Anaerobic Batch Treatment of Carbon Dioxide in Pulp and Paper Effluent

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ABSTRACT

Anaerobic Batch Treatment of Carbon Dioxide in Pulp and Paper Effluent

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Concordia University, 2013

The increasing concentration of carbon dioxide (CO_2), the most dominant component of greenhouse gases (GHG) in the atmosphere, has been of growing concern for many years. Since the beginning of the industrial revolution, atmospheric concentration of carbon dioxide has increased dramatically due to human activities. Many methods have been applied to reduce atmospheric CO_2 concentrations, including capture, sequestration, and reduction of carbon dioxide emissions. However, these methods have proved to be not efficient or economical.

The pulp and paper industry is highly pollution and energy intensive. The pulp and paper manufacturing process contributes significant amounts of pollutants that are released to the environment. The Kraft wastewater from the pulp and paper industry has high COD levels, ranging from 1000 mg/L to 33600 mg/L, and feasible to be treated by anaerobic digestion.

Anaerobic digestion has been applied in this study. In this method, CO_2 is converted to methane as a biogas during the biological treatment of industrial pulp and paper wastewater. The final step of anaerobic digestion is to use CO_2 and hydrogen or acetic acid to produce methane. In order to know the feasibility of CO_2 removal by this method, a series of batch tests on pulp and paper wastewater were performed. To determine the optimum conditions, the impact of different pH values (6.5, 7.0, 7.5) and temperatures (20, 30, 35ºC) on the efficiency of CO_2 and COD removal and methane production was investigated. The efficiency of CO_2 removal was found to be 66-90%, while the removal of COD ranged from 32% to 49%. The optimum conditions for the removal of both COD and CO_2 were established at pH 6.5 and 35ºC. The methane generation rates ranged from 4 mL/d to 19 mL/d. The optimum conditions for the maximum generation of methane were found to be the temperature of 35ºC and pH 6.5 along with the injection of carbon dioxide. In conclusion, the applied method was shown to be applicable for CO_2 removal, while producing biogas as a clean source of energy.

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List of Abbreviations

BOD	Biochemical oxygen demand
COD	Chemical oxygen demand
K	Kelvin
MLSS	Mixed liquor suspended solids
MLVSS	Mixed liquor volatile suspended solids
SS	Suspended solids
Ta	Actual temperature
TN	Total Nitrogen
Ts	Standard temperature
TS	Total solid
TSS	Total suspended solid
TVS	Total volatile solid
Va	Actual volume
Vs	Standard volume
VSS	Volatile suspended solid

VFA Volatile fatty acid

Chapter 1: Introduction

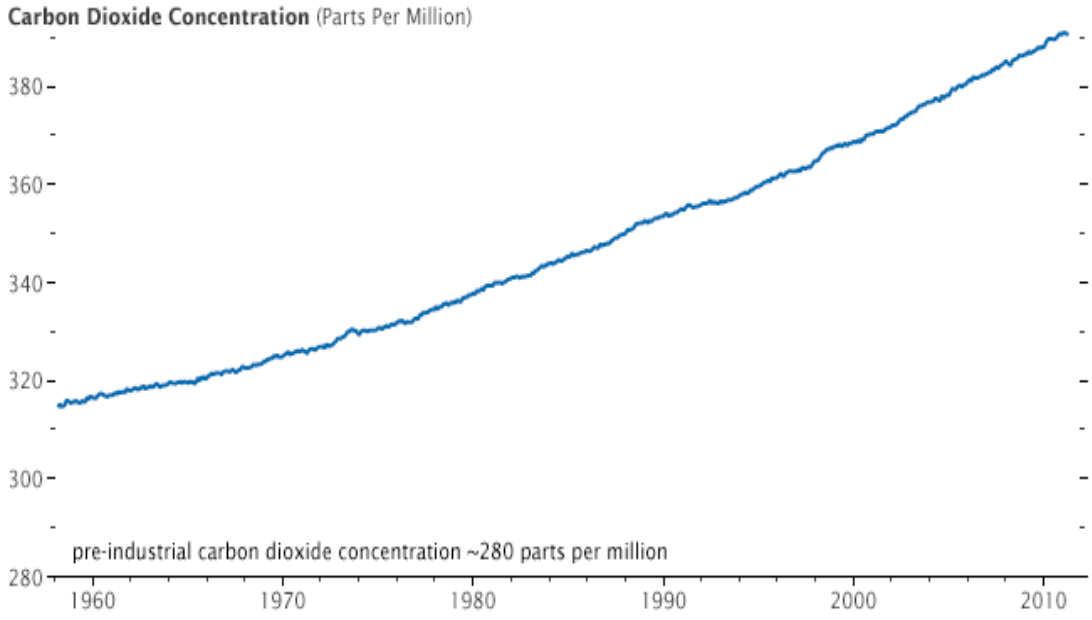
1.1 Problem Statement

1.1.1 Carbon dioxide emission

Carbon dioxide is a major greenhouse gas (GHG) that contributes to global warming and climate change. With the onset of the industrial revolution in 1750, the emission of carbon dioxide has rapidly increased due to human activities (Figure 1.1). The changes in the concentration of carbon dioxide and global temperature from 1960 to 2010 are shown in Figure 1.2. Human activities contribute to the global carbon cycle, not only by releasing carbon dioxide to the atmosphere, but also through activities that reduce the capability of natural carbon sinks, such as deforestation. Industrial operations, transportation, and commercial and residential activities have contributed to 47%, 22 % and 31% of the world's total emissions of carbon dioxide, respectively (Hallman et al., 2008). The emission of carbon dioxide from power plants is included in the industrial emissions of CO_2 (US EPA, 2010).

The emissions of CO_2 have been dramatically increased within the last 50 years and are still increasing by almost 3% each year. The amount of carbon dioxide emitted by different regions is presented in Table 1.1. Carbon dioxide is released to the atmosphere where it can remain for 100

to 200 years (US EPA, 2012). This results in an increasing concentration of carbon dioxide in our atmosphere, which in turn causes the average temperature on earth to rise and affects the climate. Therefore, the industries are more than ever faced with technical challenges to further reduce the atmospheric emissions of carbon dioxide.



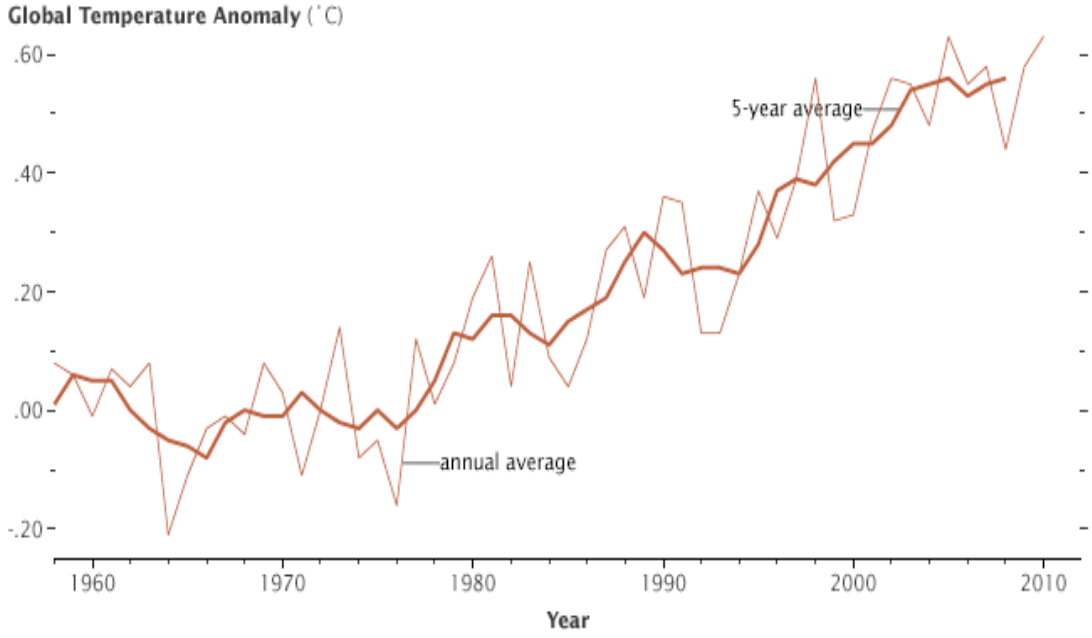


Figure 1.1 Changes of carbon dioxide concentration and global temperature by year (http://earthobservatory.nasa.gov/Features/CarbonCycle/printall.php)

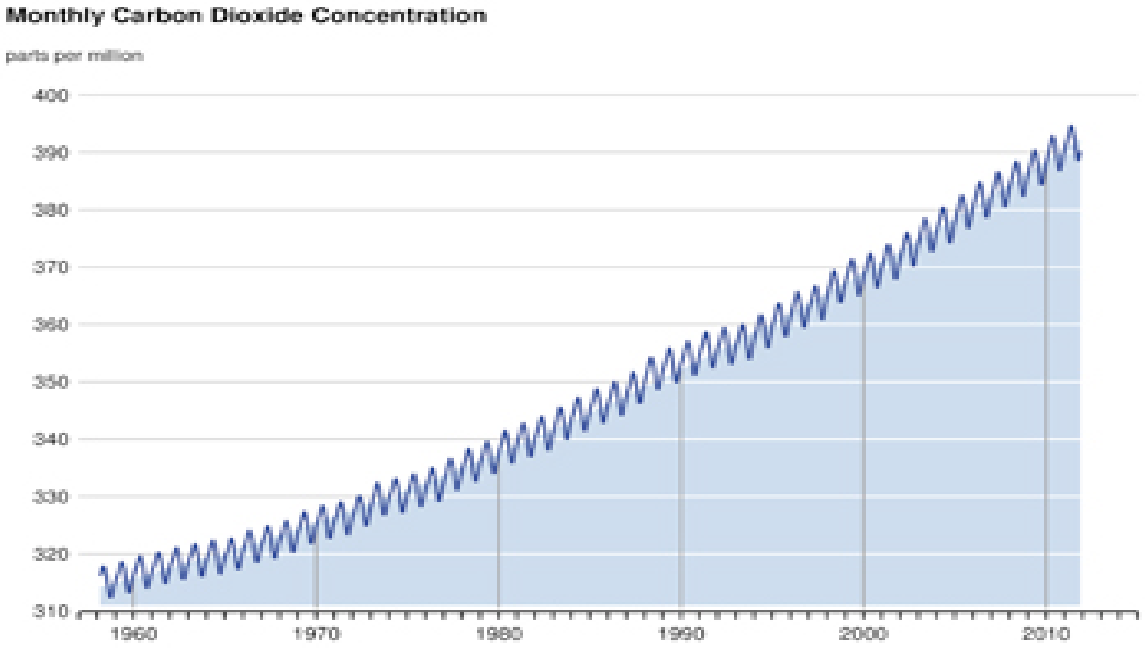


Figure 1.2 Concentration of atmospheric carbon dioxide from 1960 to 2010 (https://www2.ucar.edu/climate/faq/carbon-dioxide-atmosphere-decreased-recently)

Table 1.1 Carbon dioxide emissions from 1980 to 2006 (in million metric tons)

(http://mdgs.un.org/unsd/mdg/SeriesDetail.aspx?srid=749&crid=)

Year	North America	Central & South America	Europe	Eurasia	Middle East	Africa	Asia& Oceania	World Total
1980	5488.11	627.76	4707.50	3092.69	490.76	537.76	3558.55	18503.12
1990	5806.56	716.95	4858.17	3834.05	730.05	728.00	5299.37	21683.16
2000	6820.19	992.81	4500.07	2355.98	1093.74	892.07	7365.81	24010.66
2006	6954.03	1138.49	4720.85	2600.65	1505.30	1065.55	11219.56	29195.42

1.1.2 Effects of carbon dioxide

Effects on the marine ecosystems

Marine ecosystems are affected by the variation of their physical and biological environments, as shown by palaeological and archaeological records (Enghoff et al., 2007). Fish stock is a vital component of marine ecosystems. Atlantic cod (*Gadus morhua*) can be used as an example to demonstrate the response of fish to temperature change. Similar responses can be expected from other marine species resulting from other environmental factors. As shown in Figure 1.3, the growth rate of fish increases at higher temperatures, and smaller fish are more sensitive to temperature variations than larger fish.

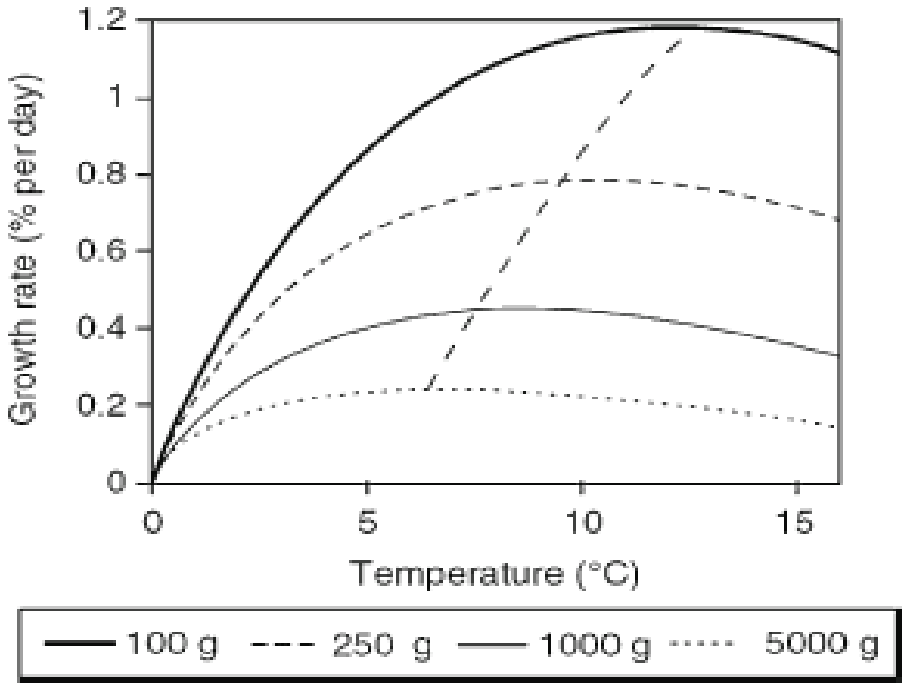


Figure 1.3 Growth rate curves at different temperatures and fish sizes (Brander, 2012)

Effects on human health

The high atmospheric concentration of carbon dioxide leads to global warming that affects climate-related parameters. Human health is closely connected to the environment; hence environmental factors may have a detrimental influence on human health. Human health possibly can be influenced by five pathways through climate change, as follows:

1) morbidity and mortality related to the temperature,
2) health effects related to air pollution,
3) influence of extreme weather events (heat waves, intensive rainfall and drought) on population health,
4) water and food borne diseases
5) vector borne diseases
6) impact of temperature on mentality and emotion (Patz et al., 2002).

Effects on ice glaciers

Carbon dioxide is associated with warm temperature that will weaken ice shelves. There are two pathways that affect the ice shelves: 1) thinning of the shelves because of melting at the upper and lower surfaces, 2) increase of the calving rates by enhancing existing lines of weakness (Robet et al., 1979). In the future, approximately one billion people will be affected either directly or indirectly due to the ice glacier melting. The ice glacier melting effects include:

1) Sea level rise, flooding low-lying coastal areas and transferring the coastal lands underwater (Figure 1.4).

2) Methane emerging from thermokast lakes increases up to 5 times higher than previously expected due to the melting of ice.

3) Shrinkage of glaciers result in the sedimentation of unstable debris and formation of ice and debris dammed lakes; thereby it increases instability of glacier ice. These conditions may increase the potential of debris flows, catastrophic flooding and ice avalanches.

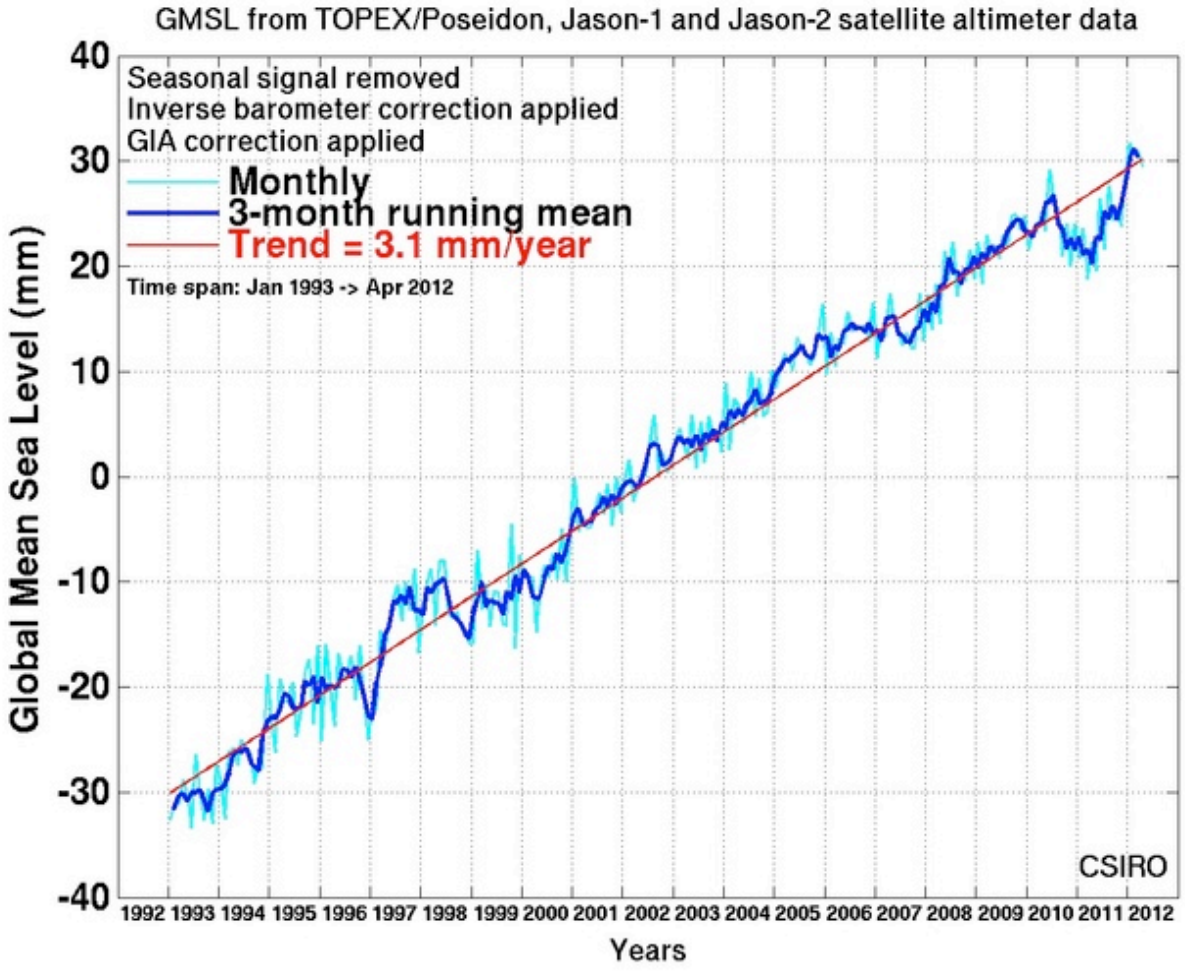


Figure 1.4 Changes in sea level from year 1992 to 2012 (http://www.cmar.csiro.au/sealevel/sl_hist_last_15.html**)**

1.2 Carbon Dioxide Mitigation

The increase of atmospheric emissions of carbon dioxide has caused a major concern, thus extensive studies have been conducted to either decrease or removal carbon dioxide from the atmosphere.

1.2.1 Clean Energy

According to the analysis made in the Energy Technology Perspectives 2008 (ETP) Project by the International Energy Agency (IEA), the emission of carbon dioxide from the energy sector will rise by 130% by the year 2050. Without new policies or supply constraints, the combustion of fossil fuel is the major factor that contributes to the increasing emission of carbon dioxide (International Energy Agency, 2008).

Carbon dioxide emission reduction can be achieved by increasing the share of renewable energy sources. While nuclear energy is a very important component of alternate energy sources, as it can decrease emissions, it is not renewable.

The action of nuclear fission (Figure 1.5) that refers to splitting the atomic nucleus yields an enormous amount of energy. This fission can emit 10^6 times more energy per atom than any chemical reaction within a nuclear reactor under controlled conditions. Moreover, the process can react without generating many of the pollutants associated with combustion such as oxides of sulphur, carbon and nitrogen (Elliott, 2009).

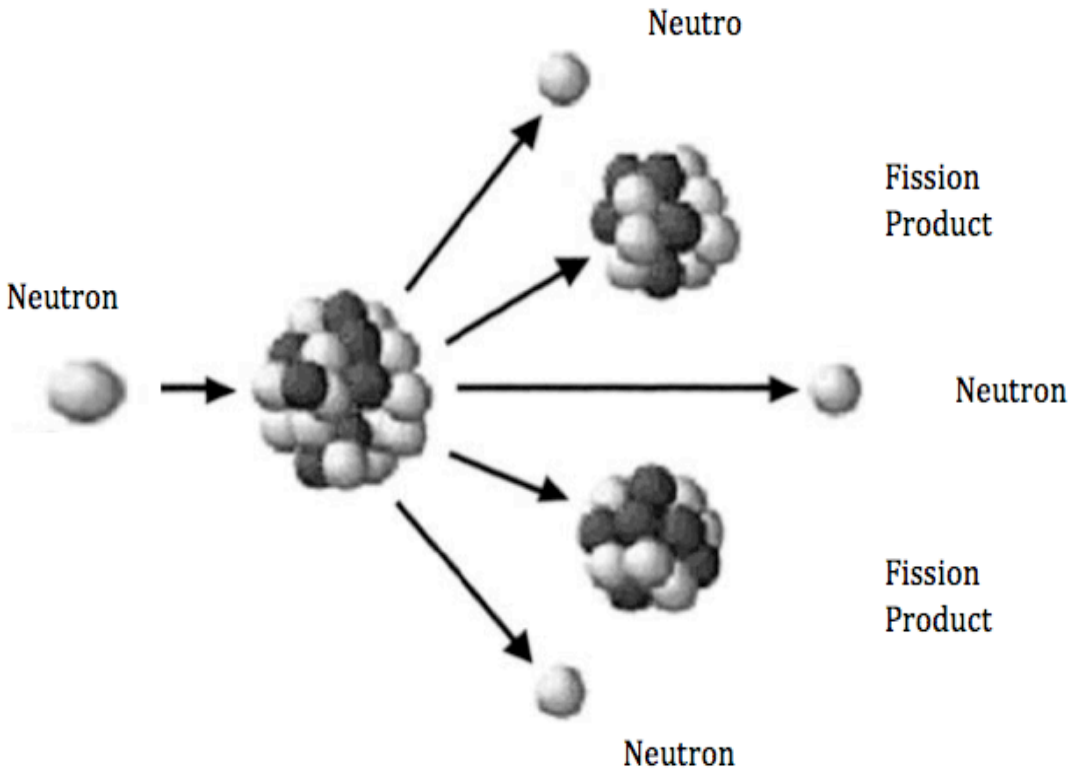


Figure 1.5 Diagram of fission action (Elliott, 2009)

However, this method of energy generation has several disadvantages that limit its application. They include:

1) Radiation risks due to involuntary leaks, causing hidden or irreversible damage which can lead to severe illnesses for future generations
2) Risk of waste disposal which is an important global issue, further complicated due to long half-lives of radioactive materials. The leakage of nuclear waste can cause significant harm to the human health and will damage the economics of energy generation (Slovi et al., 1991)
3) Threat to world peace since the nuclear source that generates nuclear energy can also be used to make nuclear weapons, especially if nuclear power plants are widely applied. Nuclear weapons are the most dangerous weapon in the world and can place the world into a dangerous situation (United Nations Office for Disarmament Affairs 2012).

1.2.2 Carbon Dioxide Capture and Storage

Carbon dioxide capture and storage (CCS) provide a viable and competitive route to reducing greenhouse gases (GHG) emissions. It involves the application of technologies that retrieve carbon dioxide from single-point sources and store it underground in geological reservoirs (Figure 1.6).

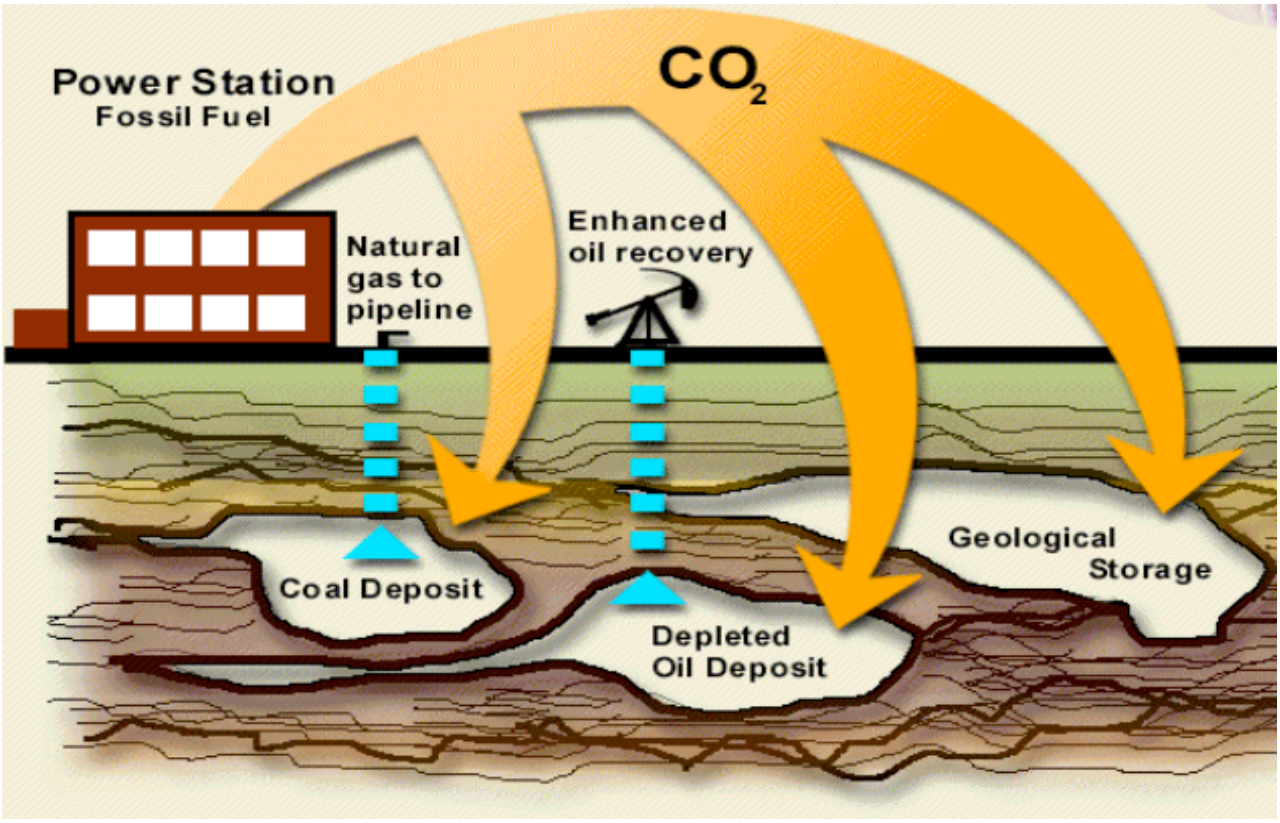


Figure 1.6 Fate of carbon dioxide by capture and storage (Natural Resources Canada, 2012)

The process of CCS can be divided into three parts:

1) Capturing carbon dioxide from industrial facilities followed by compression into a transportable form, e.g. liquid.
2) Transportation of liquefied carbon dioxide either by pipeline or by tanker to the storage place.
3) Storage of carbon dioxide in different media such as geological formations, oceans, or industrial processes (National Energy Board, 2008).

Advantages and disadvantages

1) CCS removes large amounts of carbon dioxide from non-point sources and compresses the retrieved carbon dioxide to make it transportable to save volume
2) Makes use of depleted or abandoned oil and gas fields as the storage medium
3) The captured carbon dioxide may be used as liquid or gas feedstocks in chemical processes to make valuable carbon-containing products (National Energy Board, 2008).

The disadvantages of CCS include the following:

1) During the CCS process, carbon dioxide is only transferred from one place to another place without being transformed (Hitchon, 1998; Reeve, 2000; Herzog, 2003)
2) The stored carbon dioxide has the potential of leakage from underground
3) The cost of transportation, monitoring of the stored carbon dioxide, and construction of pipeline may make the process economically unfavorable.

1.3 Anaerobic treatment of Carbon dioxide

In this work, anaerobic batch treatment of carbon dioxide in pulp and paper effluent would be a best method, because it simultaneously does:

- Bioconversion of carbon dioxide which is a major component of Greenhouse gas that can lead to global warming;

- Treat wastewater by anaerobic digestion which can have net energy gain and produce fertilizer from residuals
- Produce biogas that would be a source of energy that can be used in many ways: for heating, cooking and etc.

1.4 General objective

The main objective of this study was to develop a new sustainable process to simultaneously remove carbon dioxide and treat wastewater by anaerobic digestion.

1.5 Specific objectives

The specific objectives were designed to determine the optimum operating conditions in batch mode of operation by evaluating the impact of various parameters on CO_2 removal. These objectives are to:

1) Evaluate the biodegradability of Kraft wastewater through the reduction of COD concentrations
2) Investigate the impact of carbon dioxide injection on its removal efficiency

3) Investigate the impact of carbon dioxide injection on the efficiency of wastewater treatment
4) Evaluate the efficiency of carbon dioxide bioconversion into methane by anaerobic digestion
5) Evaluate the impact of operating parameters such as pH and temperature on carbon dioxide and COD removal and methane generation.

1.6 Organization of the thesis

This thesis includes 5 chapters as follows：

Chapter 1: Statement of the problem and objectives of research

Chapter 2: Critical review of the literature on the removal of carbon dioxide, information on the pulp-and paper industry, theoretical background of anaerobic digestion

Chapter 3: Characteristics of the examined wastewater, experimental methodology and analytical methods

Chapter 4: Presentation of the experimental results obtained under various operating conditions related to the removal of carbon dioxide, reduction of COD and generation of methane, and discussion of the findings

Chapter 5: Overall conclusions of the research work and contribution to the existing knowledge

Chapter 6: Recommendations to further the research of the conducted study.

Chapter 2: Literature Review

2.1 Anaerobic Treatment

Anaerobic digestion is a biological process with the potential to remove carbon dioxide. In the final step of this process that is called the methanogenesis stage, simple organic molecules that include short-chain fatty acids along with carbon dioxide and hydrogen are converted to biogas as shown in Figure 2.3. Therefore, it is possible to simulate this step and provide conditions to convert carbon dioxide to biogas by using methanogens. Previous research has been done by using synthetic wastewater **(**Alimahmoodi, 2008**).** *Methanogenic archaea* are obligate anaerobes. In fact, they are the strictest anaerobes discovered (Harley et al., 1990).

Anaerobic bacteria have the ability to use carbon dioxide as a source of oxygen (Mulligan, 2002). Carbon dioxide will be solubilized in water and converted by anaerobic bacteria into methane. There are four stages in the anaerobic digestion, as shown in Figure 2.3 (Cho et al., 1995):

Hydrolysis

This is the process to break complex organic matter into smaller molecules via the enzymes released by the bacteria. Larger molecules break down into small molecules which have fewer atoms of carbon.

Fermentation or acidogenesis

In this step, monomeric molecules are fermented into different volatile fatty acids via enzymes produced by the bacteria. The primary organic compounds produced in this step are acetic, propionic and butyric acids.

Acetogenesis

In this stage, fatty acids that were produced during the previous stage are converted into hydrogen, carbon dioxide and acetate with the help of acetogenic bacteria.

Methanogenesis

In this stage, a group of anaerobic bacteria called methanogens transform acetate and hydrogen/carbon dioxide into methane (CH_4). In the final stage, carbon dioxide and hydrogen produce CH_4. Therefore, a combination of a hydrogen or acetic acid with carbon dioxide provides an environment to convert carbon dioxide to CH_4 via methanogenic bacteria. It is possible to reduce carbon dioxide emissions and treat the wastewater in one complete and sustainable system.

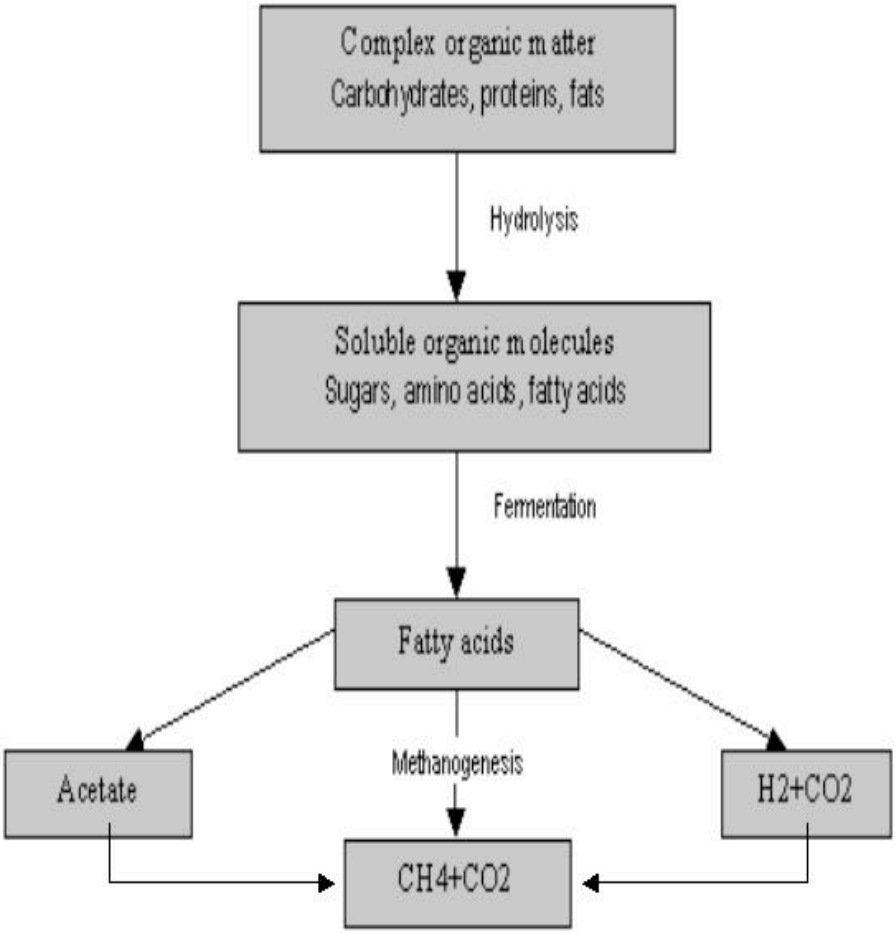


Figure 2.3 Overall scheme of anaerobic digestion process （Cho et al., 1995)

Methanogenic bacteria play an important ecological role in anaerobic environments for the removal of hydrogen and fermentation products generated during anaerobic respiration. Methanogenic bacteria can be found in different parts and conditions on earth. Methanogenic bacteria have various morphological structures and some are shown in Figure 2.4 (Preslott et al., 2001).

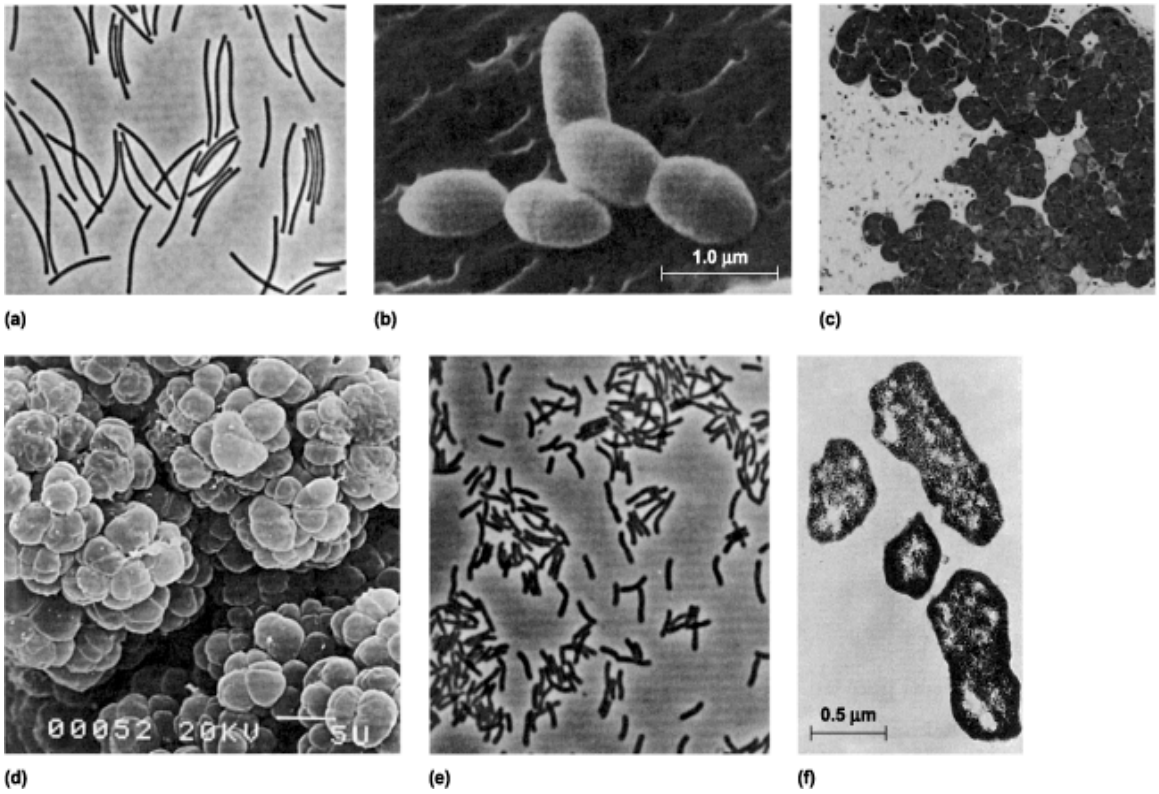


Figure 2.4 Morphological structures of selected methanogens (Preslott et al., 2001)

(a) *Methanospirillium hungatei* (b) *Methanobrevibacter smithii*. (c) *Methanosarcina barkeri* from sewage digester; transmission electron microscope (d) *Methanosarcina mazei;* (e) *Methanobacterium bryantii*; (f) *Methanogenium marisnigri*; electron micrograph

Growth environment

The activity and function of methanogens can be influenced by various environmental factors that affect the efficiency of anaerobic digestion (AD). Therefore, it is vital to know the optimum environment conditions for growth and proper activity of methanogens. The factors that affect the activity of methanogens are presented below:

Temperature

Methanogens can tolerate different ranges of temperatures. There are three main types of methanogens: psychrophilic methanogens that prefer temperatures lower than 20°C, mesophilic methanogens with the optimum temperature range of 20–45 °C, and thermophilic methanogens that can function at the temperature range of 45–65 °C. The mesophilic methanogens are commonly used in industrial operations due to the low rate of biogas production at low-temperatures by psychrophilic methanogens (Lin et al., 1987; Lettinga et al., 2001). The application of thermophilic methanogens has been limited due to poor stability of operation and low quality of supernatant, as well as high cost of temperature maintenance (Kugelman et al., 1989). Therefore, in this study, temperatures of 20°C, 30°C, and 35°C were used.

Oxygen

The activity of methanogens and the production of biogas require strict anaerobic conditions and a total lack of atmospheric oxygen. Only a limited amount of dissolved oxygen can be tolerated by the methanogens. So in this work, access to the atmospheric O_2 has been restricted.

pH

pH is a very important factor that affects the performance of AD. Methanogens are very sensitive to the liquid pH. However, different methanogens can tolerate different ranges of pH. For example, some types of methanogens can produce methane at pH 4 or even lower than 4, while

some can be active at pH 8-9. However, the optimum pH for biogas generation by most methanogens is around neutrality (Jones et al., 1987; Cerning et al., 2010). In light of the above discussion, pH values of 6.5, 7, and 7.5 were chosen to be used in this study.

Toxicity

Toxicity/inhibition is a major factor that may limit the efficiency of anaerobic digestion. Substances such as ammonia, sulfide, heavy metals and organic compounds can be toxic to the methanogens. The level of toxicity/inhibition depends on the type of compound and the level of microbial adaptation (Chen et al., 2007). Toxic levels of various inhibitors for methanogens are shown in Table 2.1 (BRTC, 1989)

Methanogenic pathway

Anaerobic bacteria use a variety of pathways for the metabolism of simple carbon substrates, including CO_2, acetate, formate, and methanol. Three pathways have been illustrated in Figure 2.5 (Joshua , 2012; Welander et al., 2005; Rother, 2008):

1) CO_2 reduction pathway: CO_2 is converted to CH_4 using hydrogen gas as an electron donor (hydrogenotrophic) and/or formate
2) Methylotrophic pathway: CO_2 and CH_4 are produced by disproportionation of methylated compounds including methanol and methylamines
3) Acetoclastic pathway: CO_2 and CH_4 are produced by the dissimilation of acetate.

Table 2.1 Toxic level of various inhibitors (BRTC, 1989)

Inhibitors	Inhibiting Concentration
Sulphate (SO_4^{2-})	5,000 mg/L
Sodium Chloride or Common salt (NaCl)	40,000 mg/L
Nitrate (Calculated as N)	0.05 mg/mL
Copper (Cu^{2+})	100 mg/L
Chromium (Cr^{3+})	200 mg/L
Nickel (Ni^{2+})	200 - 500 mg/L
Sodium (Na^{+})	3,500 - 5,500 mg/L
Potassium (K^{+})	2,500 - 4,500 mg/L
Calcium (Ca^{2+})	2,500 - 4,500 mg/L
Magnesium (Mg^{2+})	1,000 - 1,500 mg/L
Manganese (Mn^{2+})	Above 1,500 mg/L

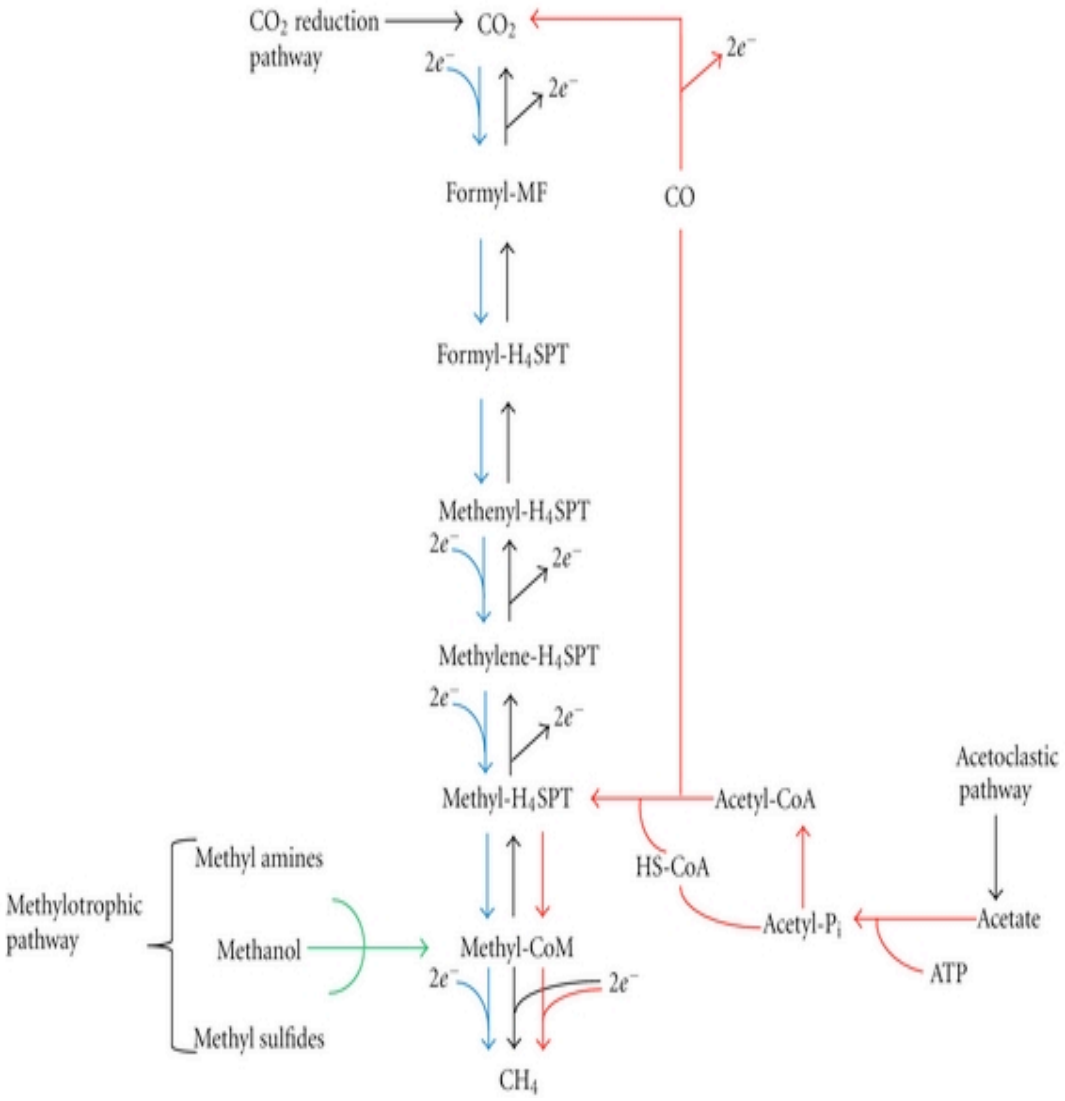


Figure 2.5 Schematic diagram, illustrating the major substrates and pathways utilized for methanogenesis (Joshua , 2012; Welander et al., 2005; Rother, 2008)

2.2 Pulp and paper industry

The pulp and paper industry is considered as one of the sources of environmental pollution (Anh, 1996). Pollutants from various sources of pulping and papermaking are shown in Figure 2.6 (USEPA, 1995). This industry generates various pollutants depending upon the type of the pulping process employed. In Canada, it has been estimated that the pulp and paper industry is responsible for 50% of all the wastes dumped into Canadian waters, and it also accounts for approximately 5.6% of the common air contaminants from known industrial sources (Murray, 1992).

The pulp and paper manufacturing process is highly energy intensive that consumes large amounts of energy, water and trees. The pulp and paper manufacturing industry consumed fuel accounted for around 14 percent of fuel consumed by the U.S. manufacturing sector in 2002. (Kramer 2009). In the United States, pulp and paper mills are now considered the third largest polluter of the USA. Natural gas, fuel oil, biomass-based materials, purchased electricity and coal are the major energy-related GHG emission sources from the U.S. pulp and paper mills (Kramer, 2009).

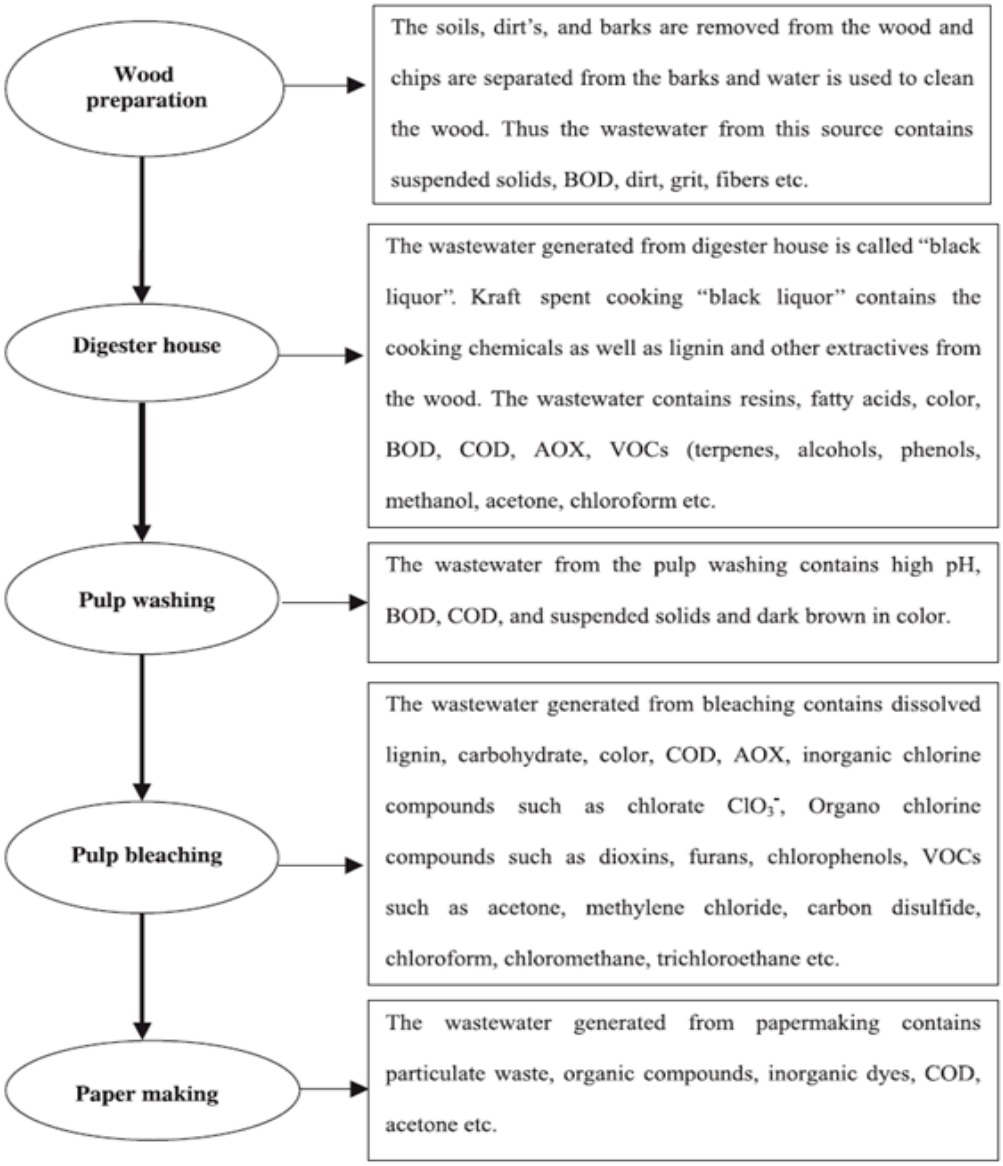


Figure 2.6 Pollutants from various sources of pulping and papermaking (US EPA, 1995)

Characterization of the Pulp and Paper Industry

The pulp and paper industry using cellulose fiber from purchased /recycled fibers or timber to produce primary products by pulping and paper or paperboard manufacturing. Pulping is the first step and the source of the most pollutant of this industry (Bahar et al. 2011). The process of pulping is shown in Table 2.2（USEPA 2002）.

Table 2.2 Process of pulping（USEPA, 2002）

Pulp process	Description/Principal Products
Dissolving Kraft	Highly bleached and purified kraft process wood pulp suitable for conversion into products such as rayon, viscose, acetate, and cellophane
Bleached Paper-grade Kraft and Soda	Bleached or unbleached kraft process wood pulp usually converted into paperboard, coarse papers, tissue papers, and fine papers such as business, writing and printing
Unbleached Kraft	
Dissolving Sulfite	Highly bleached and purified sulfite process wood pulp suitable for conversion into products such as rayon, viscose, acetate, and cellophane
Paper-grade Sulfite	Sulfite process wood pulp with or without bleaching used for products such as tissue papers, fine papers, and newsprint.
Semi-chemical	Pulp is produced by chemical, pressure, and occasionally mechanical forces with or without bleaching used for corrugating medium (cardboard), paper, and paperboard
Mechanical pulp	Pulp manufacture by stone ground wood, mechanical refiner, thermo-mechanical, chemi-mechanical, or chemi-thermo-mechanical means for newsprint, coarse papers, tissue, molded fiber products, and fine paper.

Secondary Fiber Deink	Pulps from recovered paper or paperboard using a chemical or solvent process to remove contaminants such as inks, coating and pigments used to produce fine, tissue and newsprint papers.
Secondary Fiber Non-deink	Pulp production from recovered paper or paperboard without deinking processes to produce tissue, paperboard, molded products and construction papers.
Non-wood Chemical pulp	Linters, flax, hemp, tobacco, and abaca to make cigarette wrap papers and other specialty paper products.

Paper and Paperboard Manufacturing

The process of paper manufacturing is similar for different types of pulp. The water in the pulping is removed by gravity and vacuums, and it passes through a series of rollers that results in sheets (US EPA, 2002).

The wastewater from the pulp and paper industry contains high COD concentrations that are suitable for anaerobic processes. The anaerobic treatability of different processes is given in Table 2.3.

Table 2.3 Anaerobic biodegradability of pulp and paper mill effluents (Rintala et al., 1994)

Source of wastewater	COD(mg/l)	Anaerobic biodegradability (%)
Wet debarking	1300-4100	44-78
Thermo-mechanical pulping (TMP)	1000-5600	60-87
Chemi-thermomechanical pulping (CTMP)	2500-1300	40-60
NSSC-spent liquor	40000	nr
NSSC-condensate	7000	nr
Kraft condensate	1000-33600	83-92
Spent condensate	7500-50000	50-90
Chlorine bleaching	900-2000	30-50
Sulfite spent liquor	120000-220000	nr

nr— not reported; NSSC— neutral sulphite semichemicals

Anaerobic treatment systems are feasible to treat wastewater from most types of pulp and paper mills.

2.3 Anaerobic treatment of pulp and paper industry

Anaerobic treatment of industrial wastewater has been widely applied in the pulp and paper industry since early 1980s. Various anaerobic systems are installed to treat a large variety of different pulp and paper mill wastewaters. The advantages of anaerobic treatment include: first, minimized biomass production; second, net production of energy; third, less space is needed; last but not least, less energy is required.

Anaerobic treatment is frequently applied fro the secondary treatment of industrial wastewaters. Typical COD removal for the treatment of pulp and paper mill can be achieved from 49% to 80%. Anaerobic digestion is carried out at mosephilic temperature that is from 35 ^{o}C to 37^{o}C generally. Table 2.4 and Table 2.5 show performance of biological treatment processes and existing anaerobic treatment in paper mills.

Almahmoodi and Mulligan (2008) provided a method to remove carbon dioxide from synthetic water under anaerobic digestion, their method achieved two major objectives, carbon dioxide removal and biogas generation. Abedi et al (2011) used pulp and paper industry wastewater instead of synthetic water via anaerobic digestion. The composition of substrate plays an important role in the anaerobic digestion and also the different designs of the employed systems would have impact on it.

Table 2.4 Performance of biological treatment processes (Pokhrel D et al., 2004)

Treatment process	COD		Color		Reference
	Influent (mg/l)	% Removal	Influent (mg/l)	% Removal	
Biological reactors					
HRC (TMP Mill)	3340	79	–	–	Magnus et al. (2000a)
Total plant efficiency	5000	86	–	–	
MBBR (HRT 4.5 hrs)	–	85–95	–	–	Borch-Due et al. (1997)
SBR	–	85–93	–	–	Franta and Wilderer (1997)
Anaerobic (GAC)	1400	50	1300	50	Jackson-Moss et al. (1992)
Kraft mill Windsor	2036g/d	59	–	–	Dufresne et al. (2001)

Table 2.5 Selected anaerobic process performance (Bajpai, 2001)

Mill location	Wastewater source	Loading rate (kg COD/m^3/d)	COD (mg/l)	TSS (mg/l)	COD Removal%
Anaerobic contact reactor					
Hylte Bruk AB, Sweden	TMP, groundwood, deink	2.5	3500	520	67
SAICA, Zaragoza, Spain	Waste paper alkaline cooked straw	4.8	30,000	–	66
Hannover paper, Alfred, Germany	Sulfite effluent condensate	4.2	6000	–	85
Niagara of Wisconsin of USA	CTMP	2.7	4800	3300	77
SCA Ostrand, Ostrand, Sweden	CTMP	6	7900	–	40
Alaska Pulp Corporation, Sitka	Sulfite condensate, bleach caustic and pulp whitewater	3	10,000	–	49
Upflow anaerobic sludge blanket					
Celtona, Holland	Tissue	3	1200	–	60
Southern paper converter, Australia	Wastepaper	10	10,000	–	> 80
Davidson, United Kingdom	Linerboard	9	2880	–	75
Chimicadel, Friulli, Italy	Sulfite condensate	12.5	15,600	–	80
Quesnel River Pulp, Canada	TMP/CTMP	18	7800	–	50
Lake Utopia Paper, Canada	NSSC	20	16,000	–	55
EnsoGutzeit, Finland	Bleached TMP/CTMP	13.5	4000	–	60
McMillan Bloedel, Canada	NSSC/CTMP	15	17,500	–	55
Anaerobic filter: Lanaken, Belgium	CTMP	12.7	7900	–	70
Anaerobic fluidized bed: D' Aubigne, France	Paperboard	35	3000	–	72.2

Chapter 3: Materials and Methods

3.1 Materials

The utilized material can be divided into the wastewater, inoculum, pH adjustment solution, and gaseous carbon dioxide.

3.1.1 Inoculum

The granulated biomass used in this project was obtained from Kruger Inc. Division Wayagamack , Trois-Rivieres, QC. The biomass was initially kept in the incubator for temperature acclimation and was further acclimated in the bioreactor. The characteristics are shown in Table 3.1. The methods used for the wastewater characterization are detailed in the following section.

Table 3.1 Characteristics of the biomass used in the study

Parameter	Value
pH	7.71
TS	16060 mg/L
TVS	12200 mg/L
MLSS	14250 mg/L
MLVSS	11010 mg/L

3.1.2. Wastewater

The Kraft pulp and paper wastewater was obtained from Kruger Inc. Division Wayagamack , Trois-Rivieres, QC. The wastewater was neutralized by injecting carbon dioxide. The characteristics and composition of Kraft wastewater are shown in Tables 3.1 and 3.2, respectively. The Kraft wastewater was kept refrigerated (2-4 ^{o}C) during transportation and after receiving in the laboratory to minimize changes in its properties.

Table 3.2 Characteristics of Kraft wastewater used in the study

Parameters	Value
TSS	1465 mg/L
SS	1200 mg/L
COD	1250 mg/L
BOD	384 mg/L
Alkalinity	448 mg/L
VFA	538mg/L
pH	6.76

Table 3.3 Compositions of the Kraft wastewater

Element	Concentration (mg/L)
Nitrate (NO_3^-)	7.31
Nitrite (NO_2^-)	0.261
Chromium (Cr)	0.742
Nickel (Ni)	4.63
Chlorine (Cl)	2.39
Iron (Fe)	3.48

Aluminum (Al)	0.407
Phosphate (P)	1.31
Total nitrogen (TN)	9.39

3.1.3 pH adjustment solutions

NaOH (4 N) and HCl (6 N) solutions were used to adjust the pH of solutions.

3.1.4. Gases

Carbon dioxide

A carbon dioxide gas cylinder (Praxair Inc.) was used to supply carbon dioxide to saturate the wastewater. The purity of carbon dioxide gas in the tank was 99%.

Nitrogen

An industrial grade nitrogen gas (Praxair Inc.) was used as a carrier in the gas chromatograph (GC), and also to provide an anaerobic environment for the biomass and wastewater.

Air

In order to maintain a minimum flow through the gas chromatograph, an extra dry air from a gas cylinder (Praxair Inc.) was used. The operating pressure was set at 300 kPa and a regulator was used to control the pressure.

3.2 Analytical Methods

3.2.1. Chemical Oxygen Demand (COD)

The chemical oxygen demand (20 -1500 mg/L) was measured based on the USEPA reactor digestion method (Standard Method 5220 D). In this test, COD test vials (Hach Inc.), a spectrophotometer (Cole Parmer, model DR 2800), and a DRB200 Digital Reactor Block were used.

Test procedure:

1. The reactor block was turned on and preheated to 150 °C.
2. The cap of the COD reagent vial was removed, and 2 ml sample was pipetted into each vial.
3. The cap was placed and the vials were inverted gently several times to mix the solution.
4. The vials were placed in the preheated reactor block and were heated for two hours.
5. The reactor block was turned off after two hours, and allowed the vials to cool to 120 °C.
6. The COD vials were inverted again and cleaned on the outside.
7. The COD vials were inserted into a rack and then allowed to cool down to room temperature.
8. COD vials were placed in the spectrophotometer and the value was read.

3.2.2. Alkalinity

Alkalinity represents the buffering capacity of solution and assesses the ability of a solution to neutralize acids. Alkalinity was measured by titration based on the method NO. 2320B (Standard Method, 1998).

The materials used: Bromcresol green, distilled water, sulfuric acid (0.1 N).

Procedure:

Bromcresol green solution: 100 mg dry bromcresol green was dissolved in 100 ml distilled water. It changes color at pH 4.5. Standard sulfuric acid, 0.02N: Diluted 20 ml of 0.1 N standard sulfuric acid into 100 ml by using distilled water. 1 ml of standard sulfuric acid (0.02N) is equivalent to a total alkalinity of 1 ppm calcium carbonate. The last point for the titration test was determined according to the color change of the solution (blue to pale green).

3.2.3. Dissolved Carbon Dioxide

Dissolved carbon dioxide is associated with alkalinity and pH values. It is measured by the equilibrium relationship among carbonate species. When carbon dioxide is dissolved in water, the reactions are shown by the following equations.

$$CO_2+H_2O <=> H^+ + HCO_3^-$$

$$K_1 = [H^+][HCO_3^-]/[CO_2(aq)] = 4.47\times10^{-7}M \quad (3.1)$$

$$HCO_3^- <=> H^+ + CO_3^{2-}$$

$$K_2 = [H^+][CO_3^{2-}]/[HCO_3^-)] = 4.68\times10^{-11}M \quad (3.2)$$

$$K_1K_2 = [H^+]^2[HCO_3^-]/[CO_2(aq)] = 2.1\times10^{-17} \quad (3.3)$$

The calculation of pH: $[H^+] = 10^{-pH}$ (3.4)

Alkalinity was defined by equation 3.5:

$$Alk = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] - [H^+] \quad (3.5)$$

Alkalinity was calculated by equation 3.5

$$K_w = [H^+][OH^-] \quad (3.6)$$

K_w: ionic product for water (1.00 x 10^{-14} mol^2 dm^{-6})

The concentrations of species CO_3^{2-} and HCO_3^- were calculated from equations 3.5, 3.2 and 3.4. Then the concentration of dissolved carbon dioxide was determined by equation 3.3. EXCEL was used to program the data (pH, alkalinity and temperature).

3.2.4. Volatile Fatty Acid (VFA) Analysis

The concentration of VFAs was measured by the esterification method, using Volatile Acids TNT plus Reagent purchased from Hach Inc. (Ohio, USA). A spectrophotometer (Cole Parmer, model DR 2800), and a DRB200 Digital Reactor Block were used.

Procedure:

1. The reactor block was preheated up to 150 °C.
2. The cap of VFAs reagent vial was removed, and 0.4 ml of solution A sample was pipetted to the vial. Then 0.4 ml of sample was pipetted to the test vial.
3. The cap was placed and the solution was inverted several times.
4. The vial was put in the preheated reactor block and was heated for 10 minutes.
5. After 10 minutes, the test vial was placed in the rack and was cooled down to the room temperature (15°C-25°C).
6. 0.4 ml of solution B was added to the vial and the cap was replaced. The vial was inverted several times.
7. 0.4 ml of solution C was added to the vial. The cap was replaced and the vial was inverted several times.
8. 2 ml of solution D was added to the vial. The cap was replaced and the vial was inverted several times.
9. The test vial was placed in the spectrophotometer after three minutes and the value was read.

3.2.5.Total Nitrogen (TN)

Total nitrogen refers to all nitrogen forms. TN was measured by the Persulfate Digestion method using nitrogen, Total TNT plus Reagent purchased from Hach Inc. A spectrophotometer (Cole Parmer, model DR 2800), and a DRB200 Digital Reactor Block were used.

Procedure:

1. The reactor block was heated up to 100 °C.
2. 0.5 ml of sample, 2.0 ml of solution A and 1 of reagent B tablet were added in quick succession to reaction tube and then closed. The tube immediately was placed in the preheated reactor block and heated for 1 hour.
3. The tube was taken out from the reactor and was cooled down to room temperature.
4. 1 Micro Cap C was added to the tube.
5. The cap was replaced and the vial was inverted several times until streaks could not be seen in the tube.
6. 0.5 mL of the solution from the reaction tube was pipetted into a test vial.
7. 0.2 ml of solution D was pipetted into the test vial.
8. Quickly placed the cap and inverted the vial 2-3 times until streaks could not be seen in the vial solution.
10. After 15 minutes, placed the vial in the spectrophotometer and read the value.

3.2.6. Purity of the biogas

The biogas concentration was measured by gas chromatography (GC Varian CP-3800). A 10 ml gas-tight plastic syringe was used to take gas samples. The gas samples were injected into a Varian type 1041 on-column injector fitted with a Valco instruments Co. Inc. (VICI) pressurized valve delivery system as a 0.2 ml sample plug. The operating

conditions and column specification are shown in Table 2.4. Gas samples of 20%, 40%, 60%, 80% and 90% (CH_4/CO_2 vol/vol) were used to make the reference curve.

Table 3.4 Operation conditions and column specification

Parameter	Setting or type
Column (30 mm x 0.53 mm)	CARBOXEN 1010PLOT from SUPELCO
Carrier gas	Hydrogen
Detector	TCD
Sample delivery	VICI pressurized valve system
Injector	1041 On-column
Injector temperature (^oC)	225
Column oven temperature (^oC)	50-100 (5^oC/min)
Injection flow (ml/min)	5
Gas retention time (min)	20

3.2.7. Volatile suspended solids (VSS) and total suspended solids (TSS)

VSS and TSS (mass per volume, g/L or mg/L) were used to measure the sludge concentration according to the Standard Method (Clesceri et al., 1998). The material used: Gooch crucible,

Whatman GF/C filter paper, furnace (Fisher scientific isotemp muffle furnace), automatic dehumidifying desiccator, balance, vacuum filtration, and oven.

Steps:

1) A pre-dried Gooch crucible with Whatman GF/C filter paper in a Fisher Scientific was placed in an Isotemp muffle furnace at 550 ^{o}C $\pm$ 2 ^{o}C for an hour. Then desiccator was used to cool down the sample for half an hour. Then it was weighed immediately and its weight recorded as "A".
2) The sample was taken from the biomass and put into the Gooch crucible and filtered by vacuum filtration.
3) The Gooch crucible was put in the oven (105 ^{o}C $\pm$ 2 ^{o}C) and allowed it dry for an hour, then put it into desiccator to cool down for 10 min. Then it was weighed and its weight "B" was recorded.
4) Equation 2.7 was used to calculate the TSS : $\mathrm{TSS} = \frac{\mathrm{A-B}}{1\mathrm{ml}} \times 1000(\frac{g}{L})$
5) The Gooch crucible was put in the muffle furnace at 550 ^{o}C $\pm$ 2 ^{o}C for 2 hours, and then cooled down in a desiccator for half an hour. The crucible was weighed and recorded as weight "C".
6) VSS was calculated by using equation 2.8 : $\mathrm{VSS} = \frac{\mathrm{B-C}}{1\mathrm{ml}} \times 1000(\frac{g}{L})$, the residual in the Gooch crucible represents the ash content of the biomass which was calculated per mass of dry solids by using equation 2.9： $\mathrm{Ash} = 1 - \frac{\mathrm{VSS}}{\mathrm{TSS}} (\frac{g}{g})$

Three samples were taken to measure TSS and VSS concentration each time.

3.2.8. Volume of biogas and methane

The total volume of biogas was measured by collecting the biogas in a Tedlar plastic bag (500 ml) and by using the water displacement method.

The material: acidified water (1N sulfuric acid), graduated cylinder, 1L flask sealed with cap that has one inlet and one outlet, tubes and septum.

Steps:

1) 1L flask was filled completely with acidified water to prevent any dissolution of biogas, and connected to the Tedlar plastic bag by two plastic tubes.
2) The gas bag was pressed to transfer the biogas into the acid water flask.
3) The acid water was pumped into collecting flask.
4) The volume of acid water was determined by using the graduated cylinder.
5) The volume of methane was determined from its percentage in the biogas.

3.3 Experimental set up

The experiments were performed in batch mode of operation. Pyrex solution bottles (Fisher Scientific Ltd., Montreal) were used as batch reactors. Each bottle had a 1 L total volume and was equipped with a flexible cap and a rubber septum. The cap enabled the bottle to be sealed,

prevented the produced biogas to leak from the bottles, and enabled taking gas and liquid samples by using syringes without opening the cap.

The adequate nutrient ratio (COD: N: P) for bacterial growth is 200 -300: 5: 1 (Zhu et al., 2009). In the examined wastewater, the ratio of nitrogen to phosphorus was 1068: 7: 1, and it was not satisfactory to the bacteria. Potassium hydrogen phosphate with 98% purity (Fisher scientific Ltd) and ammonium chloride (crystalline 99.5%, Fisher scientific Ltd, Montreal) were used as nutrient solutions and were added to the examined wastewater as sources of nitrogen and phosphorus to meet the bacterial growth requirements.

3.3.1 Operation and sampling

Three different temperatures (20 ^{o}C, 30 ^{o}C, 35 ^{o}C) and three pH values (6.5, 7, and 7.5) were used for the batch experiments, performed as three groups. Each group had the same set up and only the temperature was different. As an example, the first group was performed at three pH values of 6.5, 7, and 7.5 at the temperature of 20 ^{o}C, and was sub-divided in to two sets. In the first set, all bottles received 400 ml wastewater mixed with carbon dioxide, and the second set was the same as the first set but without the additional of carbon dioxide. All bottles received 2g of volatile suspended solids (VSS)/L biomass and NaOH and HCl solutions to adjust the pH to 6.5, 7, 7.5. The headspace of each bottle was purged with nitrogen gas for 5 min. Then the bottles were put in the incubator at temperatures of 20 ^{o}C, 30 ^{o}C, and 35 ^{o}C. Process parameters including the COD, biogas production, and methane content were monitored during the

experiment. A Tedlar bag with pipe and needle was used to take the gas samples and a 10 ml sterile plastic syringe was used to take liquid samples.

Chapter 4: Results and Discussion

In this chapter, the results of the batch experiments are presented and the discussion of results is provided. The sample analysis was based on the standard methods as mentioned in Chapter 3. Each series of experiments was carried out for 12 days until biogas production ceased.

4.1 Carbon dioxide removal under various conditions

The main objective of this work was to reduce carbon dioxide concentration in water. The initial and final concentrations of carbon dioxide play a major role in its removal. Figure 4.1 shows the initial concentrations of carbon dioxide.

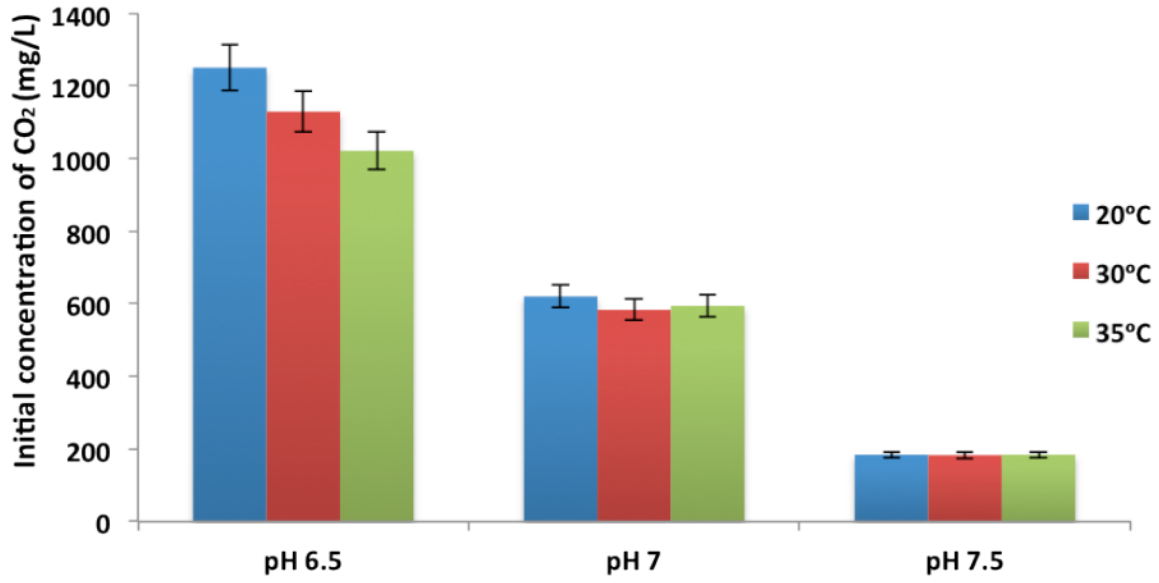


Figure 4.1 Initial concentration of carbon dioxide

As it shows in Figure 4.1, the highest initial concentration of carbon dioxide was observed at pH 6.5 while the lowest concentration was observed at pH 7.5 had. This could be related to the dissolve carbon dioxide equilibrium (Figure 4.2). At lower pH, there is more carbon dioxide in aqueous form, and at higher pH, the majority of dissolved carbon dioxide is in the form of HCO^{3-} instead of CO_2.

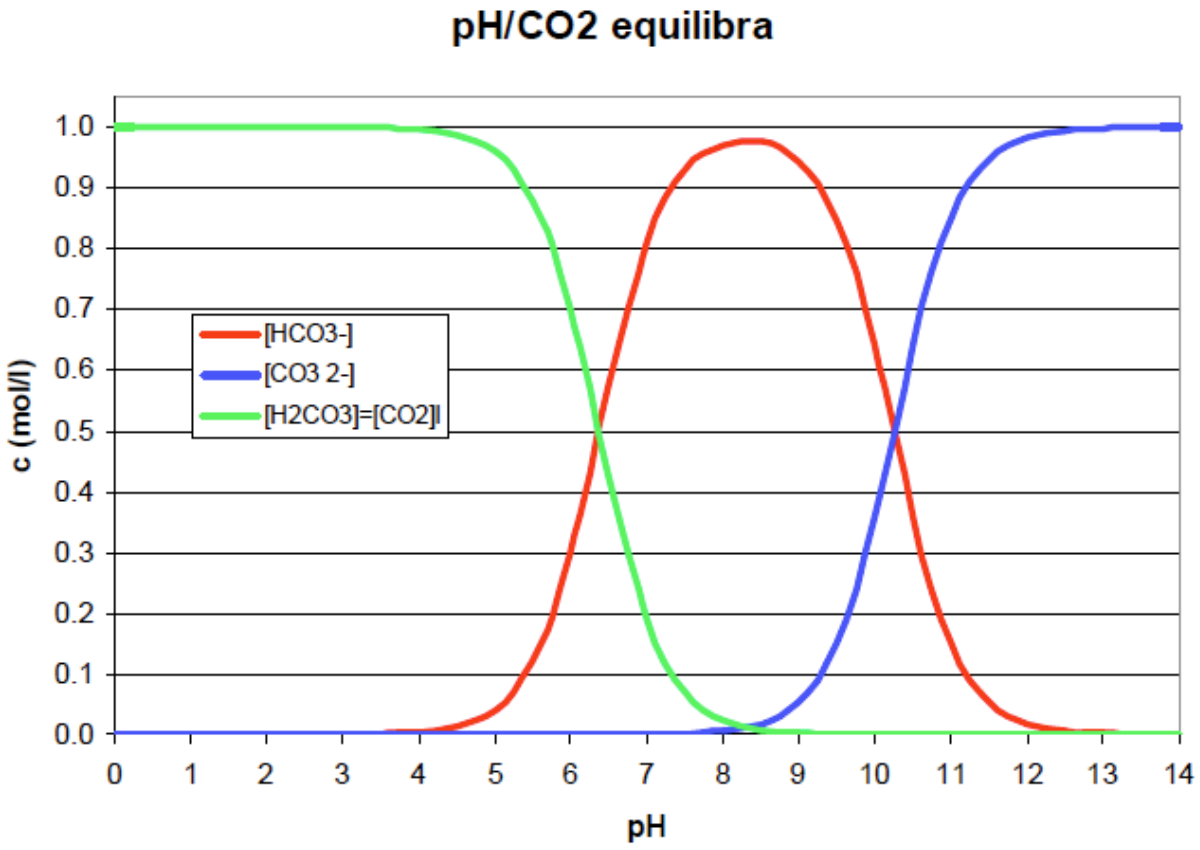


Figure 4.2. pH and CO_2 species (http://www.pwtag.org/researchchdocs/Used%20Ref%20docs/52%20Carbondioxide%20in%20water%20equilibrium.pdf)

Figure 4.3 shows the final concentration of dissolved carbon dioxide. It shows that at lower temperature, the final concentration is higher. That shows less carbon dioxide was used by the

microbial at lower temperature. Temperature has a significant impact on microbial activity by affecting the solubility of substrate, ionization equibria, and the bioavailability of nutrients. So lower temperature, the lower the microbial activity.

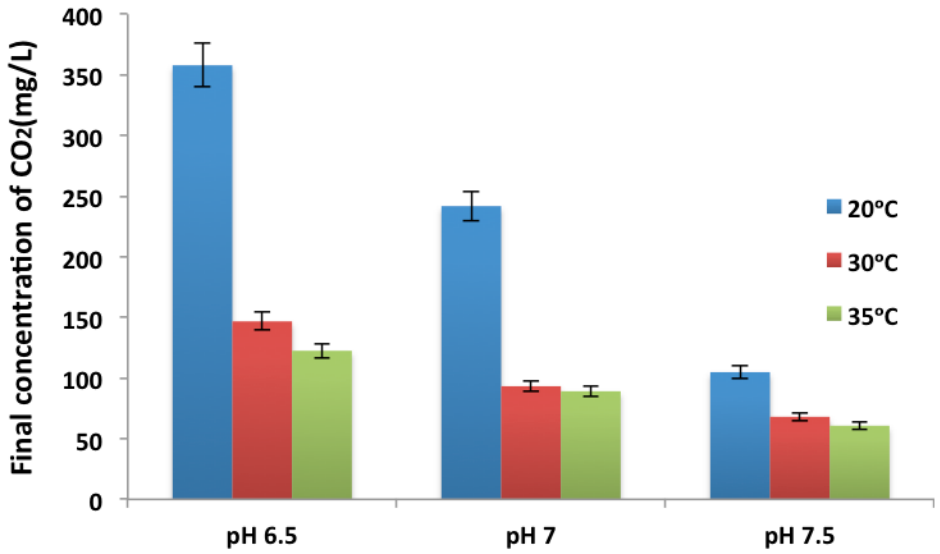


Figure 4.3 Final concentration of carbon dioxide after treatment

The remove efficiency of dissolved carbon dioxide in water at different pH values of 6, 7, and 7.5 at the temperatures of 20 °C, 30 °C, and 35 °C were calculated from the initial and final concentrations of carbon dioxide dissolved in the wastewater (Figure 4.4). The results show that the removal efficiency of dissolved carbon dioxide increased with the increase of temperature, whereas it declined with the increase of liquid pH. The removal of dissolved carbon dioxide at the temperature of 35 °C was higher compared to the results at 20 °C and 30 °C at any given pH value. For example, at pH 7.5, 67% of dissolved carbon dioxide was removed at 35 °C while 56% and 63% of dissolved carbon dioxide were removed at 20 °C and 30 °C respectively. The removal of dissolved carbon dioxide at pH 6.5 and 7 are more efficient than that at pH 7.5 at different temperatures. For example, at 20 °C, 82% of dissolved carbon dioxide was removed at

pH 6.5. However, 74% and 56% of dissolved carbon dioxide were removed at pH 7 and pH 7.5, respectively. Maximum dissolved carbon dioxide removal efficiency was obtained at a temperature of 35 °C and pH 6.5. Carbon dioxide is used by microorganisms, and as shown by the following relationship, as aqueous carbon dioxide is consumed, the equilibrium in equation 4.1 shifts to aqueous carbon dioxide side.

$$CO_{2(aq)} + H_2O \Longleftrightarrow H^+ + HCO_3^- \qquad (4.1)$$

The increase of temperature resulted in higher removal efficiency of dissolved carbon dioxide at all pH values. This could be the consequence of biomass reaction at higher temperature (35 °C). However, it is observed that temperature did not have a significant impact on CO_2 removal.

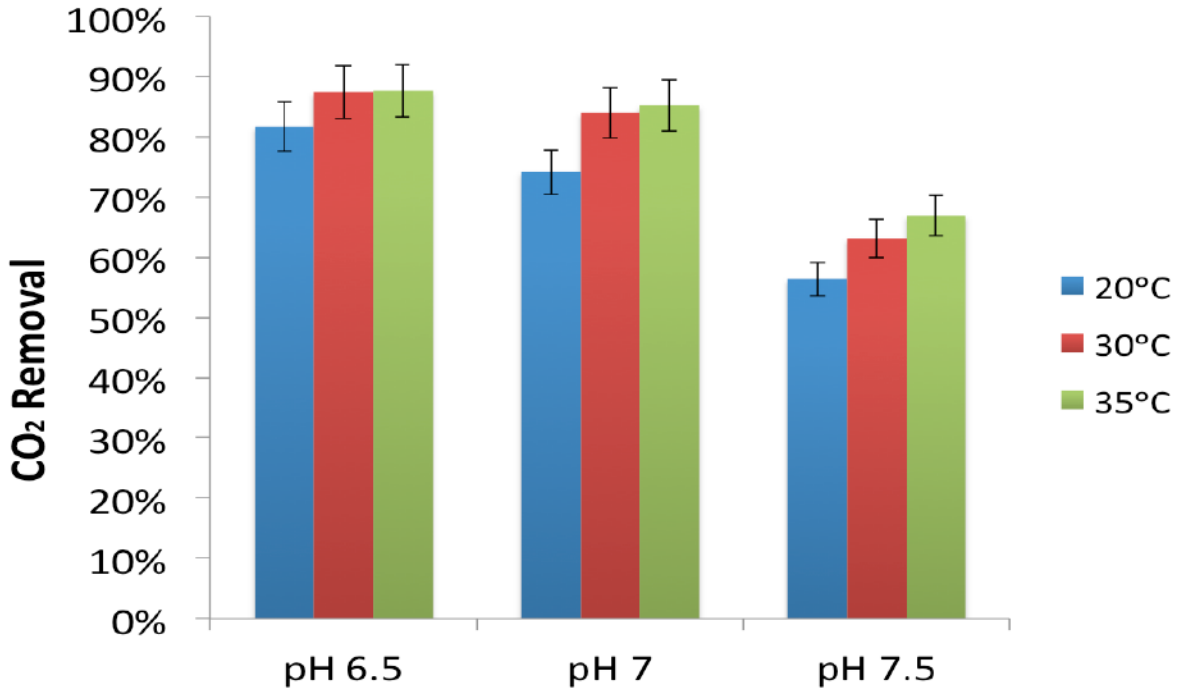


Figure 4.4 Carbon dioxide removal under various conditions of pH and temperature

4.2 Impact of carbon dioxide on COD removal under various operating conditions

In order to investigate the impact of the addition of carbon dioxide on the removal of COD, the removal of COD was tested at temperatures of 20 ^{o}C, 30 ^{o}C, and 35 ^{o}C.

4.2.1 Impact of carbon dioxide on COD removal at various pHs at 20 ^{o}C

The results of COD removal with and without carbon dioxide addition at different pH values and at the temperature of 20 ^{o}C are presented in Figures 4.5 to 4.7. The results show that while the addition of carbon dioxide has an insignificant impact on increasing the COD removal efficiency, it produced higher COD removal efficiencies at different pH values (pH 6.5, pH 7, pH 7.5) and at the temperature of 20 ^{o}C. At pH 6.5, the overall COD removal was 562 mg/L with the injection of carbon dioxide, while without carbon dioxide injection it was 520 mg/L. At pH 7, the COD removal was 517 mg/L with the injection of carbon dioxide, while without carbon dioxide injection it was 451 mg/L. At pH 7.5, COD removal was 377 mg/L with the injection of carbon dioxide, while without carbon dioxide injection, it was 345 mg/L. Thus, additional carbon dioxide can improve the efficiency of COD removal.

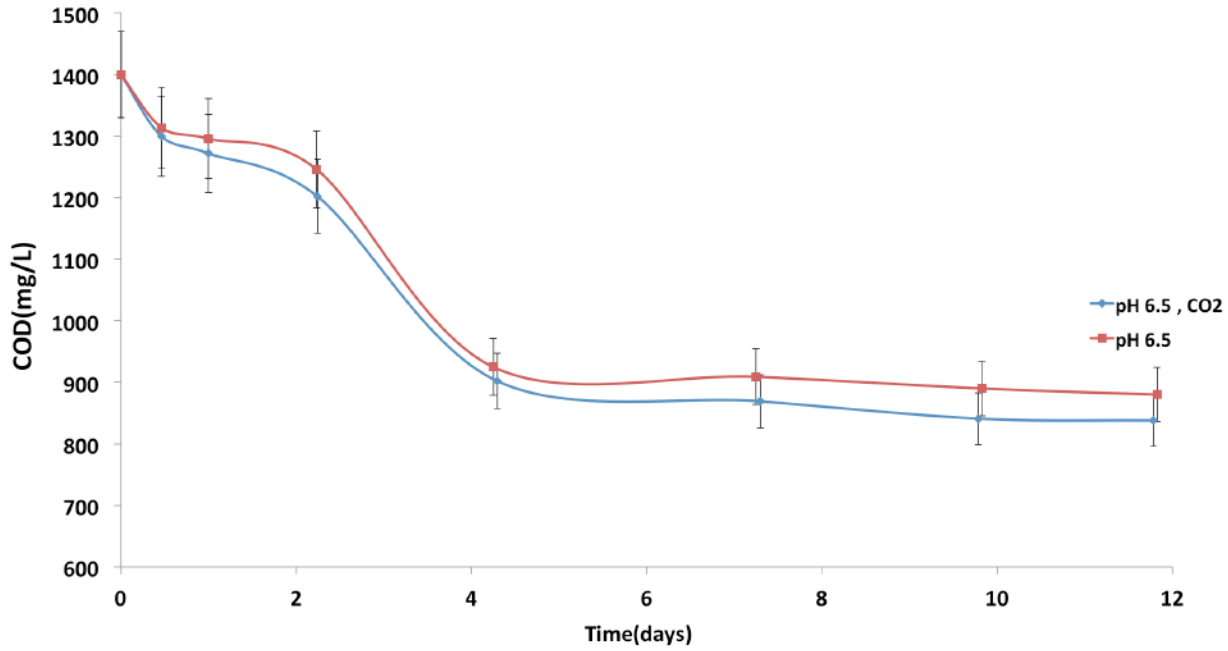


Figure 4.5 COD removal with and without carbon dioxide addition at pH 6.5 and at 20 °C

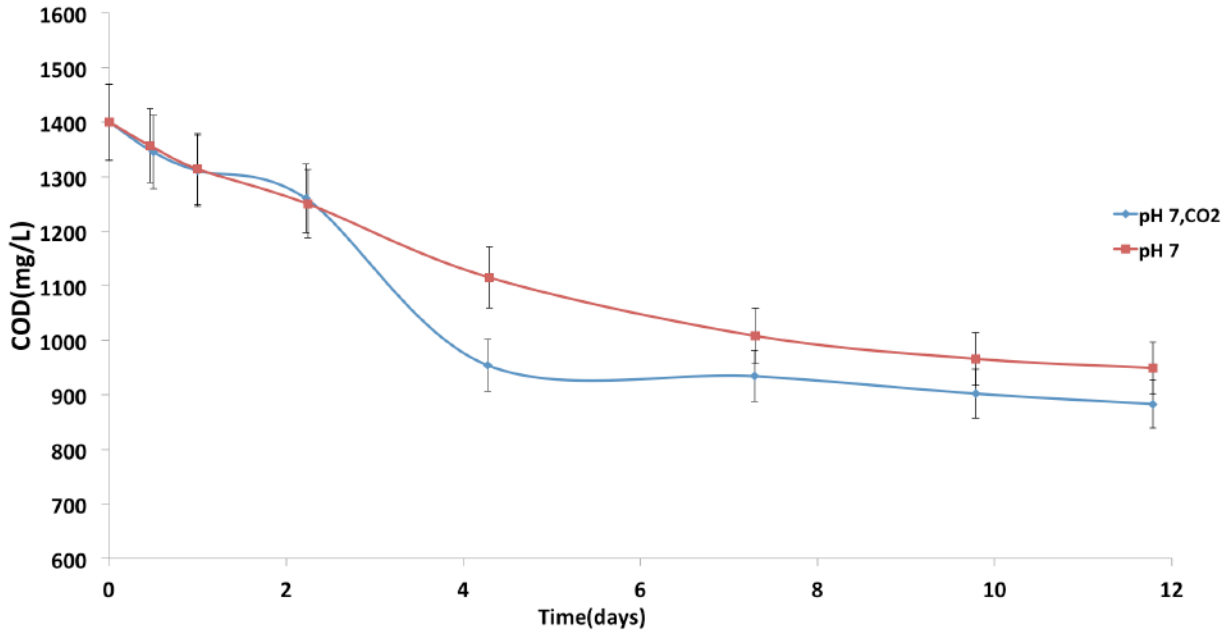


Figure 4.6 COD removal with and without carbon dioxide addition at pH 7 and at 20 °C

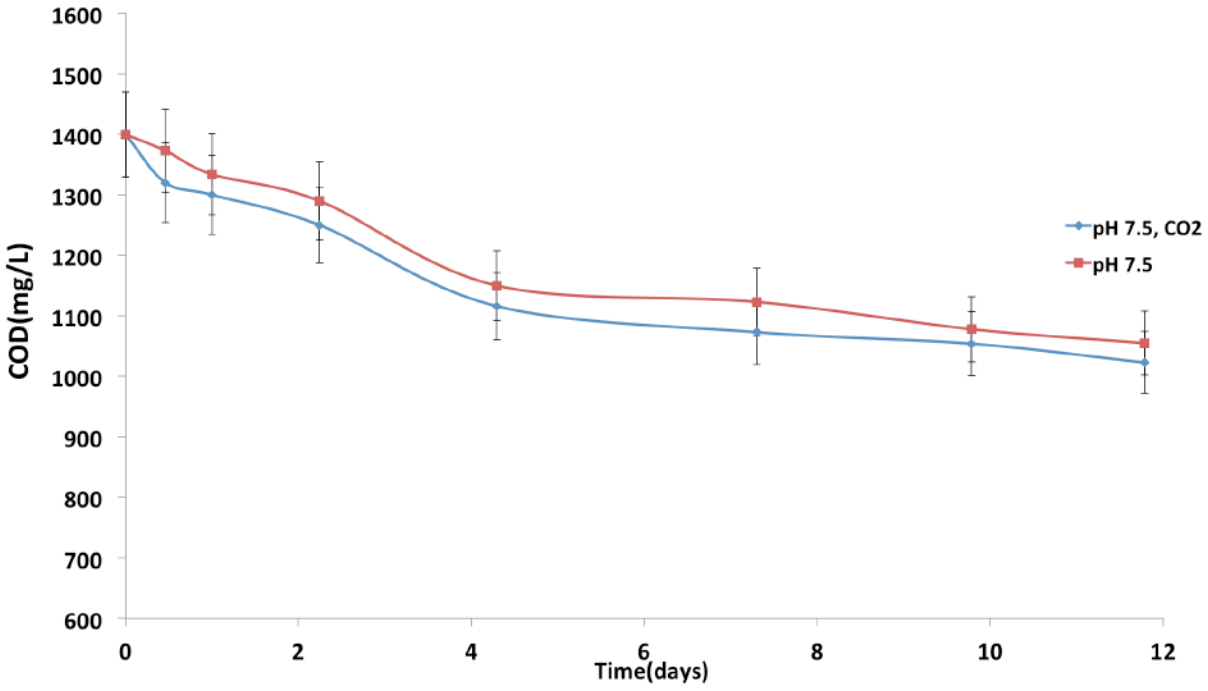


Figure 4.7 COD removal with and without carbon dioxide addition at pH 7.5 and at 20 °C

Figure 4.8 shows the results of COD removal with the injection of carbon dioxide at different pH values (6.5, 6, 7) at 20 °C. The removal of COD increased with the decrease of pH. The optimum condition for COD removal was at pH 6.5.

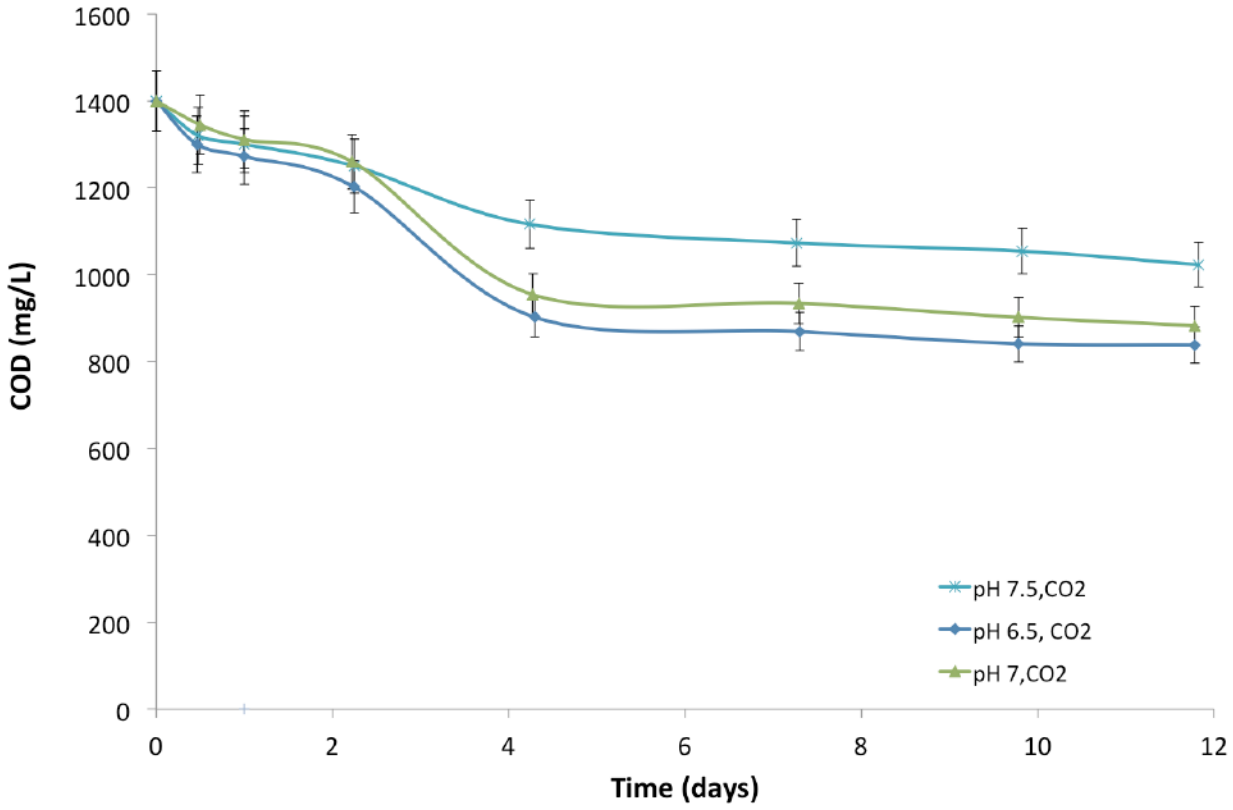


Figure 4.8 COD removal with the addition of carbon dioxide at pH values of 6.5, 7.0 , 7.5 and at 20 °C

4.2.2 Impact of carbon dioxide on COD removal at 30 °C

The results of COD removal with and without carbon dioxide addition at different pH values and at the temperature of 30 °C are shown in the Figures 4.9 to 4.11. According to the results, the impact of injected carbon dioxide is negligible on increasing the COD removal efficiency. However, the addition of carbon dioxide at different pH values (6.5, 7.0, and 7.5) and at the temperature of 30 °C resulted in a slightly better COD removal rate compared to the results

without carbon dioxide addition. At pH 6.5, the COD removal efficiency was 43 % with the injection of carbon dioxide, while without carbon dioxide injection it was 40 %. At pH 7, the COD removal was 40% with the injection of carbon dioxide, while without carbon dioxide injection it was 38%. At pH 7.5, the COD removal was 33% with the injection of carbon dioxide, while without carbon dioxide injection, it was 31%. Additional carbon dioxide can improve the efficiency of reaction at 30 °C .

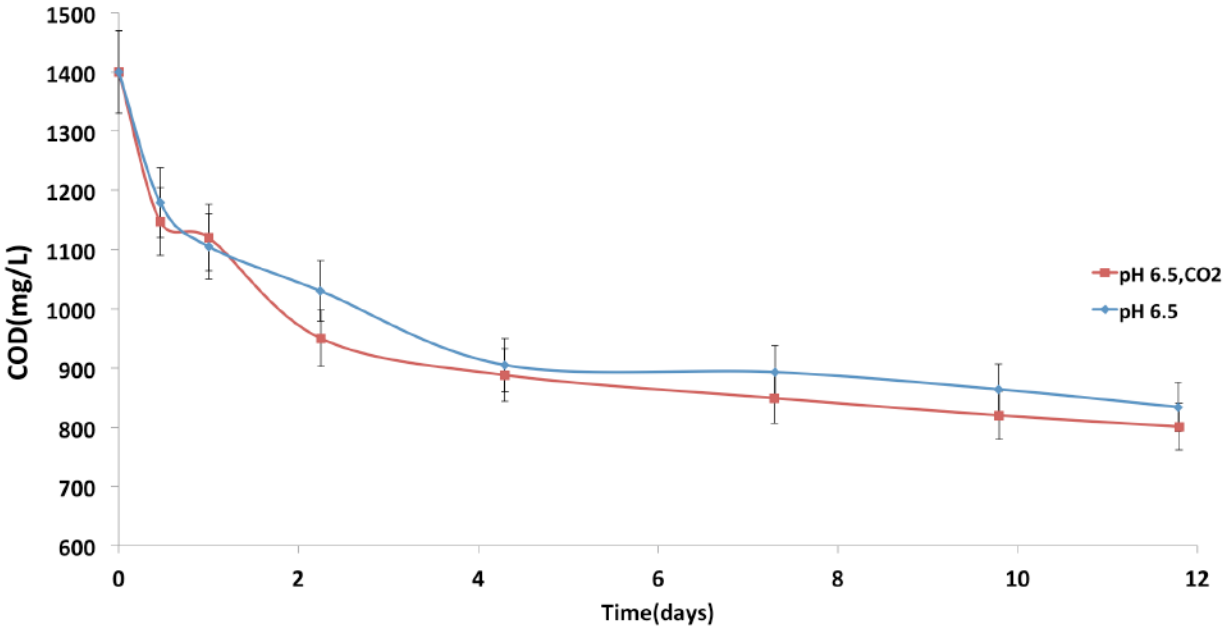


Figure 4.9 COD removal with and without carbon dioxide addition at pH 6.5 and at 30 °C

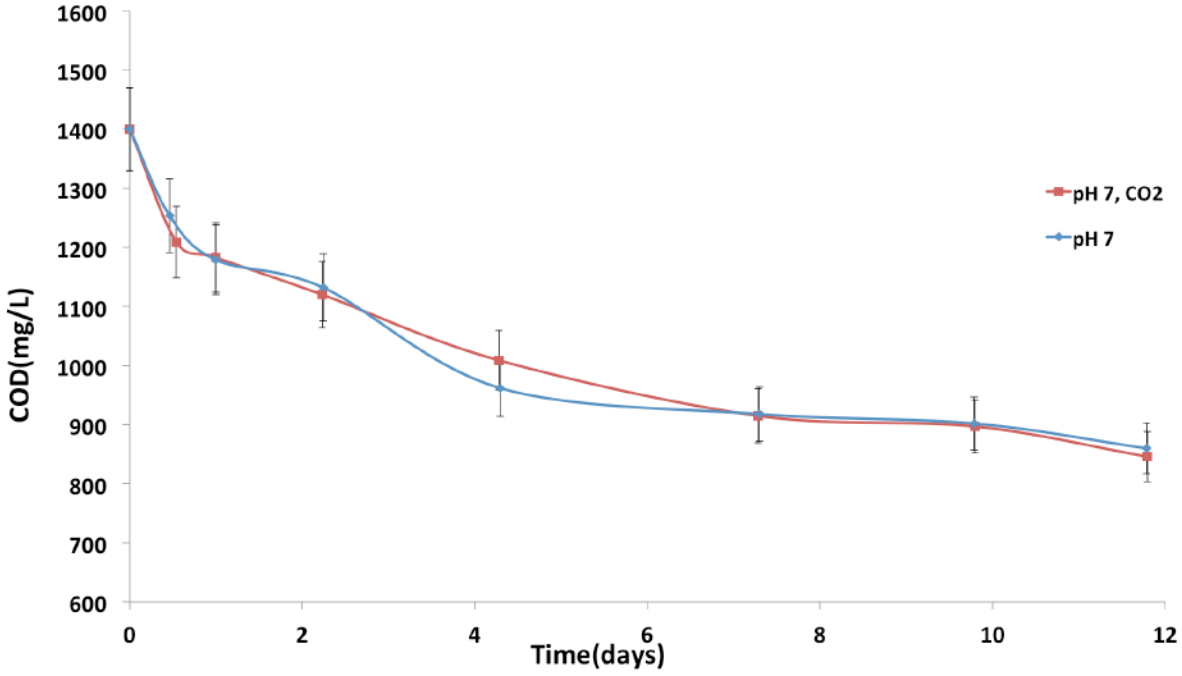


Figure 4.10 COD removal with and without carbon dioxide addition at pH 7 and at 30 °C

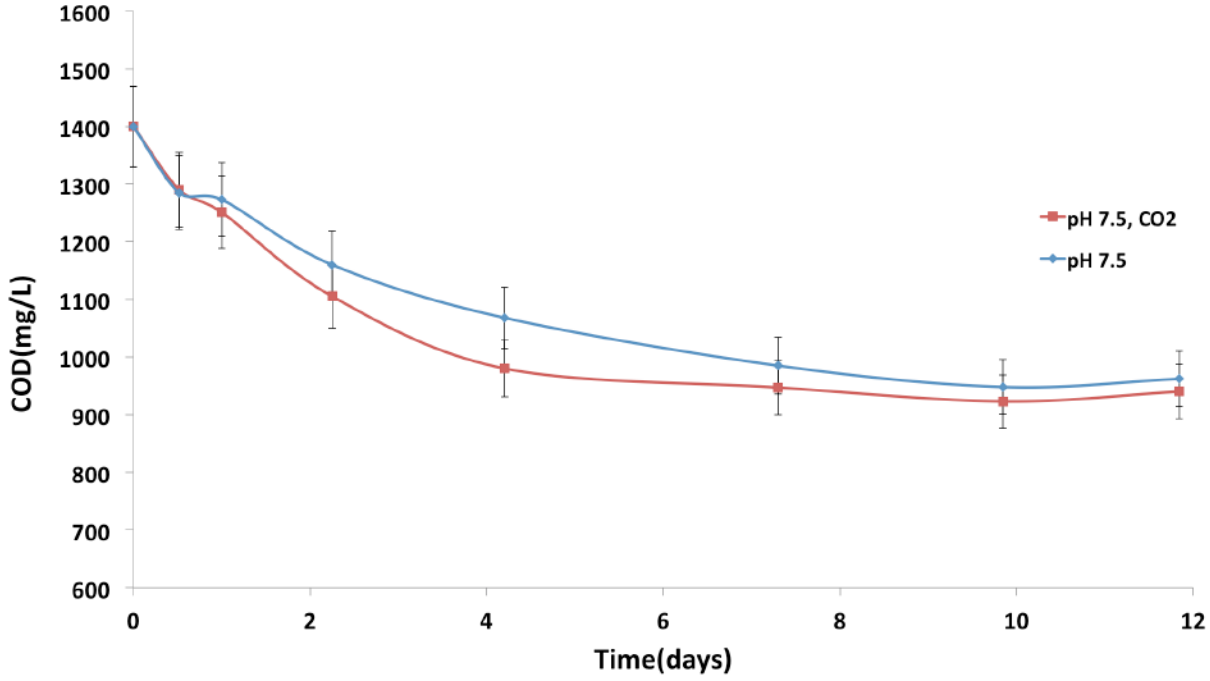


Figure 4.11 COD removal with and without carbon dioxide addition at pH 7.5 and at 30 °C

Figure 4.12 shows the removal of COD with the injection of carbon dioxide at different pH values (6.5, 7.0, 7.5) at 30 °C. While pH showed a minor effect on COD removal, the removal of COD increased with the decrease of pH, reaching a maximum value at pH 6.5.

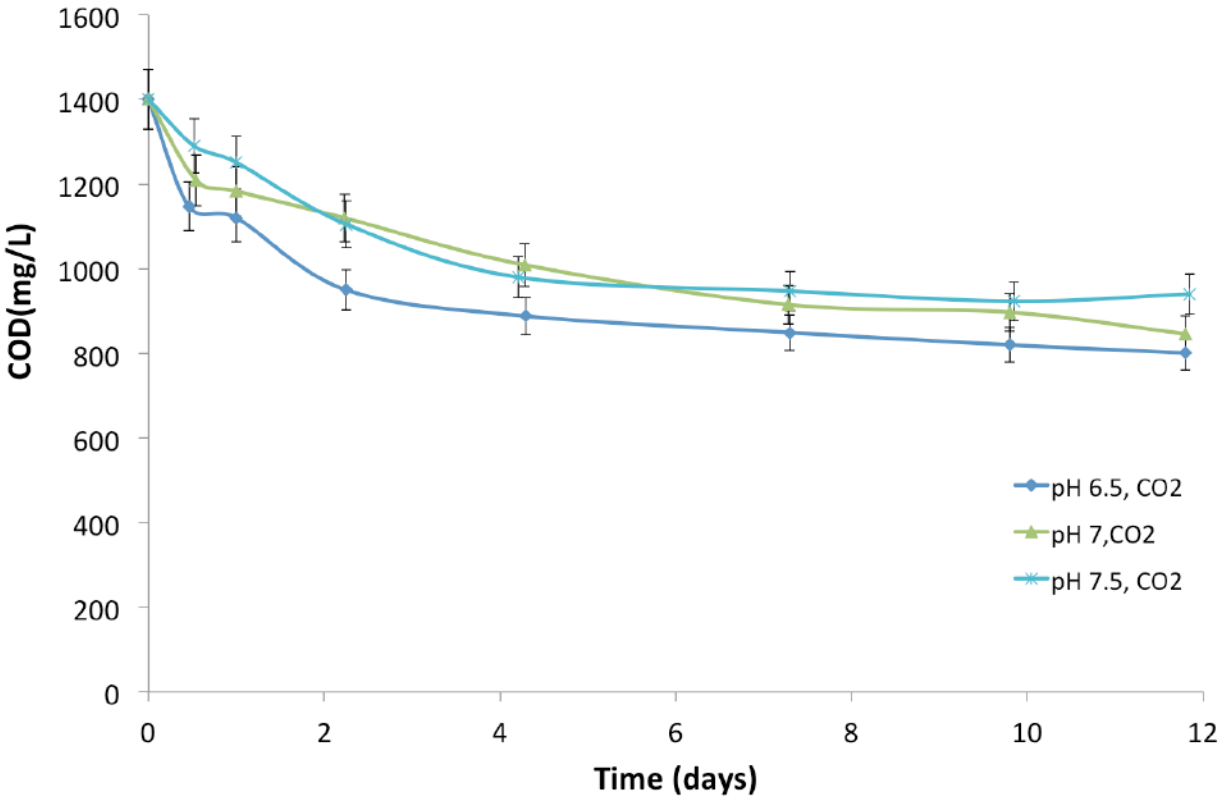


Figure 4.12 COD removal with the addition of carbon dioxide at pH values of 6.5 to 7.5 and at 30 °C

4.2.3 Impact of carbon dioxide on COD removal at 35 °C

At the temperature of 35 °C and at three pH values, respectively, the impacts of carbon dioxide addition on the reduction of COD concentration are presented in Figures 4.13 to 4.15. According

to the results, the addition of carbon dioxide at different pH values and at the temperature of 35 °C results in an insignificant increase in COD removal compared to the results without carbon dioxide addition. At pH 6.5, the COD removal efficiency was 49% with the injection of carbon dioxide, while without carbon dioxide injection, it was 47 %. At pH 7, the COD removal efficiency was 46 % with the injection of carbon dioxide, while without carbon dioxide injection, it was 43%. At pH 7.5, the COD removal efficiency was 42 % with injection of carbon dioxide, while without carbon dioxide injection, it was 39 %. It can be seen that additional carbon dioxide can improve the removal efficiency at 35 °C at any given pH.

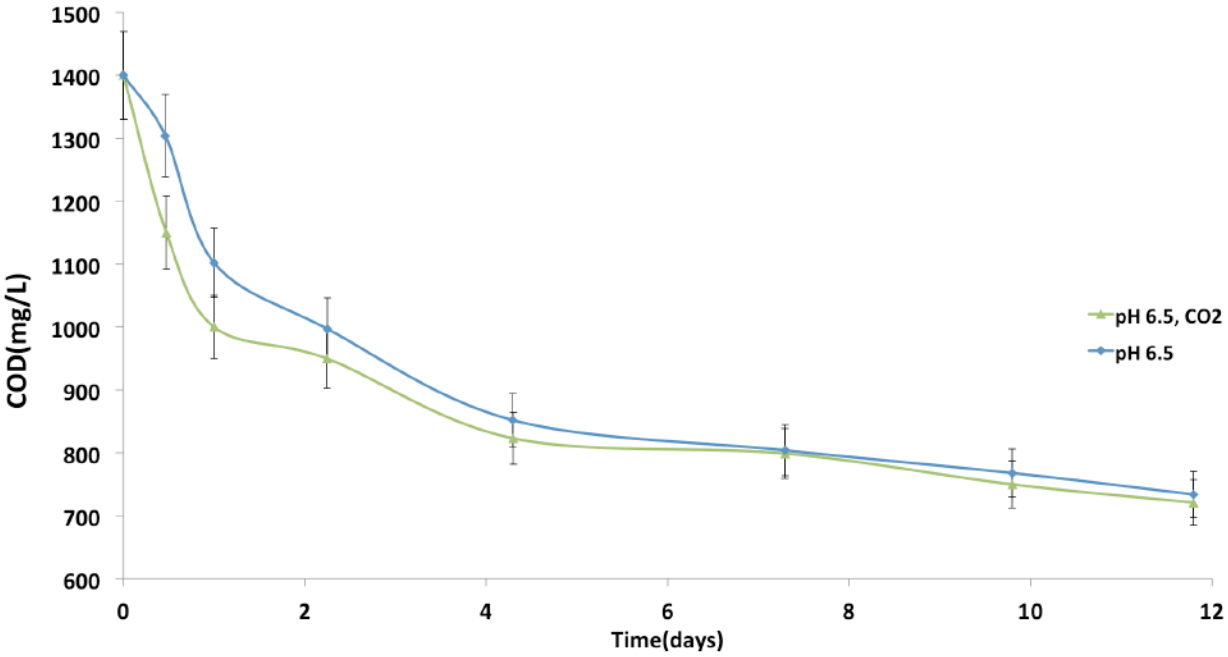


Figure 4.13 COD removal with and without carbon dioxide addition at pH 6.5 and at 35 °C

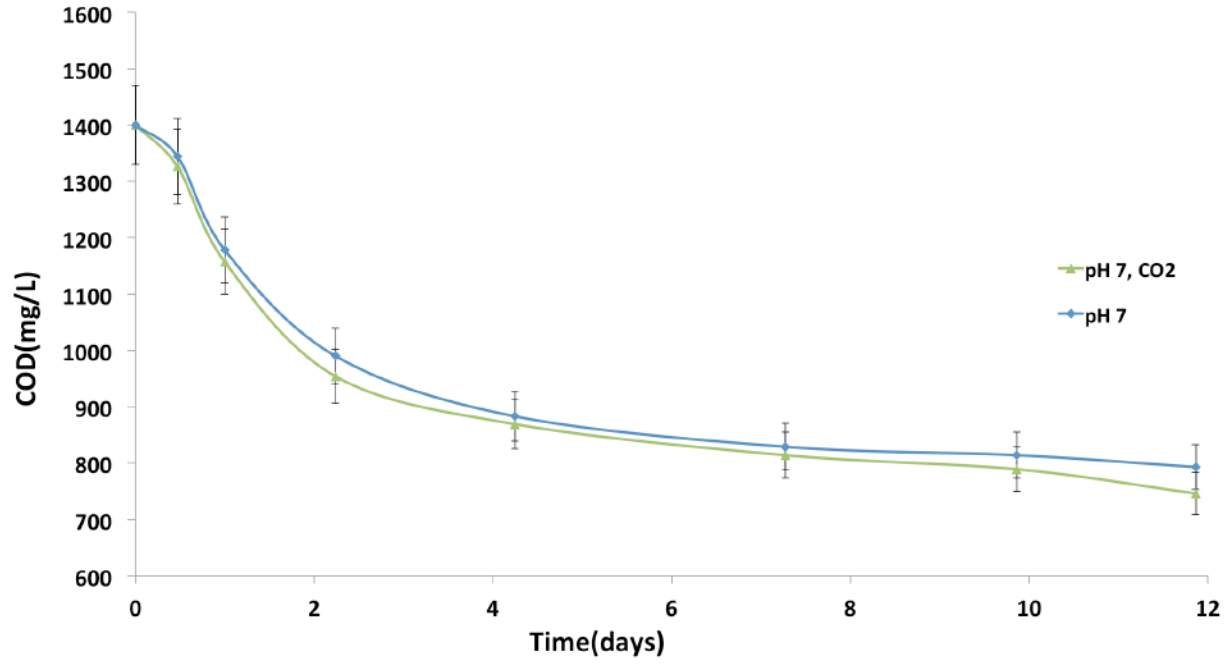


Figure 4.14 COD removal with and without carbon dioxide addition at pH 7 and at 35 °C

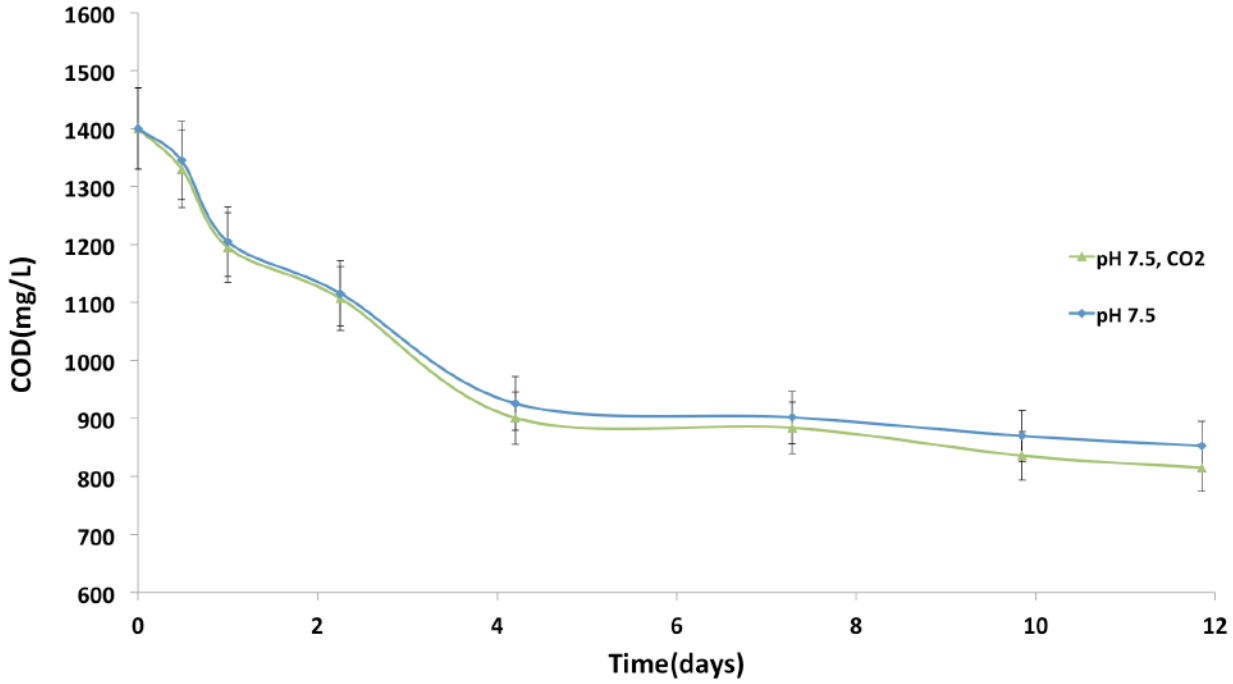


Figure 4.15 COD removal with and without carbon dioxide addition at pH 7.5 and at 35 °C

The tests at three pH values show the same trend for COD removal. All of them show a slight improvement in COD removal with the injection of carbon dioxide. Figure 4.16 presents the effect of pH on COD removal at 35 °C, and shows that the highest removal was obtained at pH 6.5. This could be related to the fact that the optimum pH for biogas generation by most methanogens is around neutrality (Jones et al. 1987; Cerning et al., 2010).

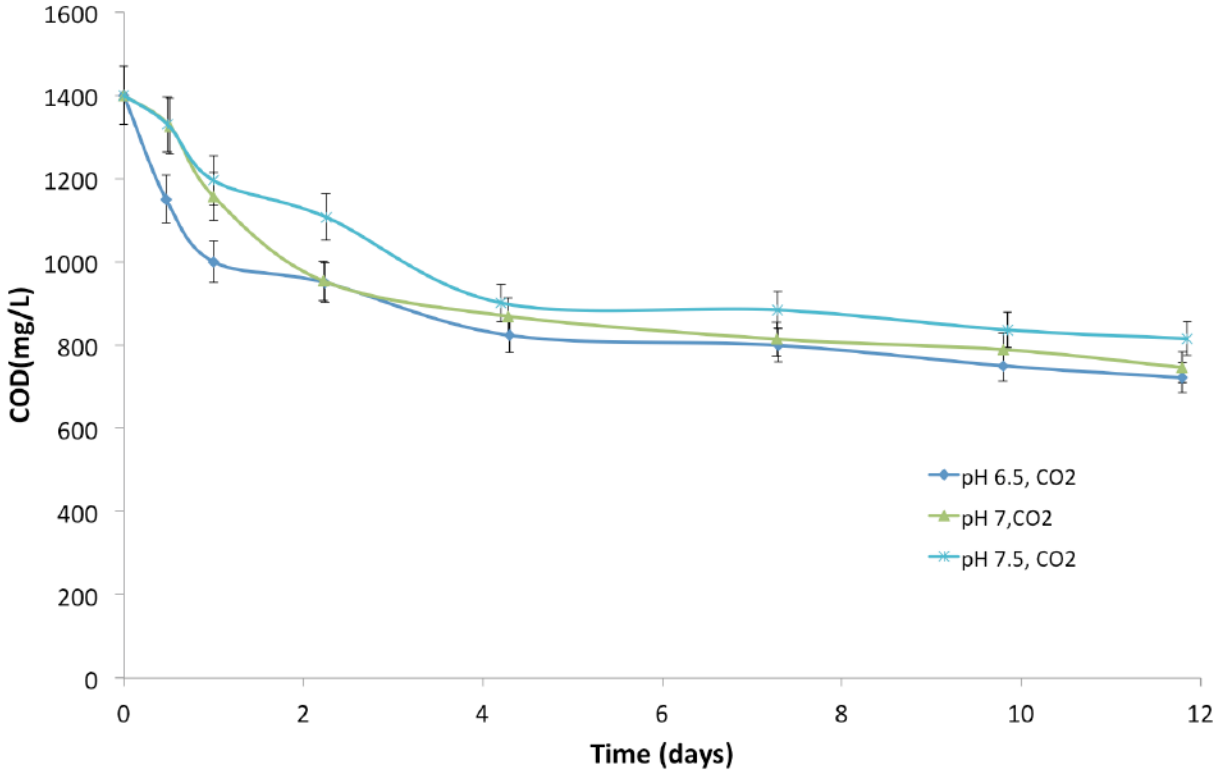


Figure 4.16 COD removal with the addition of carbon dioxide at pH values of 6.5 to 7.5 at 35 °C

4.3 Impact of temperature of COD removal

The results of COD removal at different temperatures of 20 °C, 30 °C, and 35 °C and at pH 6.5 with the addition of CO_2 are shown in Figure 4.17 The removal of COD improves with the increase of temperature, producing the highest removal efficiency at 35 °C. For example, at pH 6.5, at 35 °C in the presence of carbon dioxide, the removal efficiency was 49 %, while at 20 °C and at 30 °C it was 40% and 43%, respectively. At pH 7 and pH 7.5, the COD removal efficiency increased with the increase of pH. Figures 4.18 and 4.19 show the removal of COD at different temperatures and at pH 7 and 7.5, respectively. Similar trends were observed whereby COD removal increased with the increase of temperature.

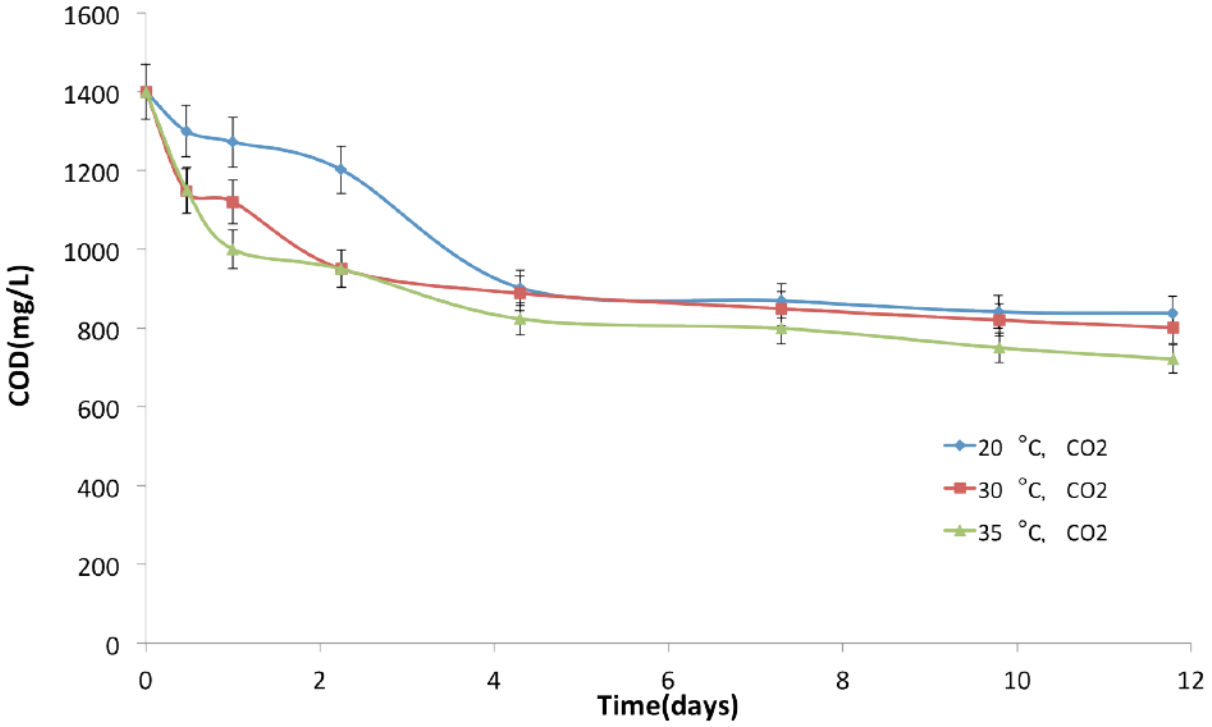


Figure 4.17 COD removal with the addition of carbon dioxide at pH 6.5 and at 20 °C, 30 °C, and 35 °C

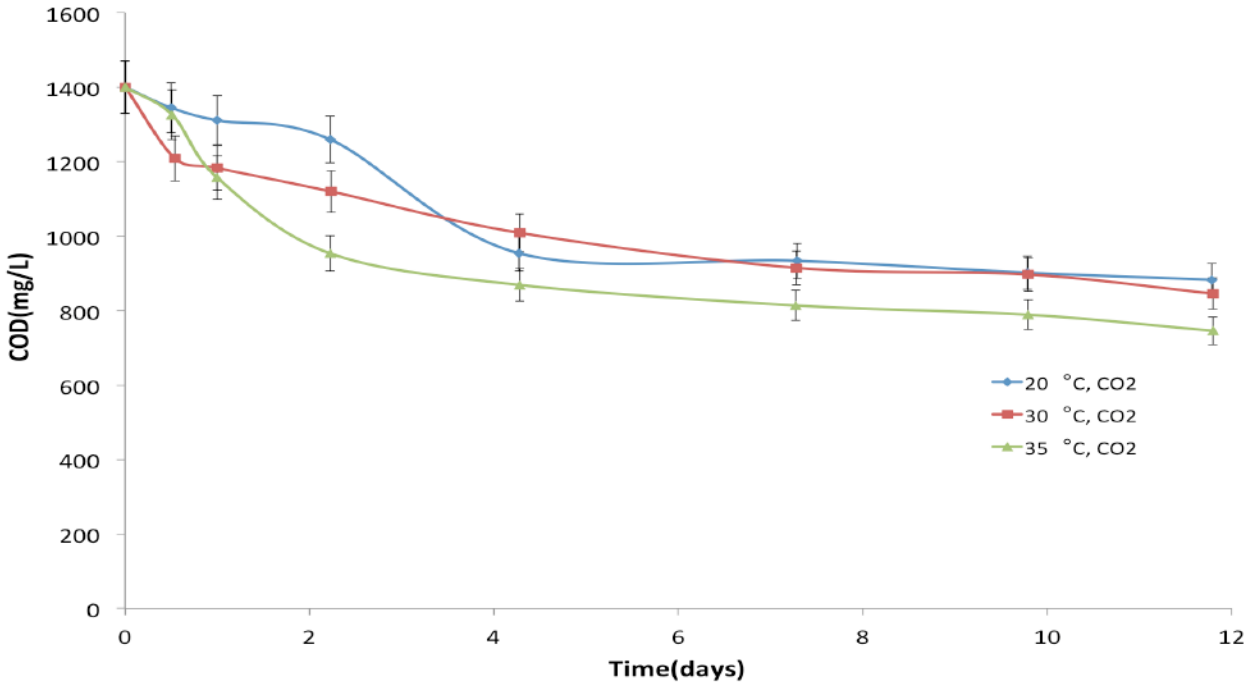


Figure 4.18 COD removal with the addition of carbon dioxide at pH 7 and at 20 °C, 30 °C, and 35 °C

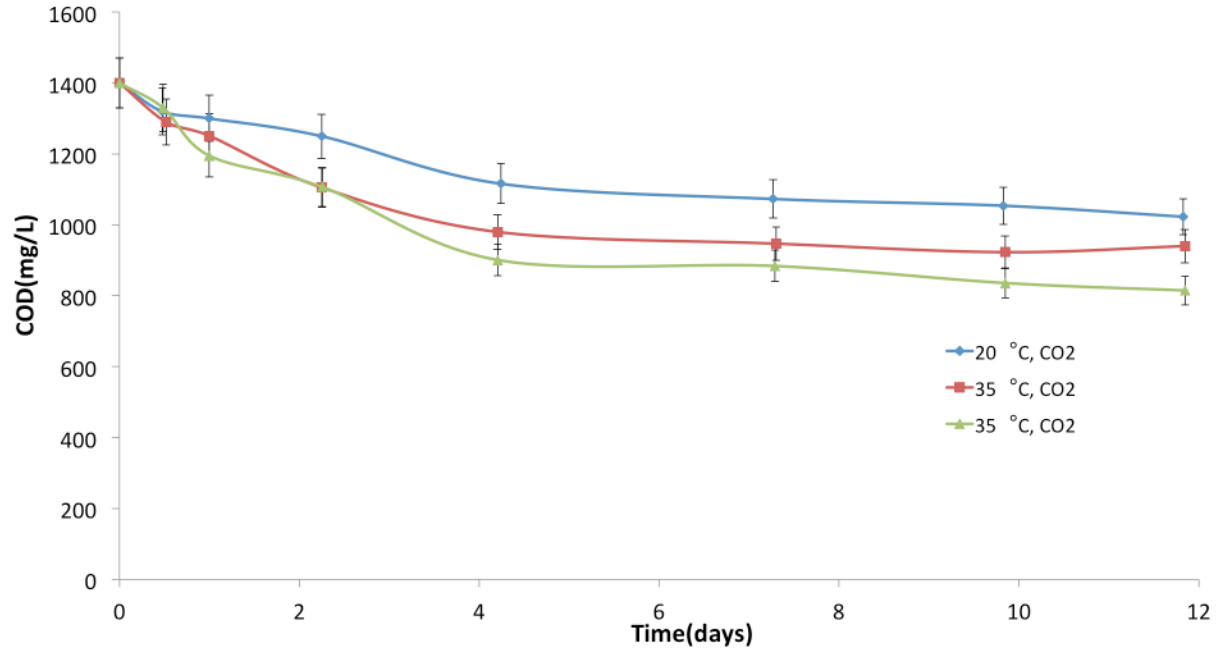


Figure 4.19 COD removal with the addition of carbon dioxide at pH 7.5 and at 20 °C, 30 °C, and 35 °C

The results show a wide variation in the remaining concentration of COD at the end of experiments at the different examined temperatures and at the same pH value. For example, at pH 7.5 and 35 ^{o}C, the remaining COD was 815 mg/L with the injection of carbon dioxide, while at 20 ^{o}C and 30 ^{o}C the remaining COD was 1023 mg/L and 940 mg/L, respectively. Similar trends were observed for pH 6.5 and pH 7.0. The observed trend could be related to the increased activity of microorganisms at higher temperatures.

4.4 Overall COD Removal and Removal Rate

Figures 4.20 to 4.23 show the COD removal rate at various operating conditions. The COD removal was highest during the first four days of experiments compared to the following days. The results of COD removal rate at 20 ^{o}C and at pH 6.5 with and without the injection of CO_2 are shown in Figure 4.20. The results show that the highest COD removal rate is reached during the first half day at any given pH at 20 ^{o}C. Also, at any given pH and in the presence of carbon dioxide a higher COD removal rate was obtained compared to the rate without the injection of carbon dioxide. For example, at pH 6.5 with the injection of carbon dioxide, the COD removal rate was 217 mg/d while without the injection of carbon dioxide it was 186 mg/d. At pH 7 with the injection of carbon dioxide, COD removal rate was 110 mg/ d, while without the injection of carbon dioxide it was 83 mg/d. At pH 7.5 with the injection of carbon dioxide, COD removal rate was 168 mg/d, while without the injection of carbon dioxide it was 54 mg/d. Figures 4.21 and 4.22 show similar trends.

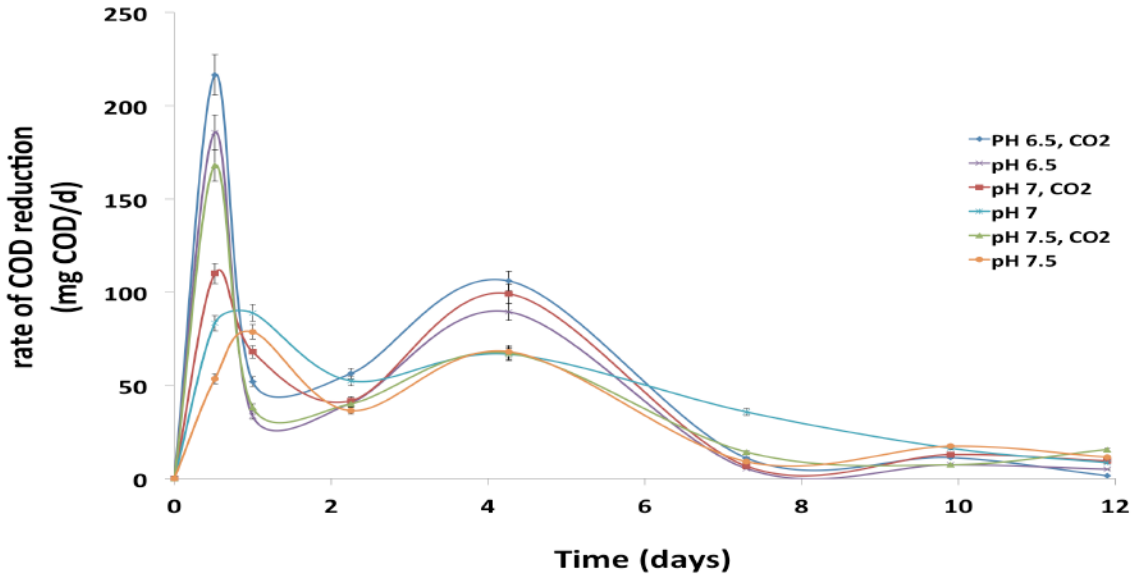


Figure 4.20 COD removal rate at various operating conditions at 20 °C

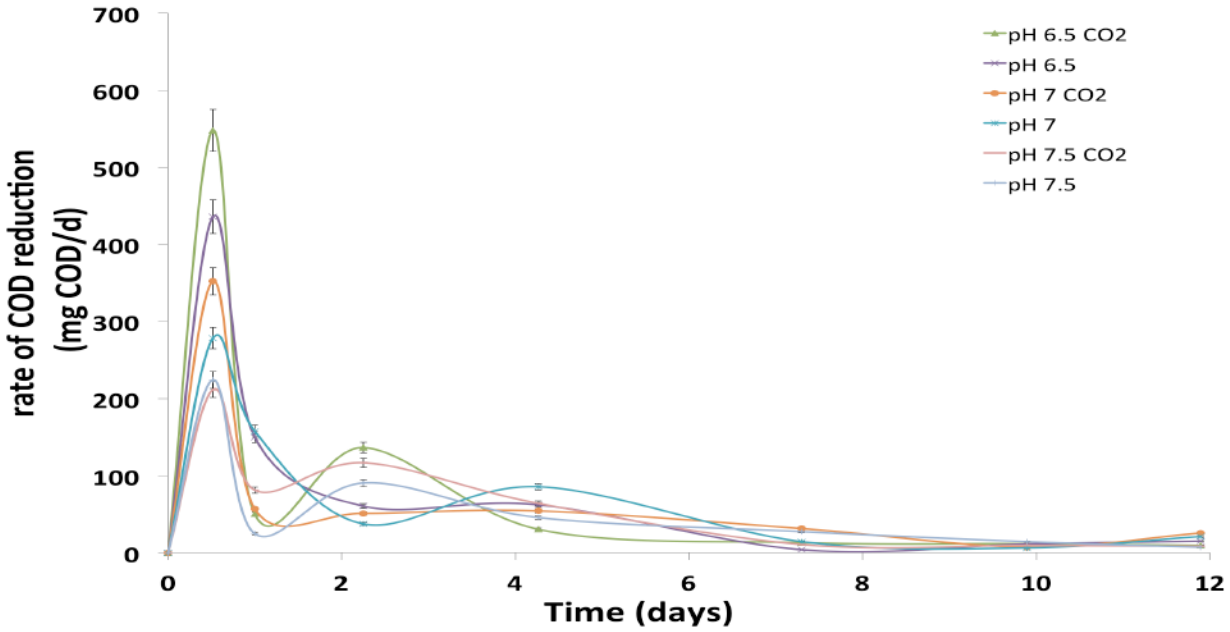


Figure 4.21 COD removal rate at various operating conditions at 30 °C

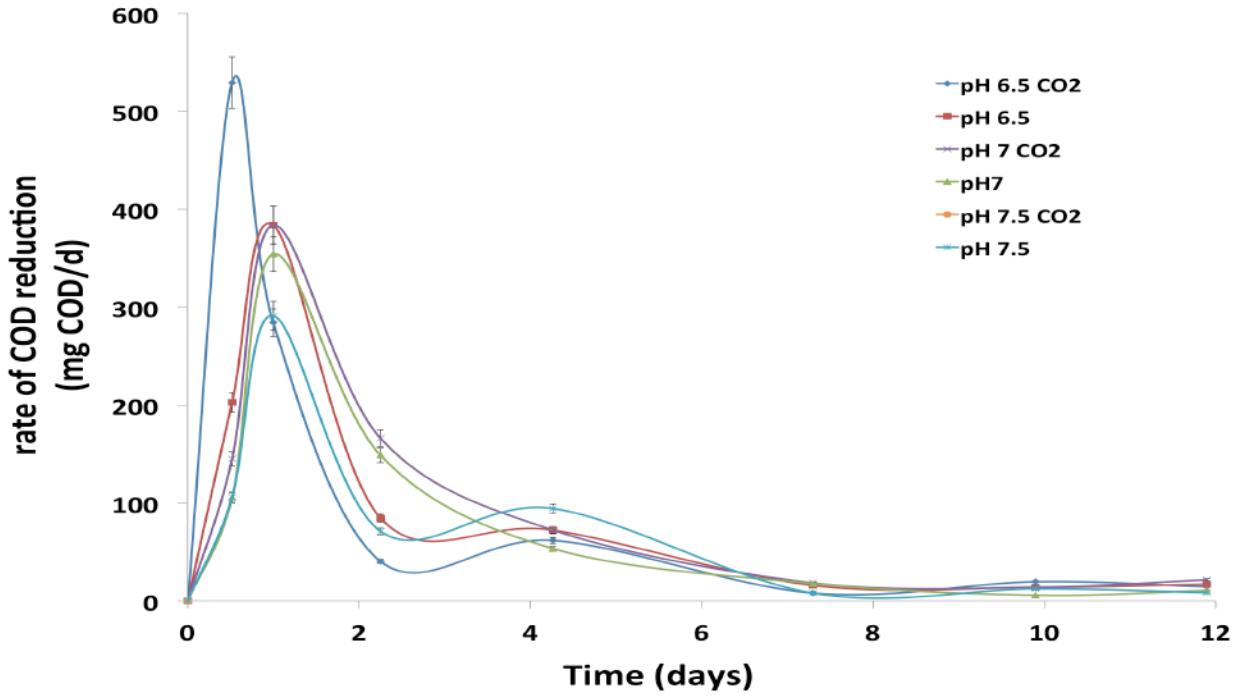


Figure 4.22 COD removal rate at various operating conditions at 35 °C

Overall COD Removal

Figure 4.23 shows the overall COD removal efficiency at different conditions and Figure 4.21 shows the COD removal rates at various conditions. Both Figures 4.23 and 4.24 show that at any given pH, COD reduction is maximum at the highest examined temperature of 35 °C, while being minimum at 20 °C. However, at any given temperature, COD reduction is maximum at pH 6.5 while being minimum at pH 7.5.

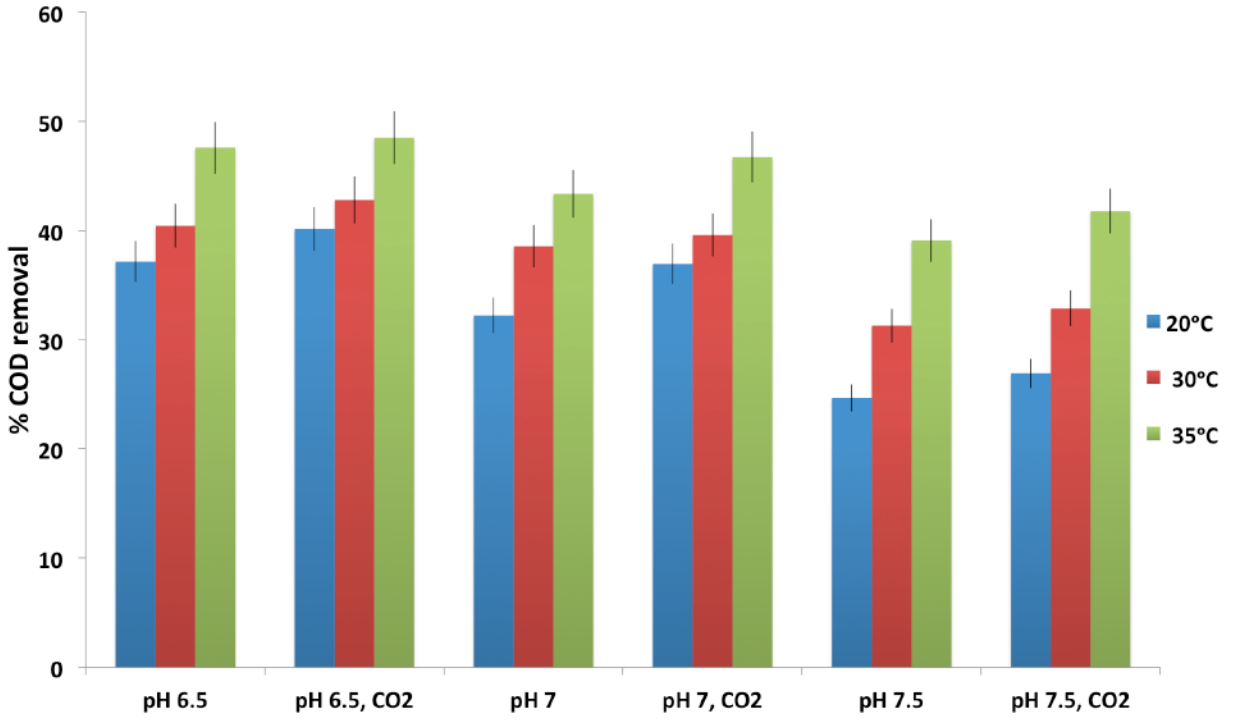


Figure 4.23 COD removal at different pH and temperatures

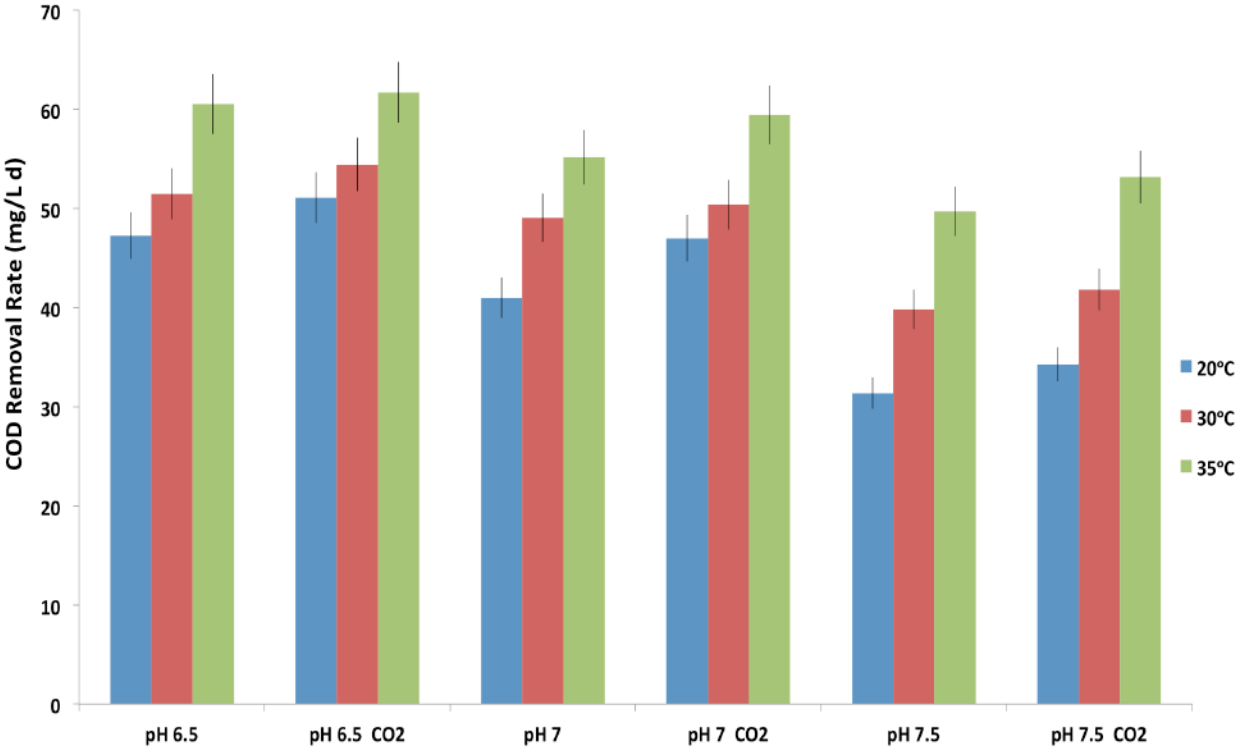


Figure 4.24 COD removal rates at Different pH and temperatures

In conclusion: Firstly, both pH and temperature have an impact on COD reduction. Secondly, the injection of carbon dioxide improves the COD reduction efficiency at any given pH. Thirdly, the injection of carbon dioxide at pH 6.5 and at the temperature of 35 ^{o}C provides the optimum conditions in this study. Wang et al. (2009) and Cakir et al. (2005) also reported that COD removal increases with the increase of temperature. The optimum pH for most methanogens is around neutrality (Jones et al. 1987; Cerning et al., 2010).

4.5 Biogas generation under various conditions

Biogas generation is another important parameter that can be used to evaluate the efficiency of CO_2 transformation process.

4.5.1 Impact of carbon dioxide on biogas generation at 20 ^{o}C

The results of methane generation at various pH values with or without carbon dioxide addition at the temperature of 20 ^{o}C are shown in Figures 4.25 to 4.27. At the temperature of 20 ^{o}C, the figures show that there is no methane generated during the first 2 days. This delay could be

related to the time required for the onset of methanogenic reactions, leading to the production of biogas during the anaerobic digestion process.

The amount of generated methane was 71 ml after 12 days of operation at pH 6.5 with the addition of carbon dioxide, while the volume of generated methane was 48 ml without carbon dioxide injection. At pH 7, these values changed to 69 ml and 64 ml while at pH 7.5 there were 71 ml and 60 ml methane generation with and without the injection of CO_2, respectively. Also, at any given pH and in the presence of carbon dioxide a higher methane generation rate was obtained than without the injection carbon dioxide. For example, at pH 6.5 with the injection carbon dioxide, the mean methane generation rate was 6.49 mL/d while without the injection of carbon dioxide it was 4.37mL/d. At pH 7 with the injection of carbon dioxide, the mean methane generation rate was 7.68 mL/d while without the injection of carbon dioxide it was 6.46 mL/d. At pH 7.5 with the injection of carbon dioxide, the mean methane generation rate was 6.46 mL/d while without the injection of carbon dioxide it was 5.85 mL/d. These results consistently showed that carbon dioxide injection into the wastewater can improve methane production at 20 ^{o}C.

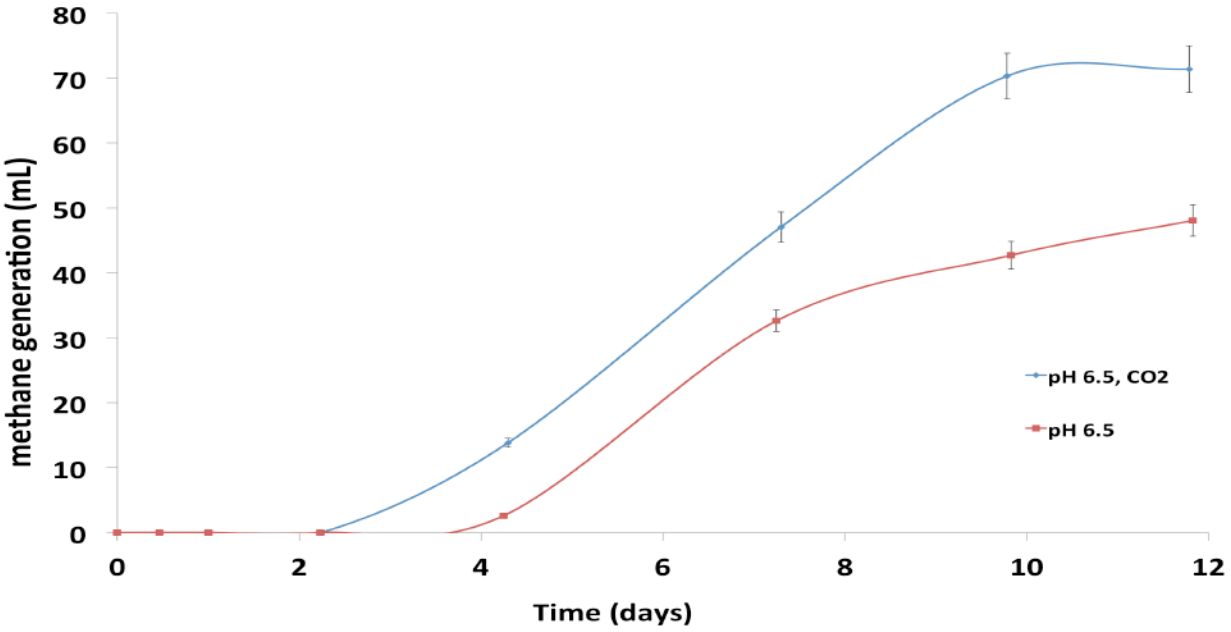


Figure 4.25 Methane generation at pH 6.5 with and without carbon dioxide addition at 20 °C

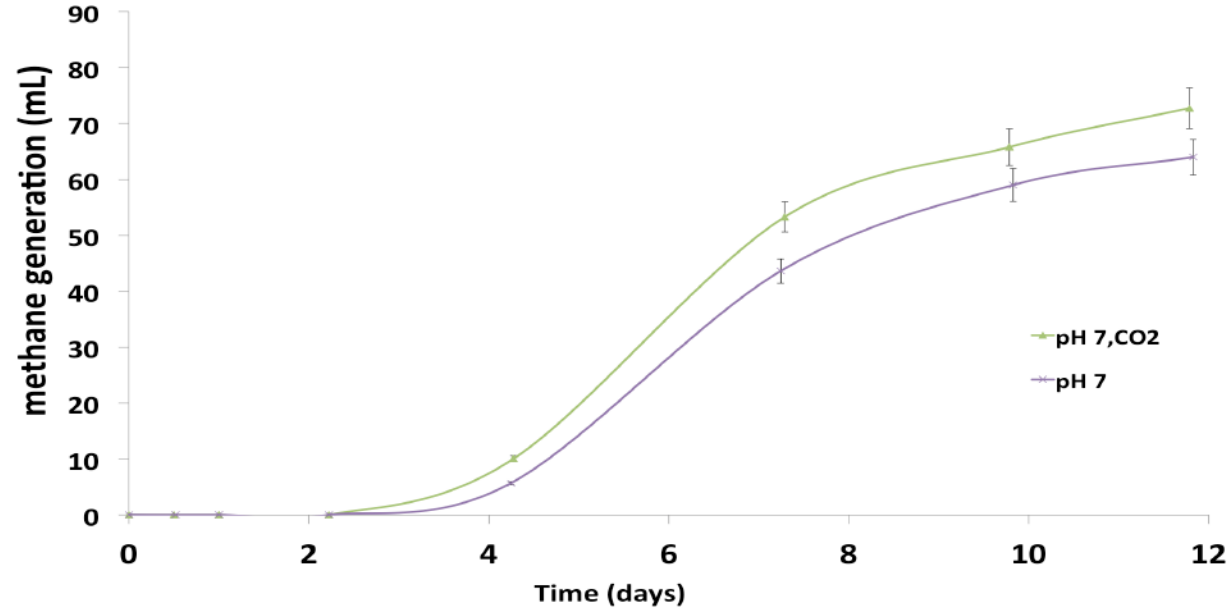


Figure 4.26 Methane generation at pH 7 with and without carbon dioxide addition at 20 °C

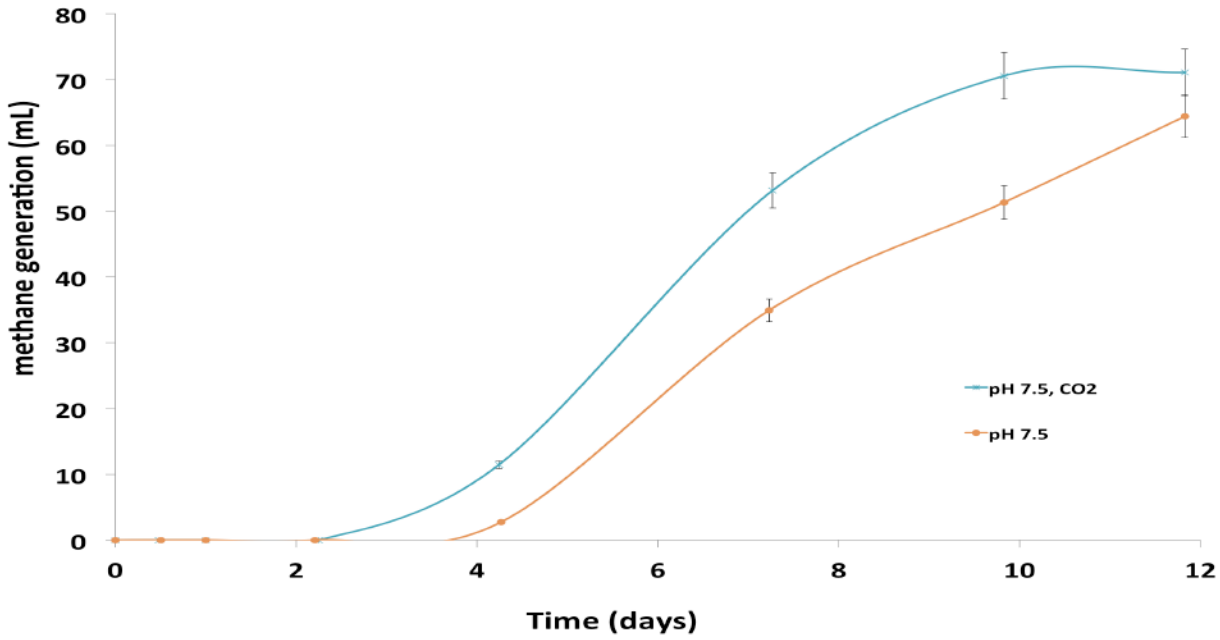


Figure 4.27 Methane generation at pH 7.5 with and without carbon dioxide addition at 20 °C

4.5.2 Impact of carbon dioxide on biogas generation at 30 °C

The results of methane generation at various pH values of 6.5, 7 and 7.5 with or without carbon dioxide addition at the temperature of 30 °C are shown in Figures 4.28 to 4.29. At the temperature of 30 °C, the figures show that there is no methane generated during the first 9 hours, possibly due to the fact that at this temperature it took 9 hours to reach the methanogenesis phase for methane production.

At pH 6.5 and at 30 °C, the amount of generated methane with and without the addition of carbon dioxide was 195 ml and 134 ml, respectively. These values changed to 189 ml and 154 ml at pH 7.0 and to 179 ml and 160 ml at pH 7.5. Also, at any given pH and in the presence of carbon dioxide a higher methane generation rate was obtained than without the injection carbon dioxide. For example, at pH 6.5 with the injection carbon dioxide, the mean methane generation rate was 17.73 mL/d while without the injection of carbon dioxide it was 14.06 mL/d. At pH 7 with the injection of carbon dioxide, the mean methane generation rate was 17.01 mL/d while without the injection of carbon dioxide it was 16.81 mL/d. At pH 7.5 with the injection of carbon dioxide, the mean methane generation rate was 16.3 mL/d while without the injection of carbon dioxide it was 14.94 mL/d. Again, these results clearly show that the addition of carbon dioxide to the wastewater can increase methane production at 30 °C.

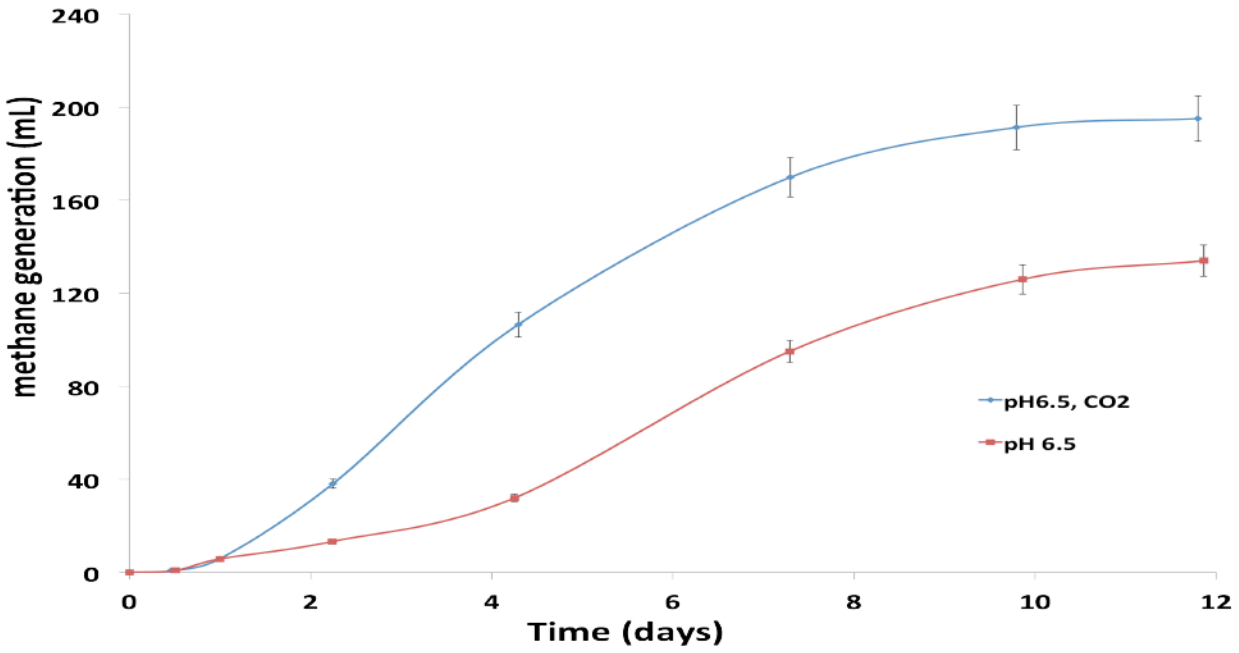


Figure 4.28 Methane generation at pH 6.5 with and without carbon dioxide addition at 30 °C

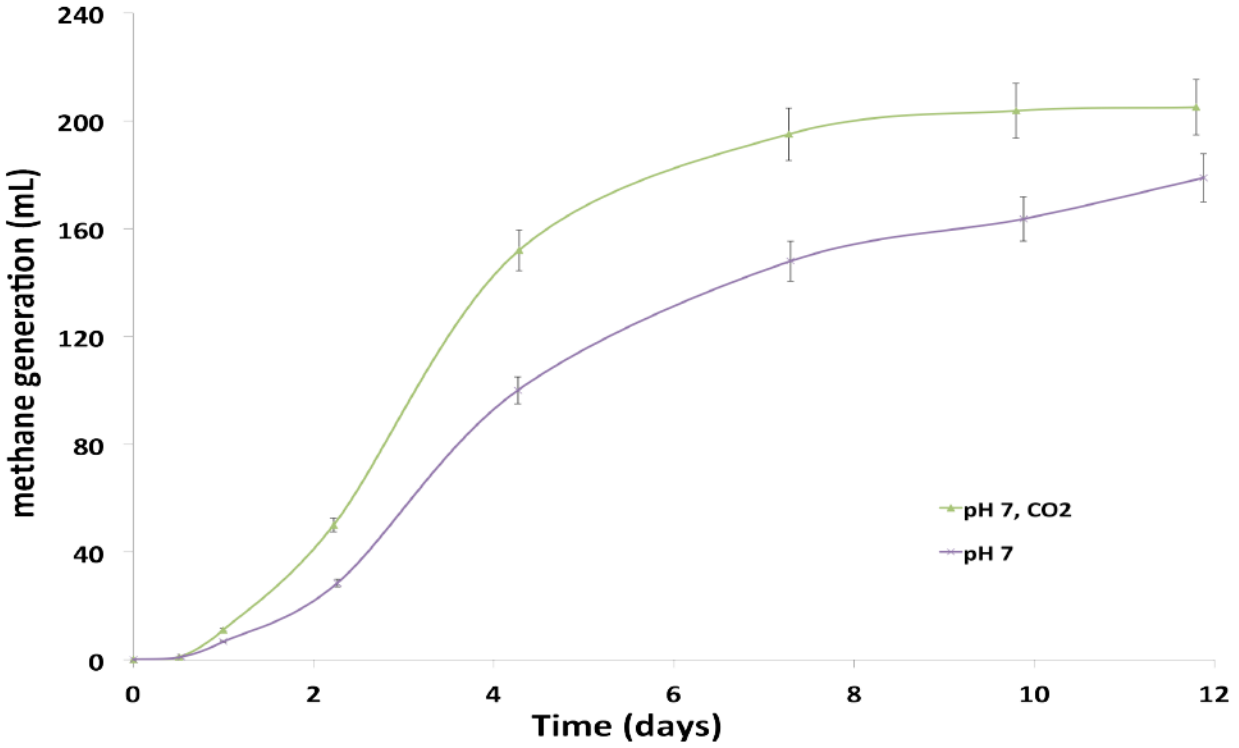


Figure 4.29 Methane generation at pH 7 with and without carbon dioxide addition at 30 °C

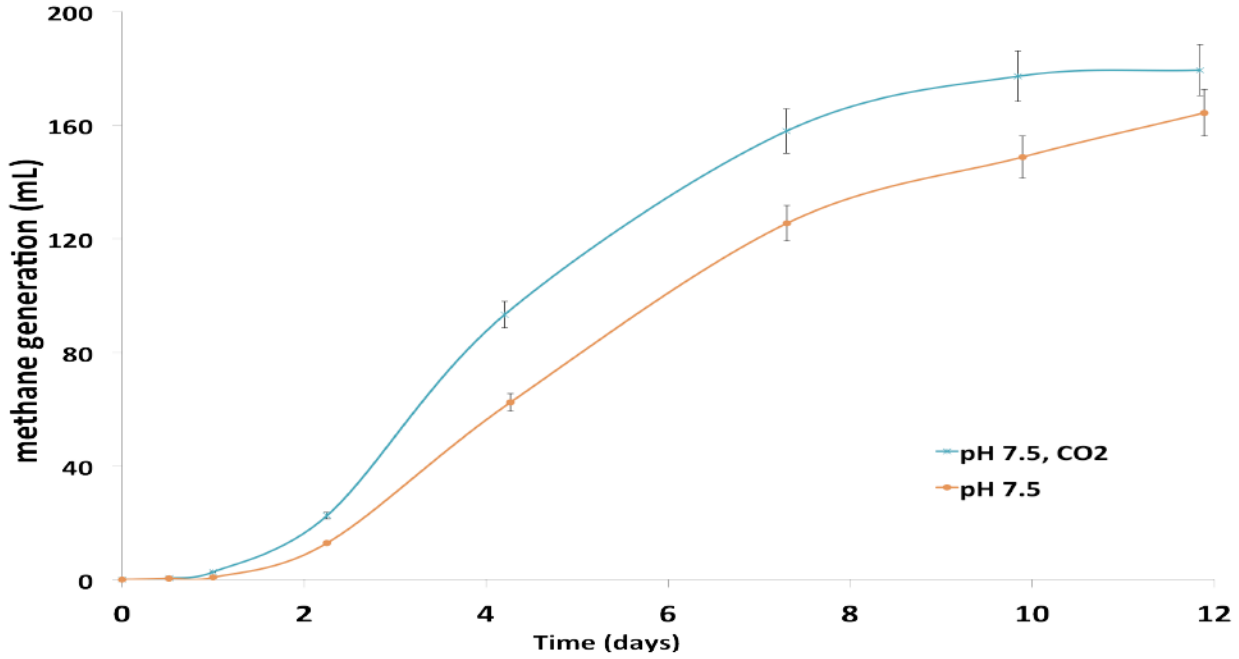


Figure 4.30 Methane generation at pH 7.5 with and without carbon dioxide addition at 30 °C

4.5.3 Impact of carbon dioxide on biogas generation at 35 ^{o}C

The results of methane generation at various pH values of 6.5, 7 and 7.5 with or without carbon dioxide addition at the temperature of 35 ^{o}C are shown in Figures 4.31 to 4.33. At the temperature of 35 ^{o}C, the injection of carbon dioxide generated more methane gas compared to the condition without the injection of carbon dioxide. The figures also show that there is no methane generated during the first 5 hours. That could be the step for breaking complex organic matter into smaller molecules via the enzymes released by the bacteria.

At pH 6.5, the amount of generated methane was 223 ml after 12 days with the injection of carbon dioxide, while without carbon dioxide addition the generated methane was 161 ml. At pH 7 the volume of generated methane was 205 ml with the injection of carbon dioxide and 178 ml without the addition of carbon dioxide. These values changed to 207 ml and 190 ml with and without the injection of carbon dioxide, respectively. Also, at any given pH and in the presence of carbon dioxide a higher methane generation rate was obtained than without the injection carbon dioxide. At pH 6.5 with the injection carbon dioxide, the mean methane generation rate was 20.28 mL/d while without the injection of carbon dioxide it was 14.66 mL/d. At pH 7 with the injection of carbon dioxide, the mean methane generation rate was 18.6 mL/d while without the injection of carbon dioxide it was 16.25 mL/d. At pH 7.5 with the injection of carbon dioxide, the mean methane generation rate was 18.83 mL/d while without the injection of carbon dioxide it was 17.91mL/d.

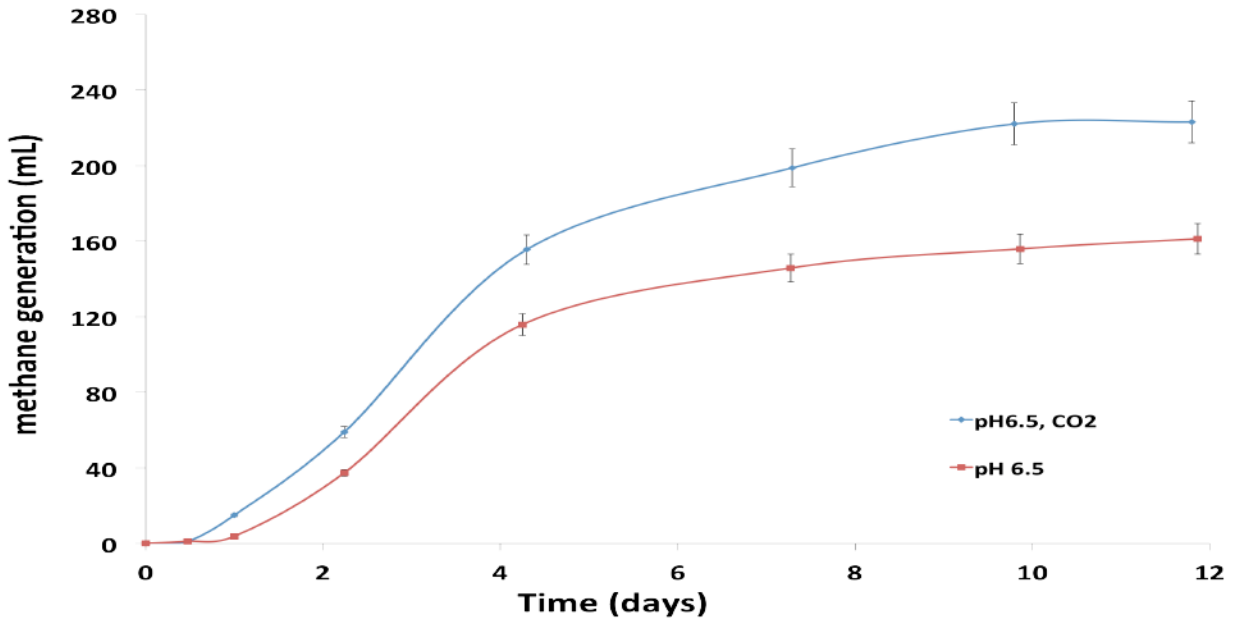


Figure 4.31 Methane generation at pH 6.5 with and without carbon dioxide addition at 35 °C

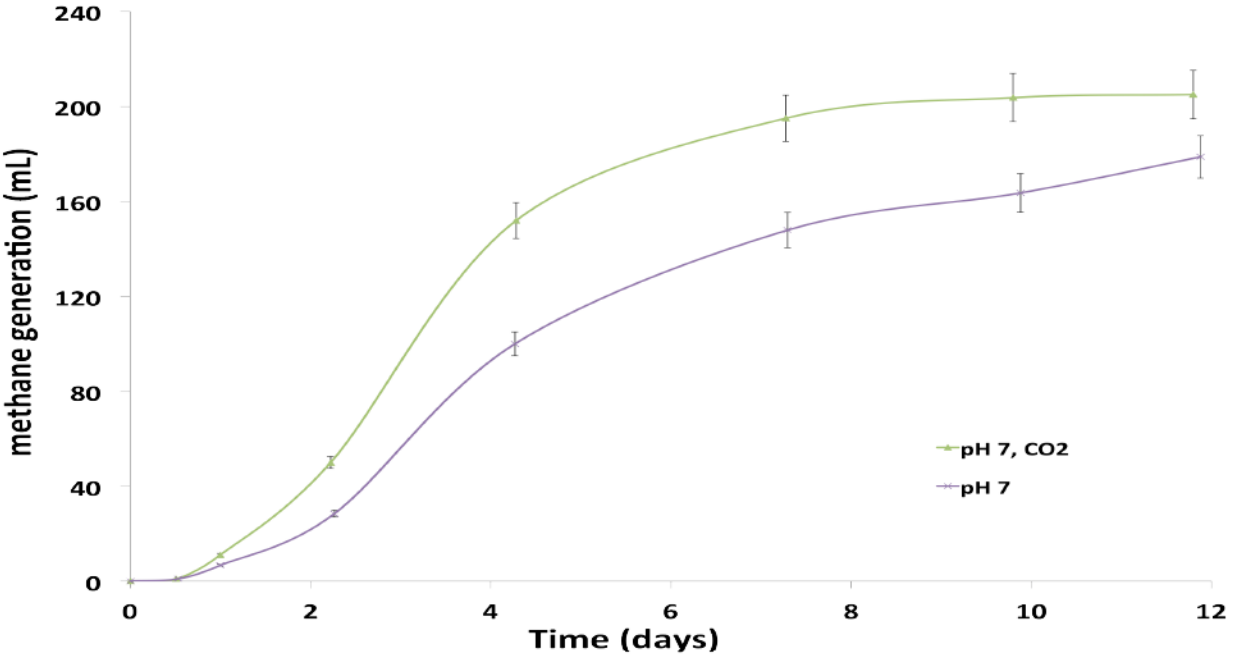


Figure 4.32 Methane generation at pH 7 with and without carbon dioxide addition at 35 °C

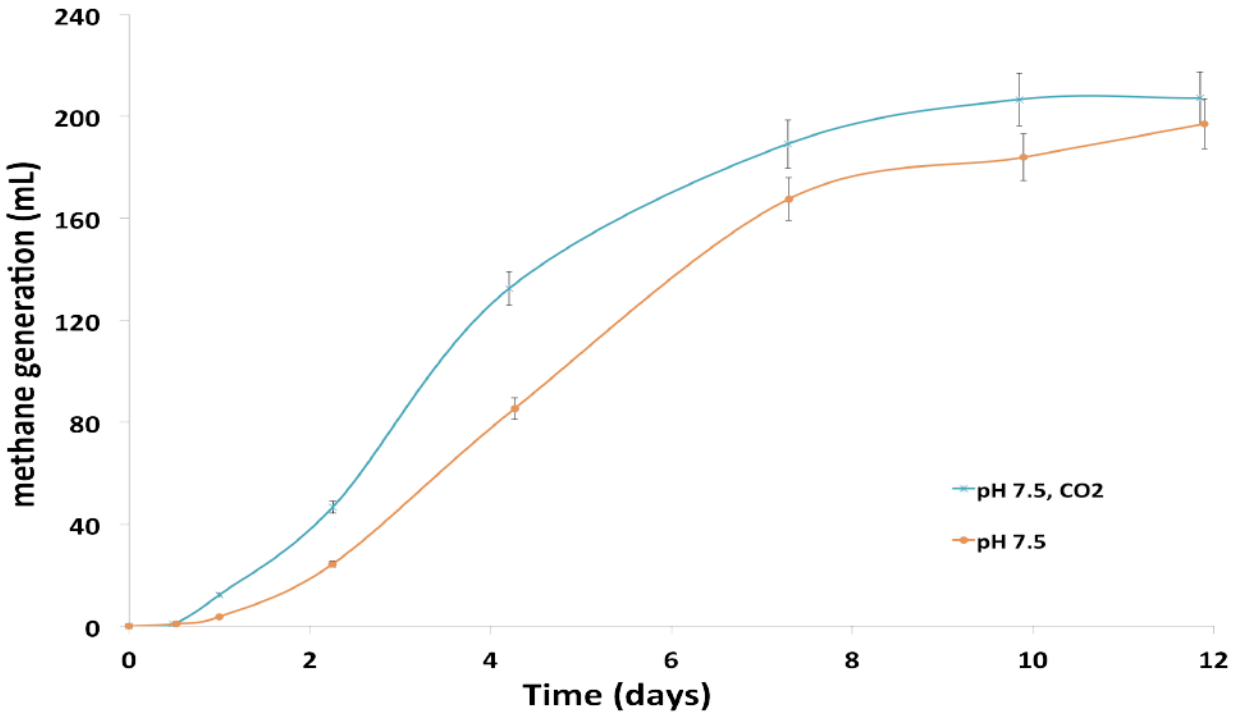


Figure 4.33 Methane generation at pH 7.5 with and without carbon dioxide addition at 35 °C

In conclusion, the results consistently show that carbon dioxide addition has a positive impact on methane generation at the three examined temperatures of 20 °C, 30 °C, and 35 °C. Higher temperatures also lead to a faster reaction.

4.6 Impact of temperature on biogas generation with the injection of carbon dioxide at various pH values

In order to investigate the impact of temperature on biogas generation, methane generation at different temperatures and at pH values of 6.5, 7, and 7.5 were determined.

4.6.1 Impact of temperature on biogas generation with the injection of carbon dioxide at pH 6.5

Figure 4.34 shows the results of methane generation with the addition of carbon dioxide at pH 6.5 and at various temperatures of 20 ^{o}C, 30 ^{o}C, and 35 ^{o}C. The results show that the highest methane generation occurred at 35 ^{o}C. The maximum amount of generated methane was 223 ml at the temperature of 35 ^{o}C.

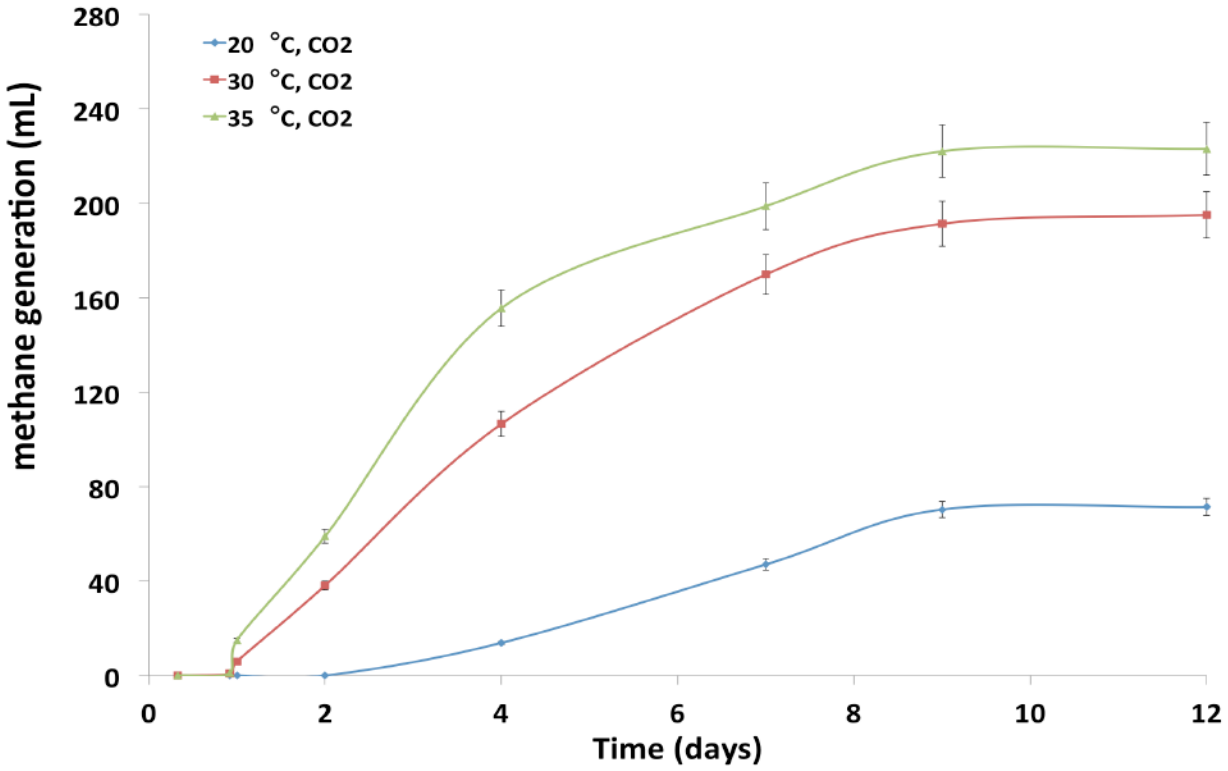


Figure 4.34 Methane generation at pH 6.5 and with carbon dioxide addition at various temperatures

4.6.2 Impact of temperature on biogas generation with the injection of carbon dioxide at pH 7

Figure 4.35 shows the results of methane generation with the addition of carbon dioxide at pH 7 and at various temperatures of 20 °C, 30 °C, and 35 °C. The results show that the highest amount of methane generation, which was 209 ml occurred at 35 °C.

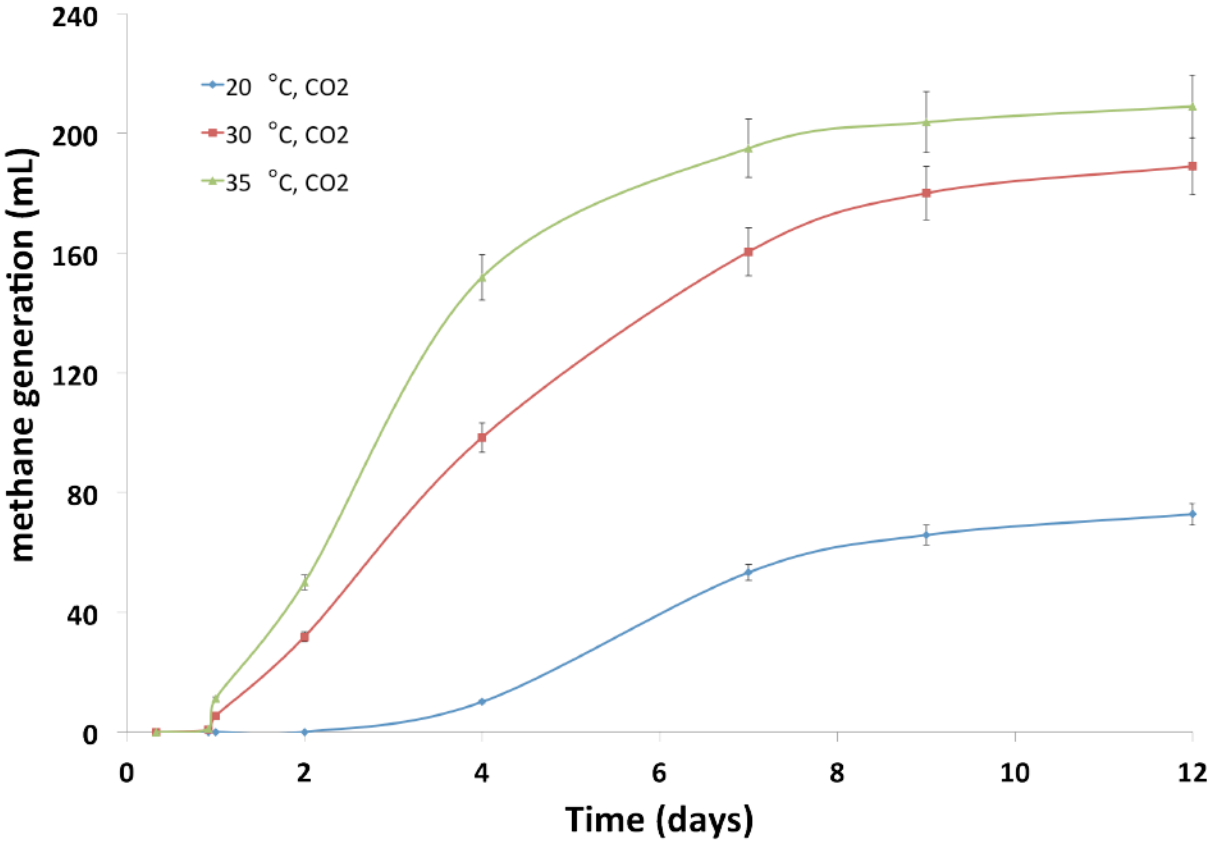


Figure 4.35 Methane generation at pH 7 and with carbon dioxide addition at various temperatures

4.6.3 Impact of temperature on biogas generation with the injection of carbon dioxide at pH 7.5

Figure 4.36 presents the results of methane generation with the injection of carbon dioxide at pH 7.5 and at three temperatures of 20 °C, 30 °C, and 35 °C. Again, the results indicate that the highest amount of methane production, which was 207 ml, occurred at 35 °C.

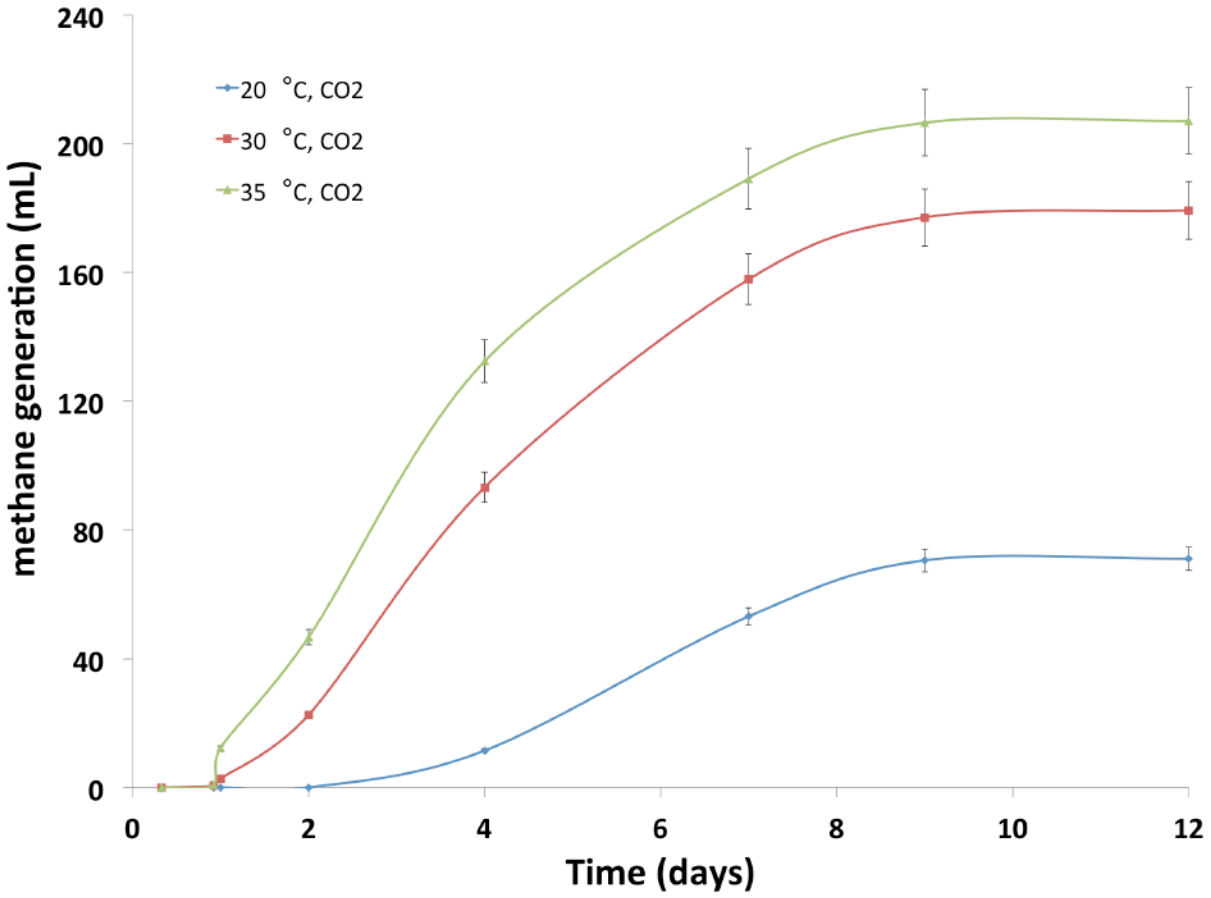


Figure 4.36 Methane generation at pH 7.5 and with carbon dioxide addition at various temperatures

In conclusion, the obtained results show that the optimum temperature for methane generation is 35 °C, as it leads to the production of the highest volume of methane and faster methane generation.

4.6.4 Optimum condition for methane generation

The optimum pH for the activity of methanogens is around neutrality (Jones et al., 1987; Cerning et al., 2010). Temperature around 35 °C has been widely applied in anaerobic treatment process. The results, presented in the previous figures, show that the most favorable temperature for methane

generation is 35 °C while the most suitable pH is 6.5. These conditions led to the generation of the highest volume of methane which was 223 ml.

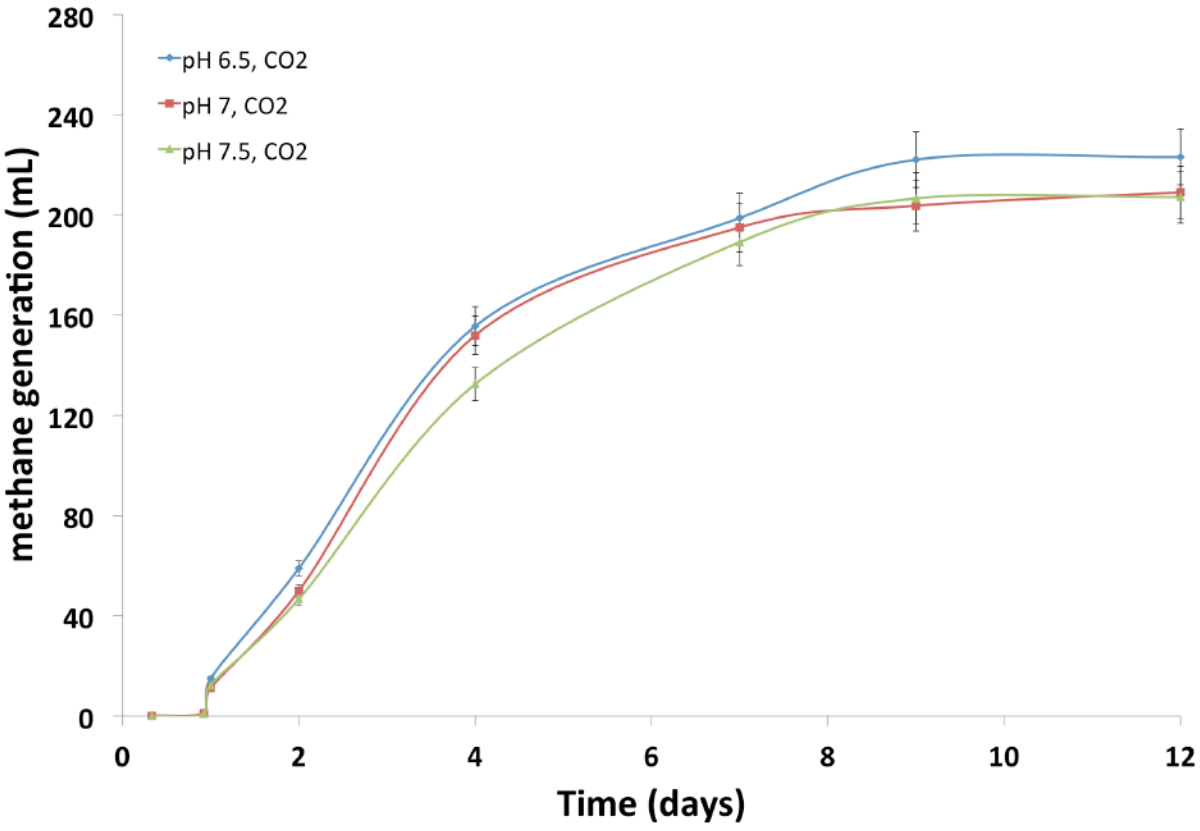


Figure 4.37 Methane generation at various pH values and at the optimum temperature of 35 °C

4.6.5 Methane generation efficiency under the various conditions

Figure 4.38 shows the overall methane generation efficiency under different conditions. The results show that at any given pH, methane generation rate was maximal at the highest examined temperature of 35 °C, while being minimal at 20 °C. Costa et al. (2009) presented methane generation increased with the increase of temperature.

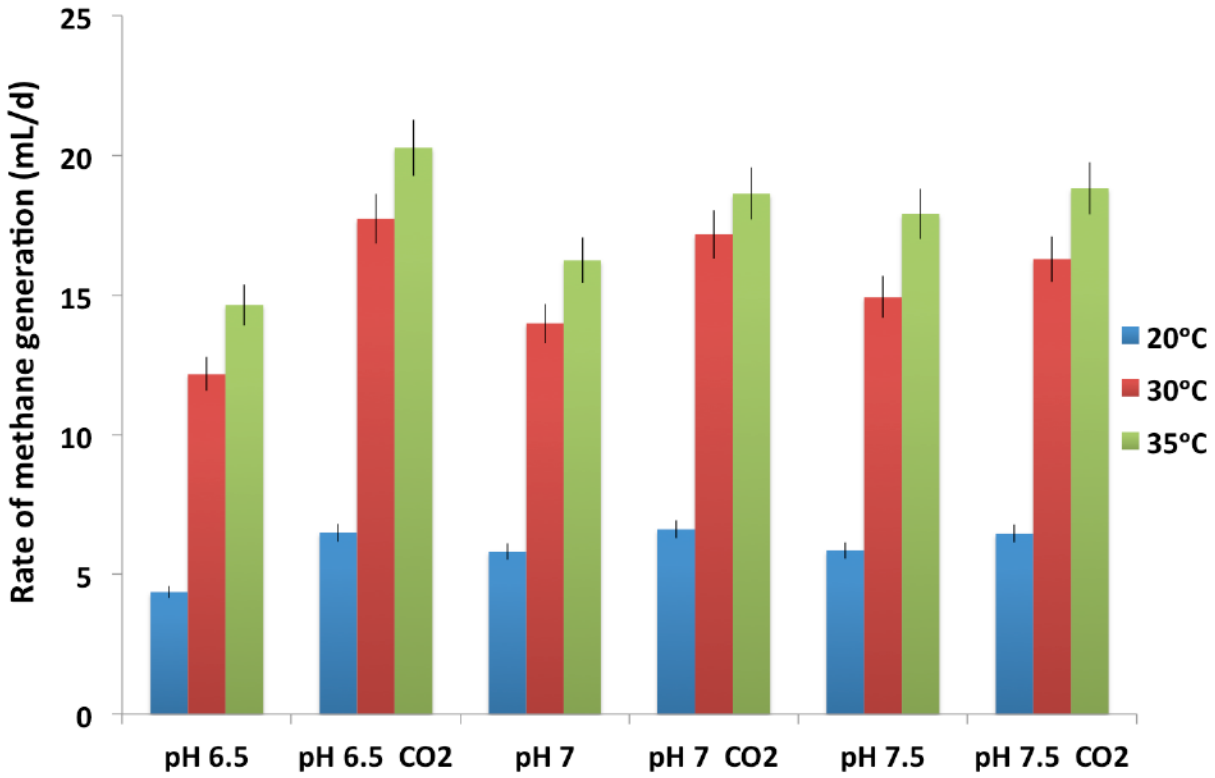


Figure 4.38 Methane generation at different pH and temperatures

Temperature and pH have an impact on the rate of biochemical reactions; they also control microbial growth and competition in biological processes. Figure 4.38 presented the effect of temperature and pH on methane generation. As Figure 4.34 shows the impact of temperature is higher than that of pH. At pH 6.5, temperature increase enhanced methane generation from 6.5 mL/d to 21.1 mL/d. pH 7 and pH 7.5 showed the same trend. For anaerobic treatment of pulp and paper industry wastewater, the increase of temperature enhances methane generation.

Also, it is shown that at pH 6.5, there is a remarkable difference between the cases with and without the addition of carbon dioxide, while at pH 7.5 the difference is negligible. The reason could be due to the fact that pH 6.5 is between the optimum pH for hydrolysis (pH 5.2 to 6.3)

and methane formation (pH 6.7 to 7.5). So, at pH 6.5 both groups of hydrolysis bacteria and methanogenic bacteria are active. There are two groups of methanogens: acetate fermenters and hydrogen oxidizers (Rittmann &McCarty, 2001). Therefore, with the addition of carbon dioxide, Acetate fermenters can use carbon dioxide to generate methane and methanogenesis dominated, while without additional carbon dioxide, hydrogen oxidizers responsible to generate methane. At pH 7.5, there is not sufficient aqueous carbon dioxide, and as shown in Figure 4.1, methane generation is mainly from acetate methanation. Under this condition, 27% to 30% of methane is generated by H_2 and CO_2 while 70% of methane is generated by acetate (Deublein and Steinhauser, 2008).

In conclusion, the addition of carbon dioxide at pH 6.5 and temperature of 35 ^{o}C is the best conditions for methane generation in this study.

Figure 4.39 shows the rate of methane generation under the best conditions in this work. There was no methane generation until 5 hours after the onset of experiment, while the rate of methane generation reaches its peak that was 96 ml/d around 4 days. By the end of the experiment, the rate of methane generation was close to zero.

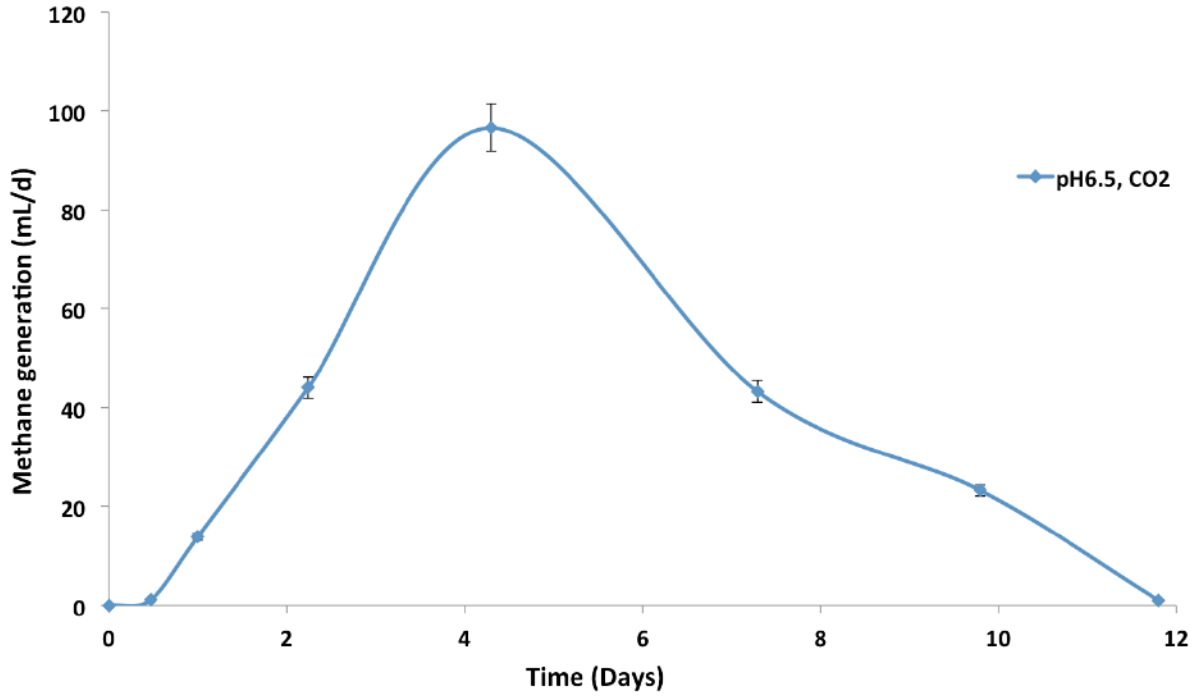


Figure 4.39 Methane generation rate under the optimum condition of pH 6.5 and 35 °C

Figure 4.41 shows the methane percentage in the biogas. Typical biogas is composed of 50-80% methane, 20-50% carbon dioxide and trace amounts of other gases (U.S. Department of Energy, 2012). In this work, the composition of methane in biogas was from 50% to 70% . The composition of biogas depends on various factors. In this work, both temperature and pH affect the composition of biogas.

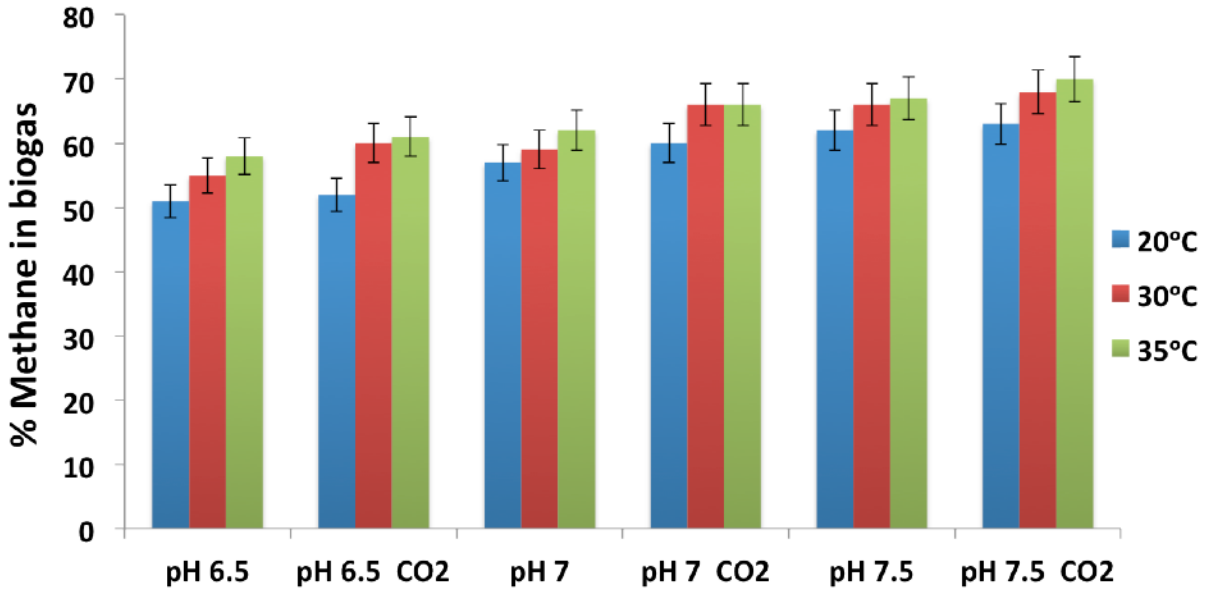


Figure 4.40 Methane content in the biogas

Tables 4.41 to 4.42 show that the methane yield, based on the consumed COD, increases with the increase of pH at a given temperature. At a constant pH, the temperature of 20 °C resulted in the lowest methane yield compared to the other temperatures. Meanwhile, the addition of carbon dioxide resulted in higher methane yields at any given temperature and pH. This shows that the addition of carbon dioxide can have a positive impact on bacterial metabolism and improve the conversion rate of organic matter.

Carbon dioxide removal trend

For the dissolved carbon dioxide, the mass balance (mg) was calculated as following;

$$CO_2(aq)_i - CO_2(aq)_{f-} - CO_2(aq)_b = CO_2(aq)_r \quad (4.2)$$

Where $CO_2(aq)_i$ = Initial dissolved CO_2

$CO_2(aq)_f$ = Final dissolved CO_2 after anaerobic digestion

$CO_2(aq)_b$ = CO_2 in biogas

$CO_2(aq)_c$ = Removed carbon dioxide

The amount of carbon dioxide dissolved in the wastewater was calculated as mentioned in section the 3.23. Dissolved carbon dioxide involved in different reactions that include its consumption and production, or the reaction among the inorganic species (Alimahmoodi, 2008). The amount of removed carbon dioxide was calculated using the equation 4.2. Figure 4.41 shows the amount of carbon dioxide removed.

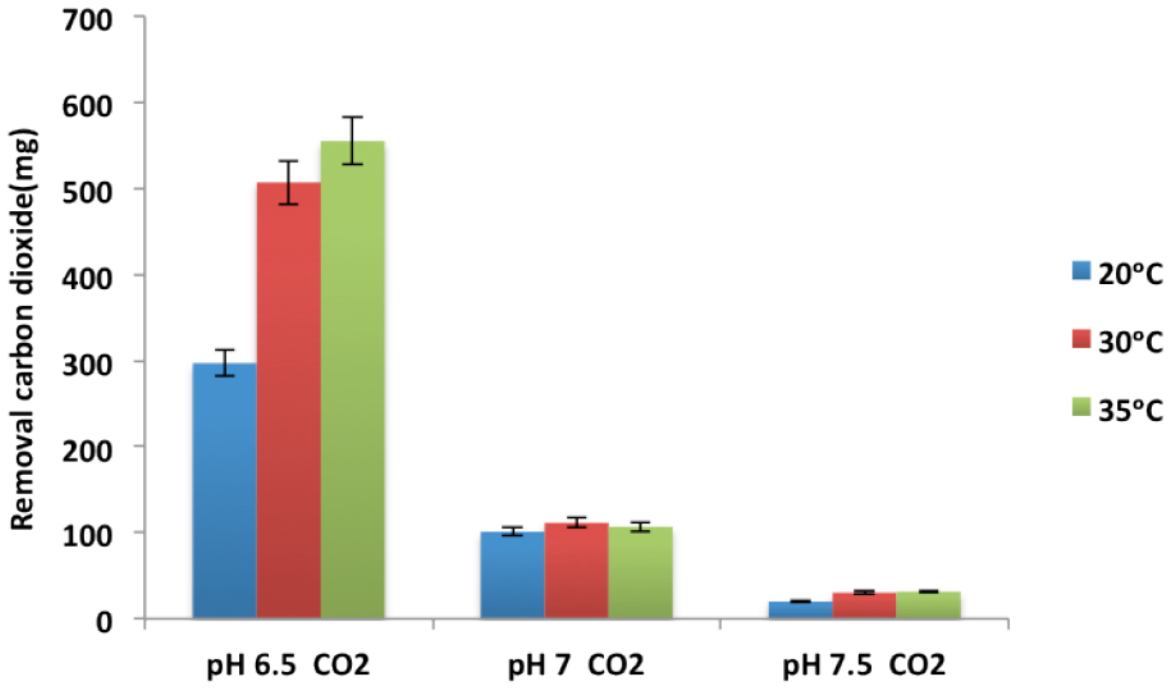


Figure 4.41 Amount of CO_2 removed after anaerobic digestion

The theoretical methane yield is 0.35 L/g COD removed (Michaud et al ., 2002) at 0 ^{o}C and pressure of 1 atm. Because this work used three temperatures, the theoretical methane yield needs to be corrected for the applied temperature. Assuming the ideal gas law for methane, the following T-V relationship can be used:

$$V_s/T_s=V_a/T_a \qquad (4.3)$$

Where V_s and T_s refer to standard conditions (T_s =273K)

V_a and T_a refer to actual conditions (T_a=293K, 303K, and 308K)

$$V_a=V_s(T_a/T_s)$$

$$0.35L*308K/273K=0.376\ L$$

$$0.35L*308K/273K=0.388\ L$$

$$0.35L*308K/273K=0.395\ L$$

The methane yields obtained at 30 ^{o}C and 35 ^{o}C are close. The highest methane yield was 0.364 L per g COD removed, obtained at pH 7.5 and 35 ^{o}C with the injection of carbon dioxide which is close to the yield obtained at 35 ^{o}C and at pH 7.5 which was 0.364 L per g COD removed.

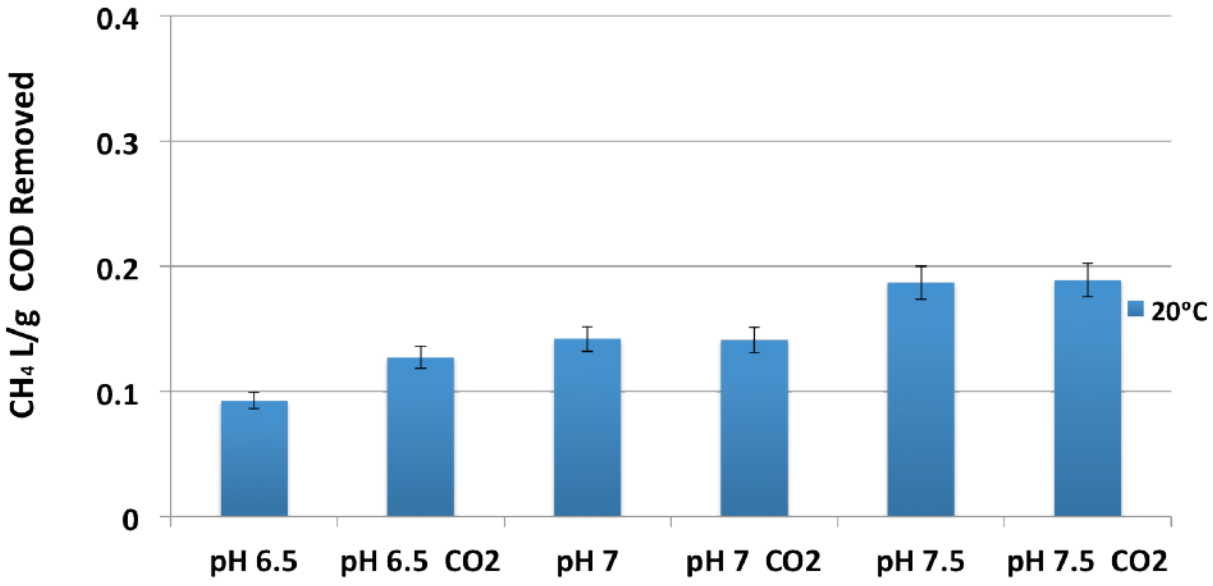


Figure 4.42 Methane yield at 20 °C

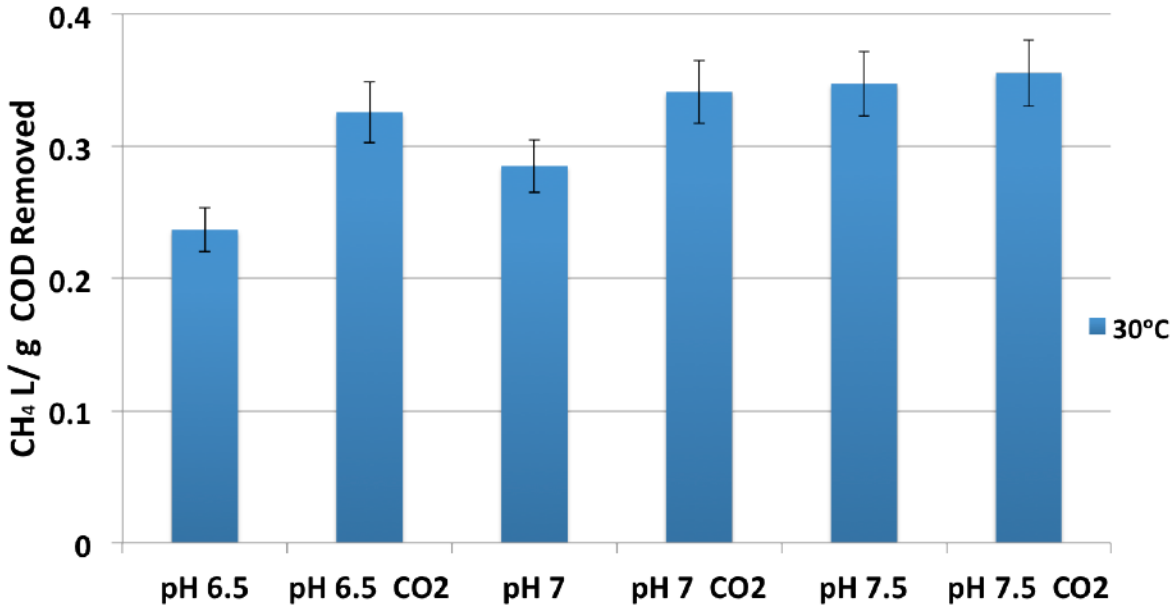


Figure 4.43 Methane yield at 30 °C

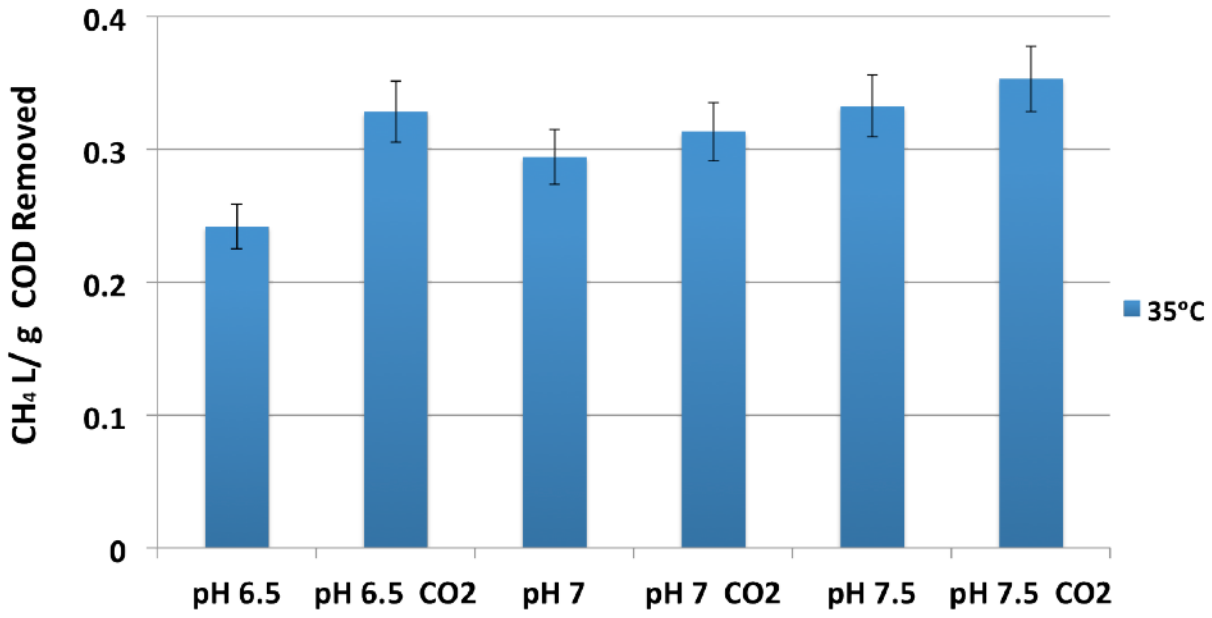


Figure 4.44 Methane yield at 35 °C

4.7 Comparison of the results with previous work

Fitzsimons et al. (1990) operated a continuous reactor for the treatment of bleach plant effluents from Swedish pulp mill. Figure 4.44 shows the experimental setup. They reported 35% to 40% COD reduction at a hydraulic retention time (HRT) of 36 hours. This system combines anaerobic and aerobic processes. In the present research, the experimental system had only one unit while reaching the same removal efficiency for COD removal.

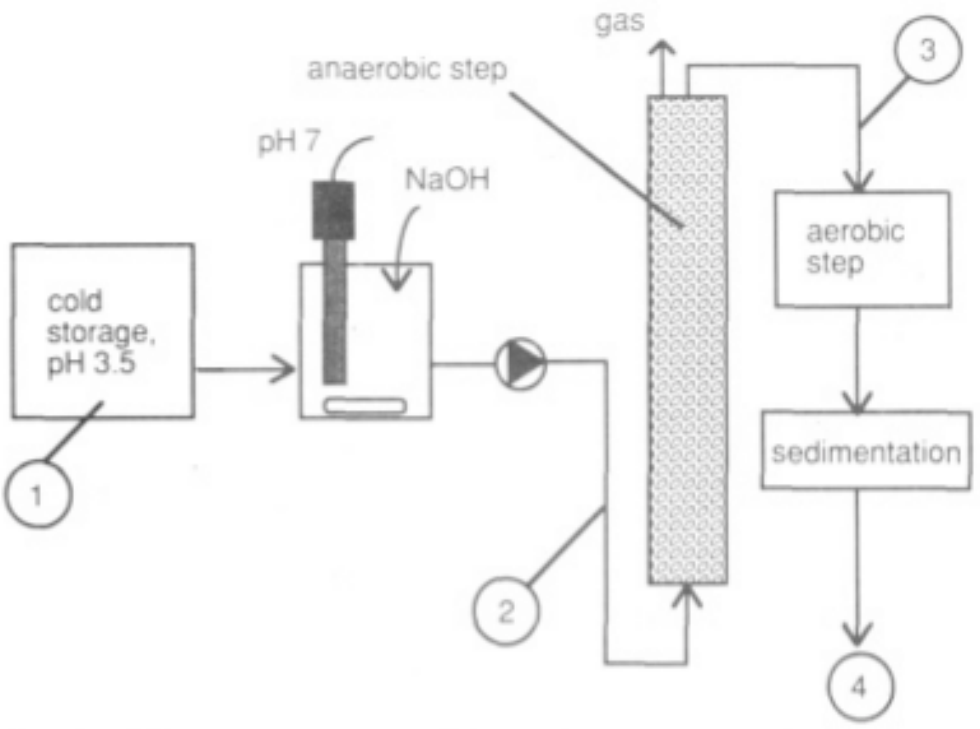


Figure 4.45 Process set up flow of the Fitzsimons et al. (1990) work

Lepisto and Rintala (1994) presented work with a thermophilic anaerobic process. Four different types of anaerobic reactors at the temperature 55 ^{o}C were used in their study: an upflow anaerobic sludge blanket (UASB) reactor; a UASB reactor enriched with sulfate; a UASB reactor with recirculation; and a fixed-bed reactor with recirculation. The COD removal rates for all the reactors were from 30% to 70%. However, mesophilic conditions were chosen for this study. Compared to thermophilic conditions, mesophilic operation is realized at a relatively low cost. In this work, temperature from 20 to 35 ^{o}C was used which needs less energy input compared to 55 ^{o}C used by Lepisto and Rintala (1994).

Yu and Welander (1994) presented work using a laboratory-scale anaerobic fixed-film process operated at different hydraulic retention times (HRTs). At an HRT of 15 hours, 20% of COD was removed and 0.19 NL of methane was produced per gram of COD. Compared to Yu and Welander (1994), this study has a minimum 25% of COD removal and maximum was 49%. Biogas production per removed COD (g) was 0.364 L.

Ali and Sreekrishnan (2000) showed anaerobic treatment of black liquor and bleach effluent. With the addition of glucose (1% w/v), the reduction of COD was 71% for black liquor, while the bleach plant effluent had 66% COD reduction. In the absence of glucose, the COD reduction was 43% for black liquor and 31% for the bleach effluent. However, the present work achieved 49% of COD removal by injection of carbon dioxide compare to Ali and Sreekrishnan's work.

In conclusion, this work achieved the following:

- Carbon dioxide removal by using an anaerobic process
- The wastewater from pulp and paper industry was treated while carbon dioxide was removed
- The developed process generated biogas that could be used as a source of energy.

Chapter 5: Conclusions and Contributions

5.1 Conclusions

This work aimed to reduce the emissions of carbon dioxide by its bioconversion into methane. The following conclusions are made based on the obtained results of this study:

1. Carbon dioxide dissolved in the pulp-and-paper wastewater can be treated by anaerobic process.
2. Anaerobic biological processes can reduce the dissolved carbon dioxide in wastewater.
3. Kraft pulp and paper effluents can be treated by anaerobic processes along with COD removal that reached 49% .
4. The injection of carbon dioxide into the wastewater can increase the reduction of COD by 4.7% and also improve the generation of biogas by 4.7%
5. The optimum temperature for the removal of COD is 35 ^{o}C, while the optimum pH is 6.5.
6. The best reduction rate of COD is around 529 mg/d.
7. Temperature exerts a more important effect on COD reduction than pH.
8. The optimum temperature for biogas generation is 35 ^{o}C, while the optimum pH is 6.5.
9. The maximum rate of biogas generation is observed around 4 days after the onset of process.
10. Both pH and temperature have an impact on the generation of methane.

5.2 Contribution to Knowledge

This work demonstrated a new method to reduce atmospheric carbon dioxide concentrations by using the anaerobic digestion process while treating pulp and paper wastewater from industrial operations along with the production of biogas. It shows a practical application to dissolving carbon dioxide in wastewater to improve the efficiency of anaerobic processes. The contribution of this work is presented in the following lines:

1. Development of a method to remove atmospheric carbon dioxide while treating Kraft pulp and paper wastewater
2. Expansion of the application of anaerobic digestion to reducing carbon dioxide emissions
3. Development of a method to remove carbon dioxide while generating additional energy in the form of biogas.

Chapter 6: Recommendations

Several recommendations are presented below to improve the efficiency of the developed method and to expand its applications:

1. Investigation of carbon dioxide removal under anaerobic conditions at a wide range of pH values during different stages of anaerobic digestion.
2. Design and development of a continuous system for the simultaneous removal of carbon dioxide and wastewater treatment
3. Investigation of the optimum operating conditions for increased dissolution of carbon dioxide in wastewater
4. Development of a mathematical model for the simulation of the developed process
5. Investigation of the applicability of the developed method to treat other types of wastewaters

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Appendix

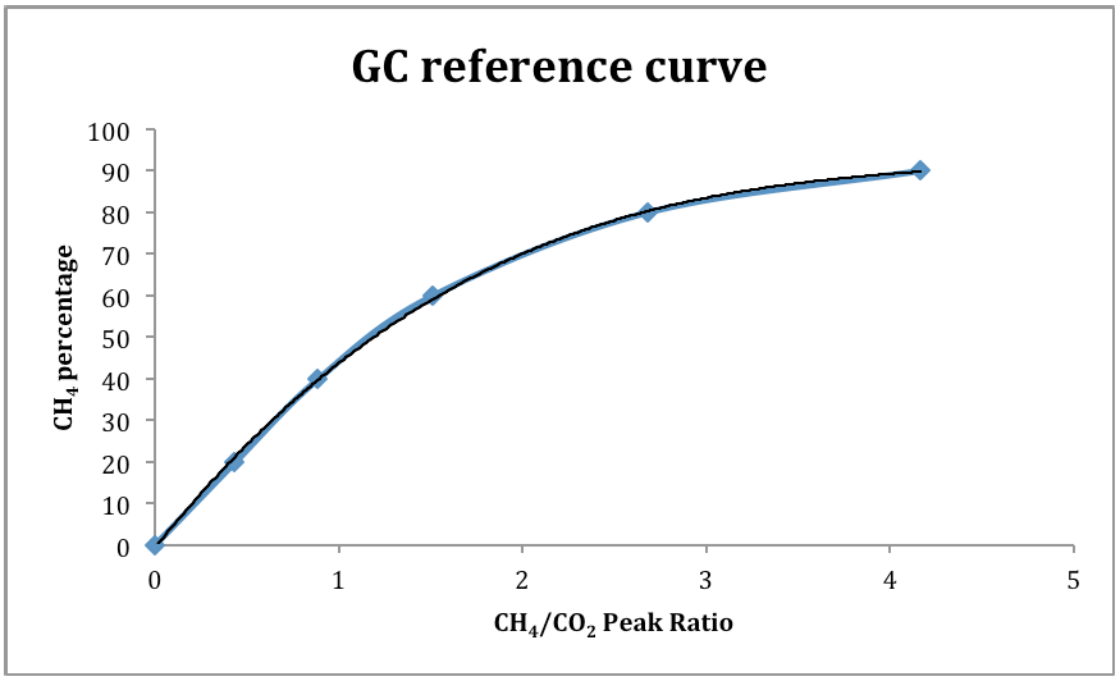

Figure A 1 Reference curve for methane content of the biogas obtained by gas chromatography (GC)