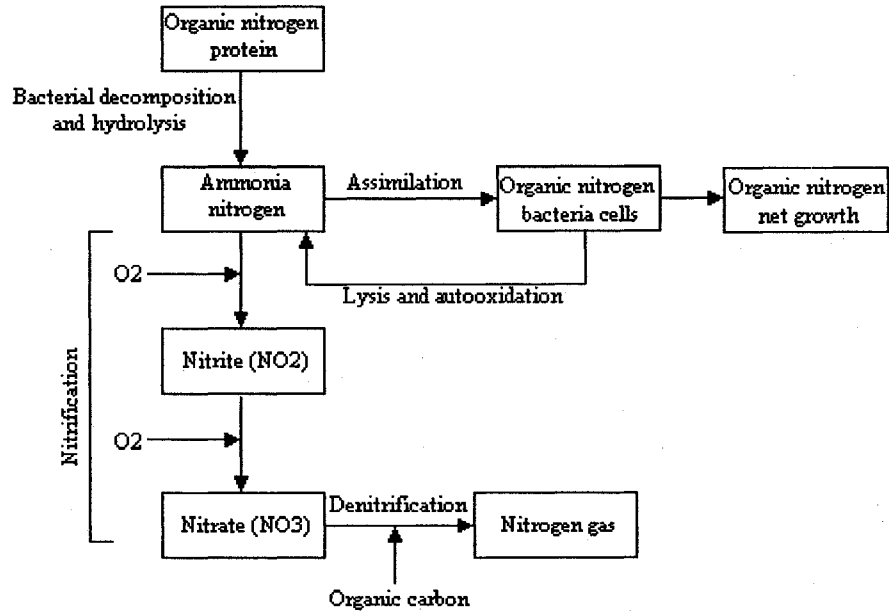


Figure 2.14- Nitrogen transformations in biological treatment (Sedlak, 1991)

In suspended growth processes, most commonly used by the industrial wastewater treatment processes, nitrification is carried out along with BOD removal in a single-sludge process that contains the aeration tank, clarifiers and sludge recycle. In the presence of toxic compounds in the wastewater that may inhibit the activity of nitrifying bacteria, a two-sludge suspended growth system is used which consists of two aeration tanks and two clarifiers in series with the first aeration tank/clarifier unit operating at short SRT for BOD removal. Figure 2.15 shows a two-sludge suspended growth system designed for nitrogen removal (Peavy et al., 1985). In this design, the BOD and toxic substances are removed in the first unit and the nitrification proceeds in the second unit. The bacteria responsible for nitrification grow more slowly than heterotrophic bacteria that are used for BOD removal, and they require longer HRTs and SRTs to ensure a complete nitrification (Metcalf and Eddy, 2003). Since the food processing wastewaters

do not contain toxic compounds, the single-sludge nutrient removal process is used for treatment of these wastewaters.

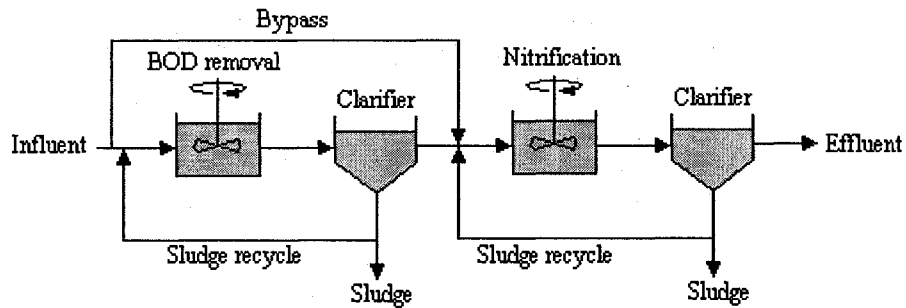
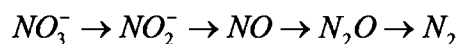


Figure 2.15- Two-sludge suspended growth system for nutrient removal

In attached growth treatment systems that include nitrification, the major fraction of BOD should be removed before a stable population of nitrifying bacteria can be established in the system. The heterotrophic bacteria have higher biomass yield and dominate the surface area of fixed films over nitrifying bacteria. Therefore in attached growth systems, nitrification is accomplished after BOD removal, or it proceeds in a separate treatment system, employed only for nitrification.

Denitrification is the biological conversion of the organic substrate using nitrate or nitrite as electron acceptor instead of oxygen in the absence of dissolved oxygen. The nitrate reduction reactions involve the following steps.



There are two common methods used for denitrification. In pre-anoxic method (U.S. EPA, 1993) the aeration tank in a complete mixing process is divided into two

zones of anoxic and aerobic. Figure 2.16 shows a typical pre-anoxic treatment method used for the removal of nutrients and COD.

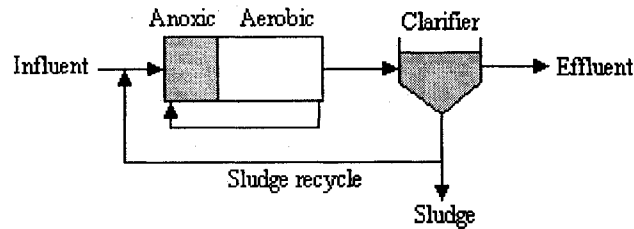


Figure 2.16- Preanoxic process

The influent wastewater is fed to the anoxic zone which is followed by the aerobic zone. Nitrate is produced in the aerobic zone and is returned to the anoxic zone via recycled sludge. Denitrification occurs in the anoxic zone by the transfer of electrons from organic carbon in wastewater (electron donor) to nitrate (electron acceptor) which transforms the produced nitrate to nitrogen gas. COD removal is carried out in the aerobic zone. The second method is called post-anoxic denitrification (Peavy et al., 1985) where denitrification occurs in the anoxic part of reactor following nitrification in aerobic section of reactor. In this method, the source of electron donor is either the decaying biomass or it must be supplied by an external carbon source such as methanol or acetate. since biodegradable carbon has mostly been depleted during the BOD removal process that precedes nitrification. Post-anoxic method can also use attached growth microbial biomass. Figure 2.17 illustrates a post-anoxic treatment method.

There is a new technology for nitrogen removal called the Anammox process. In this method only a fraction of influent nitrogen is oxidized to nitrite and it is used as the electron donor to oxidize ammonia under anaerobic conditions to nitrogen gas and small

amounts of nitrate. In this process, contrary to the traditional nitrification-denitrification process, there is no need for an external supply of carbon source.

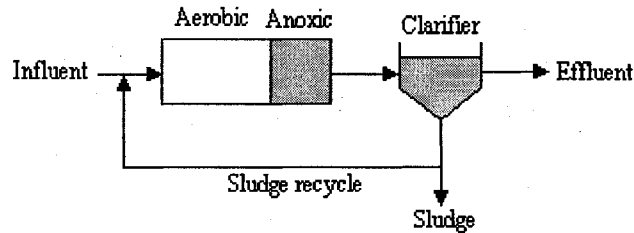


Figure 2.17- Postanoxic process for denitrification

The Annamox process is used in a technology called Sharon (single-reactor high activity ammonia removal over nitrite) for biological nitrogen removal. In the Sharon process, the recycle flow from dewatering of anaerobically digested solids which has high concentration of ammonia enters a complete-mixed reactor with intermittent aeration for nitrification and denitrification. Methanol is added to supply the electron donor for anoxic stage. For the generation of a nitrite-rich flow, the Sharon process is operated without an anoxic step or methanol addition (Metcalf and Eddy, 2003).

Phosphorous removal can be performed by chemical or biological processes. Chemical treatment uses alum or iron salts. However, biological phosphorous removal is more widely used because of the reduced chemical cost and less sludge production compared to chemical phosphorous removal processes. The reactor configuration for biological phosphorous removal aims to encourage phosphorous accumulating organisms to consume the phosphorous in the system. This is mostly accomplished by placing an anaerobic tank that has an HRT of 0.5-1 hr before the aeration tank. In this system, the

return activated sludge combines with effluent from primary clarifier before entering the anaerobic reactor.

2.5.3 Digester: In the solid treatment stage, thickening, conditioning, dewatering and drying are used primarily to remove water from the solids. These processes are not designed to remove the BOD of solids, but they are used to improve the sludge's condition for better biodegradation in biological digester. Therefore, these processes do not contribute to GHG generation because of the lack of organic matter biodegradation. Clearly, all of these processes contribute to GHG generation since they all need energy to operate. GHG production during energy consumption processes will be discussed later.

Digestion, composting, and incineration are the main processes used to stabilize and treat the organic matter present in the solids. Because during these processes biodegradation is the main reaction, these processes are responsible for GHG generation. Since the main objective of this study is to estimate GHG generation during wastewater treatment processes, only biological stabilizing and treatment processes are discussed in more details. As mentioned previously, the sources of waste solids during the treatment process include screening and grit removal processes, primary sedimentation, and secondary sedimentation. After passing through conditioning processes, the sludge enters the digestion process. There are two distinct digestion methods: 1) Anaerobic digestion, 2) Aerobic digestion. Anaerobic digestion involves the decomposition of organic and inorganic matter in the absence of oxygen. Most industrial WWTP use anaerobic digesters to treat their concentrated sludge. The processes in anaerobic digester are hydrolysis, fermentation, and methanogenesis, as discussed before. The important

environmental factors in anaerobic digestion process are: 1) Solid Retention Time (SRT), 2) Hydraulic Retention Time (HRT), 3) Temperature, 4) Alkalinity, 5) pH, 6) Presence of inhibitory substances, and 7) Bioavailability of trace metals and nutrients. Biogas is produced during solid disintegration and biodegradation processes. The biogas contains about 65% to 70% CH₄ by volume, 25% to 30% CO₂ and small portions of N₂, H₂, H₂S, water vapor, and other gases (Metcalf and Eddy, 2003). The production of biogas is an important indicator for the progress of the digestion process. As mentioned before, the generated CO₂ and CH₄ during the digestion process contribute to the overall GHG production of the treatment system. There are various types of digesters used for solid treatment. Figure 2.18 presents a typical single stage high rate anaerobic digester.

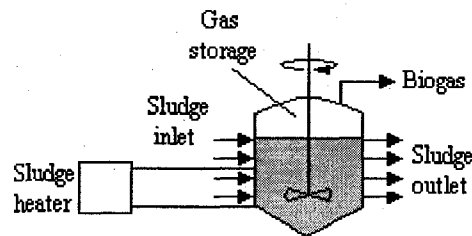


Figure 2.18- Single-stage high-rate anaerobic digester

The volume of gas produced during the digestion process is estimated from the percentage of volatile solid destruction. In large plants, the digester gas is used as fuel for boiler and internal combustion engine which are used for pumping and electricity generation. The hot water from heating boilers or the jacket water from the internal combustion engines can be used for sludge heating. The methodology to calculate the amount of produced biogas is presented in methodology section of the thesis.

Aerobic digesters are also used in the treatment of the solid waste. However, they suffer from certain disadvantages compared to anaerobic digesters including: 1) high cost of energy associated with providing the required oxygen, 2) dependency of process on temperature, location, tank geometry, concentration of influent solids, type of mixing and aeration, and the type of tank material, and 3) lack of methane generation. Aerobic digestion is similar to the activated sludge process. When the substrate has been depleted, the microorganisms (biomass) start to consume their own protoplasm to gain necessary energy by endogenous decay. In this process, the cell tissue is oxidized in the presence of oxygen to CO_2 , H_2O , and NH_4^+ . Only about 80 percent of cell material can be oxidized and the rest is inert compounds or non-biodegradable organic compounds. The ammonia produced in this process is oxidized to nitrate as digestion proceeds. Non-biodegradable solids will remain as the final product of digestion. Aerobic digesters can operate in batch or continuous flow regimes. The oxygen requirement during aerobic digestion can be calculated from the stoichiometric equation for biomass destruction inside the digester. The methodology to calculate the amount of oxygen will be presented in the methodology chapter. The oxygen residual should be kept at a minimum value, around 1 mg/L, under all operating conditions in order to support the biological reactions and prevent an unwanted anaerobic environment. Also, the contents of the aerobic digester should be well mixed to ensure its proper operation. Multiple mixing devices are often used to provide adequate mixing.

Composting is sometimes used after digestion to further stabilize the sludge. Composting is a process in which organic material undergoes complete biological degradation to stable end products. Around 20 to 30 percent of the organic solids are

converted to CO₂ and water (Metcalf and Eddy, 2003). During decomposition of the organic material, the temperature of the compost increases and pathogen organisms are destroyed. Then the composted biosolids may be used as soil conditioner. Composting is carried out under both aerobic and anaerobic conditions; however, the aerobic treatment method is more frequently used since it accelerates the material decomposition, minimizes the potential for nuisance odors, and raises the temperature which is necessary for the destruction of pathogenic microorganisms. The types of composting methods are: 1) Aerated static pile, 2) Windrow, and 3) In-vessel composting systems. The aerated static pile system is composed of a grid of aeration and exhaust piping over which a mixture of dewatered sludge and bulking material is placed. A layer of screened compost is placed on top of the pile for insulating the compost.

Windrow composting systems are similar to aerated static pile operations, but they are constructed in rows and are turned and mixed occasionally during the composting period.

In-vessel composting systems are performed in an enclosed chamber or vessel. Mechanical devices are designed to control the environmental conditions such as air flow rate, oxygen concentration, and temperature. These systems require a smaller area, have a better process control and result in a faster yield, lower odor generation, and lower labor cost compared to other types of composting.

Usually, not all of the organic matter in sludge is degraded during the digestion process, and some will remain in the effluent from the digester. This justifies the use of composting as a supplementary process for biodegradation of organic material in the sludge. For computation of the GHG produced during digestion and composting of

sludge, it is assumed that all of the organic matter is removed during digestion and no composting is required since most of Industrial Wastewater Treatment Plants (IWWTPs) do not use composting to supplement the digestion process. This issue is further described in methodology chapter. Figure 2.19 shows the stages and types of GHG produced during biological solid treatment in the digestion and composting processes.

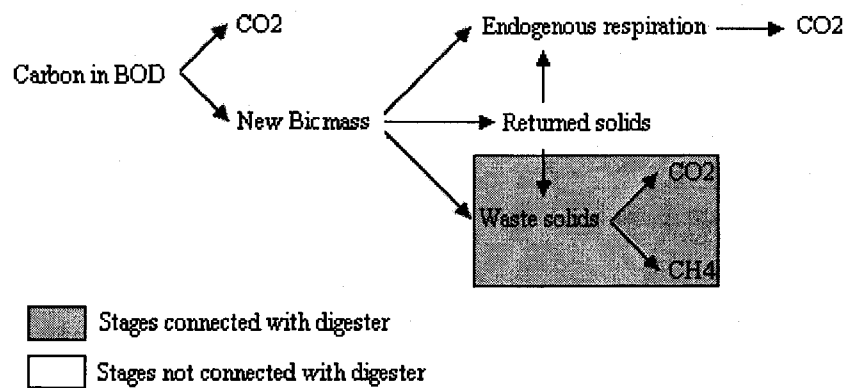


Figure 2.19- Stages and types of GHG produced during biological solid treatment in digesters (and compost)

Another option for solid treatment is the incineration of sludge. It involves the conversion of organic solids to oxidized end products that are mainly CO₂, water and ash. The major advantage of incineration is that it reduces the volume of sludge to a great extent and lessens the disposal requirement. But there are some disadvantages including: 1) High operating cost, 2) Highly skilled operators required for maintenance and operation, 3) Atmospheric emissions as well as ash that may have undesirable environmental impacts, and 4) Possible generation of hazardous waste requiring handling and disposal. For these reasons, incineration of sludge is seldom used in North America and the present study ignores this method of solid treatment.

2.6 Existing GHG estimation methodologies:

The recent GHG estimations for WWTPs focus on municipal wastewater. The methods of treatment of municipal wastewaters are different from industrial wastewaters and the GHG emission resulting from municipal wastewaters are totally different from industrial wastewaters. Aerobic treatment is more favorable for municipal wastewaters and anaerobic treatment is the preferred method of treatment for most of industrial wastewaters, among them food processing wastewaters.

In addition to different methods of GHG estimation due to different methods of industrial wastewater treatment compared to municipal wastewater treatment, the characteristics of industrial wastewaters cause unlike results in GHG estimation practice than for municipal wastewaters. Municipal wastewaters have high flow rate, low concentration, and are mostly readily biodegradable wastewaters. On the other hand food processing wastewaters have mainly low flow rate, high influent concentration and they are low in readily biochemical oxygen demand, slowly biodegradable, and nutrient deficit. Some other industrial wastewaters are even toxic or recalcitrant against treatment. Because of different characteristics of food processing wastewaters the obtained results from studies on municipal wastewaters are not applicable to this type of IWWTP and amount of contribution of different GHG producing processes are different than those in municipal wastewater treatment plant.

Some of the suggested models and methodologies of GHG emissions estimation ignore certain processes that may contribute to GHG emissions. These assumptions are avoided in the present work, resulting in the development of a more precise method for

the estimation of GHG emissions from wastewater treatment plants. A review of the literature is presented in the following paragraphs.

El-Fadel and Massoud (2001) discussed a variety of treatment systems but they did not address the combustion of the generated methane from anaerobic digestion. In North America and many other countries, the CH_4 produced from anaerobic digester is commonly combusted in large plants to generate energy or it is flared and converted to CO_2 in small plants to lessen the explosion hazard (Monteith et al., 2005). This is done to avoid possible penalties for the release of methane (Greenfield and Batstone, 2005). The estimation technique proposed by El-Fadel and Massoud (2001) overestimates the CH_4 release from many treatment plants because the CH_4 (with $\text{GWP}=23$) is a more potent GHG compared to CO_2 and the study assumes that the produced CH_4 is released into atmosphere. Because of this assumption, anaerobic treatment is presented as an improper treatment method in terms of GHG production. Also El-Fadel and Massoud (2001) used the emission factors recommended by IPCC for his estimation. The discussion about the encountered errors of using IPCC emission factors for specific wastewater treatment plant will be presented at the end of this section. Moreover, the estimation method of El-Fadel and Massoud (2001) is principally based on the influent BOD or COD and does not consider the employed method of treatment, type of wastewater, and the effect of process parameters on the final GHG production.

Monteith et al. (2005) discussed municipal wastewater treatment with activated sludge process and did not consider alternative designs or operation strategies. Their work does not address industrial operations or nutrient removal and simply focuses on carbon removal by aerobic processes in municipal wastewater treatment plant. The effect

of upstream GHG emissions is not considered in this study, but is considered in their next study (Sahely et al., 2006). The estimation procedure developed by Monteith et al. (2005) provided emissions rates ranging from 0.228 to 0.245 kg CO₂e/m³ wastewater treated. Considering the effect of upstream GHG emissions, the total GHG emission have increased 25%, 49%, 104% for the best case, base case, and worst case, respectively (Sahely et al., 2006). The study was done on WWTPs in each province of Canada and the effect of upstream GHG emissions was normalized among the treatment plants of each province. This means that the numbers given above may not be the actual total GHG emissions from each WWTP, but the average emissions across the entire municipal wastewater treatment plant for that region.

Cakir and Stenstrom (2005) discussed industrial wastewater treatment and the application of anaerobic processes; however, their work did not address GHG emissions during nutrient removal. The model was developed based on the application of UASB or AF reactors but not hybrid treatment systems. The effect of on-site material usage on upstream GHG generations is neglected and just the effect of electricity demand of WWTP on upstream GHG emissions is considered in this study. The study suggests that aerobic and anaerobic treatment methods generate 0.21 and -0.13 kg CO₂e/m³ wastewater treated at influent BOD_u concentration of 1100 mg/L, respectively. The effect of CH₄ escaped in treated wastewater from anaerobic reactor was considered in this study which was ignored in pervious anaerobic treatment studies.

Keller and Hartley (2003) also focused on domestic wastewater treatment plants and not industrial wastewater treatment plants and the results are not applicable to IWWTPs. The hybrid anaerobic/aerobic treatment is considered in his study and the

effect of power generation on upstream GHG emissions is also taken into account. The effect of material usage on upstream GHG emissions is neglected in this analysis. According to Keller and Hartley (2003), it is recommended that activated sludge process plus anaerobic digestion produces $0.89 \text{ kg CO}_2\text{e/m}^3$ wastewater treated, while hybrid anaerobic/aerobic treatment generates $0.59 \text{ kg CO}_2\text{e/m}^3$ wastewater treated. This study highlights the effect of anaerobic BOD removal in deleting the GHG production because of power generation. According to this study, with fully aerobic treatment processes, the GHG produced due to power generation outweighs the GHG produced from the treatment process itself.

Greenfield and Batstone (2005) study also focused on domestic wastewater treatment plants. This study did not consider the emissions of CO_2 from biomass decay in the GHG emissions calculation and did not examine the WWTP as an integration of processes. The study observed them as individual processes and forms mass balances around each of them and so the biomass yield was not considered in this study. For example the COD removed by sludge growth was not included in the assessment and the produced sludge was treated as output COD from the process and the GHG production because of further downstream degradation of solids was not ascribed to the process and in general to wastewater treatment plant. Furthermore, the only option of treatment processes analyzed were activated sludge combined with different types of solid digestion, among them anaerobic and aerobic solid digestion, and neither anaerobic treatment nor hybrid treatment was regarded in this study. This study is in continuation of Keller and Hartley (2003) study, and uses the many of the same assumptions and in addition to what mentioned above. It suggests that activated sludge plus nitrification and

denitrification process produces $0.53 \text{ kg CO}_2\text{e/m}^3$ wastewater treated and anaerobic digestion in ambient temperature generates $-0.73 \text{ kg CO}_2\text{e/m}^3$ wastewater treated, or in other words it removes GHG emissions by $0.73 \text{ kg CO}_2\text{e/m}^3$ WW. The study mostly focused on the effect of different types of digester on GHG producing capacity of WWTPs. Anaerobic processing of solids in low temperatures and utilization of produced CH_4 for energy generation were recommended as the most effective action among GHG mitigation strategies.

The review of published literature revealed that the previous studies failed to make a proper estimation of the upstream GHG emissions. While some investigators considered no upstream emissions in their evaluation, others ignored parts of the upstream GHG emissions. Two major sources of upstream GHG emissions are the off-site production and transportation of fuel for on-site use, and the off-site production of energy (e.g. electricity). In national GHG inventory these emissions are attributed to the energy sector, and they are not associated with the wastewater treatment. However, a more accurate measure of GHG emissions by wastewater treatment plants is presented if upstream emissions are also considered in the calculation.

Some studies such as El-Fadel and Massoud (2001) used IPCC emission factors in their GHG evaluation. The IPCC emission factors use emission factors for GHG production and multiply the GHG emission factors by incoming BOD, flow of wastewater, and percent of BOD that was removed by anaerobic treatment processes. This will result the amount of GHG produced in form of CH_4 during anaerobic processes. While this method is satisfactory for conducting national inventories, IPCC emission factor method can not be used for the wastewater treatment industry to measure the GHG

generation accurately. In national GHG inventory, GHG emissions because of off-site production and conveyance of fuel for on-site usage and the off-site production of energy are attributed to the energy sector and not to the end user, which in this example is the IWWTP. So using IPCC emission factors is misleading when the life-cycle viewpoint is considered to assign the GHG emissions to the end-user. Also IPCC emission factors neglect the effect of different operating conditions and process parameter values on the amount of GHG production and the incoming BOD value is counted on as the most responsible parameter on total GHG production. Besides, another limitation is that most of the wastewater treatment plants use aerobic treatment methods and do not produce methane. The predominant GHG produced from wastewater facilities in North America is CO₂ and even the methane that produced during anaerobic digestion is combusted and converted to CO₂ (Monteith et al., 2005) and because CH₄ is a more potent GHG than CO₂, the IPCC protocol which considers CH₄ is the principal GHG from WWTPs, leads to a significant overestimation of the amount of GHG from WWTPs. Another source of error is related to the way the CH₄ emission factor is calculated by IPCC. According to IPCC, the theoretical maximum amount of CH₄ production from waste degradation is 0.25 kg CH₄/kg COD. Furthermore, IPCC assumes that the COD of the domestic wastewater is 2.4 times greater than its BOD and concludes that the maximum CH₄ producing capacity of municipal wastewater treatment plant is $0.25 \times 2.4 = 0.6$ kg CH₄/kg BOD (IPCC, 2006). This conclusion results in overestimation of methane generation since only a fraction of COD is biologically transformed into methane while the estimations made by the IPCC are based on the total COD and not the biodegradable

COD, as pointed out by Sahely et al. (2006) and discussed in the following paragraphs.

The combustion of methane proceeds according to the following equation:



Therefore:

$$\text{Maximum } CH_4 \text{ producing capacity} = \frac{16}{2 \times 32} \text{ g } CH_4 / \text{g bCOD} = 0.25 \text{ g } CH_4 / \text{g bCOD} \quad (2.2)$$

The term bCOD is used because the CH_4 is produced by biodegradation reactions. Based on the ratio of 1/2.4 representing the biodegradable fraction of COD (according to IPCC assumption), the CH_4 production will be equal to:

$$0.25 \text{ kg } CH_4 / \text{kg bCOD} \times \frac{1}{2.4} \text{ kg bCOD} / \text{kg total COD} = 0.104 \text{ kg } CH_4 / \text{kg total COD} \quad (2.3)$$

It is clear that the existence of nonbiodegradable COD decreases the possible CH_4 production when the total COD is used in the measurement. The use of the term BOD should also be made with caution since BOD is usually reported in units of BOD_5 which is the amount of oxygen consumed in 5 days. BOD_5 is around 60-70% of the ultimate BOD (BOD_u) which is nearly equal to bCOD (Peavy et al., 1985). The emission factor for CH_4 production based on BOD_5 unit is then:

$$0.25 \text{ kg CH}_4 / \text{kg bCOD} \times \frac{1}{0.6-0.7} \text{ kg bCOD} / \text{kg BOD}_5 = 0.36 - 0.41 \text{ kg CH}_4 / \text{kg BOD}_5 \quad (2.4)$$

It is greater than 0.25 kg CH₄ based on COD because the BOD₅ measures only a part of total biodegradable matter that itself is a fraction of COD. Therefore, the factor of 0.6 kg CH₄/kg BOD, which is suggested by IPCC, significantly overestimates the CH₄ produced when the wastewater is treated anaerobically. As mentioned before, these emission factors are the maximum theoretical CH₄ producing capacity of the treatment process. If estimates are based on BOD₅ a better estimate is to use 0.38 kg CH₄/kg BOD₅ removed anaerobically (which is the average of 0.36 and 0.41) and if the estimation is based on BOD_u the best factor would be 0.25 kg CH₄/kg BOD_u. It should be noted that even the correct emission factor can not be used for industrial wastewaters because the factor 2.4 BOD/COD is based on domestic wastewater and because of varied and diverse types of industrial wastewaters this factor should be calculated for each specific IWWTP. It's important to note that this emission factor is applicable just in cases that the COD is removed anaerobically, and can't be used when aerobic treatment is used. For example, for Canadian WWTPs the on-site methane production is mostly limited to anaerobic solid digestion, because anaerobic treatment methods are incompatible with the cold climate in Canada and aerobic treatment methods are used extensively.

The following chapter describes the methodology used in this study to estimate the GHG generated during food processing WWTPs.

Chapter 3

Methodology

This Chapter discusses the development of a methodology for the estimation of GHG emissions by industrial wastewater treatment plants (IWWTPs). Different treatment methods have been addressed, making the model applicable to most treatment plants. Before presenting the model, the emission factor technique, recommended by the IPCC and most frequently used for GHG emission estimation is discussed. This method enables a quick estimation of GHG emissions from wastewater treatment plants and facilitates their comparison with national GHG inventories, which are also computed based on IPCC emission factor technique. The estimation methodology developed in this work will be subsequently presented.

3.1 Emission factor technique:

The IPCC emission factor technique is satisfactory for making national inventories and it is considered a quick and simple method, providing approximate results. In this technique, the first step to determine the mass of organic matter in wastewater removed by the WWTP. Multiplication of the appropriate emission factors by this amount will yield the total amount of GHG produced by the treatment process. For example the emission of methane from IWWTP is calculated by Equation 3.1.

$$\text{CH}_4 \text{ emissions} = EF_{\text{CH}_4} \times Q \times (BOD_{in} - BOD_{out}) \times Pr_{An} \quad (3.1)$$

Where EF_{CH_4} is methane emission factor, (kg CH₄/kg BOD removed),

Q is the wastewater flow rate, (m³/d),

BOD_{in} and BOD_{out} are the BOD concentration in the influent and effluent, (kg BOD/m³ WW), and

Pr_{An} is percent of the total BOD that is subjected to anaerobic treatment, (%).

The values of emission factors are reported in the literature, based on the type of industrial wastewater. Table 3.1 lists some emission factors estimated for wastewater treatment plants by theoretical and experimental analysis.

Table 3.1- CH₄ emission factors for municipal and industrial wastewaters

Type of WW	Type of study	EF g CH ₄ / g COD	Reference
Municipal	Theoretical	0.35	(Droste, 1997)
Municipal	Theoretical	0.21-0.25	(U.S. EPA, 1997)
Municipal	Field study	0.22	(Orlich, 1990)
Municipal	Field study	0.10	(Toprak, 1995)
Meat processing	Field study	0.26-2	(Eklund and Lacosse, 1997)
Industrial	Empirical	0.11-0.25	(Doorn et al., 1997)
Food and beverage and pulp-and-paper industry	Full- and pilot-scale digesters	0.019-0.22	(Lexmond and Zeeman, 1994)

Similar to CH₄ emission estimation, emission factors can be used to estimate N₂O emissions from IWWTPs. It has been reported that 0.01 kg N₂O-N/kg sewage N will be generated during domestic wastewater treatment (Environment Canada, 2003). As stated before, the emissions of CO₂ resulting from biomass and biomass-based wastes are not

considered by the IPCC as GHGs. Therefore, IPCC does not provide emission factors for CO₂ emission from WWTPs.

Upstream GHG emissions are not included in this method because IPCC attributed these emissions to the energy sector. In order to make a more complete estimation of emissions by wastewater treatment plants, the upstream GHG emissions must also be taken into consideration. The calculation of upstream GHG emissions is described in the following section.

3.2 Upstream GHG emissions attributed to IWWTP:

The GHG emissions associated with off-site electricity generation as well as production and transportation of fuels, and production and transmission of other material consumed on-site are considered as upstream GHG emissions. Electricity is used to satisfy the demands of various activities inside the wastewater treatment plant. It is consumed in pumps, motors, heaters, clarifiers, digesters, and other instruments and devices. In addition to electricity, external fuels (e.g. natural gas and diesel) are needed for wastewater treatment operations. To estimate the upstream emissions due to electricity generation, it is essential to evaluate the provincial or national sources of electricity generation. The estimation of GHG generation from each source will then be considered. The sources of electricity generation for Canada are included in Table 3.2 (Canadian Electricity Association. 1999). Because of the existing uncertainties in N₂O emissions during fuel combustion, only CO₂ and CH₄ emissions from the combustion of coal, oil, and natural gas are considered during electricity generation.

Table 3.2– Sources of electricity generation in Canada and each province (Canadian Electricity Association. 1999)

Province	Fuel Type, %					
	Hydroelectric	Nuclear	Coal	Oil	Gas	Other
Alberta	3.8	0	81.5	12	0	2.7
British Columbia	90.7	0	0	4.4	2	2.9
Manitoba	99	0	0.7	0.1	0	0.2
New Brunswick	20	35.2	8.5	0	34.6	1.6
Newfoundland	96	0	0	0	4	0
Nova Scotia	9	0	65.3	0	24.1	1.6
Ontario	28.6	55.8	12.8	2.4	0	0.4
Prince Edward Island	0	0	0	0	100	0
Quebec	96.7	3.1	0	0	0.2	0
Saskatchewan	26.5	0	67.7	4.4	0.3	1.1
Canada	62.4	17.3	14.8	2.5	2.2	0.8

Emission factors of each of these sources of electricity generation, based on CO₂e units, are listed in the Table 3.3.

Table 3.3- Emission factor for each method of electricity generation

	Fuel type, g CO ₂ e/kWh				
	Hydroelectric	Nuclear	Coal	Oil	Gas
Emission factors	10-400	3.2-15.41	877	604	353
Reference	(Rashad and Hammad, 2000)	(Andseta et al., 1998)	(IPCC, 2001a)	(IPCC, 2001a)	(IPCC, 2001a)

The reservoirs of large hydroelectric dams contribute to GHG generation, especially to the generation of CH₄ because of the rotting vegetation and carbon inflow. The lower end of the above range, 10 g CO₂e/kWh, has been used to represent the colder climate in Canada.

Although the nuclear fission for electricity generation does not produce GHGs, many processes in the nuclear life cycle such as the construction of the power plant and uranium enrichment depend on fossil fuels. Since there is little evidence for CH₄ and N₂O emissions during the nuclear fuel cycle, it is recommended that only the CO₂ emissions from the use of nuclear power for energy generation be considered as upstream GHG emissions (Rashad and Hammad, 2000).

In addition to GHG emissions for electricity generation, upstream GHG generation also exists because of off-site production and transmission of fossil fuels (mostly natural gas), which are commonly used in the wastewater treatment plants for on-site heating purposes such as wastewater and sludge heating. The CO₂ and CH₄ emissions from the production and transmission of fossil fuels, e.g. natural gas are also considered. The methodology to calculate the upstream GHG emissions for the Canadian wastewater treatment plants is described below:

Step 1: The amount of electricity needed to treat the wastewater can be calculated either from the IWWTP operator or according to Equation 3.2.

$$E_{Required} = \sum P_i \times T_i \quad (3.2)$$

Where $E_{Required}$ is energy required for the operation of the entire plant, (kWh/d),

P_i is the power of the i-th machinery involved in the treatment process, (kW), and

T_i is the working hours of i-th machinery during each day, (hr/d).

In the absence of precise data for electricity consumption of each electrical device or instrument, the ratio of average electricity consumed to the volume of wastewater treated may be used. A ratio of 0.2-0.5 kWh/m³ WW treated is reported in the literature (Young and Koopman, 1991; Clauson-Kaas et al., 2001; and Cheng, 2002). For large municipal wastewater treatment plants the value of 0.2 can be used since the large volumes of wastewater reduce the electricity consumption per volume of treated wastewater. For industrial wastewater treatment plants the larger value of 0.5 is used due to the lower influent flow rate compared to municipal wastewater treatment plants.

Step 2: Estimation of the quantity of fossil fuels (e.g. natural gas) consumed on-site (Q_G , m³/d). The magnitude of this parameter is calculated according to energy requirement of the IWWTP and will be described later.

Step 3: The upstream emissions related to electricity generation is:

$$P_{CO_2,electricity} = E_{Required} \times (F_i \times EF_i) \quad (3.3)$$

Where $P_{CO_2,electricity}$ is the GHG production due to electricity demands of the plant, (g CO₂e/d),

$E_{Required}$ is the energy required for the operation of the entire plant, (kWh/d),

F_i is the percentage contribution of fuel i to satisfy electricity generation needs of the IWWTP according to Table 3.2, and

EF_i is the GHG emission factor of fuel i in producing GHG, (g CO₂e/kWh) according to Table 3.3.

Step 4: The upstream GHG emissions associated with the production and transportation of natural gas plus the on-site CO₂ production due to fossil fuel burning are calculated by the following equation:

$$P_{CO_2,NG} = Q_G \times EF_{NG,CO_2} + 23 \times Q_G \times EF_{NG,CH_4} + P_{CH_4 \rightarrow CO_2} \quad (3.4)$$

Where $P_{CO_2,NG}$ is the upstream GHG production because of natural gas consumption in the plant in g CO₂e/d,

Q_G was defined before and its the quantity of natural gas consumed on-site in the wastewater treatment plant, (m³/d),

EF_{NG,CO_2} is the natural gas CO₂ emission factor, (g CO₂/m³ NG), and

EF_{NG,CH_4} is the natural gas CH₄ emission factor, (g CH₄/m³ NG).

Emission factors for CO₂ and CH₄ specific to the Canadian natural gas industry are reported in the literature and are presented in Table 3.4. The total emissions of the natural gas industry which contain both the production and transportation of natural gas in Canada are divided by the total annual production of natural gas to yield the corresponding emission factors.

Table 3.4- CO₂ and CH₄ production from NG production

	Emission Factor	Reference
EF_{NG,CO_2}	234 g CO ₂ /m ³ NG	(Natural Resources Canada, 1999)
EF_{NG,CH_4}	83 g CH ₄ /m ³ NG	(Natural Resources Canada, 1999)

Step 5: The GHG emissions related to the material used on-site are calculated by:

$$P_{CO_2,material} = \sum M_i \times EF_i \quad (3.5)$$

Where $P_{CO_2,material}$ is the upstream GHG production due to material consumption in the plant, (g CO₂e/d),

M_i is the amount of material i used daily, (kg/d), and

EF_i is the GHG emission factor for the production and transportation of material i inside the IWWTP, (kg CO₂e/kg material).

The quantity of material consumption inside the plant is calculated by mass balance and stoichiometry equations. The substances considered in this study are lime and methanol because they are widely used for alkalinity production and denitrification, respectively. The emission factors for their production and transportation are presented in Table 3.5.

Table 3.5- Emission factor for material production and conveyance

	Emissions Factor	Reference
$EF_{Alkalinity}$	1.74 g CO ₂ e/g Alkalinity	(Energy Efficiency Opportunity Guide in the Lime Industry, 2001)
$EF_{Methanol}$	1.54 g CO ₂ e/g Methanol	(Dong and Steinberg, 1997)

Step 6: The total amount of upstream GHG produced is then:

$$P_{Total\ CO_2,upstream} = P_{CO_2,electricity} + P_{CO_2,material} + P_{CO_2,NG} \quad (3.6)$$

Where $P_{Total\ CO_2,\ upstream}$ is the total upstream GHG generation, (g CO₂e/d).

It is evident that if the electricity generation relies mainly on fossil fuels, the overall upstream GHG emissions per volume of wastewater treated will be considerably higher compared to areas that use energy resources such as hydroelectric or nuclear power for electricity generation.

3.3 Estimation method - Biological technique:

Because of the diverse methods used for the treatment of food processing wastewaters, this section introduces appropriate methodologies for GHG emissions estimation related to individual treatment methods. The main treatment methods in wastewater treatment systems include: aerobic, anaerobic, and hybrid anaerobic/aerobic treatment. GHG estimation models for these treatment processes are presented in the following sections.

3.4 Aerobic treatment – GHG estimation model:

This model is developed based on a completely mixed reactor with sludge recycle. The schematic diagram is presented below in Figure 3.1. The on-site GHG producing processes are shown in a grey color.

To define the model, mass balances are formed around the treatment system for each specific component of the system such as the wastewater flow rate, microorganism

concentration and substrate concentration. These mass balances include the flow and mass of components entering and leaving the system and the reactions leading to the depletion or production of components within the system.

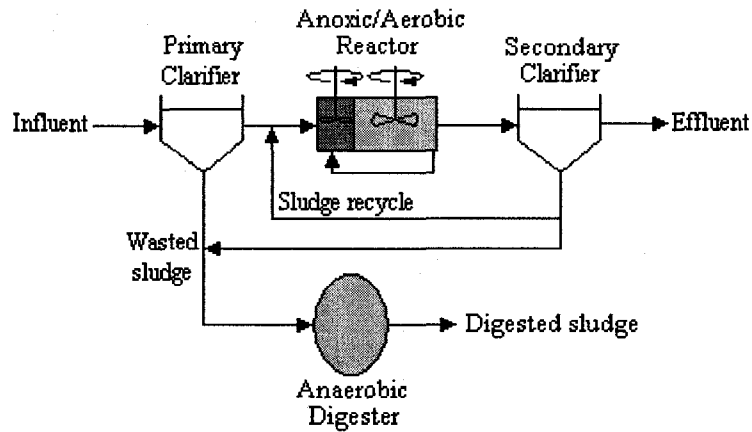


Figure 3.1- Schematic diagram of a completely mixed reactor with sludge recycle

Figure 3.2 presents the nomenclature and system boundaries used for developing the mass balance equations.

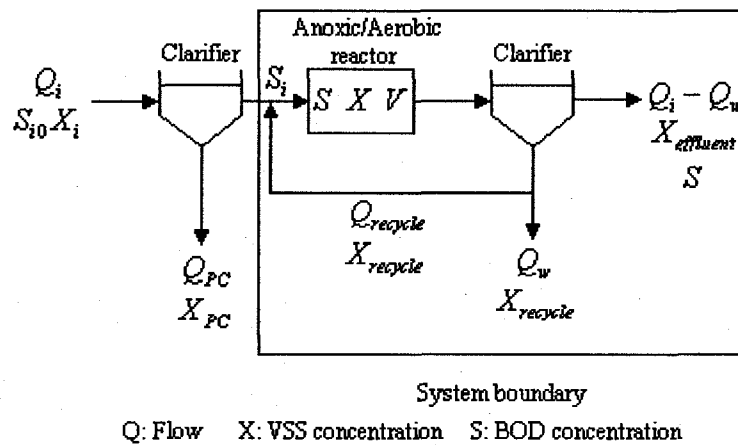


Figure 3.2- A typical aerobic treatment with a system boundary

3.4.1 Primary clarifier:

In the primary clarifier the settleable suspended solids are removed and the concentration of soluble BOD remains unchanged, since there is no biological reaction in the clarifier. The mass of solids removed by primary clarifier is calculated by Equation 3.7.

$$r_{SS,PC} = Per_X \times Q_i \times X_i \quad (3.7)$$

Where $r_{SS,PC}$ is the removal rate of suspended solids in primary clarifier, (kg VSS/d),

Per_X is the percent removal of suspended solids in primary clarifier,

Q_i is the influent wastewater flow rate, (m³/d), and

X_i is the influent volatile suspended solids (VSS), (kg VSS/m³).

Some BOD is removed in the primary clarifier due to the removal of soluble carbon. Equation 3.8 presents the mass of BOD removed during primary clarification.

$$r_{BOD,PC} = Per_S \times Q_i \times S_{i0} \quad (3.8)$$

Where $r_{BOD,PC}$ is the removal rate of BOD in primary clarifier, (kg BOD₅/d),

Per_S is the percent removal of BOD₅ in primary clarifier, and

S_{i0} is the influent BOD₅, (kg BOD₅/m³).

3.4.2 Biological aerobic reactor:

The primary clarifier's effluent enters the aerobic reactor for the biological removal of contaminants. As mentioned before, during aerobic treatment, a fraction of the carbonaceous BOD is oxidized to CO₂ by the aerobic microorganisms and the rest is incorporated into new cell mass. In the first step, the relationships between process parameters are developed. In order to calculate the amount of biomass production, mass balance equations are developed for biomass concentration within the system boundary, as shown in Figure 3.2.

Accumulation = inflow – outflow + conversion (for microorganisms)

$$V \left(\frac{dX}{dt} \right) = (Q_i - Q_{PC}) \times X_{PC} - [Q_w \times X_{recycle} + (Q_i - Q_{PC} - Q_w) \times X_{effluent}] + r_g \times V \quad (3.9)$$

Where V is the reactor volume, (m³),

X is biomass concentration in the bioreactor, (g VSS/m³),

r_g is the net rate of biomass production, (g VSS/m³.d), and

Other terms are defined previously on the Figure 3.2.

The concentration of microorganisms in the influent is negligible as compared to their concentration in the reactor ($X_{PC} = 0$), similarly Q_{PC} is negligible as compared to Q_i ($Q_{PC} = 0$). At steady state conditions, there is no accumulation of microorganisms inside the reactor. ($dX/dt = 0$), thus the above equation is simplified to the following form:

$$Q_w \times X_{recycle} + (Q_i - Q_w) \times X_{effluent} = r_g \times V \quad (3.10)$$

The biomass growth rate is proportional to the substrate utilization rate by the biomass yield coefficient. Also the biomass decay affects the actual biomass concentration. Considering these two factors, the rate of biomass growth is expressed as follows:

$$r_g = (\text{biomass growth because of substrate utilization}) - (\text{biomass decay})$$

$$r_g = -Y \times r_{su} - k_d \times X$$

$$r_g = Y \times \frac{k \times X \times S}{K_s + S} - k_d \times X \quad (3.11)$$

Where Y is synthesis yield coefficient, (g VSS/g BOD),

r_{su} is the rate of substrate utilization, (g BOD/m³.d),

k_d is the endogenous decay rate, (g VSS/g VSS.d),

k is the maximum specific substrate utilization rate, (g BOD/g VSS.d),

X is the biomass concentration, (g VSS/m³),

S is substrate concentration, (g BOD/m³), and

K_s is the half-velocity constant, (g BOD/m³).

The above equation is proposed by Monod (1949) for the specific growth rate of bacteria in which the substrate is available to the microorganisms in dissolved form.

Combining Equations 3.10 and 3.11 will result to:

$$\frac{Q_w \times X_{recycle} + (Q_i - Q_w) \times X_{effluent}}{VX} = Y \frac{kS}{K_s + S} - k_d \quad (3.12)$$

The inverse of the left term of the above equation is known as the solid retention time (SRT) which represents the mass of solids in the treatment system divided by the mass of solids removed per day. SRT is an important design and operating parameter for wastewater treatment plants because it defines the average residence time of solids in the system. So Equation 3.12 becomes:

$$\frac{1}{SRT} = Y \frac{kS}{K_s + S} - k_d \quad (3.13)$$

SRT is normally selected from the literature based on the type of treatment processes applied. According to Equation 3.13, the values of S and SRT are interrelated and the amount of substrate concentration may be expressed by the following equation:

$$S = \frac{K_s(1 + (k_d)SRT)}{SRT(Yk - k_d) - 1} \quad (3.14)$$

The mass balance equation is written once again for soluble substrate concentration within the system boundary of Figure 3.2.

Accumulation = inflow – outflow + conversion (for soluble substrate)

$$V \left(\frac{dS}{dt} \right) = (Q_i - Q_{PC}) \times S_i - [Q_w \times S + (Q_i - Q_{PC} - Q_w) \times S] + r_{su} \times V \quad (3.15)$$

Similar to the mass balance equation for biomass, Q_{PC} is negligible compared to Q_i ($Q_{PC} = 0$) and because of steady state condition there is no accumulation of soluble substrate inside the reactor ($dS/dt = 0$). Considering Equation 3.11 for the definition of r_{su} , Equation 3.15 is simplified as follows:

$$S_i - S = \left(\frac{V}{Q_i} \right) \left(\frac{kXS}{K_s + S} \right) \quad (3.16)$$

In the above equation, the volume of aeration tank divided by the influent flow rate is defined as the Hydraulic Retention Time (τ).

$$\tau = \frac{V}{Q_i} \quad (3.17)$$

If Equation 3.13 is solved for the term $S/(K_s+S)$ and substituted into Equation 3.16 the following equation will be obtained for biomass concentration in the aerobic reactor:

$$X = \left(\frac{SRT}{\tau} \right) \left[\frac{Y(S_i - S)}{1 + k_d \times SRT} \right] \quad (3.18)$$

Equation 3.18 gives the mixed liquor volatile suspended solid concentration (MLVSS) comprised of heterotrophic biomass. In addition, the autotrophic nitrifying bacteria contribute to the overall solids concentration inside the bioreactor, defined by the following equation:

$$X_n = \left(\frac{SRT}{\tau} \right) \left[\frac{Y_n(NO_x)}{1 + k_{dn} \times SRT} \right] \quad (3.19)$$

Where X_n is the nitrifying bacteria biomass concentration, (g VSS/m³),

Y_n is the synthesis yield coefficient for nitrifying bacteria, (g VSS/g BOD),

NO_x is the concentration of NH₄-N in the influent that is nitrified, (g N/m³), and

k_{dn} is the endogenous decay factor for nitrifying microorganisms, (g VSS/g VSS.d).

The concentration of cell debris, produced as a result of microbial decay and death in the bioreactor should also be considered. This debris which consists of 10 to 15 percent of cell weight remains as non-biodegradable particulate matter and contributes to the overall biological mass in the bioreactor (Metcalf and Eddy, 2003). The rate of cell debris production is:

$$r_{Xd} = f_d \times k_d \times X \quad (3.20)$$

Where r_{Xd} is rate of cell debris production, (g VSS/m³.d),

f_d is the fraction of biomass which remains as cell debris, (0.10-0.15 g VSS/g VSS).

The amount of biomass produced per day, which defines the biomass that must be removed from the bioreactor on a daily basis, can be calculated. By definition, SRT is the mass of solids present in the systems divided by the mass of solids removed per day. So:

$$SRT = \frac{XV}{P_x} \quad (3.21)$$

Where P_x is the amount of solids produced each day, (g VSS/d).

Substituting Equation 3.18 into Equation 3.21 gives the amount of daily solids production because of substrate utilization.

$$P_x = \frac{Q_i Y (S_i - S)}{(1 + k_d \times SRT)} \quad (3.22)$$

The value of S (effluent BOD concentration) is calculated according to Equation 3.14 and inserted in Equation 3.22 to yield the value of P_x . There is solids production because of: 1) substrate utilization by heterotrophic bacteria, 2) substrate utilization by nitrifying bacteria, and 3) cell debris. The solids production because of carbonaceous BOD removal and nitrification is equal to:

$$P_{x,CBOD} = \frac{Q_i Y (S_i - S)}{(1 + k_d \times SRT)}$$

$$P_{x,nit} = \frac{Q_i Y_n (NO_x)}{(1 + k_{dn} \times SRT)} \quad (3.23)$$

Where NO_x is the amount of ammonia oxidized to nitrate, (g NH_4 -N/ m^3).

The amount of cell debris production is calculated by substituting Equation 3.18 into Equation 3.20 and multiplying the rate of cell debris production (Equation 3.20) by the reactor volume (V). The amount of cell debris production is therefore equal to:

$$P_{X,Cell\ Debris} = \frac{f_d k_d Y Q_i (S_i - S) \times SRT}{(1 + k_d \times SRT)} \quad (3.24)$$

The non-biodegradable cell debris will end up in the digester and will be removed by solid waste from the digester. The wasted solids from digester contribute to off-site GHG emissions because of transportation of solids to the disposal sites. This term will be discussed later.

According to Equation 3.23, $P_{X,nit}$ is dependent on the amount of ammonia oxidized to nitrate (NO_x). For determining the NO_x amount, a nitrogen mass balance including influent TKN, nitrogen removed by biomass synthesis, and unoxidized effluent nitrogen is formed. The nitrogen removed by biomass synthesis is calculated according to the fact that there is 0.12 (g N per g biomass), considering the biomass formula ($C_5H_7NO_2$). The nitrogen mass balance equation can be expressed as follows:

$$Q_i(NO_x) = Q_i(TKN_i) - Q_i N_e - 0.12 \times P_{X,bio} \longrightarrow$$

$$NO_x = TKN_i - N_e - \frac{0.12 \times P_{X,bio}}{Q_i} \quad (3.25)$$

Where $P_{X,bio} = P_{X,CBOD} + P_{X,nit}$

In order to estimate $P_{X,nit}$, the value of NO_x must be known. Similarly, for the calculation of NO_x one should know the value of $P_{X,nit}$. Accordingly, it can be assumed that $NO_x \approx 0.8 \text{ TKN}$ (Metcalf and Eddy, 2003) and the value of NO_x is used to calculate the $P_{X,bio}$ according to Equation 3.23. Substituting the value of $P_{X,bio}$ into Equation 3.25 will yield a new value for NO_x . The iteration process continues until the difference between two successive trials approaches zero.

Following the development of equations for the analysis of the treatment process, the GHG estimation process may be initiated. A mass balance equation for BOD removal around the reactor results in the following calculations.

$$\text{Accumulation} = \text{inflow} - \text{outflow} + \text{conversion (for BOD)} \quad (3.26)$$

Due to the presence of steady state condition, the accumulation rate equals zero ($\text{Accumulation} = 0$). So:

$$0 = BOD_{in} - BOD_{out} - BOD \text{ oxidized} \rightarrow BOD \text{ oxidized} = BOD_{in} - BOD_{out} \quad (3.27)$$

BOD_{in} represents the substrate concentration in the influent of reactor and BOD_{out} signifies the substrate concentration in the effluent plus the BOD concentration of the produced biomass. So:

$$BOD_{out} = BOD_{effluent} + \text{biomass BOD} \quad (3.28)$$

Combining Equations 3.27 and 3.28 results in:

$$BOD_{oxidized} = BOD_{in} - (BOD_{effluent} + biomass\ BOD) \quad (3.29)$$

In the above equation, the BOD of the oxidized substrate is equal to the consumed oxygen. So the above equation can be rewritten as presented below:

$$r_{oxygen} = BOD_{in} - (BOD_{effluent} + biomass\ BOD) \quad (3.30)$$

Where r_{oxygen} is the oxygen removal rate because of biodegradation, (kg O₂/d).

Some BOD is removed in the primary clarifier. So the influent BOD to the aerobic reactor is calculated as follows.

$$S_i = S_{i0} - \frac{r_{BOD,PC}}{Q_i} \quad (3.31)$$

Where S_i is in (kg BOD/m³).

As mentioned before, aerobic reactions include BOD oxidation to CO₂, BOD incorporation into biomass, and nitrification. To develop the equations for each of these reactions the half reaction approach is used here. $C_5H_7O_2N$ is used as the generic biomass formula in aerobic and anaerobic environments and $C_{10}H_{19}O_3N$ is used for the substrate formula (Rittmann and McCarty, 2001). The stoichiometric relationships representing microbial biodegradation are developed based on the half reaction approach

which is most commonly employed for complex reactions (Rittmann and McCarty, 2001). The electron donor is used by microorganisms to produce energy and support cell biosynthesis reactions. A part of electrons (f_e) is transferred to the electron acceptor in order to provide energy, facilitating the transfer of other electrons (f_s) to biomass, implying that electron equivalents from the electron donor are divided between energy generation and cell biosynthesis reactions. The energy generation reaction is represented by the following equation:

$$R_e = R_a - R_d \quad (3.32)$$

Where R_e is the energy reaction,

R_a is the acceptor half reaction, and

R_d is donor half reaction.

R_d has a negative sign because the electron donor is oxidized. The synthesis reaction, R_s , can be represented as follows:

$$R_s = R_c - R_d \quad (3.33)$$

Where R_s is the synthesis reaction,

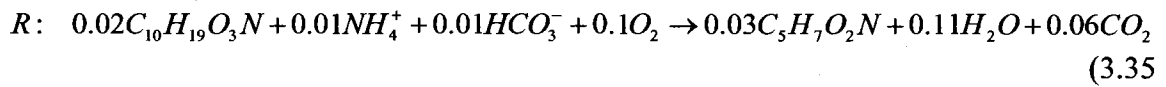
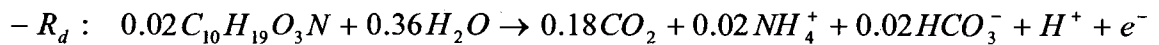
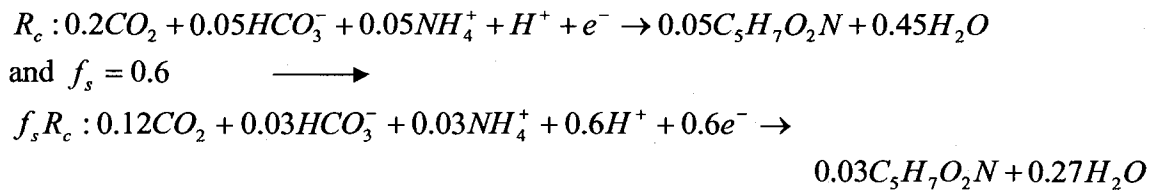
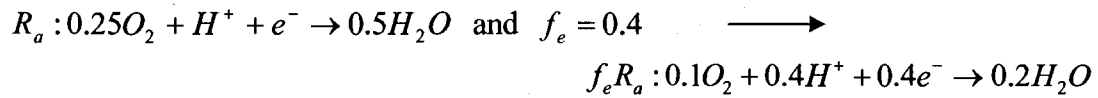
R_c is the cell half reaction.

In order to get the overall reaction (R) that includes both energy generation and cell synthesis, Equation 3.32 is multiplied by f_e and Equation 3.33 is multiplied by f_s and then they are added together as follows (Rittmann and McCarty, 2001):

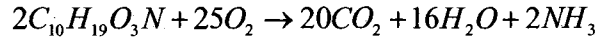
$$R = f_e(R_a - R_d) + f_s(R_c - R_d) \quad \text{and} \quad f_s + f_e = 1 \quad \longrightarrow$$

$$R = f_e R_a + f_s R_c - R_d \quad (3.34)$$

To develop the overall reaction for BOD oxidation and cell synthesis in an aerobic process, it is noted that the electron donor is an organic compound, the electron acceptor is oxygen, and ammonium is the nitrogen source. f_s is selected as 0.6 (Rittmann and McCarty, 2001).



The equation for complete oxidation of soluble BOD to produce energy for growth (Monteith et al., 2005) and the calculation of the substrate BOD are presented below:



$$BOD \text{ of substrate} = \frac{25 \times 32 \text{ g BOD}}{2 \times 201 \text{ g substrate}} = 2 \text{ gBOD} / \text{g substrate} \quad (3.36)$$

According to Equations 3.35 and 3.36, The CO_2 and VSS yield coefficients and the oxygen and alkalinity consumption rates are estimated as follows:

$$Y_{CO_2}^{Aerobic} = \frac{0.06 \times 44 \text{ g } CO_2}{0.02 \times 201 \text{ g substrate} \times 2 \text{ gBOD} / \text{g substrate}} = 0.33 \text{ g } CO_2 / \text{g BOD}$$

$$Y_{VSS}^{Aerobic} = \frac{0.03 \times 113}{0.02 \times 201 \times 2} = 0.42 \text{ g VSS} / \text{g BOD}$$

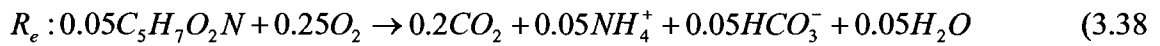
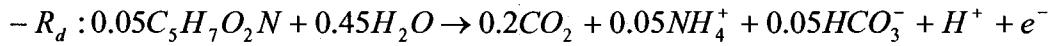
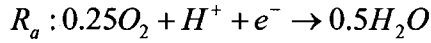
$$r_{O_2}^{Aerobic} = \frac{0.1 \times 32}{0.02 \times 201 \times 2} = 0.4 \text{ g } O_2 / \text{g BOD}$$

$$r_{Alk}^{Aerobic} = \frac{0.01 \times 50}{0.02 \times 201 \times 2} = 0.06 \text{ g } CaCO_3 / \text{g BOD} \quad (3.37)$$

Where r represents the requirement and Y represents the yield or production and the superscript aerobic accounts for aerobic process.

The endogenous decay reaction of biomass in aerobic environment is calculated considering the biomass as electron donor and oxygen as electron acceptor. Since there is no cell synthesis in endogenous decay reaction, it is enough to consider the donor half-reaction and acceptor half-reaction. In other words, the energy reaction, ($R_e = R_a - R_d$),

is enough for building the overall endogenous decay reaction (Rittmann and McCarty, 2001).



The yield coefficients for CO_2 and NH_4 , and the oxygen consumption rate are estimated as follows:

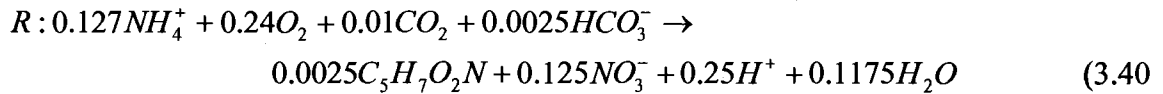
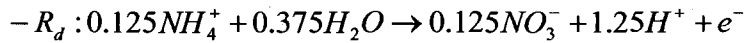
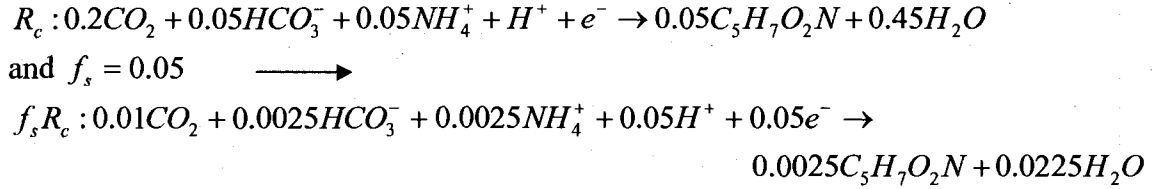
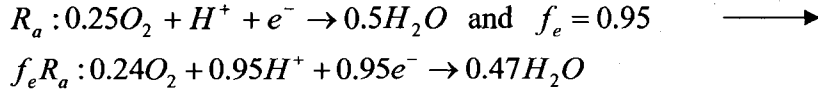
$$r_{O_2, endogenous} = \frac{0.25 \times 32}{0.05 \times 113} = 1.42 \text{ g } O_2 / \text{g VSS}$$

$$Y_{CO_2, endogenous} = \frac{0.2 \times 44}{0.05 \times 113} = 1.56 \text{ g } CO_2 / \text{g VSS}$$

$$Y_{NH_4, endogenous} = \frac{0.05 \times 14}{0.05 \times 113} = 0.124 \text{ g } N / \text{g VSS}$$

$$Y_{Alk, endogenous} = \frac{0.05 \times 50}{0.05 \times 113} = 0.44 \text{ g } CaCO_3 / \text{g VSS} \quad (3.39)$$

To obtain the nitrification reaction, half-reactions for cell synthesis (R_c), oxidation of ammonia to nitrate (R_d), and reduction of oxygen as electron acceptor (R_a) are combined. f_s is assumed to be 0.05 for nitrification (Rittmann and McCarty, 2001).



According to the above equation, for each NH_4^+ equivalent, 0.24 mole O_2 , 0.01 mole CO_2 , and 0.0025 mole alkalinity is consumed and 0.0025 mole biomass is produced. In order to maintain the liquid pH at a steady level, alkalinity is required to neutralize the 0.25 mole of hydrogen ion. The corresponding yield coefficients are:

$$r_{O_2}^{nit} = \frac{0.24 \times 32}{0.127 \times 14} = 4.32 \text{ g } O_2 / \text{g } N$$

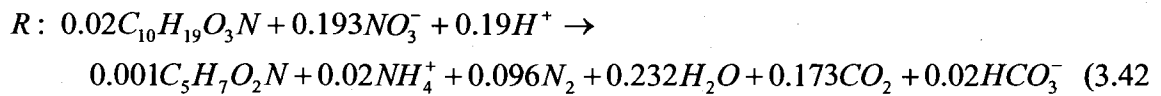
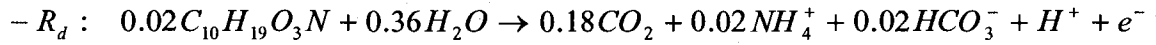
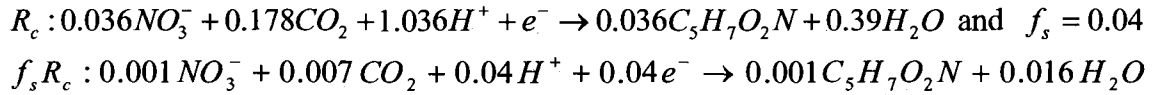
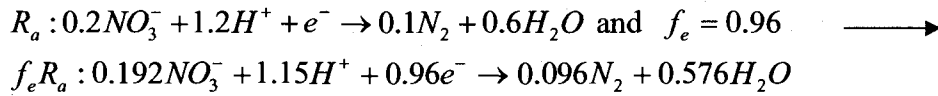
$$r_{CO_2}^{nit} = \frac{0.01 \times 44}{0.127 \times 14} = 0.247 \text{ g } CO_2 / \text{g } N$$

$$r_{Alk}^{nit} = \frac{(0.0025 + 0.25) \times 50}{0.127 \times 14} = 7.1 \text{ g } CaCO_3 / \text{g } N$$

$$Y_{VSS}^{nit} = \frac{0.0025 \times 113}{0.127 \times 14} = 0.159 \text{ g } VSS / \text{g } N$$

$$Y_{NO_3}^{nit} = \frac{0.125 \times 14}{0.127 \times 14} = 0.98 \text{ g N-Nitrate} / \text{g N} \quad (3.41)$$

The equation for denitrification process is also developed as presented below. The half-reaction for cell synthesis uses nitrate as the nitrogen source, nitrate as the electron acceptor which will be reduced to N_2 , and organic matter as the electron donor (Rittmann and McCarty, 2001). For denitrification f_s is assumed to be 0.04.



According to the above equation, the yield coefficients for denitrification process can be calculated as presented below:

$$r_{BOD}^{denit} = \frac{0.02 \times 201 \text{ g substrate} \times 2 \text{ g}^{BOD} / \text{g substrate}}{0.193 \times 14} = 2.97 \text{ g BOD} / \text{g N-Nitrate}$$

$$Y_{VSS}^{denit} = \frac{0.001 \times 113}{0.193 \times 14} = 0.042 \text{ g VSS/g N-Nitrate}$$

$$Y_{CO_2}^{denit} = \frac{0.173 \times 44}{0.193 \times 14} = 2.81 \text{ g CO}_2\text{/g N-Nitrate}$$

$$Y_{Alk}^{denit} = \frac{(0.02 + 0.19) \times 50}{0.193 \times 14} = 3.89 \text{ g CaCO}_3\text{/g N-Nitrate} \quad (3.43)$$

It can be observed that BOD oxidation to CO₂, endogenous decay of biomass, and denitrification reactions all produce GHGs in the form of CO₂ while the nitrification process consumes part of the produced CO₂ and acts as a GHG sink. The amount of CO₂ production can be calculated according to the yield coefficients calculated for each of the reactions. The oxygen equivalent of cell tissue is obtained from Equation 3.39, which is 1.42 g O₂/g VSS. So the BOD of biomass is calculated as follows:

$$\text{biomass BOD} = \text{biomass produced} \text{ g VSS/d} \times 1.42 \text{ g BOD/g VSS} \quad (3.44)$$

Thus the amount of carbonaceous BOD, oxidized to CO₂ inside the aerobic reactor equals to:

$$r_{CBOD}^{Aerobic} = Q_i \times (S_i - S) - 1.42 \times P_{X, CBOD} \quad (3.45)$$

Where $r_{CBOD}^{Aerobic}$ is the oxidized carbonaceous BOD, (kg BOD/d),

S is the BOD concentration in effluent (kg BOD/m³), and

$P_{X, CBOD}$ is the produced biomass because of carbonaceous BOD synthesis, (kg VSS/d).

Combining Equations 3.37 and 3.45, the amount of CO₂ produced due to carbonaceous BOD removal is:

$$CO_{2,CBOD} = 0.33 \times r_{CBOD}^{Aerobic} \quad (3.46)$$

Where $CO_{2,CBOD}$ is in (g CO₂/d).

According to Equation 3.41, the daily removal of CO₂ because of nitrification is:

$$\text{Daily removed } CO_2 = 0.247 \times NO_x \times Q_i \quad (3.47)$$

Where *Daily removed CO₂* is in (kg CO₂/d),

NO_x is ammonia nitrogen oxidized to nitrate, (g N/m³), and

Q_i is flow rate, (m³/d).

Combining the Equations 3.46 and 3.47, the total CO₂ production resulting from the carbonaceous BOD oxidation and nitrification is:

$$CO_{2,Aerobic} = CO_{2,CBOD} - 0.247 \times NO_x \times Q_i \quad (3.48)$$

There is also CO₂ production because of endogenous decay of cell tissue. The amount of decayed biomass, both from carbonaceous BOD utilization and nitrification that comprises heterotrophic and autotrophic microorganisms, is calculated according to the following:

$$\left. \begin{aligned}
 \text{Biomass decayed} &= V \times (k_d \times X + k_{dn} \times X_n) \\
 X &= \left(\frac{SRT}{\tau} \right) \left[\frac{Y(S_i - S)}{1 + k_d \times SRT} \right] \text{ and } X_n = \left(\frac{SRT}{\tau} \right) \left[\frac{Y_n(NO_x)}{1 + k_{dn} \times SRT} \right]
 \end{aligned} \right\} \longrightarrow$$

$$M_{X, \text{degraded, reactor}} = 0.8 \times SRT \times Q_i \times \left[\frac{k_d Y(S_i - S)}{1 + k_d \times SRT} + \frac{k_{dn} Y_n(NO_x)}{1 + k_{dn} \times SRT} \right] \quad (3.49)$$

Where $M_{X, \text{degraded, reactor}}$ is mass of endogenously decayed VSS in the reactor, (g VSS/d).

Because less than 100% of the produced solid is biodegradable, the factor of 0.8 is considered to represent the biodegradable part of the biomass (Metcalf and Eddy, 2003). The non-biodegradable biomass remains in the sludge and flows to the digester and becomes wasted sludge from the digester which contributes to off-site GHG emissions because of transportation of solids to off-site disposal sites. The CO₂ emission from endogenous decay of biomass is calculated according to Equation 3.39, as follows:

$$CO_{2, \text{reactor, endogenous}} = 1.56 \frac{\text{g } CO_2}{\text{g VSS}} \times M_{X, \text{degraded, reactor}} \quad (3.50)$$

Where the CO₂ emission rate due to endogenous decay is in (kg CO₂/d).

The total CO₂ emissions because of BOD utilization and nitrification are the sum of Equations 3.48 and 3.50.

The major difference between anaerobic and aerobic treatment processes is the aeration needs for aerobic processes. This leads to GHG emissions because of energy demands. The GHG emissions because of aeration needs are considered separately from the electricity demands of the rest of WWTP in order to identify the contribution of

aeration energy to the total GHG emissions. The first step in calculating the aeration energy is to find out the amount of oxygen delivery to the aerobic reactor. Some oxygen is consumed for the carbonaceous BOD oxidation and some for the nitrification process (denitrification is an anaerobic process). The amount of consumed oxygen for carbonaceous BOD removal and nitrification are calculated by Equations 3.51 and 3.52, respectively.

$$r_{\text{oxygen,CBOD}} = Q_i \times (S_i - S) - 1.42 \times P_{X,\text{CBOD}} \quad (3.51)$$

$$r_{\text{oxygen,nit}} = 4.33 \times Q_i \times (NO_x) \quad (3.52)$$

$$r_{\text{oxygen,total}} = r_{\text{oxygen,CBOD}} + r_{\text{oxygen,nit}} \quad (3.53)$$

Where $r_{\text{oxygen,total}}$ is the total oxygen demand of the wastewater, (kg O₂/d).

The energy required for aeration is calculated according to the following equation:

$$E_{\text{Required,Aeration}} = \frac{r_{\text{oxygen}}}{\text{Eff}_{\text{aeration}}} \quad (3.54)$$

Where $E_{\text{Required,Aeration}}$ is the energy demand, (kJ/d),

$\text{Eff}_{\text{aeration}}$ is the aeration efficiency.

If aeration energy is provided in the form of electricity, the amount of GHG emissions because of aeration energy can be calculated according to Equation 3.3. As mentioned previously, the GHG emissions for electricity generation is considered as upstream GHG emissions.

During the denitrification process, nitrate acts as the electron acceptor instead of oxygen and oxidizes the CBOD in the wastewater. This action reduces the CBOD of the wastewater available for oxidation by oxygen, and consequently less CO₂ and VSS are produced because of CBOD removal with oxygen and also less oxygen is needed for CBOD removal. On the other hand, denitrification itself produces CO₂ and VSS. The amount of removed CBOD, produced VSS, and produced CO₂ because of denitrification are calculated by Equation 3.55, considering Equation 3.43.

$$\begin{aligned}
 \text{Removed } CBOD_{denit} &= 2.97 \times NO_x \times Q_i \\
 \text{Produced } VSS_{denit} &= 0.042 \times NO_x \times Q_i \\
 \text{Produced } CO_{2,denit} &= 2.81 \times NO_x \times Q_i
 \end{aligned}
 \tag{3.55}$$

Where *Removed CBOD_{denit}* is in (g BOD/d),

Produced VSS_{denit} is in (g VSS/d), and

Produced CO_{2,denit} is in (g CO₂/d).

The impact of denitrification on the GHG estimation procedure was materialized by subtracting the CBOD removal by the denitrification process from the available CBOD for oxidation by oxygen, and by adding the CO₂ and VSS produced during the denitrification process to the CO₂ and VSS produced because of oxidation by oxygen.

The alkalinity is consumed during the treatment process because of CBOD removal and nitrification processes and it is produced because of aerobic biomass decay and denitrification processes. Considering Equations 3.37, 3.41, 3.39, and 3.43, alkalinity needs and production from each of the above processes is calculated as follows:

$$\begin{aligned}
Alk_{need,CBOD} &= 0.06 \times (S_i - S) \longrightarrow r_{Alk,CBOD} = Q_i \times Alk_{need,CBOD} \\
Alk_{need,nit} &= 7.14 \times NO_x \longrightarrow r_{Alk,nit} = Q_i \times Alk_{need,nit} \\
Alk_{produced,denit} &= 3.89 \times NO_x \longrightarrow Produced Alk_{denit} = Q_i \times Alk_{produced,denit} \\
Produced Alk_{VSS\ decay} &= 0.44 \times M_{X,degraded,reactor} \tag{3.56}
\end{aligned}$$

Where $Alk_{need,CBOD}$, $Alk_{need,nit}$, and $Alk_{produced,denit}$ are in (g CaCO₃/m³),

$r_{Alk,CBOD}$, $r_{Alk,nit}$, $Produced Alk_{denit}$, and $Produced Alk_{VSS\ decay}$ are in (g CaCO₃/d).

Mass balance equations are used to calculate the total amount of alkalinity needed during the treatment. It is recommended that alkalinity in the amount of 70 to 80 (mg/L alkalinity as CaCO₃) is needed to maintain the liquid pH (Metcalf and Eddy, 2003). The following mass balance equations are used to estimate the required alkalinity:

$$Alk\ to\ maintain\ pH = Influent\ Alk - Alk\ used + Alk\ to\ be\ added$$

$$Alk\ to\ be\ added = Alk\ to\ maintain\ pH - Influent\ Alk + Alk\ used$$

$$r_{Total\ Alk} = 80 \times Q_i - Alk_{inf} + (r_{Alk,CBOD} + r_{Alk,nit} - Produced\ Alk_{denit} - Produced\ Alk_{VSS\ decay}) \tag{3.57}$$

The terms in parenthesis stand for the alkalinity usage during carbonaceous BOD removal, and nitrification processes minus alkalinity production during denitrification reaction. As mentioned before, material consumption inside the IWWTP is one of the sources of upstream GHG emissions. The upstream GHG emissions because of alkalinity consumption during the liquid treatment process are estimated as follows:

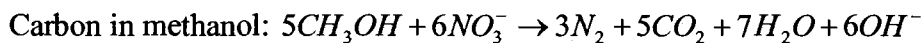
$$P_{CO_2, Alk, liquid} = EF_{Alkalinity} \times r_{Total Alk} \quad (3.58)$$

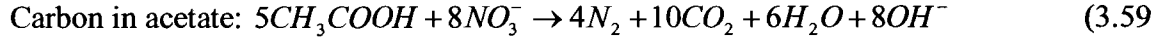
Where $P_{CO_2, Alk, liquid}$ is in (g CO₂/d),

$EF_{Alkalinity}$ is the GHG emission factor for the production and transportation of alkalinity to the IWWTP, (g CO₂e/g Alk) .

According to Equation 3.41, during the nitrification process, 7.14 g CaCO₃/g N is necessary for ammonia oxidation, and Equation 3.43 indicates that 3.89 gram of this amount is recovered during the denitrification process. This implies that if denitrification is performed along with the nitrification process, less alkalinity is needed to support the nutrient removal process as compared to the case when nitrification process is carried out alone. This of course leads to less upstream GHG emissions associated with alkalinity production and transportation.

During the biological denitrification process, as mentioned in Chapter 2, the electron donor can originate from three sources: 1) BOD in the influent wastewater, 2) BOD produced by endogenous decay of biomass, and 3) external sources such as methanol or acetate. The second method of denitrification is rarely used by the IWWTPs' operators because of unreliability and the resulting low rate of the denitrification process, so this study focuses on options one and three. The reaction stoichiometry for denitrification by the wastewater BOD was introduced in Equation 3.42. The stoichiometric reactions for denitrification using carbon in methanol or acetate are as follows (Crites and Tchobanoglous, 1998):





The CO_2 production by the denitrification process using BOD of the wastewater was given in Equations 3.43 and 3.55. If an external carbon source is used instead of the wastewater BOD to promote the denitrification process, the GHG emissions estimation procedure will proceed as follows:

a) Methanol as the external carbon source:

$$\text{CO}_2 \text{ production} = \frac{\Delta \text{CO}_2}{\Delta N} = \frac{5 \left(\frac{44 \text{ g}}{\text{mol}} \right)}{6 \times 14} = 2.62 \text{ g CO}_2 \text{ equivalent} / \text{g NO}_3 - \text{N}$$

b) Acetate as the external carbon source:

$$\text{CO}_2 \text{ production} = \frac{\Delta \text{CO}_2}{\Delta N} = \frac{10 \left(\frac{44 \text{ g}}{\text{mol}} \right)}{8 \times 14} = 3.93 \text{ g CO}_2 \text{ equivalent} / \text{g NO}_3 - \text{N} \quad (3.60)$$

The total amount of GHG production due to the denitrification process is computed as follows.

$$P_{\text{CO}_2, \text{denit}} = \begin{cases} 2.81 \times \text{NO}_x \times Q_i & \text{WW as the BOD source} \\ 2.62 \times \text{NO}_x \times Q_i & \text{Methanol as the external carbon source} \\ 3.93 \times \text{NO}_x \times Q_i & \text{Acetate as the external carbon source} \end{cases} \quad (3.61)$$

Where $P_{\text{CO}_2, \text{denit}}$ is the GHG production due to denitrification, (g CO_2/d).

The produced CO₂ due to the denitrification process is then added to Equations 3.48 and 3.50 in order to obtain the total CO₂ emissions resulting from the liquid treatment of wastewater using exogenous carbon source for denitrification.

External carbon use during the denitrification process causes additional GHG emissions because of the production and transportation of the chemical compounds to the treatment plant; that contributes to upstream GHG emissions. The use of organic carbon in the wastewater offers two advantages. First, a fraction of BOD in wastewater is removed by anoxic processes to supply the carbon needs of the denitrification process, thus lowering oxygen requirements for aerobic BOD removal process and the associated GHG productions. Second, the use of external carbon sources will be avoided, eliminating upstream GHG emission due to chemical usage.

The denitrification process using external carbon sources produces additional GHG emissions in the form of CO₂ (Equation 3.59), but it also produces alkalinity that subsides the alkalinity needs of the IWWTP, and consequently decreases the upstream GHG emissions because of on-site alkalinity usage. According to Equation 3.59, one equivalent alkalinity is produced per equivalent NO₃ reduced.

Alkalinity production as CaCO₃ = 1 × (50 g CaCO₃/eq) / 14 = 3.57 g CaCO₃/g N reduced

$$\text{Produced Alk}_{denit} = 3.57 \times NO_x \times Q_i \quad (3.62)$$

Equation 3.62 is then substituted in Equations 3.57 and 3.58 to calculate the alkalinity needs of the IWWTP and the corresponding upstream GHG emissions.

The use of methanol or acetate increases the upstream GHG emissions due to on-site material usage. According to Equation 3.59, the amount of external organic carbon needed for denitrification process is then quantified as below.

$$r_{\text{methanol,denit}} = \frac{5 \times 32 \text{ g/mole}}{6 \times 14 \text{ g/mole}} = 1.9 \text{ g CH}_3\text{OH/g NO}_3 - \text{N}$$

$$r_{\text{acetate,denit}} = \frac{5 \times 60 \text{ g/mole}}{8 \times 14 \text{ g/mole}} = 2.68 \text{ g CH}_3\text{COOH/g NO}_3 - \text{N} \quad (3.63)$$

Where $r_{\text{methanol,denit}}$ and $r_{\text{acetate,denit}}$ are the amounts of methanol and acetate needed for the denitrification process, (g/g N).

Total amount of methanol or acetate necessary for the denitrification process and the corresponding upstream GHG emissions is measured according to the following formula:

$$\text{Methanol need}^{\text{denit}} = 1.9 \times \text{NO}_x \times Q_i$$

$$\text{Acetate need}^{\text{denit}} = 2.68 \times \text{NO}_x \times Q_i$$

$$P_{\text{CO}_2,\text{denit,Methanol}} = \text{Methanol need}^{\text{denit}} \times EF_{\text{Methanol}}$$

$$P_{\text{CO}_2,\text{denit,acetate}} = \text{Acetate need}^{\text{denit}} \times EF_{\text{Acetate}} \quad (3.64)$$

Where methanol and acetate needs are in (g/d),

$P_{\text{CO}_2,\text{denit,Methanol}}$ and $P_{\text{CO}_2,\text{denit,acetate}}$ are in (g CO₂/d), and

$EF_{Methanol}$ and $EF_{Acetate}$ are the GHG emission factors for methanol and acetate production and transportation to the IWWTP, respectively, (g CO₂e/g material).

The upstream GHG emissions due to the alkalinity needs of the plant should also be added to the upstream GHG emissions attributable to IWWTP.

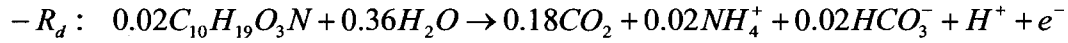
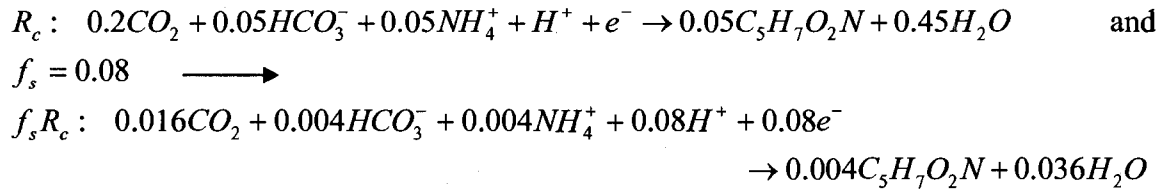
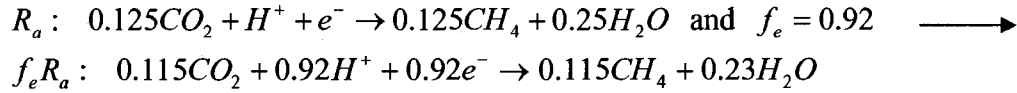
3.4.3 Anaerobic digester:

As mentioned in Chapter 2, most industrial wastewater treatment plants use anaerobic digestion for sludge stabilization and solids reduction. According to Figure 3.1, the sludge generated during the liquid treatment process and removed by primary and secondary clarifiers enter the digester for further degradation.

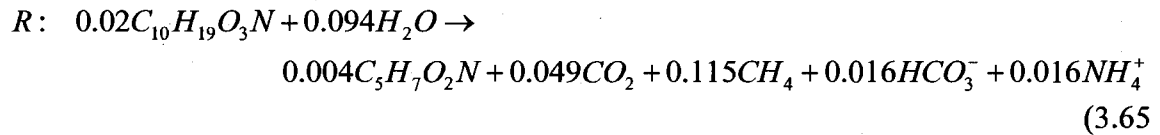
As mentioned before, anaerobic microorganisms transform part of the wastewater BOD to CO₂ and CH₄, and synthesize the rest of BOD into new biomass. The produced biomass is then decayed endogenously to provide energy for microorganisms when the BOD is consumed. In order to develop the equations for each of these reactions the half reaction approach is used as practiced before for the aerobic reactor.

The reaction for anaerobic BOD reduction to biomass and gaseous end products are developed below. In the anaerobic environment f_s is 0.05-0.08 (Rittmann and McCarty, 2001; Sawyer et al., 1994) because of low biomass yield compared to the aerobic environment. If the value of 0.08 is chosen for f_s , then $f_e = 1 - f_s = 0.92$. R_a is the half-reaction related to the electron acceptor which represents the transformation of CO₂ to CH₄ during the methanogenesis process. Ammonia is the nitrogen source for cell

synthesis (R_c) and R_d is the electron donor half-reaction which signifies the oxidation of substrate (Rittmann and McCarty, 2001).



$$R = f_e R_a + f_s R_c - R_d$$



According to the above equation, the yield coefficients for the production of CO_2 , CH_4 , VSS, Alk are calculated as follows:

$$Y_{CO_2}^{An} = \frac{0.049 \times 44 \text{ g } CO_2}{0.02 \times 201 \text{ g substrate} \times 2 \text{ g BOD} / \text{g Substrate}} = 0.27 \text{ g } CO_2 / \text{g BOD}$$

$$Y_{CH_4}^{An} = \frac{0.115 \times 16}{0.02 \times 201 \times 2} = 0.23 \text{ g } CH_4 / \text{g BOD}$$

$$Y_{VSS}^{An} = \frac{0.004 \times 113}{0.02 \times 201 \times 2} = 0.056 \text{ g VSS} / \text{g BOD}$$

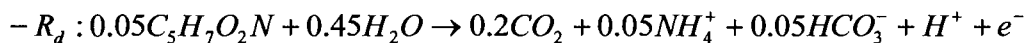
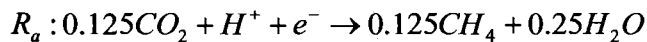
$$Y_{Alk}^{An} = \frac{0.016 \times 50}{0.02 \times 201 \times 2} = 0.1 \text{ g CaCO}_3 / \text{g BOD}$$

$$Y_{NH_4}^{An} = \frac{0.016 \times 14}{0.02 \times 201 \times 2} = 0.028 \text{ g N} / \text{g BOD} \quad (3.66)$$

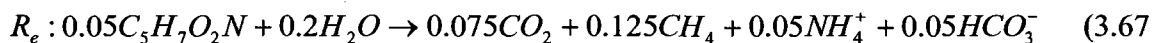
Where $Y_{CO_2}^{An}$, $Y_{CH_4}^{An}$, and Y_{VSS}^{An} are the CO_2 and CH_4 yield coefficient, and the biomass yield, in anaerobic environment, respectively,
 Y_{Alk}^{An} is the alkalinity yield as $CaCO_3$, and

$Y_{NH_4}^{An}$ is the soluble nitrogen yield.

The reaction for endogenous decay of biomass in the anaerobic environment is developed below. In the anaerobic environment, R_a is the half-reaction for CO_2 transformation to CH_4 and R_d is the half-reaction for cell destruction (reverse process of cell synthesis). Similar to the endogenous decay of aerobic microorganisms, there is no cell synthesis during the endogenous decay of anaerobic microorganisms and it is sufficient to consider the donor half-reaction and acceptor half-reaction (Rittmann and McCarty, 2001).



$$R_e = R_a - R_d$$



The yield coefficients for the endogenous decay reaction are listed below:

$$\begin{aligned}
 Y_{CO_2, endogenous}^{An} &= \frac{0.075 \times 44}{0.05 \times 113} = 0.58 \text{ g } CO_2 / \text{g VSS} \\
 Y_{CH_4, endogenous}^{An} &= \frac{0.125 \times 16}{0.05 \times 113} = 0.35 \text{ g } CH_4 / \text{g VSS} \\
 Y_{Alk, endogenous}^{An} &= \frac{0.05 \times 50}{0.05 \times 113} = 0.44 \text{ g } CaCO_3 / \text{g VSS} \\
 Y_{NH_4, endogenous}^{An} &= \frac{0.05 \times 14}{0.05 \times 113} = 0.12 \text{ g } N / \text{g VSS}
 \end{aligned} \tag{3.68}$$

By knowing the reactions occurring in the anaerobic environment, one can start the GHG emission calculation from each of the reactions in the anaerobic environment. The mass of the produced volatile suspended solids (VSS) in pervious steps which enters the digester is calculated according to Equation 3.69.

$$Total\ mass_{SS, Sludge} = r_{SS, PC} + (P_{X, bio})_{Aerobic} \tag{3.69}$$

Where $Total\ mass_{SS, Sludge}$ is the total mass of VSS enters the digester, (g VSS/d).

Some BOD enters the digester along with the solids. This BOD consists of those in the primary clarifier's sludge flow and the secondary clarifier's sludge flow. The flow that enters the digester is:

$$Q_i^D = Q_{PC} + (Q_w)_{Aerobic} \tag{3.70}$$

Where Q_i^D is the flow to the digester, (m^3/d),

$(Q_w)_{Aerobic}$ is the waste sludge flow rate from aerobic reactor, (m^3/d).

The BOD concentration in the influent and effluent of the digester are calculated as follows:

$$S_i^D = \frac{r_{BOD,PC} + (Q_w \times S)_{Aerobic}}{Q_i^D}$$

$$S^D = \frac{K_s^D (1 + (k_d^D) SRT^D)}{SRT^D (Y^D k^D - k_d^D) - 1} \quad (3.71)$$

Where S_i^D is the BOD in digester influent, ($g \text{ BOD}/m^3$),

Y^D is the yield coefficient in digester, ($g \text{ VSS}/g \text{ BOD}$),

S^D is the BOD in digester effluent, (g/m^3),

k_d^D is the endogenous coefficient in digester, (d^{-1}),

SRT^D is the solid retention time in digester, (d),

K_s^D is half velocity constant in digester, ($g \text{ BOD}/m^3$), and

k^D is the maximum specific substrate utilization rate in digester, ($g \text{ BOD}/g \text{ VSS} \cdot d$).

The gaseous end products of anaerobic digesters are CH_4 and CO_2 . The influent BOD to the digester is either converted to gaseous end products, or it is synthesized into new biomass. Because the process is anaerobic, there is no nitrification carried out in the digester. According to Equation 3.22, the mass of biological solids synthesized daily because of BOD utilization in digester is:

$$P_{X,bio}^D = \frac{Q_i^D Y^D (S_i^D - S^D)}{(1 + k_d^D \times SRT^D)} \quad (3.72)$$

Where $P_{X,bio}^D$ is in (g VSS/d).

Similar to the aerobic reactor, non-biodegradable VSS, known as cell debris, is produced in the digester following the endogenous decay of biomass. The amount of cell debris production in the digester is calculated by:

$$P_{X,Cell\ Debris}^D = \frac{f_d^D \times k_d^D \times Y^D \times Q^D \times (S_0^D - S^D) \times SRT^D}{1 + k_d^D \times SRT^D} \quad (3.73)$$

Where $P_{X,Cell\ Debris}^D$ is in (g VSS/d),

f_d^D is the fraction of biomass which remains as cell debris in digester, (0.10-0.15 g VSS/g VSS).

For a completely mixed digester, the SRT^D is similar to the hydraulic retention time in the digester (τ^D) because there is no sludge recycle in the digester. In the aerobic reactor because there was a sludge recycle the SRT differs from HRT . To determine the volume of the produced biogas, a BOD mass balance is formed around the digester in order to calculate the changes in BOD during the fermentation process. The BOD oxidation rate is then equal to:

$$r_{BOD}^D = Q_i^D (S_i^D - S^D) - 1.42 \times P_{X,bio}^D \quad (3.74)$$

Where r_{BOD}^D is the BOD removal in digester, (g BOD/d).

In anaerobic digesters, the BOD loss is determined from methane production. By recalling Equation 3.66, the CH₄ production is:

$$M_{CH_4, BOD}^D = 0.23 \text{ g } CH_4 / \text{g } BOD \times r_{BOD}^D \quad (3.75)$$

According to the literature, the value of 0.25 g CH₄/g BOD was used extensively for calculating the CH₄ production by the methanogenic microorganisms (Metcalf and Eddy, 2003). This is due to the combustion reaction of methane, as presented previously in Equations 2.1 and 2.2. The value of 0.25 g CH₄/g BOD is also selected in this study. Therefore, the CH₄ production resulting from the anaerobic BOD utilization is:

$$M_{CH_4, BOD}^D = 0.25 \text{ g } CH_4 / \text{g } BOD \times [Q_i^D (S_i^D - S^D) - 1.42 \times P_{X, bio}^D] \quad (3.76)$$

Where $M_{CH_4, BOD}^D$ is in (g CH₄/d).

Biomass is either produced inside the digester from BOD utilization or has entered the digester by the primary and mostly secondary sludge. Recalling Equation 3.18, the concentration of biomass inside the digester is estimated by the following equation:

$$X_D = \left(\frac{SRT^D}{\tau^D} \right) \frac{Y^D (S_i^D - S^D)}{(1 + k_d^D \times SRT^D)} + \frac{\text{Total mass}_{SS, Sludge}}{Q_i^D} \quad (3.77)$$

Where X_D is the concentration of biomass in the digester, (g VSS/m³).

The first term is the biomass concentration due to cell production inside the digester and the second term is the biomass that enters the digester from the primary and secondary clarifiers. Considering 80% of produced solids to be biodegradable and 0.7 be the degree of stabilization of degradable biosolids in the digester (Metcalf and Eddy, 2003) and Equation 3.77, the amount of biomass subjected to endogenous decay in the digester is calculated as follows:

$$\begin{aligned}
 \text{Biomass decayed} &= V^D \times k_d^D \times X_D \longrightarrow \\
 M_{X, \text{degraded, Digester}} &= 0.8 \times 0.7 \times \left[\frac{V^D k_d^D Y^D (S_i^D - S^D)}{(1 + k_d^D \times SRT^D)} + SRT^D \times k_d^D \times \text{Total mass}_{SS, \text{Sludge}} \right]
 \end{aligned}
 \tag{3.78}$$

Where $M_{X, \text{degraded, Digester}}$ is the amount of biomass decayed endogenously, (g VSS/d).

The total amount of CH₄ produced by endogenous decay of biomass is calculated as follows. As mentioned before, the non-biodegradable solids will accumulate as the wasted sludge from the digester and cause GHG emissions due to the transportation of solids to disposal sites. 30% of the degradable solids in the digester will be degraded off-site and contribute to off-site GHG emissions because of solid biodegradation. According to Equation 3.68, the CH₄ production resulting from the endogenous decay of biomass is:

$$M_{CH_4, \text{endogenous}}^D = 0.35 \frac{\text{g CH}_4}{\text{g VSS}} \times M_{X, \text{degraded, Digester}}
 \tag{3.79}$$

Where $M_{CH_4, \text{endogenous}}^D$ is in (g CH₄/d).

The total amount of CH₄ produced in the digester is the sum of CH₄ produced because of the sludge BOD utilization as well as the endogenous decay of biomass:

$$M_{CH_4, total}^D = M_{CH_4, BOD}^D + M_{CH_4, endogenous}^D \quad (3.80)$$

Where $M_{CH_4, total}^D$ is in (g CH₄/d).

It is clear that in addition to CH₄, CO₂ is also produced as a result of anaerobic biodegradation. The volume of CO₂ is commonly estimated by assuming that the biogas contains 65% - 70% CH₄ (v/v) and 25% - 30% CO₂ (v/v) plus small amounts of N₂, H₂, H₂S, water vapor and other gases (Metcalf and Eddy, 2003; Peavy et al., 1985; and Crites and Tchobanoglous, 1998). In this study, the mass of produced CO₂ is calculated according to Equations 3.66 and 3.68.

$$M_{CO_2}^D = 0.27 \text{ g } CO_2 / \text{g } BOD \times r_{BOD}^D + 0.58 \text{ g } CO_2 / \text{g } VSS \times M_{x, degraded, Digester} \quad (3.81)$$

Where $M_{CO_2}^D$ is the produced CO₂ from digester, (g CO₂/d).

The first term on the right hand side of Equation 3.81, defines the CO₂ production because of influent BOD and the second term is the CO₂ production because of disintegration or decay of biomass inside the digester. The mass unit of produced CO₂ and CH₄, calculated by Equations 3.81 and 3.80, may be converted to volume units in order to verify the conformity of the predicted CO₂ and CH₄ volume percentages in

biogas with the results reported before. For this purpose, the ideal gas law is used to convert the units of gases to their corresponding volume units, as presented below:

$$MG_i = g_i \times V_{DG} \times MW_i \times \frac{P}{RT} \quad (3.82)$$

Where MG_i is the mass production rate of gas i, (g/d),

g_i is the volumetric fraction of biogas that gas i occupies,

MW_i is the molecular weight of gas i, (g/mol),

P is the pressure of the biogas, (atm),

R is the gas constant, ($8.21 \times 10^{-5} \frac{\text{atm.m}^3}{\text{mol.K}}$), and

T is the biogas temperature, (K).

Because the amount of gases other than CO_2 and CH_4 in biogas is small compared to CO_2 and CH_4 , the volume fractions of these minor products are ignored and it is assumed that biogas only consists of CO_2 and CH_4 . According to Equation 3.82, the volume of CO_2 and CH_4 and the volumetric CO_2 percentage in the biogas are as follows:

$$V_{\text{CO}_2} = \frac{\frac{M_{\text{CO}_2}^D}{MW_{\text{CO}_2}} \times R \times T_{\text{reactor}}}{P}$$

$$V_{\text{CH}_4} = \frac{\frac{M_{\text{CH}_4, \text{total}}^D}{MW_{\text{CH}_4}} \times R \times T_{\text{reactor}}}{P}$$

$$X = \frac{V_{CO_2}}{V_{CH_4} + V_{CO_2}} \quad (3.83)$$

Where V_{CH_4} and V_{CO_2} are in (m^3/d).

Since there is no recycling of digester effluent, some CH_4 dissolves in the effluent and escapes the digester (Cakir and Stenstrom, 2005). It is stated that the amount of CH_4 escaped from the effluent of anaerobic digesters is small because of the low flow rate and the high concentration of solids in the anaerobic digesters' effluent (Cakir and Stenstrom, 2005). It is mentioned that this term can be as large as the recovered CH_4 in the effluent of anaerobic reactors treating low strength wastewater (Cakir and Stenstrom, 2005). This phenomenon will be considered in developing a methodology for the estimation of GHG emissions in anaerobic wastewater treatment. The escaped CH_4 should be considered if the treatment plant does not utilize a post-treatment option for the digester effluent. If there is a post treatment biological reactor after the anaerobic reactor or anaerobic digester, the dissolved methane is oxidized along with the remaining BOD in the effluent. In any case, the escaped CH_4 lowers the amount of available CH_4 in the biogas. The amount of dissolved methane in the digester effluent is calculated using Henry's law and the partial pressure of CH_4 . The partial pressure of CH_4 is the volume fraction of CH_4 in biogas and is equal to $(1-X)$, where X was calculated according to Equation 3.83. The reported partial pressure of CH_4 in the biogas is 0.65-0.70 atm (Metcalf and Eddy, 2003; Peavy et al., 1985; and Crites and Tchobanoglous, 1998). The amount of CH_4 dissolved in digester effluent is calculated by Equation 3.84:

$$DS.Methane_{Digerster\ effluent} = Q_i^D \times K_{H,CH_4\ digester} \times PP_{CH_4\ digester} \quad (3.84)$$

Where $DS.Methane_{Digerster\ effluent}$ is in (g CH₄/d),

$K_{H,CH_4\ digester}$ is the Henry's Law constant, (g/m³.atm), and

$PP_{CH_4\ digester}$ is partial pressure of methane in the digester, (atm).

If no arrangement is made to capture the methane leakage, the CH₄ is released to the atmosphere and the CO₂ equivalent of the escaped CH₄ equals to:

$$P_{CO_2\ equiv,DS\ methane}^D = 23 \times DS.Methane_{Digerster\ effluent} \quad (3.85)$$

Where $P_{CO_2\ equiv,DS\ methane}^D$ is in (g CO₂e/d).

The released CH₄ can be captured or utilized by employing a post treatment facility to oxidize the CH₄ or by using other physical methods such as air-stripping. Several other models are developed to predict the biogas production and composition (Andrews, 1969; Andrews and Graef, 1971). The models were not applicable to this study because they are based on stoichiometric relationships and assume that the acid fermentation step is the rate limiting step and not the methanogenesis or hydrolysis of particulate or complex substrate. As stated earlier, some food processing wastewaters contain high concentrations of solids that need to be hydrolyzed before biodegradation. So these models can not be applied to industrial food processing wastewaters or wastewaters with high solids content. Also these models are restricted to low strength wastewaters which is

another barrier to using them in this study. Therefore, this study does not consider the alternative models for predicting the biogas composition.

CH₄ is a source of energy and the produced biogas can be burned to heat the wastewater or to generate electricity. The recovery and combustion of methane will reduce GHG emissions associated with the treatment process and energy demand of the plant since it will reduce the use of fossil fuels for energy generation. However, in many WWTPs the generated biogas is not recovered, mainly because of economic reasons such as the low price of external energy sources, excessive cost of biogas recovery facilities and the lack of incentive to reduce GHG emissions. The recovery of the produced biogas and its use as fuel for heating purposes or generation of electricity, or even flaring of biogas to avoid explosion hazard, will reduce GHG emissions, while the release of methane to the atmosphere, as practiced in many treatment plants, contributes to considerable augmentation of GHG emissions. In this study, it is assumed that $per_{CH_4, recovered}^D$, $per_{CH_4, flared}^D$, and $per_{CH_4, vented}^D$ represent the percent (on mass basis) of the total produced CH₄ in gaseous form in the digester that is recovered, flared, or vented respectively. Therefore the mass of CH₄ entering each of these processes are:

$$\begin{aligned}
 M_{CH_4, gaseous}^D &= M_{CH_4, total}^D - DS.Methane_{Digester\ effluent} \\
 M_{CH_4, recovered}^D &= per_{CH_4, recovered}^D \times M_{CH_4, gaseous}^D \\
 M_{CH_4, flared}^D &= per_{CH_4, flared}^D \times M_{CH_4, gaseous}^D \\
 M_{CH_4, vented}^D &= per_{CH_4, vented}^D \times M_{CH_4, gaseous}^D
 \end{aligned} \tag{3.86}$$

Where all the M units are in (g CH₄/d).

According to Equation 2.1 the combustion of methane produces 44 g CO₂/16 g CH₄ or 2.75 g CO₂/g CH₄. So the CO₂ production due to CH₄ combustion during biogas recovery and biogas flaring equals to:

$$M_{CH_4 \rightarrow CO_2, recovered}^D = 2.75 \text{ g CO}_2 / \text{g CH}_4 \times M_{CH_4, recovered}^D$$

$$M_{CH_4 \rightarrow CO_2, flared}^D = 2.75 \text{ g CO}_2 / \text{g CH}_4 \times M_{CH_4, flared}^D \quad (3.87)$$

Where $M_{CH_4 \rightarrow CO_2, recovered}^D$ and $M_{CH_4 \rightarrow CO_2, flared}^D$ are in (g CO₂/d).

The vented biogas contains CH₄ which has a GWP factor 23 times higher than that of CO₂. The factor 23 is considered in the GHG release because of biogas venting.

Considering the fraction of CO₂ in the biogas as well as its production due to methane combustion (Equations 3.81, 3.85, 3.86, and 3.87), the total GHG production in the digester is:

$$M_{Total\ CO_2, biogas}^D = M_{CH_4 \rightarrow CO_2, recovered}^D + M_{CH_4 \rightarrow CO_2, flared}^D + 23 \times M_{CH_4, vented}^D + M_{CO_2}^D + P_{CO_2\ equiv, DS\ methane}^D \quad (3.88)$$

Where $M_{Total\ CO_2, biogas}^D$ is in (g CO₂e/d).

The GHG emissions savings because of biogas recovery can be calculated as described below. The energy content of CH₄ is 50.1 kJ/g (Metcalf and Eddy, 2003). If all

of the recovered CH₄ is converted to electrical energy, the total savings in electrical energy consumption of the IWWTP is:

$$E_{\text{biogas recovery}} = 50.1 \times M_{\text{CH}_4, \text{recovered}}^D \text{Eff}_{\text{electrical-conversion}} \quad (3.89)$$

Where $E_{\text{biogas recovery}}$ is in (kJ/d),

$\text{Eff}_{\text{electrical-conversion}}$ is the electrical conversion efficiency.

Conversion of CH₄ in biogas to electricity decreases the upstream GHG emissions associated with electricity production. The amount of GHG saving is calculated by Equation 3.3. On the other hand, if the recovered CH₄ is converted to heating energy in the boilers for warming up the wastewater, the total savings in energy will be as follows:

$$E_{\text{biogas recovery}} = 50.1 \times M_{\text{CH}_4, \text{recovered}}^D \text{Eff}_{\text{heat-conversion}}$$

Where $\text{Eff}_{\text{heat-conversion}}$ is the heat conversion efficiency. (3.90)

This energy saving eliminates the need for fossil fuel importation for on-site combustion and as a result eliminates the upstream GHG emissions associated with fossil fuel preparation and transmission to the IWWTP and additional GHG production because of fossil fuel burning. The total GHG savings due to the absence of fossil fuel transportation to the IWWTP is calculated according to Equations 3.4 and 2.2.

Off-site GHG emissions are also produced because of off-site degradation of the remaining constituents in the treated water, and the off-site degradation of biodegradable solids that were not degraded in the IWWTP. The treated water is discharged from both

aerobic reactor and digester but the biosolids are discharged solely by the digester. In order to calculate the off-site GHG emissions resulting from the remaining BOD, it is assumed that the soluble BOD degradation is carried out aerobically in the receiving water bodies. The overall reaction for BOD oxidation and cell synthesis in the aerobic environment (Equation 3.2) is used for calculating the corresponding GHG emissions. For each gram of BOD used, 0.42 g VSS and 0.33 g CO₂ are produced directly because of BOD oxidation. The produced VSS will be further degraded (Equation 3.38) and generates CO₂. 1.56 g CO₂ is produced from the degradation of 1 g VSS. So the total amount of CO₂ production because of BOD oxidation in the aerobic environment is:

$$0.33 \text{ g CO}_2 / \text{g BOD} + 0.42 \text{ g VSS} / \text{g BOD} \times 1.56 \text{ g CO}_2 / \text{g VSS} = 0.985 \text{ g CO}_2 / \text{g BOD}$$

Assuming that the effluent BOD is x g BOD/m³, the resulting CO₂ emissions are:

$$P_{CO_2, \text{remaining eff BOD}} = 0.985 \times x \times Q_i \quad (3.91)$$

Where $P_{CO_2, \text{remaining eff BOD}}$ is in (g CO₂/d).

Equation 3.91 represents the GHG emissions from the effluents of aerobic reactor and digester. Off-site degradation of remaining biosolids is carried out either aerobically or anaerobically. Under aerobic conditions, Equation 3.38 is used to estimate the amount of biodegradable solids remained in the sludge. The amount of biodegradable solids remaining in the sludge and the corresponding GHG emissions are calculated as follows:

$$X_{Sludge}^{Degradable} = \frac{30\%}{70\%} \times M_{x,degraded,Digester}$$

$$P_{CO_2,Sludge\ Degradation} = 1.56 \frac{g\ CO_2}{g\ VSS} \times X_{Sludge}^{Degradable} \quad (3.92)$$

Where $X_{Sludge}^{Degradable}$ is in (g VSS/d),

$P_{CO_2,Sludge\ Degradation}$ is in (g CO₂/d).

The factor of $\frac{3}{7}$ is considered because it was assumed that the digester stabilizes 70% of the biodegradable solids and the rest 30% will end up in sludge and degrade off-site (Metcalf and Eddy, 2003). The factor of 1.56 was derived from Equation 3.39 for aerobic solid decay. Equation 3.67 is used for the anaerobic off-site degradation of the remaining biosolids. During the anaerobic degradation of biosolids, CH₄ is generated along with CO₂. This increases the overall GHG emissions compared to the aerobic degradation of biosolids since CH₄, having a higher GWP compared to CO₂, is directly released to the atmosphere. The amount of the remaining biodegradable solids in the sludge and the corresponding GHG emissions is calculated as follows:

$$X_{Sludge}^{Degradable} = \frac{30\%}{70\%} \times M_{x,degraded,Digester}$$

$$P_{CO_2,Sludge\ Degradation} = 0.58 \frac{g\ CO_2}{g\ VSS} \times X_{Sludge}^{Degradable}$$

$$P_{CH_4,Sludge\ Degradation} = 0.35 \frac{g\ CH_4}{g\ VSS} \times X_{Sludge}^{Degradable}$$

$$P_{Total\ GHG,Sludge\ Degradation} = P_{CO_2,Sludge\ Degradation} + 23 \times P_{CH_4,Sludge\ Degradation} \quad (3.93)$$

Where $P_{CO_2, Sludge\ Degradation}$ and $P_{Total\ GHG, Sludge\ Degradation}$ are in (g CO₂/d),

$P_{CH_4, Sludge\ Degradation}$ is in (g CH₄/d).

The factors of 0.58 and 0.35 were derived from Equation 3.68 for anaerobic solid decay. The GHG emissions associated with the off-site degradation of BOD and the remaining biosolids are then added to the total upstream GHG emissions.

The concentration of alkalinity is of great concern during anaerobic processes. A fraction of CO₂ produced during the fermentation and methanogenesis processes dissolves in liquid and produces carbonic acid which is the main consumer of alkalinity in the anaerobic digestion process. So the CO₂ concentration in biogas, which is in equilibrium with the dissolved CO₂, reflects the alkalinity needs. In order to maintain the liquid pH at a neutral level, alkalinity concentrations of 2000-4000 mg/L as CaCO₃ are normally required in anaerobic treatment processes (Metcalf and Eddy, 2003). A well stabilized digester has the total alkalinity requirements of 2000-5000 mg/L (WEF, 1996). However, the precise alkalinity demands of anaerobic processes must be calculated in order to ensure the supply of adequate alkalinity. In most anaerobic treatment processes, the required alkalinity is rarely available in the influent wastewater and it is commonly supplied by external sources. However, during anaerobic digestion processes used for sludge treatment, a part of the alkalinity demand is produced as ammonium bicarbonate due to the breakdown of protein and amino acids in sludge. The total alkalinity production in a digester is proportional to the solid concentration in the influent. GHG emissions associated with the production and transportation of alkalinity must also be considered in the calculation of the total GHG emissions of the treatment plant. In

anaerobic treatment processes, because of high CO₂ content of biogas, the required alkalinity is proportional to the partial pressure of CO₂. The carbonic acid concentration is calculated using Henry's law and the partial pressure of CO₂ in the digester.

$$x_w = \frac{P}{H} x_a \quad \text{and} \quad x_w = \frac{[H_2CO_3]}{[H_2CO_3] + [55.6 \text{ mole/L}]} \quad (3.94)$$

Where x_w is the mole fraction of CO₂ in water, (*mole gas/(mole gas + mole water)*),

x_a is the mole fraction of CO₂ in air, (*mole gas/mole air*),

P is the total pressure, (atm), and

H is the Henry constant, (*atm.(mole gas/mole air)/(mole gas/mole water)*).

The coefficient 55.6 is moles of water per litre. Solving the above two equations will yield the concentration of carbonic acid ($[H_2CO_3]$). Once the carbonic acid concentration is determined by using Equation 3.94, the bicarbonate alkalinity (HCO_3^-) needed to maintain the liquid pH near 7 is calculated as follows:

$$K_{a1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} \quad (3.95)$$

Where K_{a1} is the first acid dissociation constant,

$[HCO_3^-]$ is the concentration of alkalinity in solution, (mole/L).

Knowing $[H^+]$, K_{a1} , and $[H_2CO_3]$, the required alkalinity concentration ($[HCO_3^-]$) is estimated. Alkalinity is normally calculated in CaCO₃ unit.

$$1 \text{ eq CaCO}_3 = \frac{MW}{2} = \frac{(100 \text{ g/mole})}{2} = 50 \text{ g CaCO}_3/\text{eq}$$

$$1 \text{ eq HCO}_3^- = \frac{(61 \text{ g/mole})}{1} = 61 \text{ g HCO}_3^-/\text{eq}$$

$$\text{Equivalents of HCO}_3^- = \frac{[\text{HCO}_3^-] \times 61 \text{ g/mole}}{61 \text{ g HCO}_3^-/\text{eq}} = [\text{HCO}_3^-] \text{ eq/l}$$

Alkalinity as CaCO₃ =

$$50 \text{ g CaCO}_3/\text{eq} \times [\text{HCO}_3^-] \text{ eq/l} \times 10^3 \text{ mg/g} = 5 \times 10^4 \times [\text{HCO}_3^-] \text{ mg CaCO}_3/\text{l}$$

$$\text{Alkalinity need}^D = (5 \times 10^4 \times [\text{HCO}_3^-] - \text{inf}_{Alk}) \times Q_i^D \quad (3.96)$$

Where alkalinity need is in (g CaCO₃/d),

inf_{Alk} is the influent alkalinity, (g CaCO₃/m³).

Alkalinity is generated in the digester because of BOD utilization and VSS destruction. Therefore, a fraction of the alkalinity demand is supplied by the degradation process itself. The alkalinity production because of BOD utilization is calculated by Equations 3.66 and 3.74. The alkalinity production due to VSS destruction is calculated by Equations 3.68 and 3.78.

$$\text{Alk Production (BOD utilization)} = 0.1 \text{ g CaCO}_3/\text{g BOD} \times r_{BOD}^D$$

$$\text{Alk Production (VSS destruction)} = 0.44 \text{ g CaCO}_3/\text{g VSS} \times M_{X, \text{deg raded, Digester}} \quad (3.97)$$

Where the alkalinity production is in (g CaCO₃/d).

The GHG emissions associated with alkalinity needs of the treatment plant are related to the production and transportation of chemicals and they are considered as part of the upstream GHG emissions. The total GHG emissions related to the alkalinity demand in the digester is calculated as follows.

$$P_{CO_2\text{-equiv, Alkalinity}}^D = EF_{Alkalinity} \times (Alkalinity\ need^D - Alk\ Production) \quad (3.98)$$

Where $P_{CO_2\text{-equiv, Alkalinity}}^D$ is in (g CO₂/d),

Alk Production is the sum of the two parts of Equation 3.97, (CaCO₃/d).

The anaerobic reactor and the digester both need heating to promote the anaerobic biological reactions. This is due to low activity of anaerobic bacteria at low temperatures. Temperatures of 25 °C to 35 °C are preferred to support a high rate of anaerobic biological reactions and to provide a more stable treatment. At lower temperatures, slower reactions occur, requiring longer SRTs, larger reactor volumes and lower organic loads. As mentioned before, because of high BOD concentrations of industrial wastewaters, generally sufficient amounts of CH₄ are produced during anaerobic treatment to heat the wastewater without the requirement of an external fuel source. Usually, the influent wastewater to a treatment plant has a temperature of 20 – 30 °C and the influent sludge to anaerobic digester has a temperature of 10 – 15 °C. So the heating needs of anaerobic reactors treating wastewaters are less than that of an anaerobic digester that treats sludge. The heating requirements of reactors are comprised of the amount needed to elevate the incoming wastewater temperature to the reactor's temperature, compensate the heating losses through walls, floor and roof of the reactors,

and to make up the losses in the piping between the heating source and the reactors. Calculation of the heating energy needs of the incoming wastewater assumes that its specific heat is similar to that of water. The heat loss through the reactor walls, floor and roof is calculated by the following equation:

$$q = U \times A \times \Delta T \quad (3.99)$$

Where q is the heat loss, (kJ/s),

U is the overall coefficient of heat transfer, (kJ/m².s.°C),

A is the cross sectional area through which the heat escapes, (m²), and

ΔT is the temperature drop, (°C).

For the heat transfer coefficient (U), different values are reported for walls, floor and roof of the reactors and so q should be separately calculated for each area. For computing the conductive heat loss, the reactor areas, heat transfer coefficients, and exterior temperatures of the walls, roof and the floor of the reactor are assumed to be A_{wall} , A_{roof} , A_{floor} and U_{wall} , U_{roof} , U_{floor} and T_{wall} , T_{roof} , T_{floor} respectively. The total heat loss by conduction is then equal to:

$$q_{heat\ loss} = [A_{wall} \times U_{wall} \times (T_{reactor} - T_{wall}) + A_{roof} \times U_{roof} \times (T_{reactor} - T_{roof}) + A_{floor} \times U_{floor} \times (T_{reactor} - T_{floor})] \times 86400 \text{ s/d} \quad (3.100)$$

Assuming that the specific gravity of wastewater is similar to that of water, the heating requirements to raise the temperature of wastewater to the temperature of reactor is computed as follows:

$$H_{WW} = Q^D \times 1000 \frac{\text{kg}}{\text{m}^3} \times (T_{\text{reactor}} - T_{\text{incoming}}) \times 4200 \frac{\text{J}}{\text{kg} \cdot ^\circ\text{C}} \times \frac{1}{1000} \frac{\text{kJ}}{\text{J}}$$

$$H_{WW} = Q^D \times (T_{\text{reactor}} - T_{\text{incoming}}) \times 4200 \quad (3.101)$$

Where H_{WW} is in (kJ/d),

T_{reactor} is the temperature of reactor, ($^\circ\text{C}$),

T_{incoming} is the temperature of incoming wastewater, ($^\circ\text{C}$), and

4200 J/kg. $^\circ\text{C}$ is the specific heat of water.

The required total heating energy, E_{heating} (kJ/d) is:

$$E_{\text{heating}} = H_{WW} + q_{\text{heat loss}} \quad (3.102)$$

The heating energy is provided by using biogas, on-site fossil fuel burning, or electric heaters. Using biogas for heating yields no additional GHG emissions, while fossil fuel burning and electric heaters generate extra GHG emissions. The method for the calculation of GHG emissions in each case was presented before.

The generated biosolids also produce GHG emissions because of their transportation and off-site degradation. There are different methods of biosolids handling and treatment; each resulting in the generation of a specific amount of GHG emissions.

For example, dewatering and drying of biosolids results in GHG emissions as a result of the energy demands of the process, while they have no effect on the carbon content of biosolids since biodegradation does not take place during drying processes. The GHG emissions related to the transportation of biosolids to the disposal sites are also a function of the dryness of biosolids, travel distance and fuel type. The emissions resulting from the degradation of biosolids during their disposal are contingent on the method of disposal. For example, the use of biosolids as soil amendment reduces GHG emissions since it removes the need for other products and energy to generate soil amendment. Therefore, the GHG emissions related to solid disposal should be estimated on a case by case basis because of the variety of treatment methods and available options for solid disposal. It is suggested that the GHG emissions from waste transportation are 10 kg CO₂e/t solid waste for short trips (between WWTP and the solid disposal site) and 20 kg CO₂e/t solid waste for longer distance trips for Canadian sources (Torrie, 2003). Due to the long distances between the source of waste production and the location of disposal, 20 kg CO₂e/t waste is chosen in this study. Moreover, it is recommended that bulldozers, loaders, and other machinery at landfills consume 1.5L of diesel with the rate of 2.7 kg CO₂e/kg diesel (Torrie, 2003), generating 4 kg CO₂e/t wastes. Therefore, if the solids are to be disposed in landfills, 24 kg CO₂e/t waste is produced that is assigned to the source of waste production, i.e. the WWTP.

The mass of dried biosolids wasted each day is based on the total suspended solids (TSS) which comprises both the VSS and inorganic solids. Inorganic solids enter the treatment system by the wastewater influent and also, the biomass includes 10% to 15% inorganic solids (w/w dry weight). In this study, it is assumed that VSS/TSS ratio is 0.85

(Metcalf and Eddy, 2003). The amount of inorganic solids produced in the treatment process is calculated as follows:

$$X_{Disposal}^{inorganic} = \left(\frac{P_{X,bio}}{0.85} - P_{X,bio} \right)_{Aerobic} + \left(\frac{P_{X,bio}}{0.85} - P_{X,bio} \right)_D \quad (3.103)$$

Where $X_{Disposal}^{inorganic}$ is in (g solid/d).

The inert TSS content in the influent wastewater is calculated as follows:

$$X_{Disposal}^{Inert} = Q_i \times iTSS \quad (3.104)$$

Where $X_{Disposal}^{Inert}$ is in (g solid/d),

$iTSS$ is the inert TSS in the influent in (g solid/m³).

As mentioned before, 80% of the organic solids produced in the aerobic reactor and digester that result from BOD utilization are biodegradable (Metcalf and Eddy, 2003). The rest of the produced biosolids is not biodegradable and will form a part of the wasted sludge from the digester, calculated as follows:

$$X_{Disposal}^{Nonbio} = \frac{20\%}{80\%} \times (M_{X,degraded,Aerobic} + M_{X,degraded,Digester}) \quad (3.105)$$

Where $X_{Disposal}^{Nonbio}$ is in (g solid/d).

The non-biodegradable cell debris is also produced from endogenous decay of biomass, as described before, and ends up in the wasted sludge. The amount of cell debris production in terms of TSS is calculated by using Equations 3.24 and 3.73, as follows:

$$X_{Disposal}^{Cell\ debris} = \frac{(P_{X,Cell\ Debris})_{Aerobic} + (P_{X,Cell\ Debris})_{Digester}}{0.85} \quad (3.106)$$

Where $X_{Disposal}^{Cell\ debris}$ is in (g solid/d).

The total amount of biosolids destined for disposal and the corresponding GHG emissions can be calculated based on Equations 3.103, 3.104, 3.105, and 3.106, as follows:

$$X_{disposal} = X_{Disposal}^{inorganic} + X_{Disposal}^{Inert} + X_{Disposal}^{Nonbio} + X_{Disposal}^{Cell\ debris}$$

$$P_{CO_2, Solid\ disposal} = 24 \times 10^{-3} X_{disposal} \quad (3.107)$$

Where $X_{disposal}$ is in (g solid/d),

$P_{CO_2, Solid\ disposal}$ is in (g CO₂/d).

The electricity consumption rate of 0.2 kWh/m³ WW for aerobic treatment was used in this study for the mixing of liquid in the reactors, illumination of plants and operation of electrical devices such as pumps. This value does not take into consideration the heating of wastewater and aeration requirements which were calculated independently from the total electricity needs of the plant. The electricity needs are consequently calculated as follows:

$$E_{Elec-Required} = Q_i \times 0.2 \frac{kWh}{m^3 WW} \quad (3.108)$$

Where $E_{Elec-Required}$ is in (kJ/d),

Q_i is the flow rate, (m^3/d).

The GHG emissions related to the electricity needs of the plant are calculated from Equation 3.3. The energy demands of the plant originate from aeration (Equation 3.54), heating (Equation 3.102), and electricity (Equation 3.108). The energy produced by the plant is in the form of biogas (Equations 3.89 and 3.90). If the biogas energy exceeds the energy needs of the plant, there is no need for the importation of electricity or fossil fuel to the IWWTP, thus reducing GHG emissions. However, if the biogas energy is less than the energy needs of the plant, then energy importation in the form of electricity or fossil fuels is inevitable, thus contributing to GHG emissions. In any case, the biogas usage lessens the need for energy importation and the related GHG emissions. If energy is imported in form of electricity, the related GHG emissions are calculated by Equation 3.3, and if the energy is supplied by fossil fuels, the GHG emissions are estimated as described below. Assuming methane to be the imported fuel, the required amount of CH_4 is:

$$r_{Imported\ Methane} = \frac{Needed\ energy}{50.1 \frac{kJ}{g\ CH_4} \times Eff_{heat-conversion}} \quad (3.109)$$

$$n = \frac{r_{Imported\ Methane}}{16}$$

Where $r_{Imported\ Methane}$ is the needed CH_4 to be imported, ($g\ CH_4/d$),

Needed energy is the difference between the produced energy in form of biogas and the total plant's needed energy, (kJ/d),

$Eff_{heat-conversion}$ is the heat conversion efficiency, and

n is number of moles of CH₄ to be imported, (mol CH₄/d).

The volume of the imported CH₄ according to ideal gas law can be calculated as:

$$V_{Imported\ Methane} = \frac{nRT}{P} \quad (3.110)$$

Where $V_{Imported\ Methane}$ is in (m³/d),

P is the pressure which is 1 (atm),

R is the gas constant, ($8.21 \times 10^{-5} \frac{atm.m^3}{mol.K}$), and

T is the biogas temperature, which is assumed to be 20(°C) or 293(K).

The GHG generation related to the on-site CH₄ combustion originates from the following sources: 1) upstream GHG emissions because of production and transportation of natural gas and 2) on-site combustion of natural gas. GHG emissions associated with CH₄ importation and on-site burning are estimated from Equations 3.4, 3.109, and 3.110. The above equations are used in the estimation of GHG emissions from aerobic IWWPs.

3.4.4 On-site GHG emission:

At this stage, the total amount of on-site GHG emissions associated with aerobic treatment ($P_{Total\ CO_2, onsite}$) may be calculated. These emissions are the sum of CO₂

generation from CH₄ burning related to fossil fuel importation (last term of Equation 3.4), biological processes in aerobic reactor (sum of Equations 3.48 and 3.50) and biological processes in the digester (Equation 3.88).

3.4.5 Upstream GHG emission:

The upstream GHG emissions, $P_{Total\ CO_2,\ upstream}$, are the sum of GHG emissions because of alkalinity needs in the aerobic reactor (Equation 3.58), alkalinity needs in the digester (Equation 3.98), methanol or acetate requirements for denitrification (Equation 3.64), CH₄ production and transportation for on-site burning (if CH₄ is imported) (Equation 3.110 and first two terms of Equation 3.4), electricity production (if electricity importation is needed) (Equation 3.108), solid disposal (Equation 3.107), off-site degradation of effluent BOD (Equation 3.91 is used for effluents from both aerobic reactor and digester), off-site degradation of solids (Equation 3.92 or 3.93).

3.4.6 Total GHG emissions:

Total GHG emissions attributable to IWWTP are the sum of upstream GHG emissions and on-site GHG emissions.

$$P_{Total\ CO_2} = P_{Total\ CO_2,\ upstream} + P_{Total\ CO_2,\ onsite} \quad (3.111)$$

3.5 Anaerobic treatment – GHG estimation model:

The model for anaerobic treatment is developed based on AF or UASB reactor with sludge recycle. The schematic diagram of a typical anaerobic process is presented in Figure 3.3. The processes responsible for on-site GHG production are identified in grey color.

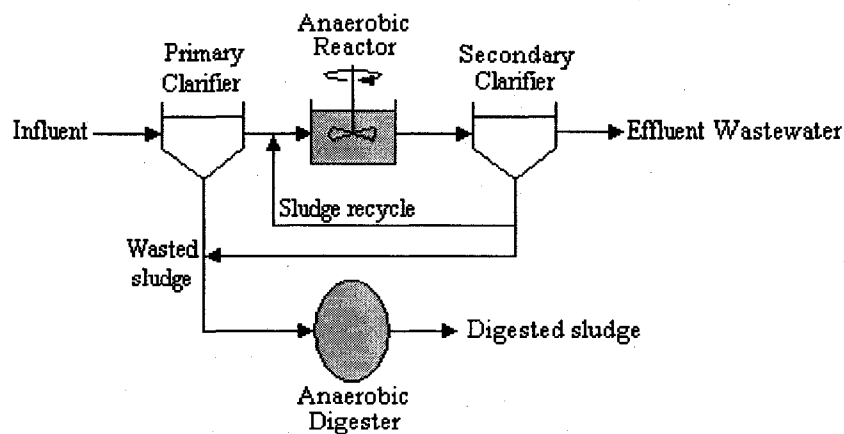


Figure 3.3- Schematic diagram of anaerobic reactor with sludge recycle

Similar to the aerobic treatment system, mass balance equations are formed around the defined processes for each specific component of interest such as the flow rate, and biomass and substrate concentrations. Figure 3.2 presents the nomenclature and system boundary. The methodology for the estimation of GHG emissions is similar to that used in the aerobic treatment system.

3.5.1 Primary Clarifier:

Equations 3.7 and 3.8 are used for calculating the VSS and BOD removal rate of the primary clarifier.

3.5.2 Biological anaerobic reactor:

There is no major difference in the equations developed in the digester section of aerobic treatment and those corresponding to the anaerobic treatment. In the anaerobic reactor, the oxidation of soluble BOD is the main source of biogas production while solid digestion deals with low flow rates of solids (sludge) that carry organic biodegradable carbon. The production of biogas in these systems results from biomass disintegration and its further biodegradation. It is important to note that some biogas is produced in anaerobic treatment systems due to endogenous biomass respiration, and similarly, some biogas is produced due to the soluble BOD flow into the anaerobic digesters.

Equation 3.31 is used to calculate the concentration of influent BOD in the anaerobic reactor (S_i^{An}). According to Equation 3.14, the effluent BOD concentration in the anaerobic reactor is calculated as follows:

$$S^{An} = \frac{K_s^{An} (1 + k_d^{An} \times SRT^{An})}{SRT^{An} (Y^{An} k^{An} - k_d^{An}) - 1} \quad (3.112)$$

Where Y^{An} is yield coefficient in the anaerobic reactor, (g VSS/g BOD),

S^{An} is the effluent BOD concentration in the anaerobic reactor, (g/m³),

k_d^{An} is the endogenous coefficient in the anaerobic reactor, (d^{-1}),

SRT^{An} is the solid retention time in the anaerobic reactor, (d),

K_s^{An} is half velocity constant in the anaerobic reactor, (g BOD/ m^3), and

k^{An} is the maximum specific substrate utilization rate in the anaerobic reactor, (g BOD/g VSS.d).

Biomass production in the anaerobic reactor because of BOD utilization and cell debris production resulting from endogenous decay of biomass are calculated as follows:

$$P_{X,bio}^{An} = \frac{Q_i Y^{An} (S_i^{An} - S^{An})}{(1 + k_d^{An} \times SRT^{An})}$$

$$P_{X,Cell Debris}^{An} = \frac{f_d^{An} \times k_d^{An} \times Y^{An} \times Q^{An} \times (S_i^{An} - S^{An}) \times SRT^{An}}{1 + k_d^{An} \times SRT^{An}} \quad (3.113)$$

Where $P_{X,bio}^{An}$ and $P_{X,Cell Debris}^{An}$ are in (g VSS/d),

f_d^{An} is the fraction of biomass which remains as cell debris in anaerobic reactor, (0.10-0.15 g VSS/g VSS).

Based on Equations 3.74 and 3.76, the rate of BOD reduction in the anaerobic reactor, as well as CH_4 production are estimated by the following equations:

$$r_{BOD}^{An} = Q_i (S_i^{An} - S^{An}) - 1.42 \times P_{X,bio}^{An}$$

$$M_{CH_4,BOD}^{An} = 0.25 \frac{g CH_4}{g BOD} \times r_{BOD}^{An} \quad (3.114)$$

Where r_{BOD}^{An} is BOD removal in the anaerobic reactor, (kg BOD/d),

$M_{CH_4, BOD}^{An}$ is CH₄ production, (g CH₄/d).

As mentioned before, in anaerobic environment, the BOD loss is expressed in terms of methane production instead of oxygen requirement.

GHG is also produced in the form of CH₄ or CO₂ because of biomass endogenous decay. The biomass concentration inside the anaerobic reactor is:

$$X^{An} = \left(\frac{SRT^{An}}{\tau^{An}} \right) \left[\frac{Y^{An} (S_i^{An} - S^{An})}{1 + k_d^{An} \times SRT^{An}} \right] \quad (3.115)$$

Where X^{An} is the concentration of biomass in the anaerobic reactor, (g VSS/m³),

τ^{An} is the hydraulic retention time in anaerobic reactor, (d).

Considering 80% of the produced biosolids to be biodegradable (Metcalf and Eddy, 2003), the amount of biomass decayed inside the reactor is calculated as follows:

$$M_{X, degraded, An} = 0.8 \times V \times k_d^{An} \times X^{An} = 0.8 \times \frac{V k_d^{An} Y^{An} (S_i - S)}{(1 + k_d^{An} \times SRT^{An})} \quad (3.116)$$

Where $M_{X, degraded, An}$ is the amount of biomass decayed endogenously inside anaerobic reactor, (kg VSS/d),

V is the volume of anaerobic reactor, (m³).

According to Equation 3.68 for VSS endogenous decay in anaerobic environment, the amount of CH₄ produced because of biomass decay is:

$$M_{CH_4, endogenous}^{An} = 0.35 \frac{g CH_4}{g VSS} \times M_{x, degraded, An} \quad (3.117)$$

Where $M_{CH_4, endogenous}^{An}$ is in (g CH₄/d).

The total amount of CH₄ produced in anaerobic reactor is then equal to:

$$M_{CH_4, total}^{An} = M_{CH_4, BOD}^{An} + M_{CH_4, endogenous}^{An} \quad (3.118)$$

Where $M_{CH_4, total}^{An}$ is in (g CH₄/d).

As described before (Equation 3.81), CO₂ is produced along with CH₄ in the anaerobic reactor. The production of CO₂ is estimated by the following equations:

$$M_{CO_2}^{An} = 0.27 \frac{g CO_2}{g BOD} \times r_{BOD}^{An} + 0.58 \frac{g CO_2}{g VSS} \times M_{x, degraded, An} \quad (3.119)$$

Where $M_{CO_2}^{An}$ is the produced CO₂ in anaerobic reactor, (g CO₂/d).

Similar to Equation 3.83, the production volume of CO₂ and CH₄, and the volume fraction of CO₂ in the produced biogas are estimated as follows:

$$V_{CO_2} = \frac{\frac{M_{CO_2}^{An}}{MW_{CO_2}} \times R \times T_{reactor}}{P}$$

$$V_{CH_4} = \frac{\frac{M_{CH_4, total}^{An}}{MW_{CH_4}} \times R \times T_{reactor}}{P}$$

$$X = \frac{V_{CO_2}}{V_{CH_4} + V_{CO_2}} \quad (3.120)$$

Where V_{CH_4} and V_{CO_2} are in (m^3/d).

The magnitude of dissolved CH_4 in the effluent of anaerobic reactors can be as large as the recovered CH_4 in biogas, particularly for low strength wastewaters (Cakir and Stenstrom, 2005). In the absence of a post treatment process, methane in the liquid effluent is considered to escape from the anaerobic reactor. The dissolved CH_4 in the reactor effluent is calculated similar to Equation 3.84.

$$DS.Methane_{An\ effluent} = Q_i \times K_{H,CH_4\ An} \times PP_{CH_4\ An} \quad (3.121)$$

Where $DS.Methane_{An\ effluent}$ is dissolved CH_4 in the anaerobic reactor effluent, ($g\ CH_4/d$),

$K_{H,CH_4\ An}$ is the Henry's Law constant, ($g/m^3 \cdot atm$), and

$PP_{CH_4\ digester}$ is the partial pressure of methane in digester, (atm).

Considering the GWP of CH_4 , the GHG emissions resulting from CH_4 leakage in dissolved form is equal to:

$$P_{CO_2\ equiv,DS\ methane}^{An} = 23 \times DS.Methane_{An\ effluent} \quad (3.122)$$

Where $P_{CO_2\ equiv,DS\ methane}^{An}$ is in ($g\ CO_2e/d$).

The remaining CH₄ in the biogas can be recovered for reuse as fuel, flared, or it may be directly vented into the atmosphere. If the percentage of the total CH₄ in biogas distributed in each of these processes is shown by $per_{CH_4, recovered}^{An}$, $per_{CH_4, flared}^{An}$, and $per_{CH_4, vented}^{An}$, respectively, then the mass of CH₄ in each of these processes can be calculated based on Equation 3.86, as follows:

$$\begin{aligned}
 M_{CH_4, gaseous}^{An} &= M_{CH_4, total}^{An} - DS_{Methane} \text{ }_{An \text{ effluent}} \\
 M_{CH_4, recovered}^{An} &= per_{CH_4, recovered}^{An} \times M_{CH_4, gaseous}^{An} \\
 M_{CH_4, flared}^{An} &= per_{CH_4, flared}^{An} \times M_{CH_4, gaseous}^{An} \\
 M_{CH_4, vented}^{An} &= per_{CH_4, vented}^{An} \times M_{CH_4, gaseous}^{An}
 \end{aligned} \tag{3.123}$$

Where all the mass units are in (g CH₄/d).

According to Equation 2.1, the production of CO₂ related to methane combustion during the recovery of biogas and its flaring is equal to:

$$\begin{aligned}
 M_{CH_4 \rightarrow CO_2, recovered}^{An} &= 2.75 \frac{g \text{ } CO_2}{g \text{ } CH_4} \times M_{CH_4, recovered}^{An} \\
 M_{CH_4 \rightarrow CO_2, flared}^{An} &= 2.75 \frac{g \text{ } CO_2}{g \text{ } CH_4} \times M_{CH_4, flared}^{An}
 \end{aligned} \tag{3.124}$$

Where $M_{CH_4 \rightarrow CO_2, recovered}^{An}$ and $M_{CH_4 \rightarrow CO_2, flared}^{An}$ are in (g CO₂/d).

The estimated amount of CH₄ that escapes the treatment system or is vented should be multiplied by the GWP factor of CH₄ in order to yield the overall GHG emissions.

Considering the total CO₂ in biogas, the total GHG production in anaerobic reactor can be estimated based on Equation 3.88, as follows:

$$M_{Total\ CO_2, biogas}^{An} = M_{CH_4 \rightarrow CO_2, recovered}^{An} + M_{CH_4 \rightarrow CO_2, flared}^{An} + 23 \times M_{CH_4, vented}^{An} + M_{CO_2}^{An} + P_{CO_2\ equiv, DS\ methane}^{An} \quad (3.125)$$

Where $M_{Total\ CO_2, biogas}^{An}$ is in (g CO₂e/d).

Similar to Equations 3.89 and 3.90, the total savings in energy depends on the use of biogas for electricity production or for heating of wastewater, and it is estimated by the following equations:

$$E_{biogas\ recovery} = 50.1 \times M_{CH_4, recovered}^{An} \times Eff_{electrical-conversion}$$

$$E_{biogas\ recovery} = 50.1 \times M_{CH_4, recovered}^{An} \times Eff_{heat-conversion} \quad (3.126)$$

Where $E_{biogas\ recovery}$ is in (kJ/d).

As discussed before, the energy saving eliminates the need for fossil fuel or electricity importation to the IWWTP and as a result, eliminates the upstream GHG emissions because of fossil fuel handling or electricity generation. The amount of GHG saving due to the removal of fossil fuel importation to the IWWTP is calculated according to Equations 3.4 and 2.2.

The amount of alkalinity that should be provided to maintain the stability of anaerobic treatment process, as well as the corresponding upstream GHG emissions are

calculated from Equation 3.127 which is developed based on Equations 3.96, 3.97, and 3.98 following the methodology developed in the digester section of aerobic treatment process.

$$Alkalinity\ need^{An} = \left(5 \times 10^4 \times [HCO_3^-] - inf_{Alk}\right) \times Q_i - 0.1 \frac{g\ CaCO_3}{g\ BOD} \times r_{BOD}^{An} - 0.44 \frac{g\ CaCO_3}{g\ VSS} \times M_{X, degraded, An}$$

$$P_{CO_2-equiv, Alkalinity}^{An} = EF_{Alkalinity} \times Alkalinity\ need^{An} \quad (3.127)$$

Where $Alkalinity\ need^{An}$ is the alkalinity need, (CaCO₃/d),

$P_{CO_2-equiv, Alkalinity}^{An}$ is upstream GHG production because of alkalinity need, (g CO₂/d).

The heating energy required to warm up the influent wastewater and maintain the anaerobic reactor's temperature is similarly calculated according to Equations 3.100, 3.101, and 3.102, as presented before. The heating energy is supplied by on-site burning of fossil fuels, electric heaters, or biogas. Using biogas for supplying heating energy saves GHG emissions. The calculation method for GHG emissions from on-site burning of fossil fuels and electric heaters were described before.

Here again, the GHG emissions related to the degradation of the remaining BOD in the effluent of anaerobic treatment are calculated from Equation 3.91.

The electricity consumption rate of 0.2 kWh/m³ WW for anaerobic treatment was used to cover the mixing of liquid in the reactors, illumination of plants and operation of electrical devices such as pumps. As mentioned before, this value does not take into account the heating of wastewater which was calculated independently from the total

electricity needs of the plant. This value is therefore calculated according to Equation 3.108 and the corresponding GHG emissions are estimated based on Equation 3.3.

After leaving the anaerobic reactor, the produced biosolids enter the digester for further degradation. The estimation of GHG emissions from the digester was presented before and will not be presented here.

3.5.3 On-site GHG emission:

The total amount of on-site GHG emissions, $P_{Total\ CO_2,\ upstream}$, generated during anaerobic treatment system are the sum of CO₂ production from the combustion of CH₄ related to fossil fuel importation (last term of Equation 3.4), biological processes in anaerobic reactor (Equation 3.125), and biological processes in the digester (Equation 3.88).

3.5.4 Upstream GHG emission:

The upstream GHG emissions, $P_{Total\ CO_2,\ upstream}$, are the sum of GHG emissions related to the alkalinity needs in the anaerobic reactor (Equation 3.127), alkalinity needs in the digester (Equation 3.98), CH₄ production and transportation for on-site combustion (if CH₄ is imported) (Equation 3.110 and first two terms of Equation 3.4), electricity production (if electricity importation is needed) (Equation 3.108), solid disposal (Equation 3.107), off-site degradation of effluent BOD (Equation 3.91 applied for

effluents from both anaerobic reactor and digester), and off-site degradation of solids (Equation 3.92 or 3.93).

3.5.5 Total GHG emission:

Total GHG emission attributable to IWWTP is the sum of on-site and upstream GHG emissions, as presented in Equation 3.111.

3.6 Hybrid treatment – GHG estimation model:

Hybrid treatment is the integration of anaerobic and aerobic treatment processes. The schematic diagram of a typical hybrid treatment system is presented in Figure 3.4 and the on-site GHG producing processes are defined in grey.

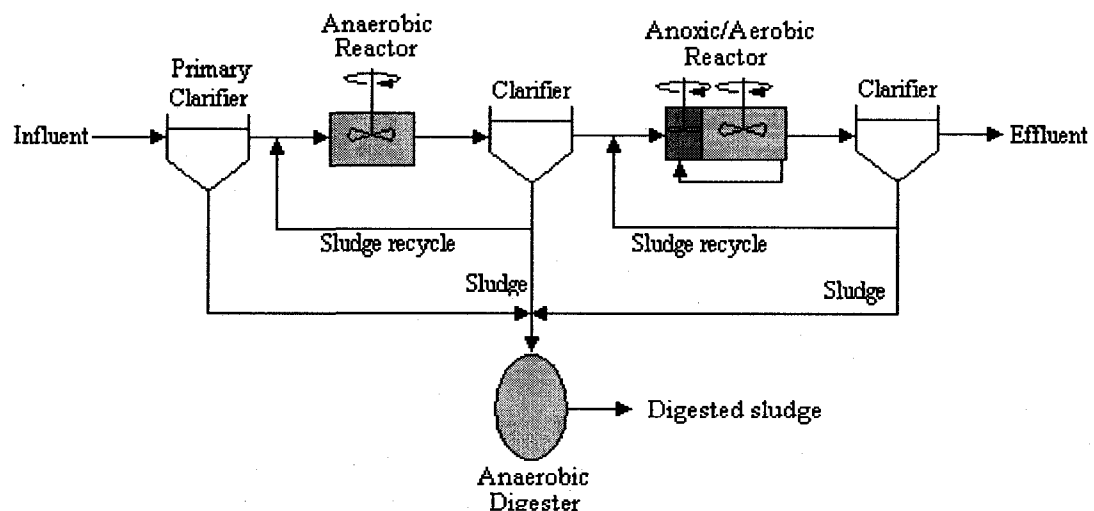


Figure 3.4- Schematic diagram of hybrid treatment system

The GHG estimation model for the hybrid treatment system comprises the estimation of GHG emissions from anaerobic reactor, aerobic reactor, and anaerobic digester. The estimation of emissions associated with these treatment processes was described before. On-site and upstream GHG emissions are also estimated for hybrid treatment systems based on the developed methodology, similar to those applied to aerobic and anaerobic treatment systems.

The developed mathematical model and relevant process parameters were used to estimate GHG emissions by the different treatment systems examined in this study. Tables 3.6 and 3.7 present the major operating and process parameters used during this work.

Table 3.6- Major operating and process parameters of the wastewater treatment plant of a food processing industry

Parameter	Value	Reference
Energy		
Electricity consumption rate		(Sahely et al., 2006)
Hybrid treatment	0.3 kWh/m ³ WW	
Aerobic treatment	0.2	
Anaerobic treatment	0.2	
Aeration efficiency ($Eff_{aeration}$)	7.2 g O ₂ /kJ	(Cakir and Stenstrom, 2005)
Heat conversion efficiency ($Eff_{heat-conversion}$)	0.83	(Cakir and Stenstrom, 2005)
Electricity conversion efficiency ($Eff_{electrical-conversion}$)	0.5	(Cakir and Stenstrom, 2005)
Material		
Emission factor for alkalinity production and transmission ($EF_{Alkalinity}$)	1.74 g CO ₂ e/g Alk	(Energy Efficiency Opportunity Guide in the Lime Industry, 2001)
Emission factor for methanol production and transmission ($EF_{Methanol}$)	1.54 g CO ₂ e/g Methanol	(Dong and Steinberg, 1997)

Table 3.7- Major operating and process parameters of the wastewater treatment plant of food processing industry (continued)

Parameter	Value	Reference
Influent		
Flow rate (Q_i)	1000 m ³ /d	(Xu and Nakhla, 2006)
BOD _u (S_{i0})	2000 g BOD/m ³	(Xu and Nakhla, 2006)
Nitrogen	100 g N/m ³	(Xu and Nakhla, 2006)
VSS (X_i)	10 g VSS/m ³	(Xu and Nakhla, 2006)
Temperature (T)	25 °C	(Xu and Nakhla, 2006)
Primary Clarifier		
VSS removal percentage (Per_X)	0.2	(Monteith et al., 2005)
BOD removal percentage (Per_S)	0.3	(Monteith et al., 2005)
Underflow rate (Q_{PC})	30 m ³ /d	(Monteith et al., 2005)
Anaerobic Reactor		
Temperature	25 °C	(Metcalf and Eddy, 2003)
Heterotrophic Yield (Y^{An})	0.08 g VSS/g BOD	(Metcalf and Eddy, 2003)
Decay rate (k_d^{An})	0.01 g/g.d	(Metcalf and Eddy, 2003)
Solid retention time (SRT^{An})	15 d	(Metcalf and Eddy, 2003)
Sludge wasting ratio (Q_w/Q_i)	0.01	(Metcalf and Eddy, 2003)
Aerobic Reactor		
Temperature	20 °C	(Metcalf and Eddy, 2003)
Nitrifying Yield (Y_n)	0.12 g VSS/g N	(Metcalf and Eddy, 2003)
Heterotrophic Yield (Y)	0.4 g VSS/g BOD	(Metcalf and Eddy, 2003)
Nitrifying decay rate (k_{dn})	0.08 g/g.d	(Metcalf and Eddy, 2003)
Heterotrophic decay rate (k_d)	0.12 g/g.d	(Metcalf and Eddy, 2003)
Solid retention time (SRT)	5 d	(Metcalf and Eddy, 2003)
Sludge wasting ratio (Q_w/Q_i)	0.01	(Metcalf and Eddy, 2003)
Anaerobic Digester		
Temperature	35 °C	(Metcalf and Eddy, 2003)
Heterotrophic Yield (Y^D)	0.08 g VSS/g BOD	(Metcalf and Eddy, 2003)
Decay rate (k_d^D)	0.03 g/g.d	(Metcalf and Eddy, 2003)
Solid retention time (SRT^D)	30 d	(Metcalf and Eddy, 2003)

Similar characteristics of the influent wastewater have been used during all analysis for all types of treatment systems.

Chapter 4

Results and discussion

The mathematical model developed in this study for greenhouse gas (GHG) emissions estimation was validated by using literature-cited values of kinetic parameters and comparing the obtained results with those reported in previous studies.

As mentioned before, earlier models and methodologies of GHG emission estimation ignored certain GHG producing processes. Accordingly, these processes were eliminated during the validation stage of the current study in order to create similar conditions as the previous studies. The validity of models used for the simulation of aerobic treatment system was verified by using the data reported by Monteith et al. (2005) and Keller and Hartley (2003), while the model used for the hybrid treatment system was validated by using the data reported by Keller and Hartley (2003). These studies were chosen due to the completeness of their data.

Since the effluent of anaerobic treatment systems commonly needs a post treatment stage to reach the discharge limits, most prior studies did not consider anaerobic treatment as the sole treatment method. Furthermore, the hybrid treatment system considered in this study includes both aerobic and anaerobic processes. Therefore, it is proven sufficient to only verify the correctness of the developed models for hybrid and aerobic treatment systems without the need for an independent verification of the model for anaerobic treatment system. Cakir and Stenstrom (2005) used anaerobic treatment in their study and compared GHG emissions by aerobic and anaerobic treatment systems.

However, their treatment system could not be simulated by the model developed in the present work since they did not provide sufficient data to quantify the process parameters.

4.1 Aerobic treatment model examination:

The developed models were verified by using the process parameters reported by Monteith et al. (2005). The employed parameters included: 1) influent and effluent parameters such as the influent flow rate, influent and effluent BOD and VSS removal rates, 2) primary clarifier's process parameters such as the underflow rate, BOD and VSS removal rate, 3) aerobic reactor's process parameters such as temperature, SRT, MLVSS concentration, k_d , Y , VSS/TSS ratio, and Q_w/Q_i , and 4) anaerobic digester's process parameters such as SRT, k_d , and Y . As mentioned before, the study of Monteith et al. (2005) was based on municipal wastewaters, hence the selected process parameters were all identified for municipal wastewaters. Under these conditions, the model verification stage used modified values of process parameters and ignored material consumption and the associated upstream GHG emissions as well as nitrification and denitrification processes, GHG emissions due to solid disposal, and GHG emissions associated with off-site degradation of remaining biodegradable constituents in treated water and sludge. Biogas recovery and GHG savings due to biogas reuse as fuel are considered in the reference study. Neither the reference study nor our model verification study considered the upstream GHG emissions due to the energy requirement related to on-site electrical and natural gas consumption. Only on-site CO_2 production because of natural gas burning is taken into account in both studies. The model developed in our

study resulted in the estimation of 4674 kg CO₂/d or 1706 Mg CO₂/y emissions which is equal to 0.20 kg CO₂/m³ wastewater treated. The reference study's generic estimation procedure for conventional activated sludge plus anaerobic digester provided emissions rates ranging from 0.228 to 0.245 kg CO₂/m³ wastewater treated. This demonstrates the close agreement between the model developed in the present work and that used in the reference study. The difference in emissions estimation, which is about 12%, primarily stems from the following sources:

- 1) In the reference study, biogas production volume was measured by the operators and the CO₂ and CH₄ volumes were calculated by assuming volume fractions of 0.65 and 0.32 for CH₄ and CO₂ in the biogas. In the present study the production volumes of CH₄ and CO₂ were calculated based on stoichiometric equations.
- 2) In the reference study, energy requirements of the plant in the form of electricity and natural gas were measured by WWTP operators while in the present study the energy demand is calculated based on the energy need of each section of the WWTP. More energy demand needs more electricity and natural gas importation and results in the production of additional on-site CO₂ emissions due to fossil fuel burning and off-site GHG emissions due to production of electricity and natural gas. As mentioned before, the upstream GHG emissions because of energy need of the WWTP were not examined in the reference study.

The validity of the developed model was further verified through comparison with another reference study which was conducted by Keller and Hartley (2003). As practiced

during the previous verification, similar process parameters and input model parameters were considered in the reference study and the present study. The process parameters of concern were introduced before. Again, material consumption and the associated upstream GHG emissions, nitrification and denitrification processes, GHG emissions due to solid disposal, and GHG emissions related to off-site degradation of remaining biodegradable constituents in treated water and sludge were ignored in order to conform to the employed conditions in the reference study. Biogas recovery and GHG savings due to biogas reuse as fuel are considered in the reference study. In Keller and Hartley (2003), electricity is produced from coal burning but in the present study combination of different methods of electricity generations are considered. Since the energy production method of the reference study was different from our study, only the GHG emissions from BOD removal processes are compared between the two studies. According to the predictions of our model, GHG emission from the BOD removal processes is equal to 10148 kg CO₂/d or 0.44 kg CO₂/m³ WW. The study of Keller and Hartley (2003) suggests that activated sludge system plus anaerobic digester produce 0.438 kg CO₂/m³ WW, closely corresponding to the results of our model.

4.2 Hybrid treatment model examination:

The study of Keller and Hartley (2003) was used again as the reference study to verify the accuracy of the developed model for hybrid treatment system. Again, similar process parameters and input model parameters were considered in the reference study and the present study. Also, material consumption and the associated upstream GHG emissions, nitrification and denitrification processes, GHG emissions due to solid

disposal, and GHG emissions related to off-site degradation of remaining biodegradable constituents in treated water and sludge were ignored in order to conform to the employed conditions in the reference study. Biogas recovery and GHG savings due to biogas reuse as fuel are considered in the reference study. Since the energy production method of the reference study was different from our study, only the GHG emissions from BOD removal processes are compared between the two studies.

According to the predictions of our model, GHG emission from the BOD removal processes is equal to 9003 kg CO₂/d or 0.39 kg CO₂/m³ WW. The study of Keller and Hartley (2003) suggests that anaerobic/aerobic process produces 0.35 kg CO₂/m³ WW. Again, a close agreement is observed between the predictions of both models with a difference of 10%, which confirms the validity of the model developed in the present study. Thus, the validity of the model developed in the present study for the estimation of GHG emissions from wastewater treatment plants was verified for aerobic and hybrid treatment systems through direct comparison of results, and by reasoning, for anaerobic treatment systems.

4.3 Estimation of GHG emissions from wastewater treatment plants of food processing industry:

The developed model was further employed for the estimation of greenhouse gas (GHG) emissions by wastewater treatment plants of the food processing industry. This estimation considers three different types of treatment systems, namely aerobic, anaerobic and hybrid systems.

It is assumed that 70% of VSS is stabilized in the digester and the remaining 30% is degraded anaerobically outside the digester (Metcalf and Eddy, 2003). The heating losses from the anaerobic reactor and anaerobic digester are assumed to be 20% of the total heating needed in each reactor (Metcalf and Eddy, 2003).

Substrate driven denitrification (preanoxic denitrification) is chosen as the method of denitrification which exists before the aerobic reactor, as described in Chapter 2. In this anoxic process the substrate BOD is used by the heterotrophic microorganisms as the carbon source for denitrification process. Since the aerobic reactor is the only location of biological processes in an aerobic treatment system, there is adequate BOD for substrate driven denitrification processes in anoxic reactor, which precedes the aerobic reactor, and there is no need for an external carbon source. In the hybrid treatment system, the major fraction of substrate BOD is removed during the primary anaerobic treatment, leaving little carbon source for a complete preanoxic denitrification in the following anoxic/aerobic reactor. In this process, an external carbon source such as methanol is used to ensure a complete reduction of nitrate.

Energy is commonly supplied to the wastewater treatment plants in the form of electricity and fossil fuel. The electricity consumption rate ($0.3 \text{ kWh/m}^3 \text{ WW}$ for hybrid treatment and $0.2 \text{ kWh/m}^3 \text{ WW}$ for aerobic and anaerobic treatment systems) (Sahely et al., 2006) is related to the mixing of liquid in the reactors, illumination of plants and operation of electrical devices such as pumps. These values do not take into consideration the heating of wastewater and aeration requirements which were calculated independently from the total electricity needs of the plant in order to determine the contribution of aeration energy and heating energy demands to the total GHG emissions.

Two scenarios are considered for the fate of biogas during the treatment process. The first scenario assumes the flaring of biogas without recovery and reuse. In this case, heating energy for wastewater is supplied by on-site fossil fuel combustion while the rest of the plant's energy demand is provided by electricity importation. The second scenario assumes the recovery and combustion of biogas for heating of wastewater. If heating requirements exceed the biogas energy, natural gas should be imported to the WWTP to compensate for the shortage of energy. This will augment both on-site GHG emissions due to natural gas combustion, and off-site emissions due to the production and transmission of natural gas to the WWTP. However, if biogas energy exceeds the heating requirements, then the surplus biogas is used in the generators for electricity production, further reducing GHG emissions of the WWTP related to energy consumption.

Computer simulation studies used the raw data presented in Tables 3.6 and 3.7 along with the equations presented in the pervious chapter, and employed Microsoft Excel software. Due to the excessive number of equations involved in the computation of each GHG emission source in the industrial WWTP and the interrelationship between equations, circular referencing is used until the results from two consecutive runs converge. Table 4.1 presents the estimated GHG emissions by individual processes in the three studied types of treatment systems.

In order to describe the estimation process, aerobic treatment systems are selected as an example. Equation numbers correspond to those presented in the previous chapters. GHG emissions of biological processes result from the following sources:

- 1- CO₂ emissions from the aerobic reactor

- 1-1 Total CO₂ emissions in the aeration tank: Equations 3.48 and 3.50

1-2 CO₂ produced during the denitrification process in the anoxic tank:

Equation 3.55

2- CO₂ and CH₄ emissions from the anaerobic digester: Equation 3.88

3- CO₂ and CH₄ emissions related to the remaining constituents in treated wastewater

3-1 CO₂ and CH₄ emissions related to the off-site BOD degradation in the treated water: Equation 3.91

3-2 CO₂ and CH₄ emissions related to the off-site carbon degradation in the treated sludge: Equation 3.93

In the aerobic treatment system, GHG emissions related to the material usage result from alkalinity consumption:

1- Alkalinity needs in the aerobic reactor: Equation 3.58

2- Alkalinity needs in the anaerobic digester: Equation 3.98

The GHG emissions related to the energy demands of the IWWTP originate from:

1- Upstream GHG emissions due to natural gas importation plus GHG emissions related to on-site natural gas burning: Combination of Equations 3.110 and 3.4.

2- GHG emissions because of electricity needs of the plant

2-1 Aeration energy: combination of Equations 3.54 and 3.3

2-2 Electricity consumption of the rest of plant: combination of Equations 3.108 and 3.3

During the first scenario for the fate of biogas that assumes its flaring without recovery and reuse, heating energy for wastewater (Equation 3.102) is supplied by on-site fossil fuel combustion while the rest of the plant's energy demand is provided by electricity

importation. During the second scenario that assumes the recovery and combustion of biogas, the resulting extra savings indicate additional reductions in GHG emissions since biogas recovery covers the entire energy demands of the plant.

GHG emissions associated with solid disposal are calculated according to Equation 3.107. The total GHG emissions are the sum of the preceding columns in Table 4.1. For example if biogas recovery is performed, the total GHG emissions are calculated by the addition of GHG emissions due to biological processes, material usage, energy demand (with biogas recovery), extra savings due to biogas recovery, and solid disposal. The same procedure was followed to obtain the results for anaerobic and hybrid treatment systems.

Table 4.1- Comparison of the estimated GHG emissions by the three different types of treatment systems examined

Process identification	On-site Biological processes (kg CO ₂ /d)	Off-site Biological processes (kg CO ₂ /d)	Material used (kg CO ₂ /d)	Energy Demand (kg CO ₂ /d)		Extra Saving due to biogas recovery (kg CO ₂ /d)	Solid Disposal (kg CO ₂ /d)	Total GHG Emissions (kg CO ₂ /d)	
				No biogas recovery	With biogas recovery			No biogas recovery	With biogas recovery
Aerobic Treatment	1759	781	206	512	0	-58	6	3265	2694
Anaerobic Treatment	1702	844	3403	673	0	-128	0.7	6623	5822
Hybrid Treatment	2035	475	4138	988	0	-34	3.6	7640	6617

According to Table 4.1, biogas recovery and reuse as fuel covers the total energy needs of the treatment plants for aeration, heating and electricity for all three types of

operations, and considerably reduces GHG emissions. The recovery and reuse of biogas eliminate the need to import fossil fuels for on-site energy generation and the excess energy from the produced biogas may be used for the generation of electricity and sold to the power grid. It also reduces the dependence of treatment plants on other forms of electricity generation and consequently becomes a carbon credit for the WWTP while reducing the total GHG emissions attributed to the plant. The amount of GHG reduction achieved by this action equals 58, 128, and 34 kg CO₂/d for aerobic, anaerobic, and hybrid treatments, respectively. Furthermore, this action can offset some of the biogas recovery costs (such as those related to the recovery equipment) and makes it favorable and economical for the operation of WWTPs. Figure 4.1 shows the contribution of different processes to GHG production for all three types of treatment, with the implementation of biogas recovery.

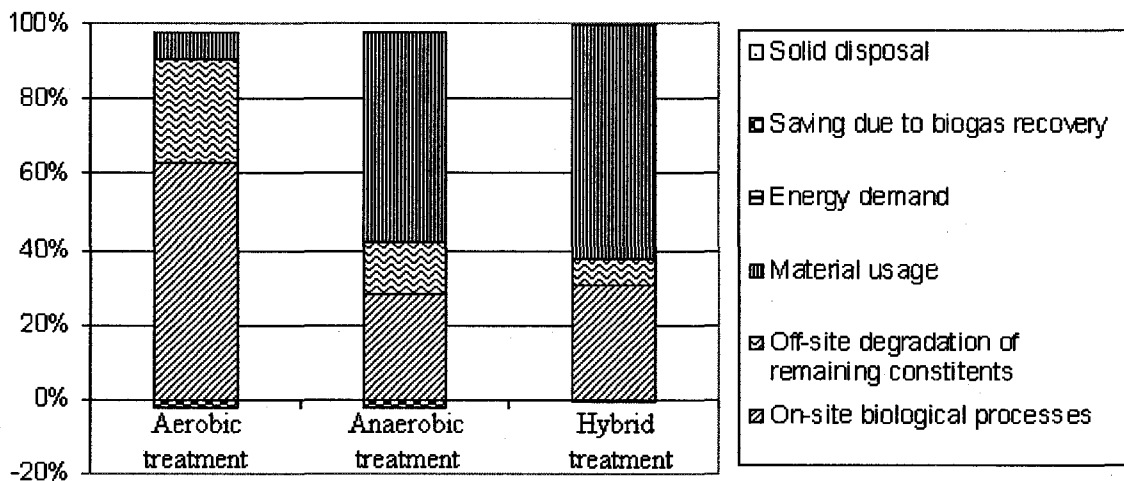


Figure 4.1- GHG emissions by different treatment systems

It can be observed that on-site biological processes are accountable for 65%, 29%, and 31% of total GHG emissions, off-site degradation of carbon is responsible for 29%, 14%, and 7% of total GHG emissions, and material usage is responsible for 7%, 58%, and 62% of total GHG emissions from aerobic, anaerobic, and hybrid treatment systems, respectively. This estimation can be used as a guide for the development of GHG reduction strategies by targeting specific processes. For example in hybrid treatment systems, GHG reduction strategies must focus on reducing material usage in the plant or using materials with less off-site GHG emissions.

As presented in Figure 4.1, off-site degradation of the remaining carbonaceous material in the effluent and sludge makes a considerable contribution to the overall GHG emissions of the plant. Therefore, an increase in the efficiency of treatment will reduce the degradable constituents in the effluent and sludge while producing biogas which can serve as a source of energy for the plant, further reducing the overall GHG emissions. Biogas recovery and use as fuel will supply the energy demands of all three types of treatment systems while providing savings equal to 2.2%, 2.2%, and 0.5% of total GHG emissions in aerobic, anaerobic, and hybrid treatment systems, respectively. Saving due to biogas recovery is shown below the horizontal axis in Figure 4.1. It can be observed that the GHG emissions due to solid disposal are very small and do not appear on the chart. Table 4.2 presents the on-site and off-site GHG emissions of the treatment plants.

Aerobic treatment is selected again as an example to describe the estimation process. When biogas recovery is not conducted, the sources of off-site GHG emissions are:

- 1- Alkalinity needs in the aerobic reactor and digester: Equations 3.58 and 3.98

- 2- Fossil fuel importation for on-site consumption: combination of Equations 3.110 and 3.4 (just the first two terms)
- 3- Solid disposal: Equation 3.107
- 4- Electricity consumption:
 - 4-1 Aeration energy: Combination of Equations 3.54 and 3.3
 - 4-2 Electricity needs of the rest of plant: Combination of Equations 3.108 and 3.3
- 5- GHG emissions associated with the remaining constituents in treated wastewater:
 - 5-1 Off-site BOD degradation in the treated water: Equation 3.91
 - 5-2 Off-site carbon degradation in the treated sludge: Equation 3.93

In the presence of biogas recovery, the sources of off-site GHG emissions are the same as those without biogas recovery, except that the biogas energy eliminates, partially or completely, the heating and electricity energy requirements (options 2 and 4, as described above). Additional savings due to biogas recovery is also added to the off-site GHG emissions.

In the absence of biogas recovery, the sources of on-site GHG emissions are:

- 1- On-site biological processes:
 - 1-1 CO₂ emissions from the aerobic reactor
 - 1-1-1 Total CO₂ emissions in the aeration tank: Equations 3.48 and 3.50
 - 1-1-2 CO₂ produced during the denitrification process in the anoxic tank: Equation 3.55
 - 1-2 CO₂ and CH₄ emissions from the anaerobic digester: Equation 3.88

2- On-site fossil fuel burning: Combination of Equations 3.110 and 3.4 (only the last term)

If biogas recovery is carried out, the sources of on-site GHG emissions are the same as those without biogas recovery, except that the biogas energy eliminates, partially or completely, the fossil fuel importation needs (option 2).

Table 4.2- Comparison of on-site and off-site GHG emissions by the three types of treatment examined in this study

Process identification	Off-site GHG emissions (kg CO ₂ /d)		On-site GHG emissions (kg CO ₂ /d)	
	No biogas recovery	With biogas recovery	No biogas recovery	With biogas recovery
Aerobic Treatment	1313	935	1952	1759
Anaerobic Treatment	4631	4120	1992	1702
Hybrid treatment	5205	4582	2435	2035

According to Table 4.2, biogas recovery and use eliminate the off-site GHG emissions resulting from the use of fossil fuels for all three types of treatment systems. According to Table 4.2, GHG production due to material usage during the treatment process, off-site energy generation, and off-site degradation of carbonaceous material are substantially higher than the GHG production resulting from the treatment process itself in anaerobic and hybrid treatment systems. The contribution of off-site GHG emissions to

the total GHG emissions is much higher in the anaerobic and hybrid treatment systems compared to that in the aerobic treatment system.

The comparison of different types of treatment shows that, when all on-site and off-site emissions are considered, aerobic treatment systems produce the least amount of GHG emissions compared to hybrid and anaerobic treatment systems. Biological processes produce almost the same amount of GHG during each type of treatment but the GHG emissions because of material usage and energy demand in the anaerobic and hybrid treatment systems are well above the corresponding values in the aerobic treatment system. Although the amount of produced biogas in anaerobic and hybrid treatment systems is considerably higher than that obtained in aerobic treatment operations, the increased off-site GHG emissions in the former systems lead to considerably higher emissions as presented in Table 4.2. Previous studies suggested that anaerobic treatment is the favorable type of treatment in terms of GHG production (Cakir and Stenstrom, 2005; Keller and Hartley, 2003; and Greenfield and Batstone, 2005). However, when upstream GHG emissions are also taken into consideration, anaerobic and hybrid treatment systems produce more GHGs compared to aerobic treatment. Table 4.3 identifies the processes responsible for GHG production in each type of treatment system. It is assumed that biogas is recovered and reused as a source of energy under all studied conditions. The sources of data and the equations used are similar to those described before. The normalized GHG emissions by the influent BOD and wastewater are calculated by dividing the total GHG emissions of the plant by the influent wastewater BOD and flow rate, respectively.

Table 4.3- GHG emission sources in different types of treatment system

Process identification	Aerobic treatment (kg CO ₂ /d)	Anaerobic treatment (kg CO ₂ /d)	Hybrid treatment (kg CO ₂ /d)
Anaerobic reactor			
Biological process	-	957	613
Alkalinity	-	3392	3392
Aerobic reactor			
Biological process	681	-	492
Alkalinity	206	-	579
Methanol	-	-	167
Anaerobic digester			
Biological process	1078	745	930
Alkalinity	0	12	0
BOD in the effluent	781	844	475
Solid disposal	6	0.7	4
Total energy demand	0	0	0
Additional saving because of biogas recovery	-58	-128	-34
Total	2694	5822	6617
Normalized GHG emissions by influent BOD (g CO ₂ /g BOD)	1.35	2.91	3.31
Normalized GHG emissions by influent WW (kg CO ₂ /m ³ WW)	2.69	5.82	6.62

As indicated in Table 4.3, anaerobic digester produces the highest amount of GHGs in the aerobic treatment system, while alkalinity needs in anaerobic reactors produce the highest GHGs in the anaerobic and hybrid treatment systems. The residual BOD in the effluent (comprised of both BOD in the treated water and remaining degradable carbon in the treated sludge) also makes a substantial contribution to the generation of GHGs in all the studied systems. The improved efficiency of treatment will reduce the residual BOD in the effluent while increasing biogas generation, further decreasing GHG emissions. Solid disposal has minimal impact on GHG emissions in all three types of treatment. The biogas recovery covers the total energy demand of all three types of treatment and further

reduces the total GHG emissions. As mentioned before, additional savings in GHG emissions are obtained when the residual biogas (after compensating for the total energy demand of the WWTP) is exported to the energy market as a source of energy, either in the form of CH₄ or electricity. In this study, it is assumed that the remaining biogas is transformed to electrical energy and it is sold to the power grid. In order to compare the GHG producing capacity of different WWTPs with different characteristics, the normalized GHG emissions by the influent BOD of wastewater are very useful and convenient tools. The energy needs and generation during different processes are presented in Table 4.4.

Table 4.4- Energy needs and generation by various processes in different types of treatment systems

Process identification	Aerobic treatment (MJ/d)	Anaerobic treatment (MJ/d)	Hybrid treatment (MJ/d)
Energy need	4478	5105	8046
Anaerobic reactor's heating	-	1473	1473
Aeration	846	-	924
Digester's heating	2912	2912	4569
Electricity need of the rest of the WWTP	720	720	1080
Energy produced	7122	9097	10314
Energy from anaerobic reactor biogas	-	4098	4098
Energy from digester biogas	7122	4999	6216

Aerobic treatment is selected again as an example to describe the estimation process. The sources of data and the equations used are similar to those described before. The energy needs of the aerobic treatment system result from:

- 1- Aeration energy in the aerobic reactor: Equation 3.54

2- Digester's heating: Equation 3.102

3- Electricity needs of the rest of plant: Equation 3.108

The energy is produced in the form of biogas from anaerobic digester in aerobic treatment system and it is calculated by Equation 3.90. In this study, it is assumed that the recovered biogas is converted to heating energy in the boilers for warming up the wastewater.

As mentioned before (Tables 4.1, 4.2, and 4.3), biogas recovery compensates the total energy needs of the plant. The most energy producing process is the anaerobic digestion that generates 100%, 55%, and 60% of the total produced energy in the form of biogas in aerobic, anaerobic, and hybrid treatment systems, respectively. The most energy consuming process is the digester heating that accounts for 65%, 57%, and 57% of the total energy needs of the plant in aerobic, anaerobic, and hybrid treatment systems, respectively. Efficient digesters with less heating needs and a higher degree of VSS stabilization will reduce the energy needs of the treatment plant and increase the biogas production, leading to an overall GHG reduction of the WWTP.

Previous studies have reported lower GHG productions by anaerobic/aerobic processes compared to the values obtained in the present study. This is attributed to the fact that those studies ignored nutrient removal along with CBOD removal operations, confined their studies to municipal wastewaters, ignored the effect of off-site GHG emissions, and used incorrect values for some parameters. For example, Keller and Hartley (2003) suggested 1.04 kg CO₂ produced per kg COD removed from anaerobic/aerobic treatment plant. Based on the IPCC guidelines (IPCC, 2001a), the

COD of municipal wastewaters is 2.4 times greater than the BOD_u. So by converting the suggested values of Keller and Hartley (2003) to BOD unit, the following will result:

$$1.04 \text{ kg CO}_2/\text{kg COD} \times 2.4 \text{ kg COD}/\text{kg BOD} = 2.5 \text{ kg CO}_2/\text{kg BOD}$$

According to the present study, GHG emissions from the target hybrid industrial wastewater treatment plant is 3.31 kg CO₂/kg BOD, which is almost 32% higher than the values reported in pervious studies. The values of 0.44 kg CO₂/m³ WW (Keller and Hartley, 2003) and 0.228-0.245 kg CO₂/m³ WW treated for municipal wastewaters (Monteith et al., 2005) were suggested for treatment processes using activated sludge plus anaerobic digestion. The values for food processing wastewaters according to the present study are estimated to be 2.69 kg CO₂/m³ WW or 1.35 kg CO₂/kg BOD (Table 4.3, normalized GHG emission factors for aerobic treatment), considering all upstream GHG emissions and nutrient removal processes.

One strategy for GHG reduction is to use alternative nutrient removal processes such as the anaerobic process Anammox that offers nitrogen removal with a lower consumption of energy and lower carbon use (Greenfield and Batstone, 2005). The reduced aeration energy consumption reduces GHG production related to energy demands of the treatment plant while the extra available carbon can be converted to methane via anaerobic processes, further reducing GHG emissions.

In order to minimize the consumption of energy in digesters, psychrophilic treatment can be used instead of mesophilic or thermophilic treatments. Psychrophilic treatment yields a higher effluent quality as a result of lower maintenance needs for

microorganisms, thermodynamic reasons, and reduced decay of biomass which causes lower soluble microbial products and lower loss of energy for heating the influent stream (Batstone and Keller, 2003). Under this treatment condition, heating requirements for sludge digestion will be minimized, while solids digestion, solids separation and activated sludge production will be increased by reducing the sludge age in the preceding aerobic or anaerobic reactor. By reducing the sludge age (SRT) in the aerobic or anaerobic reactor, more sludge is transferred to the digester for solid treatment and more biogas is produced, as the digester was proved to be the most biogas generator in all three types of treatment (Table 4.4). Reduction of sludge age should be done carefully to avoid jeopardizing the treatment efficiency of the WWTP. Therefore, the biomass concentration in the anaerobic digester will increase, making it the dominant energy producing stage compared to anaerobic reactor. Insulation of the digester reduces energy demands by removing the need to heat the digester influent in order to compensate the heating losses through the digester walls. This will reduce by 411 MJ/d (Equation 3.100) the required heating energy of the digester which are 2912 MJ/d, 2912 MJ/d, and 4569 MJ/d in the aerobic, anaerobic, and hybrid treatment systems, respectively (Table 4.4), further reducing the overall energy needs of the plant and decreasing GHG emissions.

The effect of nutrient removal processes are examined on total GHG generation by the treatment plants. Only aerobic and hybrid treatment systems are taken into consideration because anaerobic treatment systems do not remove nutrients. The effect of nutrient removal operation is shown in Table 4.5 for hybrid treatment and in Table 4.6 for aerobic treatment systems.

Table 4.5- Effect of various nutrient removal processes on GHG generation by hybrid treatment systems

Types of hybrid treatment	On-site biological processes (kg CO ₂ /d)	Off-site degradation of carbon (kg CO ₂ /d)	Material usage (kg CO ₂ /d)	Energy demand (kg CO ₂ /d)	Additional saving due to biogas recovery (kg CO ₂ /d)	Solid disposal (kg CO ₂ /d)	Total (kg CO ₂ /d)
Nitrification+ BOD & methanol denitrification	2035	475	4138	0	-34	4	6617
Without nitrification	1881	481	3402	0	-67	4	5700
Nitrification without denitrification	1873	494	4406	0	-36	4	6741
Nitrification+ methanol denitrification	2056	494	4176	0	-36	4	6694

Table 4.6- Effect of various nutrient removal processes on GHG generation by aerobic treatment systems

Types of aerobic treatment	On-site biological processes (kg CO ₂ /d)	Off-site degradation of carbon (kg CO ₂ /d)	Material usage (kg CO ₂ /d)	Energy demand (kg CO ₂ /d)	Additional saving due to biogas recovery (kg CO ₂ /d)	Solid disposal (kg CO ₂ /d)	Total (kg CO ₂ /d)
Nitrification+BOD denitrification	1759	781	206	0	-58	6	2694
No nitrification	1734	853	0	0	-87	7	2507
Nitrification without denitrification	1614	777	551	0	-58	6	2890
Nitrification+ methanol denitrification	1748	777	383	0	-58	6	2856

Tables 4.5 and 4.6 are extensions for Table 4.1 to verify the effect of nutrient removal processes on total GHG emissions. Therefore the GHG emissions in each process and at each scenario are estimated by the same equations as those used in Table 4.1. For the hybrid treatment system, when CBOD is not sufficient for complete

denitrification, an external carbon source, commonly methanol, is added to support the denitrification process (option 1 in Table 4.5). In order to remove the impact of denitrification while nitrification was present in the system, Equation 3.55 along with the alkalinity production due to denitrification, i.e. Equation 3.56, were eliminated during the estimation process. For nitrification along with methanol denitrification, Equation 3.55 and the alkalinity production due to denitrification, i.e. Equation 3.56 were eliminated and Equations 3.61 and 3.62 were considered for the CO₂ and alkalinity production due to denitrification. Equation 3.63 was employed to calculate the upstream GHG emissions due to methanol consumption.

Table 4.6 compares the individual nutrient removal processes to a base case which is selected as the CBOD removal with nitrification and denitrification using the combined BOD and methanol as the carbon source. This case is primarily selected because most industrial WWTP are required to perform tertiary treatment including both nitrification and denitrification on the effluent and the most economic and less GHG generating means of denitrification is to exploit the wastewater BOD as the carbon source to lessen the methanol import that imposes extra expenditure and more off-site GHG emissions.

As presented in Table 4.5 and 4.6, GHG emissions are lowest in the absence of nitrification. This is expected since the removal of nitrification process eliminates the need for excessive aeration and partially removes the need for material usage. In addition, more savings in GHG emissions are made due to the recovery and reuse of biogas when there is no nitrification.

For both hybrid and aerobic treatment systems, when nitrification is carried out without denitrification, although GHG emissions from on-site biological processes

decline, the overall GHG emissions of the treatment plant increase because there is additional need for material supply (to control alkalinity) for on-site consumption. As described earlier, denitrification compensates some of the alkalinity needs of the nitrification process. Therefore, in the absence of denitrification, alkalinity needs of the plant must be supplied by external material. In both aerobic and hybrid treatment systems, nitrification without denitrification generates the highest GHG emissions compared to the other nutrient removal processes.

Nitrification/denitrification using methanol as the carbon source presents the second highest GHG producing process for both aerobic and hybrid treatment systems among the examined processes. In this case, GHG emissions because of material usage increase the overall emissions compared to the base case.

The order of GHG producing capacity of all types of nutrient removal processes examined in this study from higher to lower are as follows: Nitrification without denitrification, Nitrification/denitrification using methanol as the carbon source, Nitrification/denitrification using BOD and methanol as the carbon source, absence of nitrification.

4.4 Impact of Process Parameters on GHG emissions

The impacts of pertinent process parameters on GHG emissions by wastewater treatment systems were evaluated. This evaluation identified the parameters that closely control GHG emissions and facilitated the development of strategies for the reduction of emissions by the plant. Of course, the implementation of any strategy is site-specific and

should consider the economics of the treatment process. These aspects are not addressed in the present study.

Each treatment method is considered separately. The process parameters are divided into four sets depending on the type of treatment investigated. They include: primary clarifier, anaerobic reactor, aerobic reactor, and digester. The major controlling parameters are selected and the impacts of process parameters on GHG emissions are presented in the following paragraphs:

4.4.1 Aerobic treatment:

4.4.1.1 Primary clarifier: Figure 4.2 (a to c) present the dependence of GHG emissions on the primary clarifier's VSS removal rate, BOD removal rate, and underflow rate.

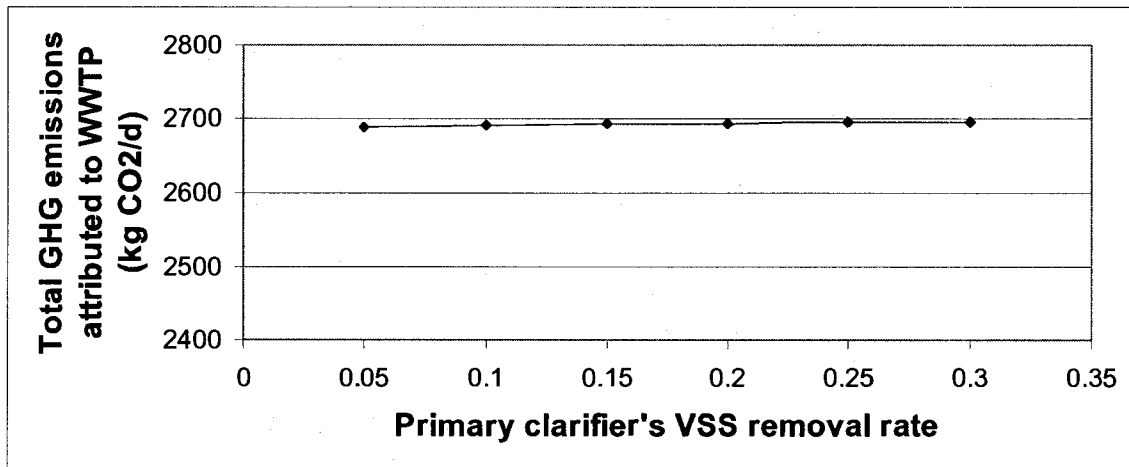


Figure 4.2(a)- Effect of primary clarifier's VSS removal rate on total GHG emissions in an aerobic treatment system

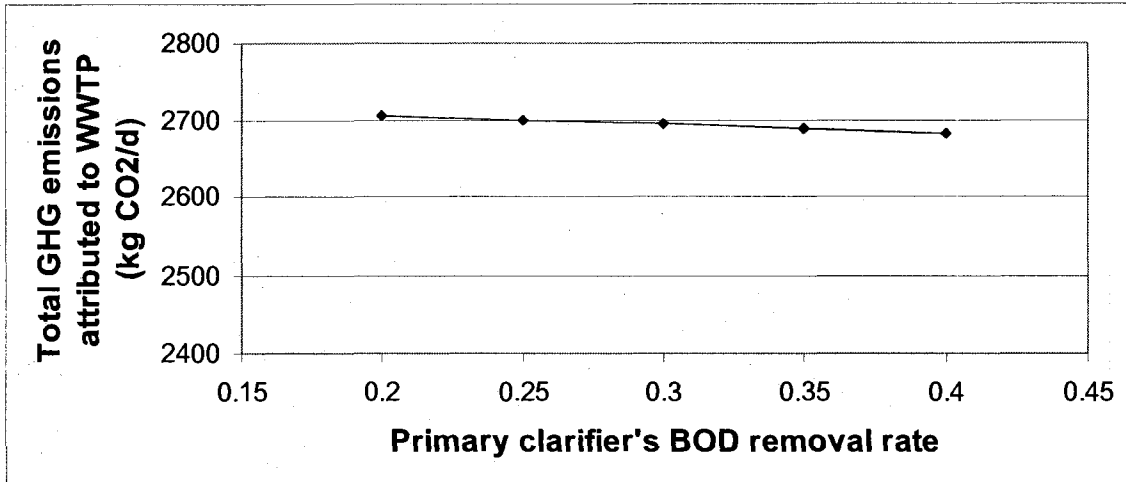


Figure 4.2 (b)- Effect of primary clarifier's BOD removal rate on total GHG emissions in an aerobic treatment system

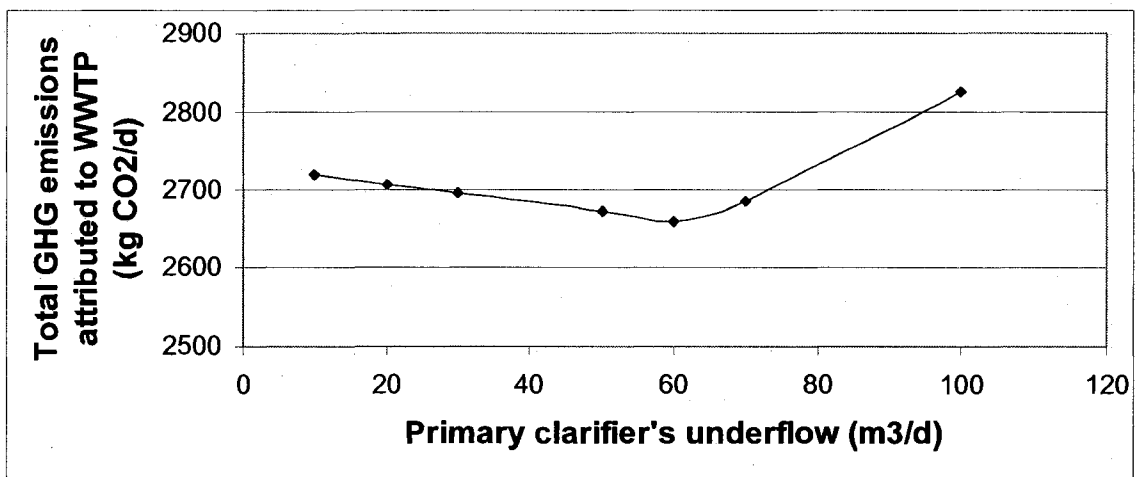


Figure 4.2 (c)- Effect of primary clarifier underflow rate on total GHG emissions in an aerobic treatment system

As presented in Figure 4.2 (a to c), the process parameters of primary clarifier do not have a significant impact on total GHG emissions of the aerobic treatment system. The most effective parameter is the primary clarifier's underflow rate (Figure 4.2 c). Increasing the underflow rate increases the flow rate of untreated wastewater that feeds the digester. More biogas is produced by the anaerobic digestion of untreated wastewater, leading to more savings in GHG emissions. On the other hand, a higher underflow rate

and a higher wastewater flow rate to digester imply more energy demands for the operation of digester with the resulting production of additional GHG because of energy needs. Of course, there is a balance between the observed gains and losses. According to this study, at underflow rates below 60 m³/d, the savings due to biogas production offset the additional GHG productions that result from the energy needs for the operation of digester. So with the increase of underflow rate, the total GHG emissions decrease. Above 60 m³/d, the effects of energy demand become more apparent than the biogas savings. Possible strategies for the reduction of GHG emissions will be to make the underflow rate close to 60 m³/d. As shown in Figures 4.2 a and b, the increase in BOD removal rate and the reduction of VSS removal rate in primary clarifier lower the total GHG emission, although the effect is not significant.

4.4.1.2 Aerobic reactor: The effect of aerobic reactor's process parameters including solid retention time (SRT), reactor's temperature, and wasting ratio on total GHG emissions by the aerobic treatment system is displayed in Figure 4.3 (a to c).

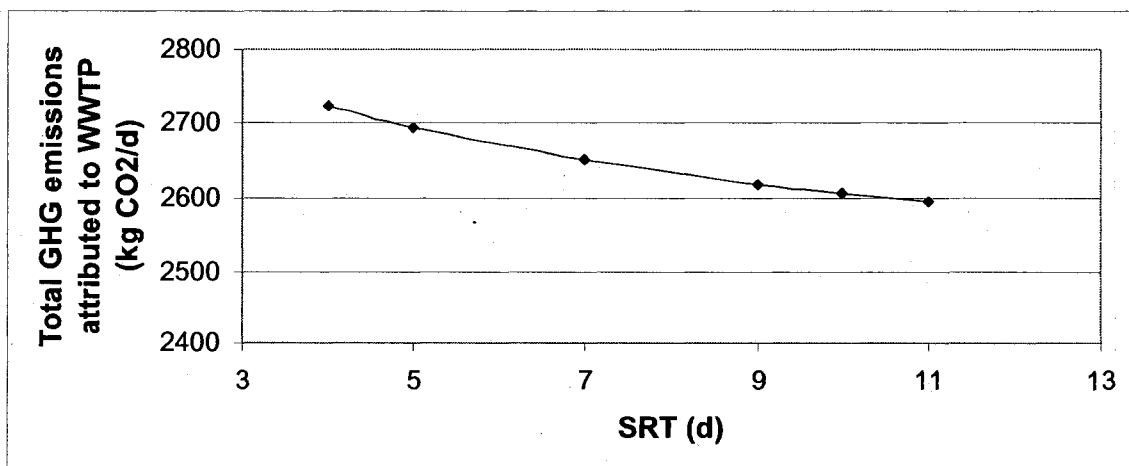


Figure 4.3 (a)- Effect of aerobic reactor's SRT on total GHG emissions in an aerobic treatment system

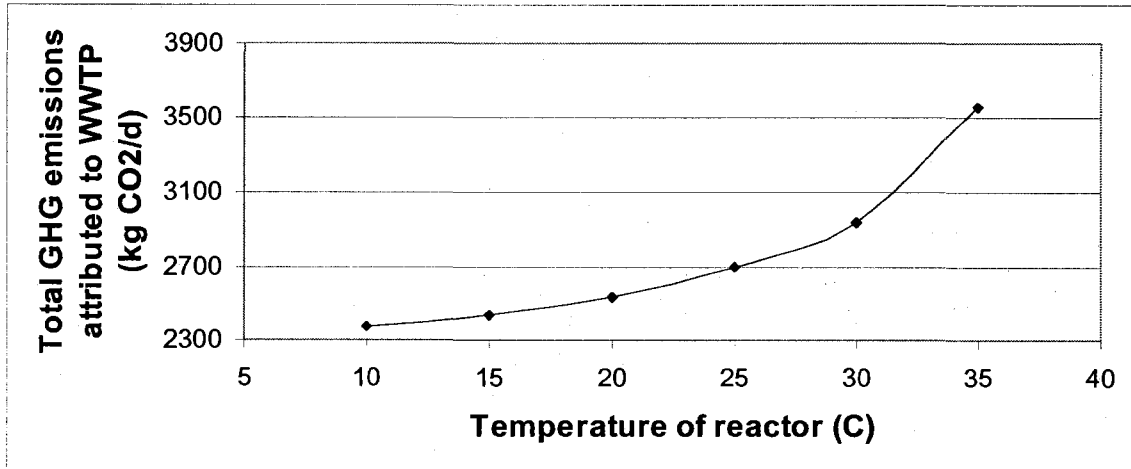


Figure 4.3 (b)- Effect of aerobic reactor's temperature on total GHG emissions in an aerobic treatment system

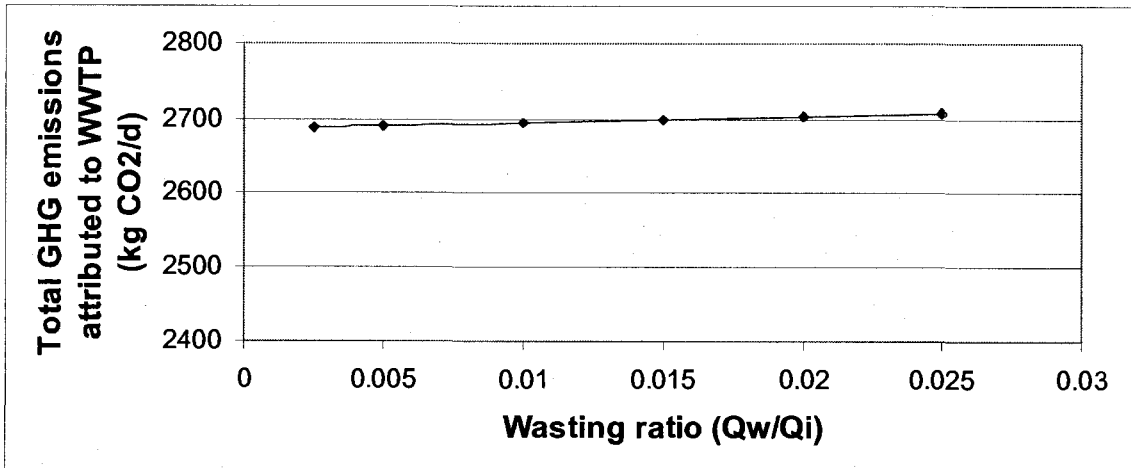


Figure 4.3 (c)- Effect of aerobic reactor's wasting ratio on total GHG emissions in an aerobic system

GHG emissions decrease with the increase of solid retention time (SRT) while they increase with increased reactor temperature and wasting ratio. The increase of SRT from 4 to 11 days decreased the GHG emissions by 4.7% while an increase of wasting ratio from 0.0025 to 0.025 increased the emissions by 0.7%. The most significant impact was observed with the temperature which increased the emissions by 50% upon increasing from 10 °C to 35 °C. In fact, a non-linear trend was observed indicating a considerably

higher rate of increase above 25 °C. Increasing the SRT of aerobic reactor, decreases the production of degradable sludge from aerobic reactor. This will lower the amount of generated sludge that feeds the anaerobic digester. The outcome is a lower demand for the heating energy to warm up the wastewater in the digester and also less biogas production from the digester. According to Figure 4.3 (a) the effect of lower heating energy requirements on total GHG emissions is higher than the effect of lower biogas production. Therefore, with the lowering of sludge production in aerobic reactor, less GHG is produced from the industrial WWTP. Heating of the wastewater in aerobic reactor, increases the energy demand of the industrial WWTP which is provided by fossil fuels. This will increase the upstream GHG emissions of the treatment plant. Increasing the wasting ratio from aerobic reactor boosts the GHG emissions from the WWTP. A higher wasting ratio results in a higher wastewater flow into the anaerobic digester, which on one hand, increases the heating demand of the digester and on the other hand, increases the biogas production form anaerobic digester. Similar to the effect of SRT, the influence of heating energy demands on total GHG emissions is more than the savings due to biogas production. Recommended strategies for the reduction of GHG emissions will be to keep the reactor's temperature as low as possible, increase the SRT of aerobic reactor, and decrease the wasting ratio.

4.4.1.3 Digester: The effect of digester's process parameters including solid retention time (SRT), and temperature of the digester on total GHG emissions by the aerobic treatment system is displayed in Figure 4.4 (a and b).

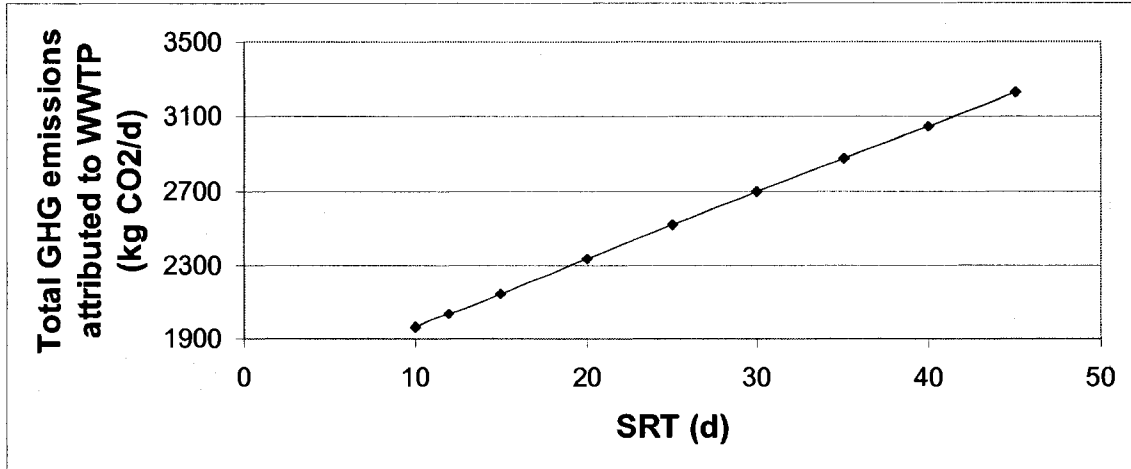


Figure 4.4 (a)- Effect of digester's SRT on total GHG emissions in an aerobic treatment system

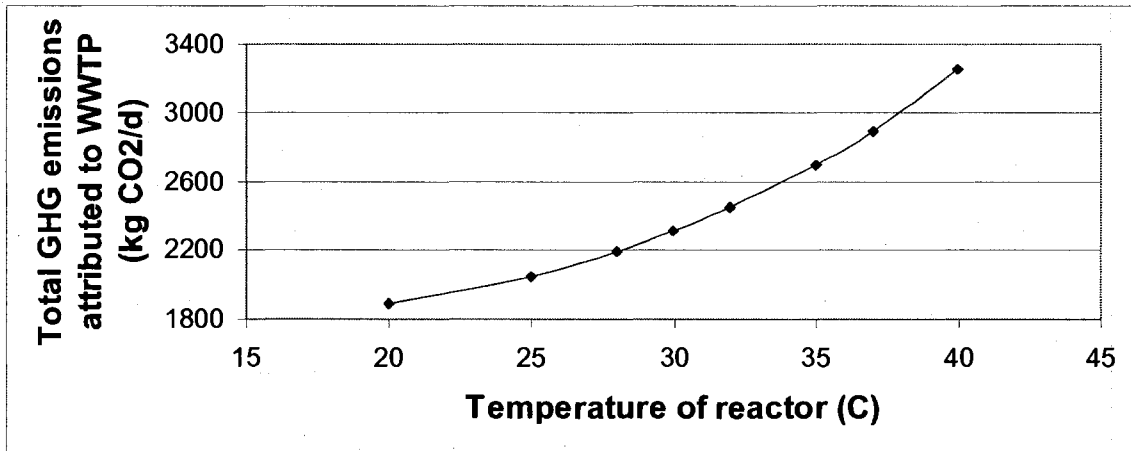


Figure 4.4 (b)- Effect of digester's temperature on total GHG emissions in an aerobic treatment system

Solid retention time (SRT) and digester temperature both have a great influence on total GHG emissions by the aerobic treatment system. As shown in Figure 4.4 (a and b), GHG emissions increased by 64.6% with the increase of SRT from 10 to 45 days while they increased by 72.5% with the increase of temperature from 20 °C to 40 °C. The increase of SRT and temperature both cause higher heating demands by the digester and consequently, more upstream GHG emissions because of on-site fossil fuel consumption.

Recommended strategies for the reduction of GHG emissions will be to reduce the digester temperature and SRT to the lowest acceptable values that do not compromise the efficiency of treatment.

4.4.2 Anaerobic treatment:

4.4.2.1 Primary clarifier: Figure 4.5 (a to c) present the dependence of GHG emissions on the primary clarifier's VSS removal rate, BOD removal rate and underflow rate.

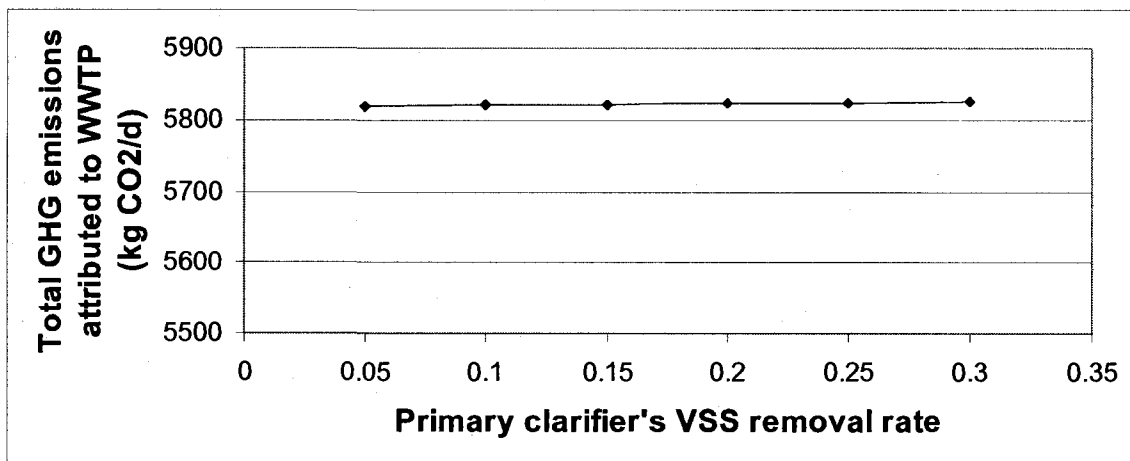


Figure 4.5 (a)- Effect of primary clarifier's VSS removal rate on total GHG emissions in an anaerobic treatment system

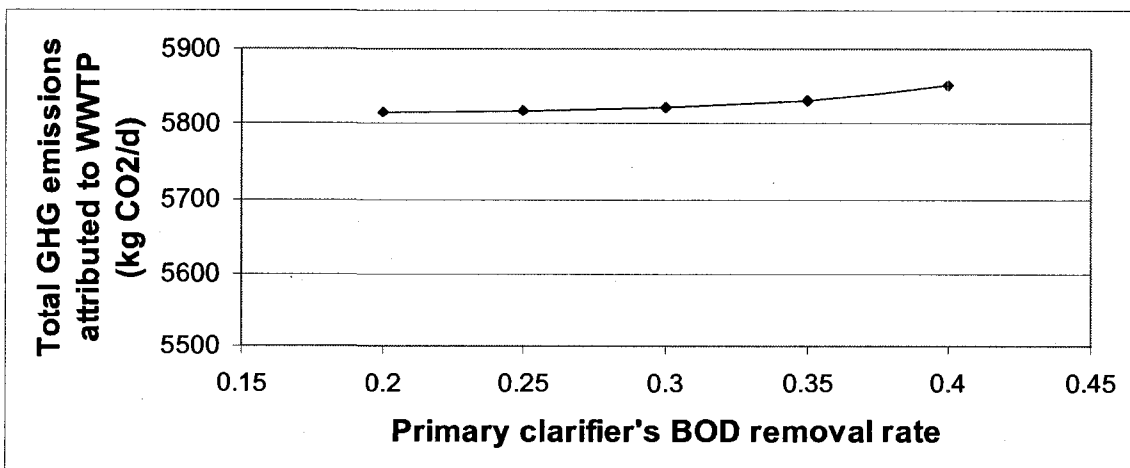


Figure 4.5 (b)- Effect of primary clarifier's BOD removal rate on total GHG emissions in an anaerobic treatment system

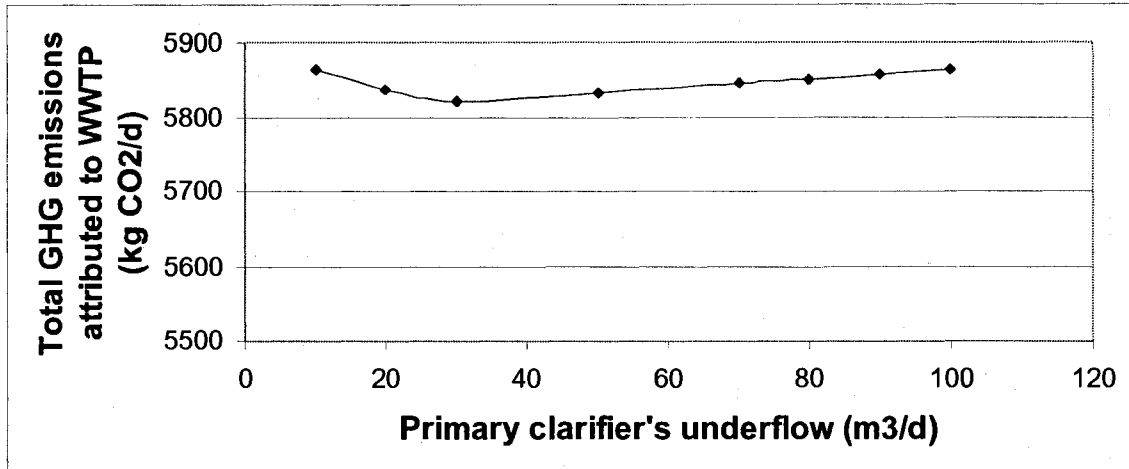


Figure 4.5 (c)- Effect of primary clarifier underflow on total GHG emissions in an anaerobic treatment system

VSS removal rate has a minor impact on the total GHG emissions by the wastewater treatment plant, while BOD removal rate and the underflow rate exert a higher influence on this parameter. As shown in Figure 4.5 a, b and c, GHG emissions increased by 0.1% with the increase of VSS removal rate from 0.005 to 0.3 while they increased by 0.6% with the increase of BOD removal rate from 0.2 to 0.4. The response of GHG emissions to the clarifier's underflow rate (Figure 4.5(c)) indicates a decrease of 0.7% with the increase of the underflow rate from 10 to 30 m³/d following an increase of 0.7% with further increase of underflow rate from 30 to 100 m³/d. The trend observed in Figure 4.5 (c) is similar to that observed in Figure 4.2 (c). Recommended strategies for the reduction of GHG emissions will be to keep the underflow rate close to 30 m³/d, decrease the BOD removal rate and the VSS removal rate as much as possible.

4.4.2.2 Anaerobic reactor: Figure 4.6 (a to c) present the dependence of GHG emissions on solid retention time (SRT), temperature, and the waste ratio from anaerobic reactor.

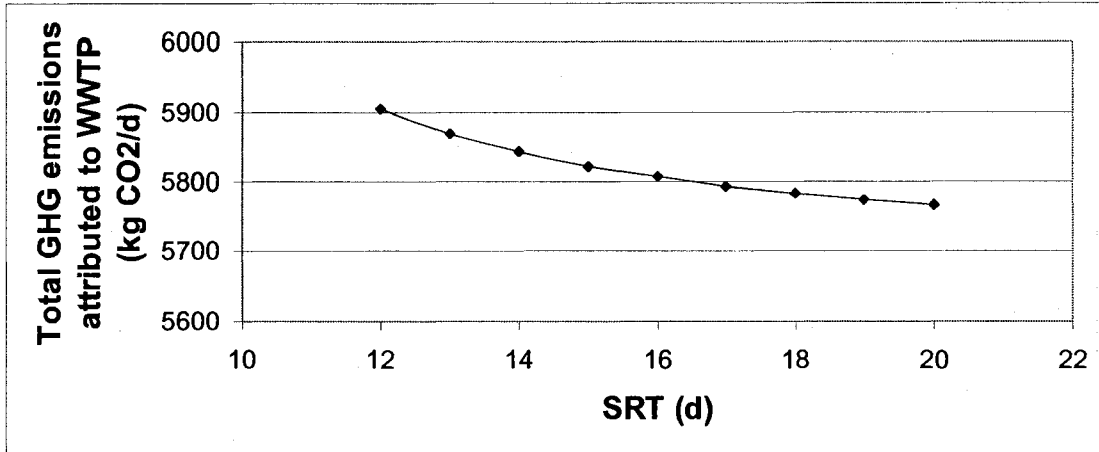


Figure 4.6 (a)- Effect of anaerobic reactor's SRT on total GHG emissions in an anaerobic treatment system

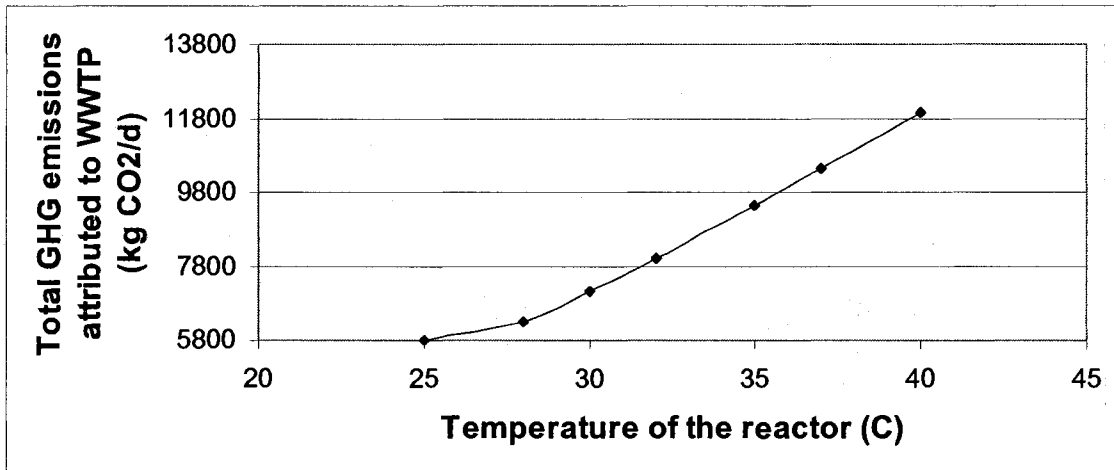


Figure 4.6 (b)- Effect of anaerobic reactor's temperature on total GHG emissions in an anaerobic treatment system

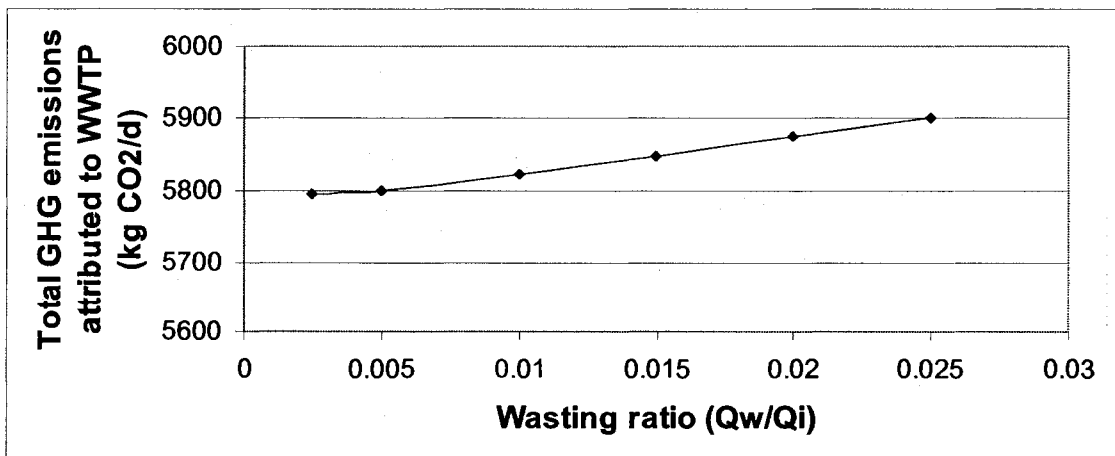


Figure 4.6 (c)- Effect of anaerobic reactor's wasting ratio on total GHG emissions in an anaerobic treatment system

GHG emissions decrease with the increase of solid retention time (SRT) while they increase with increased reactor temperature and wasting ratio. Similar effects were observed with the aerobic reactor in the aerobic treatment system. The increase of SRT from 12 to 20 days decreased the GHG emissions by 2.3% while an increase of wasting ratio from 0.0025 to 0.025 increased the emissions by 1.8%. The most significant impact was observed with temperature which increased the emissions by 105.6% upon increasing from 25 °C to 40 °C. A non-linear trend was observed, indicating a considerably higher rate of increase above 40 °C. Similar explanations apply to the trends observed in Figure 4.6 (a to c) and Figure 4.3 (a to c). Recommended strategies for the reduction of GHG emissions will be to keep the reactor's temperature as low as possible, increase the SRT of anaerobic reactor, and decrease the wasting ratio.

4.4.2.3 Digester: The effect of digester's process parameters including solid retention time (SRT), and temperature on total GHG emissions by the anaerobic treatment system is displayed in Figure 4.7 (a and b).

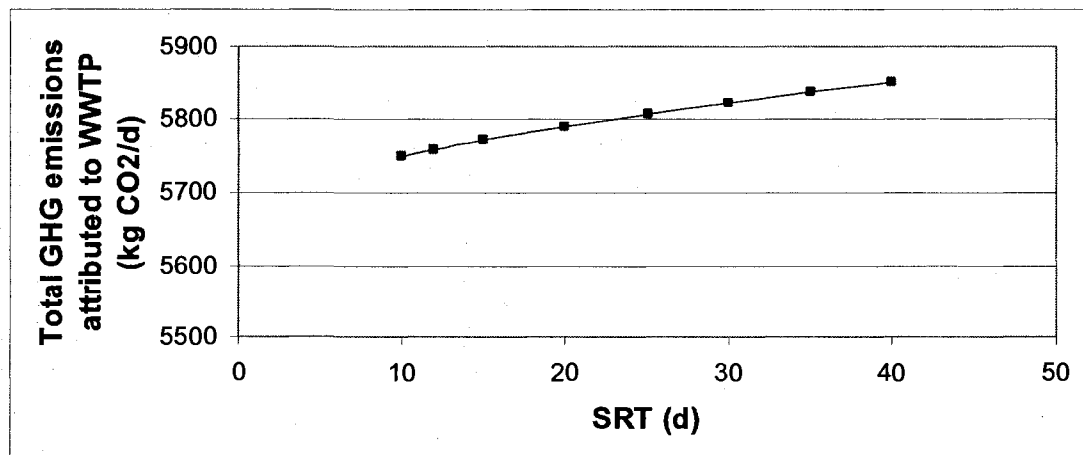


Figure 4.7 (a)- Effect of digester's SRT on total GHG emissions in an anaerobic treatment system

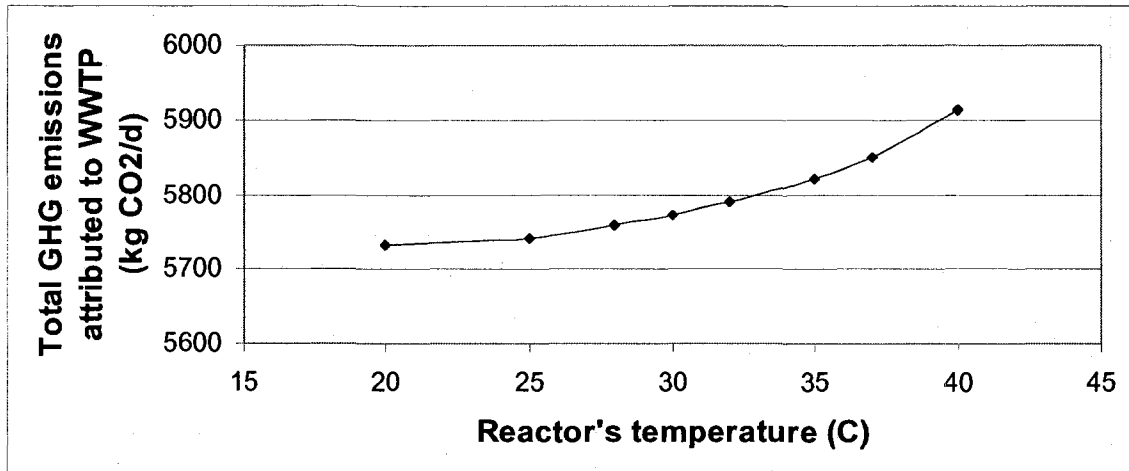


Figure 4.7 (b)- Effect of digester's temperature on total GHG emissions in an anaerobic treatment system

Solid retention time (SRT) and digester temperature both have a moderate impact on total GHG emissions by the anaerobic treatment system. As shown in Figure 4.7 (a and b), GHG emissions increased by 1.7% with the increase of SRT from 10 to 40 days while they increased by 3.1% with the increase of temperature from 20 °C to 40 °C. The increase of SRT and temperature lead to heating demands by the digester, thus resulting in higher upstream GHG emissions because of on-site fossil fuel consumption. Comparison of the effects of variations of the digester's process parameters in aerobic and anaerobic treatment on total GHG emissions reveals that a considerably higher impact is observed in the aerobic treatment system. The increase of SRT caused 64.6% increase in emissions in the aerobic system compared to 1.7% in the anaerobic system while the increase of temperature led to 72.5% increase in emissions in the aerobic system compared to 3.1% in the anaerobic system. Recommended strategies for the reduction of GHG emissions will be to reduce the digester temperature and SRT to the lowest acceptable values that do not compromise the efficiency of treatment.

4.4.3 Hybrid treatment:

4.4.3.1 Primary clarifier: Figure 4.8 (a to c) present the dependence of GHG emissions on primary clarifier's VSS removal rate, BOD removal rate, and underflow rate.

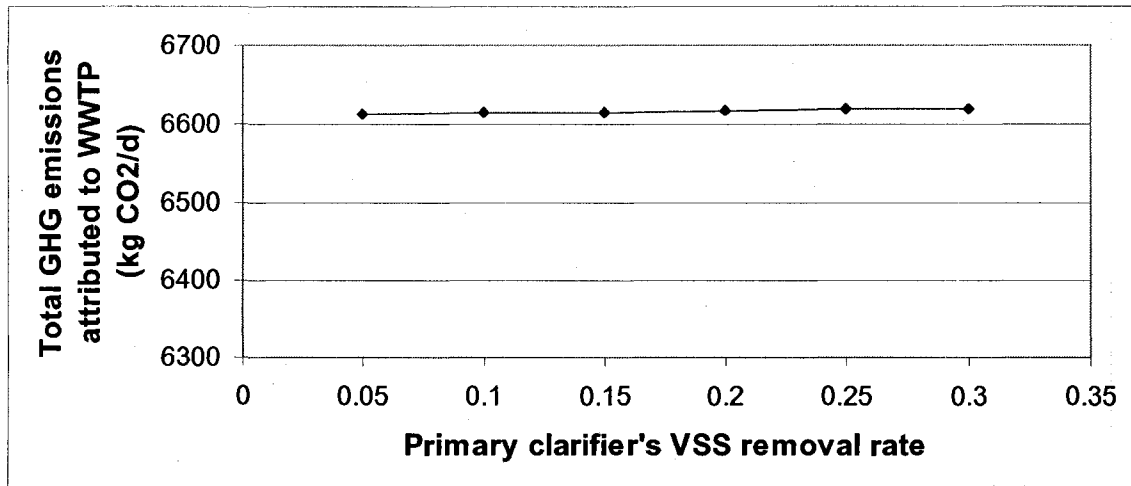


Figure 4.8 (a)- Effect of primary clarifier's VSS removal rate on total GHG emissions in a hybrid treatment system

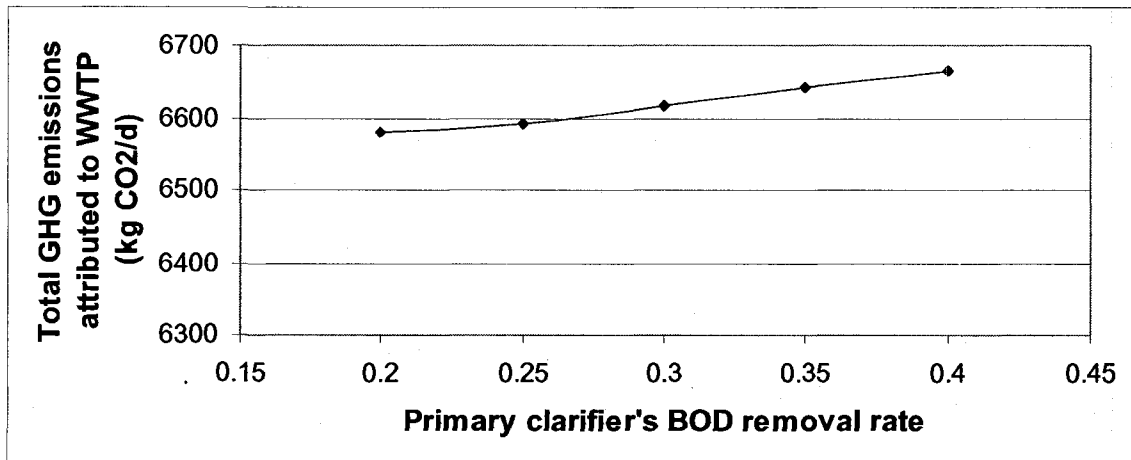


Figure 4.8 (b)- Effect of primary clarifier's BOD removal rate on total GHG emissions in a hybrid treatment system

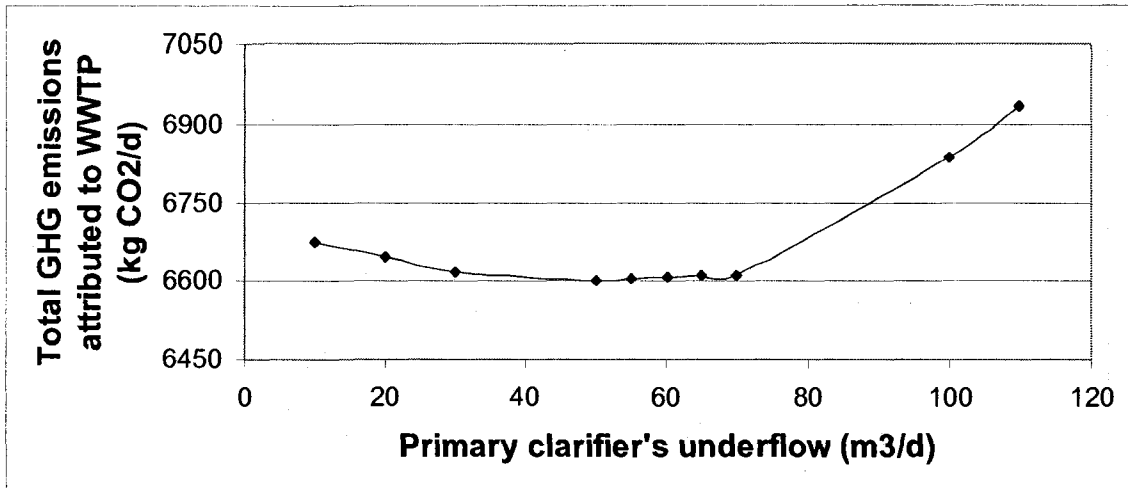


Figure 4.8 (c)- Effect of primary clarifier underflow on total GHG emissions in a hybrid treatment system

These figures demonstrate that the VSS removal rate has a minor impact on the total GHG emissions by the wastewater treatment plant, while BOD removal rate and the underflow rate exert a higher influence on this parameter. As shown in Figure 4.8 a, b and c, GHG emissions increased by 0.1% with the increase of VSS removal rate from 0.005 to 0.3 while they increased by 1.3% with the increase of BOD removal rate from 0.2 to 0.4. The response of GHG emissions to the clarifier's underflow rate (Figure 4.8(c)) indicated a decrease of 1.1% with the increase of the underflow rate from 10 to 50 m³/d following an increase of 5% with further increase of underflow rate from 50 to 110 m³/d. Similar explanations apply to the trends observed in Figure 4.8 (c), Figure 4.2 (c) and Figure 4.5 (c). Recommended strategies for the reduction of GHG emissions will be to keep the underflow rate close to 50 m³/d, while decreasing the BOD removal rate and the VSS removal rate as much as possible.

4.4.3.2 Anaerobic reactor: Figure 4.9 (a to c) present the dependence of GHG emissions on solid retention time (SRT), temperature, and the waste ratio from the anaerobic reactor.

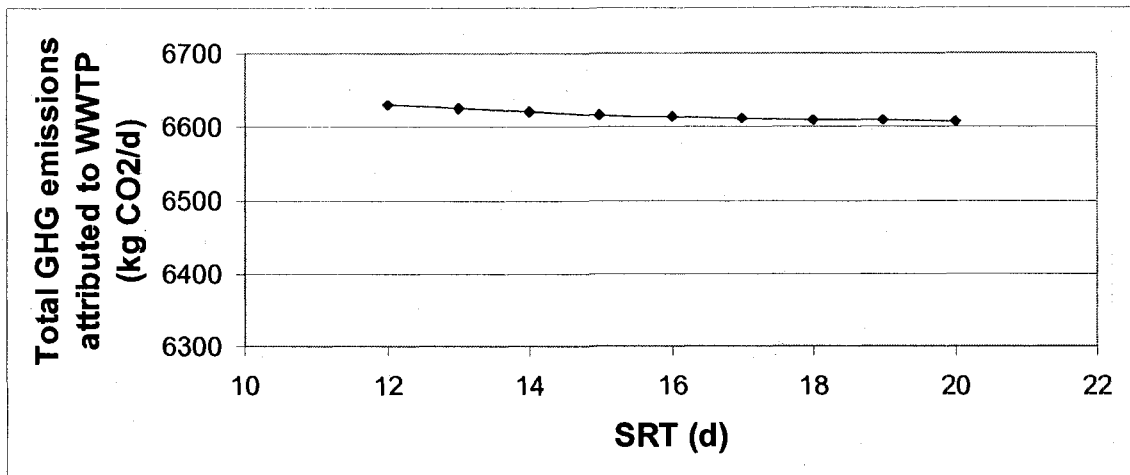


Figure 4.9 (a)- Effect of anaerobic reactor's SRT on total GHG emissions in a hybrid treatment system

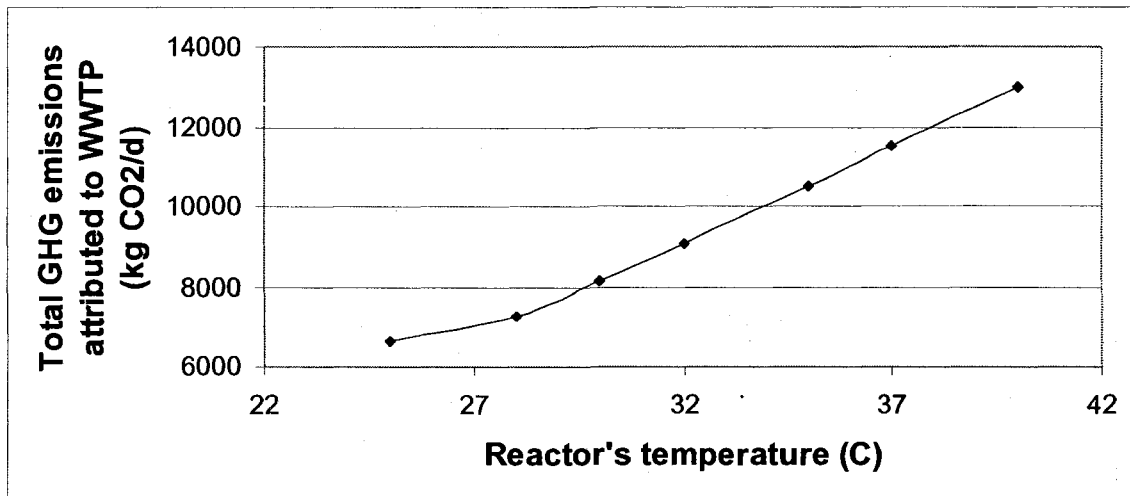


Figure 4.9 (b)- Effect of anaerobic reactor's temperature on total GHG emissions in a hybrid treatment system

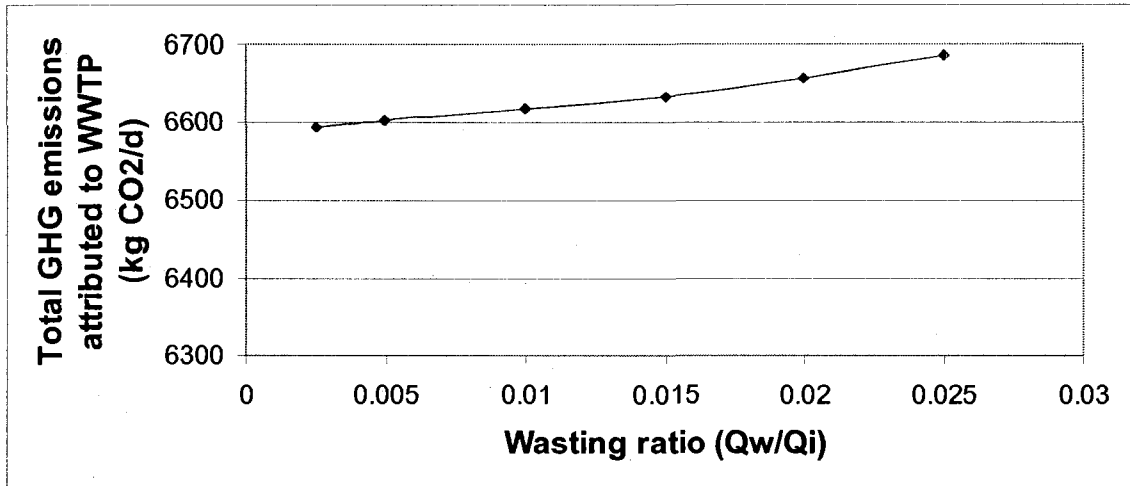


Figure 4.9 (c)- Effect of anaerobic reactor's wasting ratio on total GHG emissions in a hybrid treatment system

GHG emissions decrease with the increase of solid retention time (SRT) while they increase with the increased reactor temperature and wasting ratio. The increase of SRT from 12 to 20 days decreased the GHG emissions by 0.3% while an increase of wasting ratio from 0.0025 to 0.025 increased the emissions by 1.4%. The most significant impact was observed with temperature which increased the emissions by 96.5% upon increasing from 25 °C to 40 °C. The observed non-linear trend indicates a considerably higher rate of increase above 40 °C. Similar explanations apply to the trends observed in Figure 4.9 (a to c), Figure 4.3 (a to c) and Figure 4.6(a to c). Recommended strategies for the reduction of GHG emissions will be to keep the anaerobic reactor's temperature as low as possible, increase the SRT of anaerobic reactor, and decrease the wasting ratio.

4.4.3.3 Aerobic reactor: The effect of aerobic reactor's process parameters including the solid retention time (SRT), reactor's temperature, wasting ratio, and percent NO_x

removed by wastewater BOD in the denitrification process on total GHG emissions by the hybrid treatment system is displayed in Figure 4.10 (a to d).

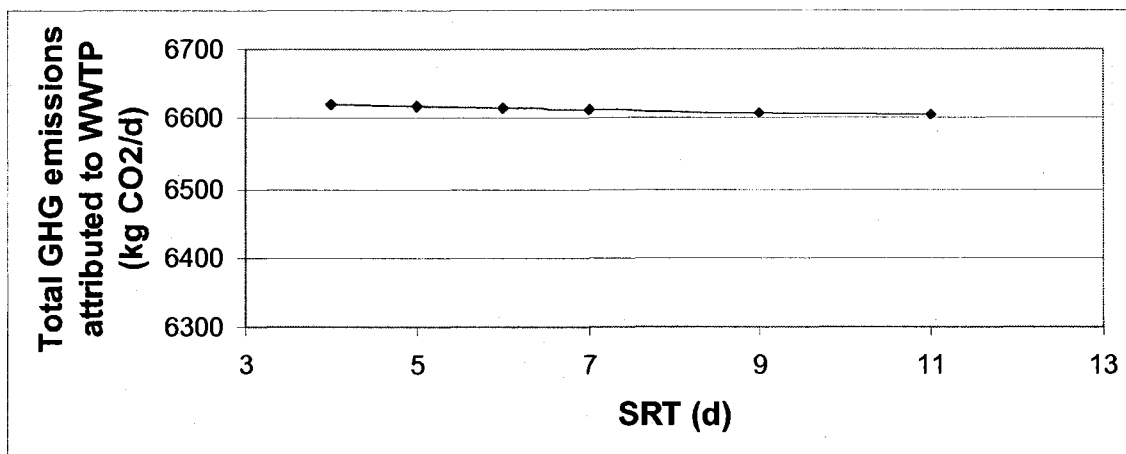


Figure 4.10 (a)- Effect of aerobic reactor's SRT on total GHG emissions in a hybrid treatment system

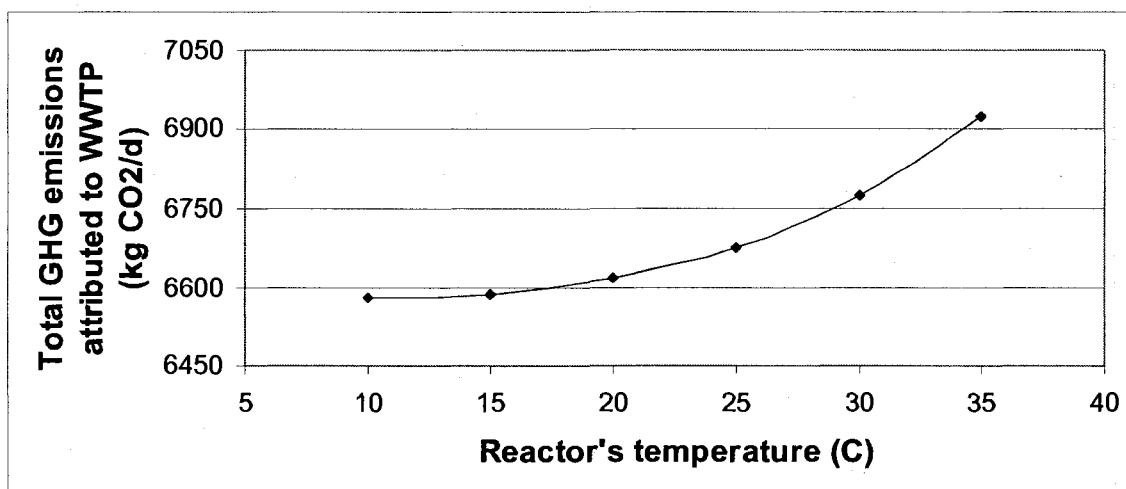


Figure 4.10 (b)- Effect of aerobic reactor's temperature on total GHG emissions in a hybrid treatment system

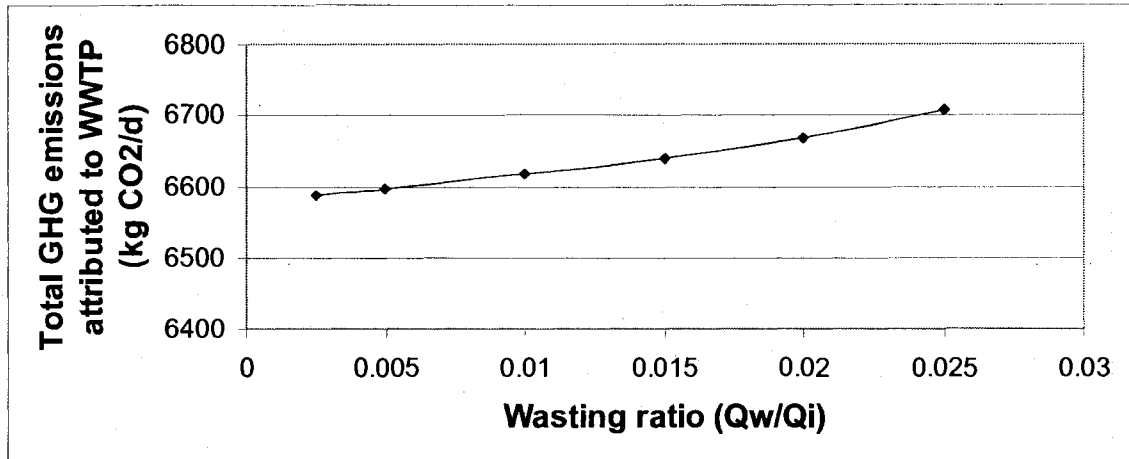


Figure 4.10 (c)- Effect of aerobic reactor's wasting ratio on total GHG emissions in a hybrid treatment system

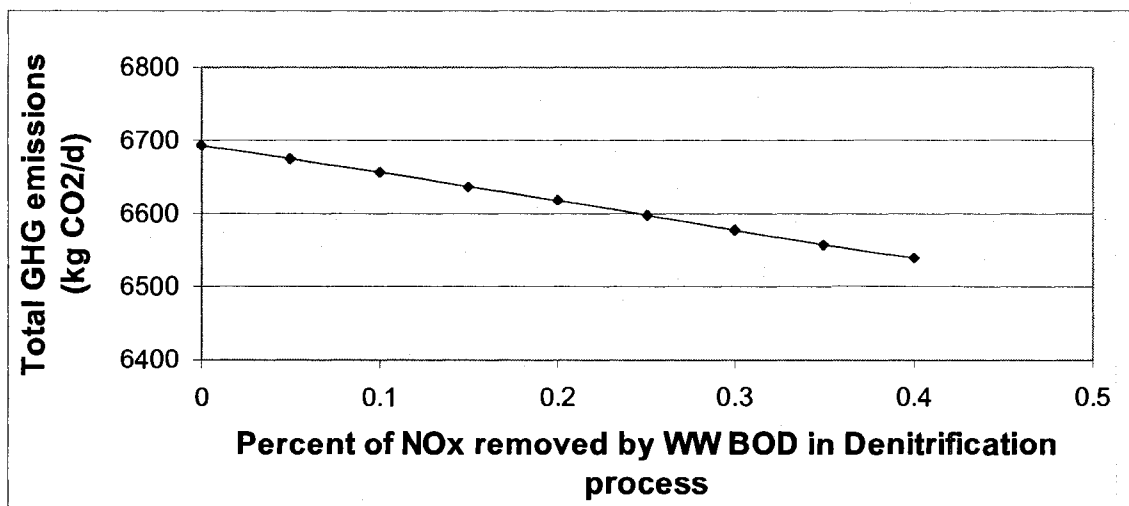


Figure 4.10 (d)- Effect of percent of NO_x removed by WW BOD during denitrification on total GHG emissions in a hybrid treatment system

GHG emissions decrease with the increase of solid retention time (SRT) while they increase with the increased reactor temperature and wasting ratio. The increase of SRT from 4 to 11 days decreased the GHG emissions by 0.2% while an increase of wasting ratio from 0.0025 to 0.025 increased the emissions by 1.8%. The most significant impact was observed with temperature which increased the emissions by 5.2% upon increasing

from 10 °C to 35 °C. Non-linear trend indicates a considerably higher rate of increase above 35 °C. Similar explanations apply to the trends observed in Figure 4.10 (a to c) and Figure 4.3 (a to c). According to Figure 4.10 (d), the total GHG emissions decreased with the increase of the percentage of NO_x removal by the BOD of wastewater. Lower NO_x removal by the wastewater BOD in denitrification process increases the need for external carbon sources (in this study methanol) and therefore enhances the upstream GHG emissions because of material usage. Recommended strategies for the reduction of GHG emissions will be to keep the reactor's temperature as low as possible, increase the SRT of aerobic reactor, decrease the wasting ratio, and remove as much NO_x as possible by means of wastewater BOD.

4.4.3.4 Digester: The effect of digester's process parameters including solid retention time (SRT), and temperature of the digester on total GHG emissions by the hybrid treatment system is displayed in Figure 4.11 (a and b).

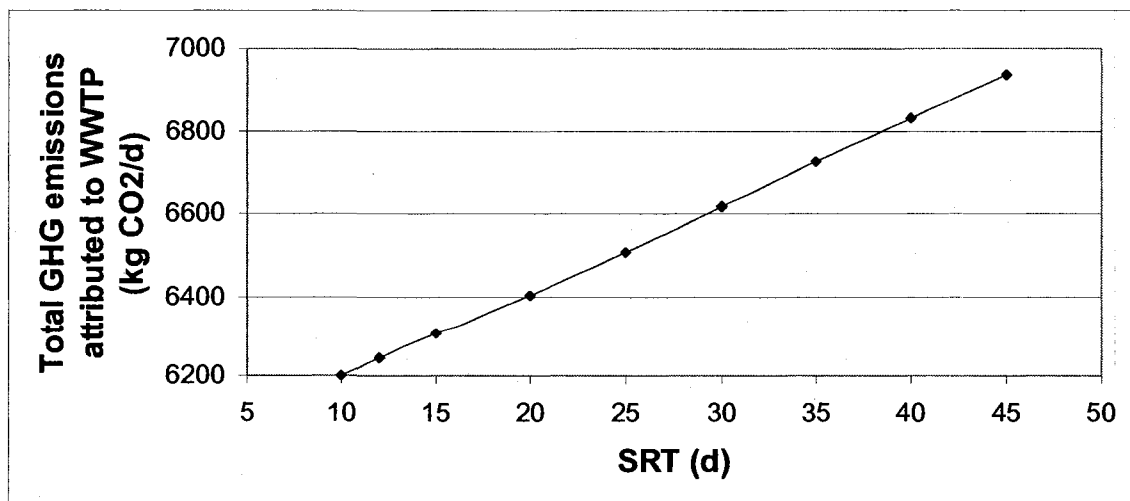


Figure 4.11 (a)- Effect of digester's SRT on total GHG emissions in a hybrid system

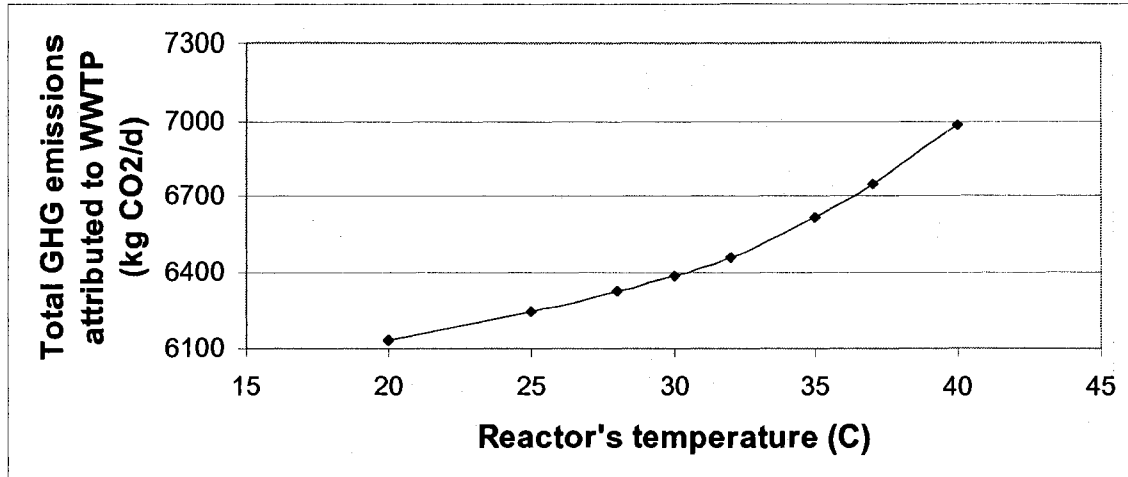


Figure 4.11 (b)- Effect of digester's temperature on total GHG emissions in a hybrid system

Solid retention time (SRT) and digester temperature both have a great influence on total GHG emissions by the hybrid treatment system. As shown in Figure 4.11 (a and b), GHG emissions increased by 11.8% with the increase of SRT from 10 to 45 days while they increased by 13.9% with the increase of temperature from 20 °C to 40 °C. Increased SRT and temperature both cause higher heating demands by digester and consequently more upstream GHG emissions because of on-site fossil fuel consumption. Recommended strategies for the reduction of GHG emissions will be to reduce the digester temperature and SRT to the lowest acceptable values that do not compromise the efficiency of treatment.

Chapter 5

Discussion and conclusions

Based on the analysis of process parameters' impacts on GHG emissions and the results provided in Figures 4.2 to 4.11, the following strategies are recommended to reduce GHG emissions in a wastewater treatment plant. This study is just based on GHG emission calculation and other factors, like the cost for mitigation strategies, are not considered as the decision making criteria in this study.

Biogas recovery and reuse reduce GHG emissions in all different treatment systems studied. Biogas recovery should be conducted more effectively to obtain additional greenhouse gas emission (GHG) reductions. Increasing the energy efficiency in industrial wastewater treatment plant (IWWTP) processes will reduce the electricity needs of the plant, thus reducing the associated GHG emissions. In an aerobic treatment system, the most effective GHG reducing strategies are: reduction of aerobic reactor and digester's temperatures, and reduction of digester's solid retention time (SRT). Minor GHG reductions can be achieved by controlling other process parameters. For example, reductions in volatile suspended solid (VSS) removal rate and increase of biochemical oxygen demand (BOD) removal rate in the primary clarifier, optimization of the primary clarifier's underflow rate, reduction of wasting ratio and increase of SRT in aerobic reactor.

The dominant GHG reducing strategies in anaerobic treatment systems are: reduction of anaerobic reactor and digester's temperatures, reduction of digester's SRT and increase of anaerobic reactor's SRT. Minor reductions in GHG emissions will be

achieved by reducing VSS and BOD removal rates of primary clarifier, optimizing the primary clarifier's underflow rate, and reducing the wasting ratio of anaerobic reactor.

In hybrid treatment systems, the most effective GHG reducing strategies are: reduction of temperatures of aerobic reactor, anaerobic reactor, and digester. Minor GHG reductions are accomplished by reductions in VSS and BOD removal rates of primary clarifier, optimization of the primary clarifier's underflow rate, increase of SRT and decrease of the wasting ratio of anaerobic reactor, increase of SRT and decrease of the wasting ratio and increase of the NO_x removal by using the influent BOD as the source of carbon in aerobic reactor, and decrease of the SRT of digester.

An alternative for abatement strategies for all types of treatment is to increase the effectiveness of anaerobic digester to produce more biogas. Using alternative nutrient removal processes, like the anaerobic process Anammox, offers nitrogen removal with a lower consumption of energy and carbon. Materials which are consumed on-site such as methanol or carbonate (for alkalinity control) should be produced by less GHG producing methods to reduce the upstream GHG emissions attributed to the IWWTP. Electricity and fossil fuels should be generated by more efficient methods to reduce the total GHG emissions.

It must be emphasized that the implementation of strategies to reduce GHG emissions must be accomplished while maintaining the treatment objectives, the efficiency of contaminant removal and the quality of effluent. Economic considerations also play an important role during the implementation of the recommended strategies.

5.1 Future work

Future research should concentrate on the application of the recommended strategies for GHG emissions reduction in full-scale wastewater treatment plants. Future experimental studies should be accompanied with the mathematical model developed in this study in order to acquire more precise information about the operation of treatment plants. Respirometric analysis of the mixed liquor, influent, and effluent of each reactor determines the amount of carbonaceous biochemical oxygen demand (CBOD) and $\text{NH}_3\text{-N}$ removed, and the amount of biomass produced and decayed. Mass balance equations and oxidation-reduction reactions are used to predict the GHG production in each reactor. Energy consumption (either electricity or fossil fuel) of the IWWTP should be calculated based on site-specific observations. The effect of nutrient removal processes on GHG emissions are needed to be considered with more elaboration and precision. Alternative and more efficient processes for nutrient removal should be considered in the prospective studies. Reliable methods should also be developed to estimate non-carbon based GHG emissions such as nitrous oxide (N_2O) which has a more potent GHG impact compared to CO_2 and CH_4 . The life cost analysis of using GHG abatement strategies should be also studied in near future. This must be handled on a case by case basis.

Global warming effect has strongly changed our viewpoint from economical to environmental. It is essential to include environmental consideration in the programming and management of environmental technologies and be prepared to face the presented challenges and opportunities.

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