The Capacity of Industrial Pulp-and-Paper Wastewater in the Absorption of CO_2 and its Removal from Gas Phase

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Abstract

The Capacity of Pulp-and-Paper Wastewater in the Absorption of CO_2 and its removal from the gas phase

Hamed Kazemi

Carbon dioxide is a major contributor to the greenhouse gas (GHG) emission, mainly generated by industrial and anthropogenic activities. Numerous investigations have been conducted on the reduction of atmospheric CO_2 emission with considerable attention paid to studying the applicability of gas-liquid absorption. The present research studied CO_2 absorption by the wastewater of a pulp-and-paper plant in an effort to determine the capacity of wastewater to absorb CO_2 as well as CO_2 emission reduction. In a series of experiments, the ability of pulp-and-paper wastewater to absorb CO_2 from a CO_2 - air mixture was studied. The examined wastewater had an average alkalinity of 2700 mg/L and an initial pH of 6.5. The impact of operating conditions including the wastewater temperature, gas composition, and liquid and gas flow rates on CO_2 absorption by the wastewater and CO_2 removal efficiency was investigated. The results showed that the gas composition had a considerable impact on the final $CO_{2(aq)}$ concentration and removal efficiency of CO_2 while temperature and flow rate had less significant effects. Higher $CO_{2(aq)}$ concentrations were achieved at lower temperatures and higher gas-phase CO_2 concentrations, as well as lower liquid flow rates. CO_2 removal efficiencies were higher at lower temperatures, lower gas-phase CO_2 concentrations, and higher liquid flow rates. The gas flow rate showed to mainly affect the absorption rate. The maximum CO_2 concentration during continuous mode of operation was 11.9 g/L which was obtained at the liquid flow rate of 200 mL/min and gas flow rate of 2.5 L/min. In terms of CO_2 emission reduction, the maximum removal efficiency was found to be 23%. Although the

capacity of wastewater in the absorption of CO_2 was shown to be lower than that of conventional caustic solutions, wastewater has been proven to be an effective alternative to reducing CO_2 emissions.

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List of Abbreviations

AD: Anaerobic Digestion

aq: aqueous

ATC: Automatic Temperature Compensation

CCS: Carbon (dioxide) Capture and Storage

COD: Chemical Oxygen Demand

CTMP: Chemi-thermo Mechanical Pulping

D: Diameter

DEA: Diethanolamine

FM: Flowmeter

GC: Gas Chromatograph

GHG: Greenhouse Gas

HDPE: High Density Polyethylene

K: Kelvin

L: Litre

LFG: Landfill Gas

MDEA: Methyldiethanolamine

MEA: Monoethanolamine

P: Pump

PSA: Particle Size Analyzer

PSD: Particle Size Distribution

ppm: parts per million

PVC: Polyvinyl Chloride

RPM: Rotations per Minute

TA: Total Alkalinity

TPAD: Two-Phase Anaerobic Digestion

WW: Wastewater

Chapter 1: INTRODUCTION

1.1 Problem Statement

1.1.1 Global Warming and Climate Change

The Earth's temperature is influenced by the sun. Some part of the solar energy received by the Earth is absorbed while some part is reflected. A large portion of the reflected energy is absorbed by certain gases in the atmospheric layer and is released back to the earth, warming the Earth's surface. This is known as natural greenhouse effect. In the absence of natural greenhouse effect, the Earth's temperature would be much colder. Figure 1-1 shows a schematic of the greenhouse effect that occurs naturally on the planet.

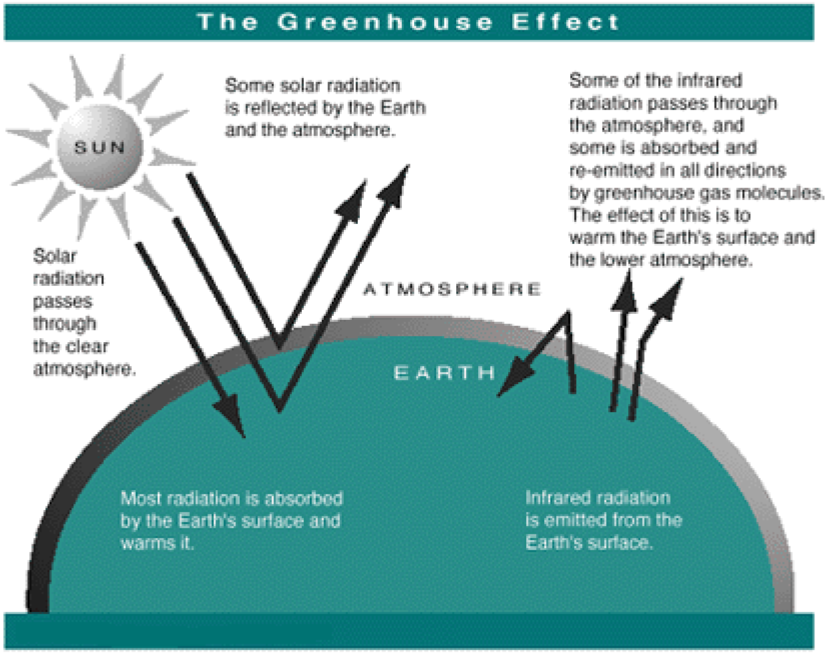


Figure 1-1 Natural greenhouse effect (Environmental Protection Agency 1995)

Recently, it has been observed that due to the increase of emission of certain gases, the greenhouse effect has significantly increased, leading to Earth's temperature rise. The term "Global Warming" refers to the increase of mean surface temperature of the earth due to the emission of greenhouse gases. In the U.S., CO_2 is the largest contributor among greenhouse gases, accounting for 85% of released greenhouse gases with methane standing in the second position. CO_2 is mainly released from the combustion of fossil fuels, while methane emissions result from agricultural activities, landfills, etc. (Environmental Protection Agency 2010).

Nitrous oxide and fluorinated gases are other greenhouse gases with the first mainly produced through agricultural activities and the latter released by industrial activities, refrigeration, etc. (Environmental Protection Agency 2010).

The mean temperature of the Earth has increased 0.4 – 1.0 °C since the beginning of 20th century and is expected to rise by 1 – 3.5 °C in the next hundred years if the rate of greenhouse gas emission is not reduced (Environmental Protection Agency 2010) . Figure 1-2 shows the temperature change trend from the late 19th century to recent years.

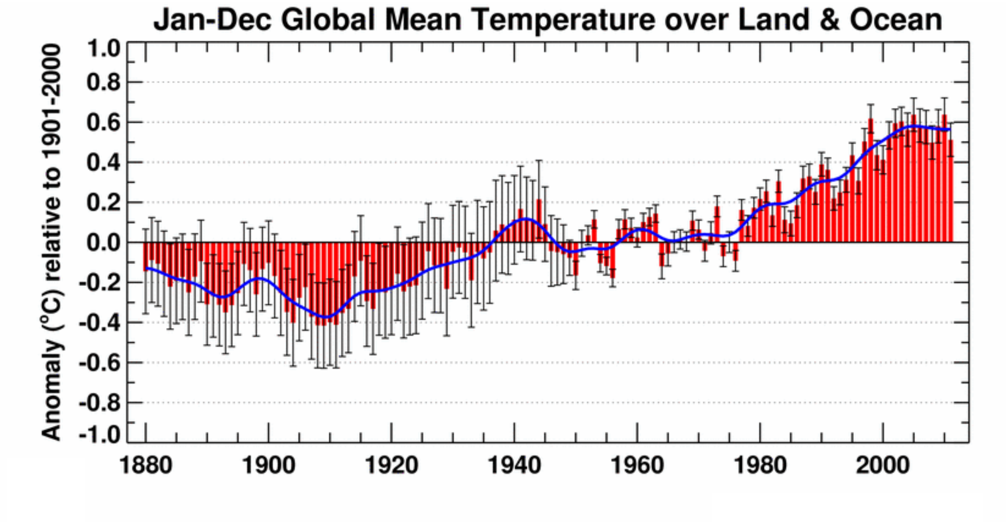


Figure 1-2 Temperature change (National Climatic Data Center 2012)

The already observed impacts of the temperature rise include the decrease in snow cover in northern hemisphere and floating ice in Arctic Ocean as well as sea level rise of 10-20 cm in the past hundred years. The ongoing rate of greenhouse gas emission and the expected temperature rise will cause significant climate change all over the planet. The results of the climate change could be:

- Extreme weather events such as frequent storms and hurricanes

- Changes in evaporation and precipitation patterns
- Threatening coastal resources and wetlands as a result of sea level rise
- Increased transmission of certain pathogens (Kilpatrick et al. 2008)

1.1.2 Carbon Dioxide

As mentioned before, carbon dioxide makes the major contribution to the greenhouse effect, having the highest rate of production compared to other greenhouse gases. The main sources of carbon dioxide production are combustion of fossil fuels and anthropogenic activities which lead to a gigantic annual production of CO_2. Figure 1-3 shows the trend of carbon dioxide emission from the beginning of industrial revolution, i.e. end of the 19th century.

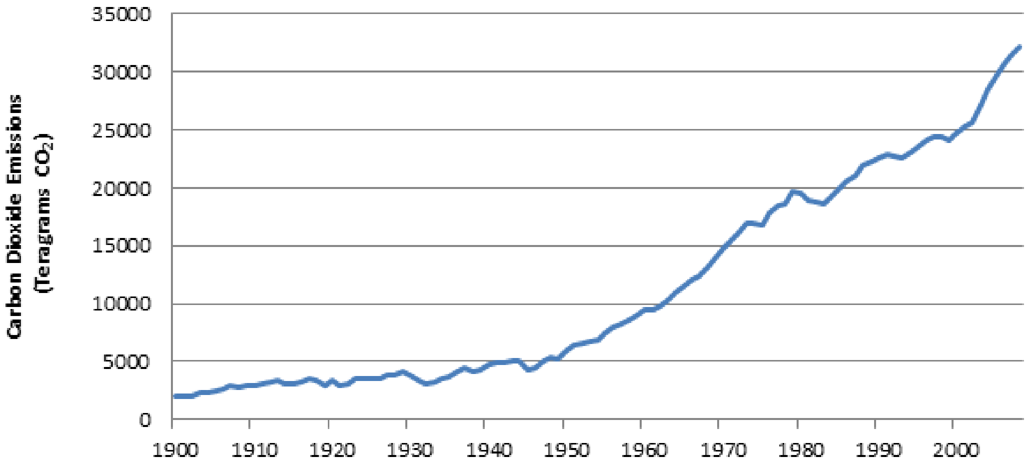


Figure 1-3: Carbon dioxide emission trend (Boden et al. 2010)

Due to a large emission of carbon dioxide in the past two hundred years, the concentration of this greenhouse gas has dramatically changed. As Figure 1-4 shows, the concentration of CO_2 in the atmosphere has changed from around 290 ppm in 1900 to 390 ppm in 2010.

Carbon dioxide is also produced through respiration and natural decomposition of organic material which is much more than that produced by industrial and anthropogenic activities. However, natural production of CO_2 has always been in balance with its absorption by oceans and plants (during photosynthesis). The whole process of CO_2 production + absorption is called the "Carbon Cycle".

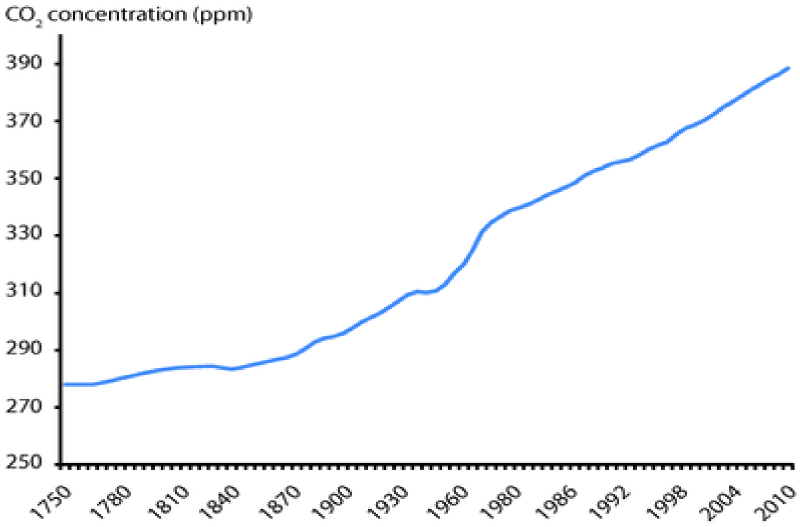


Figure 1-4 CO_2 concentration trend in atmosphere (European Environment Agency 2012)

As a result of the balance caused by the natural carbon cycle, the concentration of CO_2 in the atmosphere remained constant (with negligible fluctuations) for thousands of years. However, due to the increase in anthropogenic activities and especially industrial revolution, an excessive amount of CO_2 has been introduced to the atmosphere, causing an imbalance in the rates of production and absorption, leading to a considerable increase in the atmospheric CO_2 level. Figure 1-5 shows a schematic of the carbon cycle. The impact of industrial production of carbon dioxide on unbalancing the cycle is evident.

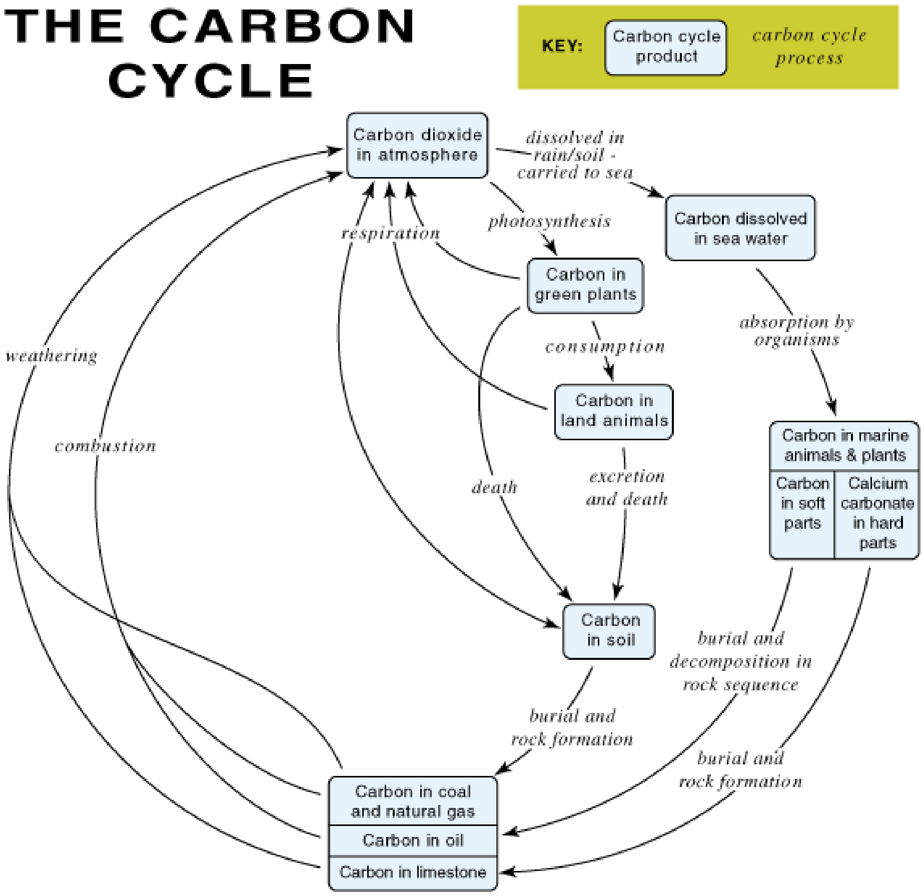


Figure 1-5 Carbon cycle (RSC 2012)

1. 1. 3 Carbon Dioxide Emission Reduction

The increasing atmospheric CO_2 level has turned into an international concern. Hence, numerous studies and research projects have been carried out on different methods of CO_2 emission reduction. In general, there are three ways to reduce CO_2 introduction to the atmosphere:

1- Process improvement, efficiency increase, and fuel consumption optimization.
2- Technology development and using biofuels instead of conventional fossil fuels.
3- Applying CO_2 separation methods.

Various methods exist for CO_2 sequestration. These methods can be categorized in two general groups:

1- Physical/chemical processes
2- Biological processes

Physical and chemical processes include the absorption process (Tontiwachwuthikul et al. 1992), membrane separation process to separate CO_2 from the flue gas (Hägg and Lindbråthen 2005), air separation and gas recycling methods (Shao and Golomb 1996), and CO_2 absorption via photocatalysis (Wang et al. 2011).

In biological processes, CO_2 is consumed by microorganisms and is converted to other substances. The aim of these processes is to convert CO_2 to other compounds that make little or no contribution to the greenhouse effect, or can be used as a fuel or raw material for other processes. Conversion of CO_2 to methane/ acetate in thermophilic bioreactors (Zinder 1990) or CO_2 bio-mitigation using microalgae (Wang et al. 2008) are examples of biological CO_2 mitigation processes.

1.2 Objectives of This Study

As mentioned before, biological conversion of CO_2 to biofuel is one of the common and highly-emphasized methods that not only reduces CO_2 emission but also produces valuable substances such as methane.

Carbon dioxide can be converted to methane by an anaerobic process. This process can include single or multiple stages and involve several types of microorganisms.

Usually, this process starts with gas-liquid contact to dissolve CO_2 into the liquid phase, followed by acidogenesis and methanogenesis steps (Salomoni et al. 2011).

Abedi et al. (2011) used pulp-and-paper industry wastewater to study the bioconversion of dissolved CO_2 in the wastewater via anaerobic digestion and the impacts of operating conditions, such as pH and temperature, on the removal efficiency of COD and conversion of CO_2 to methane. They reported a maximum COD and CO_2 removal of 50% and 94%, respectively. Xue Jiao (2012) performed similar tests on a different type of pulp-and-paper wastewater and obtained 49% and 90% for the maximum COD and CO_2 removal efficiencies, respectively. These investigations imply that the pulp-and-paper wastewaters have high potential in terms of biotreatability and conversion of dissolved CO_2 to methane.

In this project, the main focus was on the first step of the process which is absorption of CO_2 from gas phase into the liquid phase. Although numerous studies have focused on designing CO_2 capturing systems by synthetic alkaline solutions, the literature is relatively poor in terms of studying the applicability of wastewater generated by industrial/ municipal activities as an absorbent of CO_2 in a continuous system, with the aim of CO_2 conversion to biofuel. On the other hand, the dissolution of gases into liquids is a very strong function of operating conditions. Hence in this work, the ability of the wastewater generated in a pulp-and-paper plant to absorb CO_2 under different operating conditions was studied.

Based on the reported high biotreatability potential of pulp-and-paper effluents and the dissolved CO_2 in it as mentioned above, this type of effluent was worthy to undergo a general and detailed study on different stages of AD, starting from absorption of CO_2 by this wastewater.

The main objectives of this project were:

1- To evaluate CO_2 absorption capacity of pulp-and-paper wastewater.
2- To determine the impact of operating conditions on the final CO_2 dissolution capacity of wastewater.
3- To compare wastewater to low-concentration alkaline solutions for their respective CO_2 absorption capacity.

Chapter 2: LITERATURE REVIEW

2.1 Carbon Dioxide Capture and Storage/ Conversion

2.1.1 Introduction

As briefly mentioned in Chapter 1, a great deal of effort has been devoted to decreasing carbon dioxide emissions to the atmosphere through efforts such as energy consumption reduction, replacing fossil fuels with green fuels or zero carbon fuels, increasing process and fuel efficiency, and carbon dioxide capture and storage (CCS). Carbon dioxide capture and storage is a very common method. An assessment has shown that CCS contributes to approximately 20% of CO_2 emission reduction (Lakeman and Tofani 2010). One very conventional method of CCS, commonly used in power generation plants and oil extraction industries, is to inject CO_2 into underground reservoirs for storage and/or use. Enhanced Oil Recovery, in which CO_2 is used to improve oil extraction from underground oil reservoirs, is one of the main applications of CO_2 injection into underground (Alimahmoodi and Mulligan 2011).

Although CCS is a very useful method, there are many problems associated with this process (Kaplan et al. 1983) such as waste production, uncontrolled air emission/leakage, pollution of land and surface water due to possible spills, corrosion and other process problems (Millemann et al. 1982). Hence, alternative methods should be considered such as conversion of the generated CO_2.

Carbon dioxide can be converted to other compounds by chemical processes. Many other products such as acids, alcohols, esters, lactones, carbamates, urethanes, urea derivatives, various copolymers, and polymers can be produced from CO_2 (Xiaoding and Moulijn 1996). Carbon dioxide can also be converted to cyclic carbonate via a homogeneous catalytic reaction (Tian et al. 2008). Methane can be produced from CO_2 through both catalytic hydrogenation and by photoelectrocatalysis at room temperature (Ichikawa 1995).

Catalytic hydrogenation of CO_2 is generally expressed by the following reaction:

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O \qquad (2\text{-}1)$$

This reaction is exothermic (Ma et al. 2009) and requires a catalyst in order to reduce fully oxidized and highly stable carbon to methane at acceptable rates (Wang, et al. 2011).

Another method for CO_2 conversion is through application of biological processes. One technology is to convert CO_2 to methane by hydrogenotrophic methanogens in a fixed-bed bioreactor (Lee et al. 2012). The reaction taking place is similar to Equation (2-1). However, less energy is required for the reaction to take place and depending on the retention time in the reactor, up to 100% conversion can be achieved in this process.

Another proposed method is to capture and utilize the generated CO_2 in power plants by microalgae (Benemann 1997). Based on this approach, the microscopic algae could grow in large and open ponds in which CO_2 from power plant flue gas was sparged. A similar approach was used to convert CO_2 by microalgae in a photobioreactor (Watanabe and Hall 1996). The application of algae, in general, can be costly and requires further research on technology development.

A highly focused technique for CO_2 conversion to biofuel is anaerobic digestion (AD). In this process, as briefly described in Chapter 1, anaerobic microorganisms convert CO_2 to other substances such as methane. Since the present research intends to examine the potential of anaerobic conversion of CO_2 to methane, this process will be discussed in further detail in the following sections.

2.2 Anaerobic Digestion

2.2.1 Introduction

Anaerobic digestion can occur in any oxygen depleted environment where organic materials are converted to CO_2 and methane. This uncontrolled process can lead to the emission of CO_2 and methane which are the two major contributors to the greenhouse effect and global warming.

However, a controlled anaerobic biodegradation can be profitable and beneficial (Banks et al. 2007, Georgacakis and Dalis 1993). CO_2 can undergo AD which leads to the production of methane. By capturing the effluent gas of this process, the generated methane can be used as a source of energy. This implies that the CO_2 from effluents of industrial plants and/or from the atmosphere can be captured and converted to energy-rich methane.

Several reactions take place during the AD process under four main steps, as follows:

1- Hydrolysis
2- Acidogenesis
3- Acetogenesis
4- Methanogenesis

In each step, different reactions take place and complex organic materials are broken down to simple materials. The final products generated in the last step are methane and CO_2. Each step is briefly described in the following paragraphs.

2.2.1.1 Hydrolysis

Hydrolysis is the step in which complex proteins, carbohydrates, lipids, and other organic and inorganic compounds that exist in waste material are broken down to simpler compounds. In this step, bacteria convert polymeric compounds to monomeric substances. For instance, cellulose is broken down to glucose and proteins are converted to amino acids.

2.2.1.2 Acidogenesis

In this step, monomers produced in hydrolysis are converted to simple acids by acid-generating bacteria under anaerobic conditions.

2.2.1.3 Acetogenesis

Acetogenic bacteria convert generated acids to hydrogen, CO_2, and acetate.

2.2.1.4 Methanogenesis

Methanogenesis is the last step of AD in which methanogenic bacteria (methanogens) convert the product of previous steps to methane. Methane, in this stage, is produced in two ways: either by breaking down acetic acid, and converting it to CO_2 and methane, or through the reduction of CO_2 by hydrogen. The latter is the dominant method as long as enough H_2 is available to the methanogens (Verma 2002). Methanogens are strictly anaerobic and are very sensitive to environmental conditions.

2.2.2 Anaerobic Digestion Systems

Anaerobic digesters vary in terms of stages and design. In general, AD can be performed in a single or multiple-stage process. Single-stage is a simple process in which all the four steps mentioned above take place in one reactor, while in a multi-stage process, acidogenesis and methanogenesis take place in separate reactors. The latter is often called a two-phase anaerobic digestion (TPAD). In general, TPAD is preferred due to better process control. Acidogens and acetogens exhibit different activities, growth rates, and pH optima compared to methanogens. Optimum pH range for acidogens is 4-6 while methanogens exhibit activity in the range of 6.5-8, thus requiring different operating conditions. The TPAD process can facilitate the establishment of optimum operating conditions for each step and will provide a better control of process parameters, hence enhancing the process efficiency (Fezzani and Ben Cheikh 2010).

The first stage in TPAD is to absorb CO_2 from the flue gas or from the atmosphere by a liquid absorbent. The dissolved CO_2 can further undergo biological treatment and be converted to methane. Since this project focuses on the first stage of process, methods for CO_2 absorption will be discussed in the following section.

2.3 Carbon Dioxide Absorption Techniques

Various techniques have been proposed and studied for the absorption of CO_2 from the atmosphere or from gas effluents of industrial plants. These methods mainly consist of absorption of CO_2 into a liquid phase through gas-liquid contact. However, other methods such as absorption on solid surfaces have been proposed in a more limited extent. Absorption of CO_2 on PbO at ambient temperature was studied (Mu et al. 2011). They dispersed PbO on a support material made from silica gel, providing a large specific absorbing surface area of 710 m^2/g. An absorbing capacity of 59 mg/g was achieved in their experiments for the prepared absorber under ambient temperature and pressure with low CO_2 concentration.

Capturing CO_2 on a solid surface is a recent development but it has a limited application compared to physico/chemi-sorption by a liquid absorbent. Liquid absorbents are usually alkaline solutions that exhibit a good capacity to absorb CO_2. Alkaline (NaOH or KOH) and buffering (Na_2CO_3 or $NaHCO_3$) aqueous solutions are among the most effective chemical absorbents that are frequently used (Brettschneider et al. 2004). Furthermore, primary ($R{-}NH_2$) and secondary ($RR'{-}NH$) alkanolamines are also very popular reagents (Mandal et al. 2003). In general, the reactions between CO_2 and the absorbents, as discussed above, can be expressed by the following relationships: (Georgiou et al. 2007):

$$CO_2 + 2OH^- \longrightarrow CO_3^{2-} + H_2O \tag{2-2}$$

$$CO_2 + CO_3^{2-} + H_2O \longrightarrow 2HCO_3^- \tag{2-3}$$

$$CO_2 + R{-}NH_2 + H_2O \longrightarrow R{-}NH_3^+ + HCO_3^- \tag{2-4}$$

$$CO_2 + RR'{-}NH \longrightarrow RR'{-}NCOO^- + H^+ \tag{2-5}$$

The detailed mechanisms and overall reactions of CO_2 with NaOH and NH_3 absorbents are also available in the literature. For NaOH (Javed et al. 2010):

$$CO_2 + H_2O \longrightarrow HCO_3^- + H^+ \tag{2-6}$$

$$CO_2 + OH^- \longrightarrow HCO_3^- \tag{2-7}$$

$$HCO_3^- + OH^- \longrightarrow CO_3^{2-} + H_2O \tag{2-8}$$

The overall reaction of CO_2 and NaOH:

$$CO_2 + 2OH^- \longrightarrow CO_3^{2-} + H_2O \tag{2-9}$$

For NH_3, two mechanisms exist (Li et al. 2003). The first mechanism includes reactions (2-10) to (2-12):

$$NH_{3(g)} + H_2O_{(l)} \longleftrightarrow NH_4OH_{(l)} \tag{2-10}$$

$$2NH_4OH_{(l)} + CO_{2(g)} \longleftrightarrow (NH_4)_2CO_{3(s)} + H_2O_{(l)} \tag{2-11}$$

$$(NH_4)_2CO_{3(s)} + CO_{2(g)} + H_2O_{(l)} \longleftrightarrow 2NH_4HCO_{3(s)} \tag{2-12}$$

where NH_4OH is the aqueous form of NH_3. The other mechanism is:

$$CO_{2(g)} + 2NH_{3(g)} \longrightarrow NH_2COONH_{4(s)} \tag{2-13}$$

$$NH_2COONH_{4(s)} + CO_{2(g)} + 2H_2O_{(g/l)} \longleftrightarrow 2NH_4HCO_{3(s)} \tag{2-14}$$

The overall reaction of CO_2 and NH_3 for both mechanisms:

$$NH_{3(g)} + CO_{2(g)} + H_2O_{(l)} \longrightarrow NH_4HCO_{3(s)} \tag{2-15}$$

Carbon dioxide capture by liquid absorption under different conditions and with various absorption systems and absorbers has been studied. Chen et al. (2005) used a spray dryer, with NaOH + $Ca(OH)_2$, DEA + $Ca(OH)_2$, and $Ca(OH)_2$ at different concentrations to absorb CO_2. The operating temperature was reported to be around 150°C. NaOH showed the best removal efficiency of 48 % at the concentration of 10% NaOH + 5% $Ca(OH)_2$ and inlet CO_2 concentration of 10%. Diethanolamine (DEA) showed a lower performance under the same conditions. They suggested that at high temperatures, DEA participates in a reverse reaction that releases CO_2, and hence was not found suitable for their experiments. However, DEA was reported to function well when used at the temperature range of 30-70 °C in a wet scrubber rather than at higher temperatures in a spray dryer (Wey et al. 2003). For NaOH, the best absorbent concentration was reported to be 10 % when tested at 5, 10, and 20%. The impact of higher concentration on the viscosity of the absorbent and hence the diffusion coefficient of CO_2 from gas to liquid absorbent was the reason for the lower capacity of 20% solution compared to 10%. Increasing the inlet CO_2 concentration also decreased the removal efficiency of all absorbents. In conclusion, sodium hydroxide showed the best results compared to the other absorbents under all examined conditions, while pure $Ca(OH)_2$ showed an irregular and random behavior. They also compared the results of their experiments to the results of a wet scrubber experiment performed by Chen (2000). Table 2-1 shows the comparison of the spray dryer and wet scrubber systems using NaOH as the absorbent.

Table 2- 1 Comparison of wet scrubber and spray dryer (Chen et al. 2005)

Comparisons of spray dryer and wet scrubber		
Operating conditions	Spray dryer	Wet scrubber
Absorbents	10% NaOH + 5% $Ca(OH)_2$	2 N NaOH
Liquid/gas ratio (mL $^{-1}$)	2.82	10
Gas flow rate (L min^{-1})	11	10
Liquid flow rate (L min^{-1})	31	100
Inlet concentration of CO_2 (%)	10	15
Reaction temperature (°C)	150	50
Removal efficiency of CO_2 (%)	48	37

Based on the results presented in Table 2-1, it can be concluded that besides higher efficiency, less liquid flow rate is required in a spray dryer and consequently less absorbing reagent would be consumed.

The impact of temperature on the removal efficiency of CO_2 by different absorbents was also studied as a part of experiments carried out by Wey et al. (2003). Their results indicated that each absorbent exhibited a different behavior in the range of the examined temperature. In other words, different absorbents showed their best performance at different temperatures.

Different absorbers have also been compared in terms of kinetics and removal efficiency. Gonzalez-Garza et al. (2009) compared the efficiency and absorption kinetics of ammonia (NH_3), monoethanolamine (MEA), diethanolamine (DEA), and methyldiethanolamine (MDEA) as the chemical absorbents of CO_2. The experimental NH_3 concentration range was 2-5% wt. at a temperature range of 278-303 K. Their results showed that the best performance was observed by using 5% NH_3 at 278 K, with 303 K standing in the second place. In general, they reported a faster kinetics for NH_3 except at 2% NH_3 and 288 K and 3% NH_3 and 278 K.

In a different study by Yincheng et al. (2011), ammonia and NaOH were used as two different absorbents and the impact of operating conditions were studied and compared in a fine spray column. Their system consisted of an absorption tower with an inner diameter of 12 cm and height of 130 cm, equipped with two atomizers at the top of the tower, producing droplets with 30-40 μm average diameters based on the liquid pressure (0.69 – 1.11 MPa). The gas influent was an artificial mixture of pure CO_2 and N_2 and the temperatures of the gas and liquid were controlled by electroheaters before being fed into the contactor. In order to take samples from the gas outlet and for the gas composition analysis, an infrared analyzer was used to measure the CO_2 content. The gas sample passed through specific absorbents in order to protect the analyzer from ammonia or water vapor. In their study, the effect of absorbent concentration, absorbent volume flow rate, total gas flow rate, inlet concentration of CO_2, initial temperature of column, and CO_2:absorbent molar ratio were investigated. Tables 2-2 and 2-3 show the studied parameters in their research for each absorbent.

Table 2- 2 Experimental parameters for NH_3 (Yincheng et al. 2011)

NH_3 concentration (% w/w)	Liquid (sorbent) flow rate (mL/min)	Total gas flow rate (L/min)	Initial temperature (°C)	CO_2 inlet concentration (% v/v)
2-10	180	7.6	28	15
5	120-200	13	28	15
8	160	7.6 – 24.7	28	15
5	180	7.6	28-38	15
5	180	7.6	28	7-15

To study the effect of absorbent concentration on the CO_2 removal efficiency, liquid flow rate of 180 mL/min and gas flow rate of 7.6 L/min with an inlet CO_2 volumetric concentration of 15% were used at the operating temperature of 28 °C. The concentration range of 2-10 % for both NaOH and NH_3 were examined. According to their reported results, the concentration increase from 2% to 8% notably increased the removal efficiency while NH_3 showed a better efficiency compared to NaOH. A maximum removal of 98.4% at NH_3 concentration of 8% was reported while the maximum efficiency of removal by NaOH was about 90% at concentrations greater than 5%.

To study the effect of absorbent volume flow rate, Yincheng et al. (2011) carried out a series of experiments at the solution concentration of 5 % (w/w) for both absorbents, inlet CO_2 concentration of 15% (v/v), and temperature of 28 °C. The gas flow rates were 13 L/min and 7.6 L/min for the tests with NH_3 and NaOH solutions, respectively. Based on the results, as the flow rate of NH_3 increased from 120 mL/min to 200 mL/min, the absorption efficiency increased from 76.4% to 85.4%. This is mainly due to an increase in the gas-liquid interface area that enhances the absorption of CO_2. Since the gas flow rate was lower during NaOH experiments, the efficiency was higher than that of NH_3.

Table 2- 3 Experimental parameters for NaOH (Yincheng et al. 2011)

NaOH concentration (% w/w)	Liquid (sorbent) flow rate (mL/min)	Total gas flow rate (L/min)	Initial temperature (°C)	CO_2 inlet concentration (% v/v)
2-10	180	7.6	28	15
5	120-200	13	28	15
8	160	7.6 – 24.7	28	15
5	180	7.6	28-38	15
5	180	7.6	28	7-15

The effect of gas flow rate on CO_2 removal efficiency was also studied at the total flow rate of 7.6 L/min to 24.7 L/min at an initial temperature of 28 °C and inlet CO_2 concentration of 15% (v/v). The NaOH concentration was 5% (w/w) and the gas flow rate was 180 mL/min while for NH_3, the concentration and gas flow rate were 8% and

160 mL/min, respectively. The results showed that as the gas flow rate increased, the removal efficiency considerably decreased since the molar ratio of the absorbent to carbon dioxide decreased. The decrease in the efficiency when using NaOH as the absorbent was much higher. For the effect of temperature, the investigators showed that with an increase from 28 to 38 °C, the removal efficiency increased from 91.8% to 96.4% when using NH_3. Also for NaOH, a temperature range of 28 to 54 °C was studied, which exhibited higher removal efficiency at higher temperatures, mainly due to an increase in the absorption rate. Finally, for the effect of absorbent to carbon dioxide ratio, an optimum ratio of 4.43 was determined for NaOH. A higher ratio barely increased the efficiency but increased the quantity of consumed absorbent and hence the costs. For NH_3, the optimum ratio was reported to be 9.68.

Using a basic solution as an absorbent seems to be desirable in terms of high CO_2 removal efficiency. However, the costs associated with the production of the synthetic basic solutions as well as the regeneration process and other consequences such as corrosion in system are to be considered. In some research works, attempts have been made to replace the absorbent with other material. The main focus is to use an already-existing absorbent which can be regenerated later and/or does not require regeneration.

The separation of CO_2 from landfill gas (LFG) through the application of alkaline industrial wastewater was examined in a lab-scale study (Gaur et al. 2009). These authors compared the capacity of wastewater to those of NaOH and NH_3 solutions. LFG is a rich source of CO_2 and CH_4. It consists of an average value of 45% CO_2 (Themelis and Ulloa 2007, EIA 1997). Hence removing CO_2 can lead to obtaining a rich methane gas which can be subsequently used as a fuel. The wastewater (WW) used in the experiments had a very high alkalinity, contained 2-5% of NH_3 and was compared to NaOH and NH_3 solutions. A total alkalinity of 34,000 mg/L of $CaCO_3$ and a pH of 10.4 was reported for the WW. Their experimental apparatus mainly consisted of a LFG source, activated carbon filter, saturator, reactor, pH meter, and an infrared (IR) gas analyzer. The LFG samples were taken from the site and were transferred to the lab in proper gas containers. Since LFG can contain trace toxic materials, an activated carbon filter was used. In the reactor, one liter of the absorbent was contacted with the gas. The gas was sparged in the reactor through a ceramic diffuser for an efficient and even distribution. The pH of the liquid absorbent was constantly monitored by a pH meter and the gas phase CO_2 content was monitored by the IR analyzer. The results indicated that the WW showed a different behavior compared to NaOH solutions in terms of the final pH, pH change, and reaction rate. However, similarities were observed with the NH_3 solutions, confirming the existence of NH_3 in the WW. A final pH of 7-8 was achieved which is ideal for WW neutralization. Their result also showed that for a one liter volume of WW, it takes almost an hour for the liquid to saturate while for NaOH solutions, this time was much shorter, within 10-20 minutes.

In another research, the capacity of a dye-bath effluent with very high alkalinity to absorb CO_2 was investigated (Georgiou et al. 2007). The experimental system in this research consisted of a packed column with 5 cm inner diameter and 60 cm height, randomly packed with cylindrical glass rings (1x1). Figure 2- 1 shows the layout of their experimental setup.

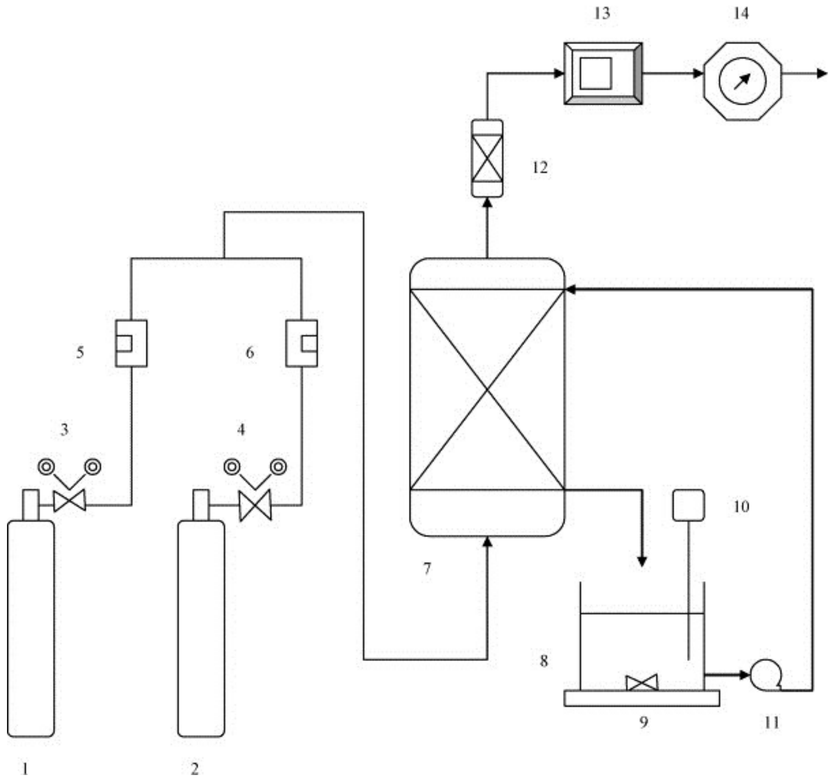


Figure 2- 1 Experimental apparatus (Georgiou et al. 2007): (1) gas cylinder (20% CO_2, 80% N_2), (2) gas cylinder (pure N_2), (3 and 4) pressure-release valves, (5 and 6) gas-flow controllers, (7) packed-tower, (8) liquid solvent vessel, (9) magnetic stirrer, (10) pH-meter, (11) peristaltic pump, (12) silica-gel trap, (13) CO_2–IR analyzer and (14) gas-flow meter

A gas flow of ~1 L/min with a CO_2 concentration of ~10% was used during the experiments. An IR analyzer was used to measure the inlet and outlet CO_2 content of gas and a silica gel desiccator was used to protect the analyzer. The pH of the liquid solvent was measured by a pH meter. One liter of liquid absorbent (filtered) was used during the experiments and it was re-circulated in each set. The researchers concluded that this type of wastewater can be successfully used to absorb CO_2 due to its high alkalinity and hydroxyl groups in the form of azo-reactive dyes that exist in the wastewater. Their results also showed that CO_2 injection can be used to neutralize dye-bath effluents.

In all work done on CO_2 capture by waste material, the main focus was to use alkaline wastewaters with a high pH to remove CO_2 and for pH adjustment. As mentioned earlier, the absorbed CO_2 in the liquid phase can undergo biological treatment and be converted to energy-rich methane. In research work by Salomoni et al. (2011), CO_2 was captured from a gas mixture in a scrubber by a basic solution (NaOH). After the capture, the solution was required to go through a regeneration process in order to separate basic solution and aqueous CO_2. Aqueous CO_2 was then mixed with sludge in order to undergo biological conversion. Simulated WW of enhanced oil recovery containing dissolved CO_2 and its capability to convert to methane was studied (Alimahmoodi 2009).

2.4 Pulp-and-Paper Process

Pulp-and-paper refers to a large industry in which paper and other derivatives are produced from wood. Canada is one of the leading countries in the pulp-and-paper industry and several leading companies work in this field across the country. In December 2011, a total number of 868 establishments in paper manufacturing with 228 pulp, paper, and paperboard mills were reported in Canada (Industry Canada 2011) which shows the extent and importance of this industry in Canada.

In general, the process starts with wood preparation in which the wood is debarked and chipped for the next steps. The next step is pulping in which cellulose fibers are separated from impurities, especially from a substance called lignin. The technologies used to separate lignin are different and can be mechanical, chemical, semi-chemical, or recycling. Kraft technology is an example for chemical pulping. There are also hybrid technologies that are commonly being used for better performance. Thermomechanical and chemi-thermomechanical pulping are examples of hybrid pulping technologies.

After pulping, bleaching is applied to remove color from the pulp and finally the pulp is ready for the paper process. The WW effluents of pulp-and-paper plants are different with respect to their constituents based on the technology and materials used during the process. As for gas effluents, pulp-and-paper contributes to a significant amount of greenhouse gas (GHG) emission. The GHG from the pulp-and-paper industry is mainly CO_2, and the emission sources are the fossil fuel combustion as a source of energy and CO_2 is emitted as a product of reactions.

Based on the brief description provided in this section as well as the potential of pulp-and-paper WW to undergo biological treatment for conversion of CO_2 to methane which was explained in the previous chapter, it can be concluded that a study on the WW of the pulp-and-paper industry which would also contribute to the reduction of CO_2 emission would be preferable and of great benefit.

Chapter 3: MATERIALS AND EXPERIMENTAL METHODS

3.1 Materials Used

3.1.1 Wastewater Sample

Wastewater samples were taken from various pulp-and-paper plants that use chemi-thermomechanical pulping (CTMP), Kraft, and paper recycling technologies. Wastewater samples were shipped in 20L buckets containing wastewater after primary treatment. The sampling point was chosen based on the fact that this project was intended for biological treatment of wastewater, and hence the treatment process had to occur after the primary treatment. In addition, raw wastewater that has not gone through primary treatment may contain large particles which cause operational difficulties. Also, if CO_2 injection takes place before primary treatment, some dissolved CO_2 may escape to the atmosphere before secondary treatment.

3.1.2 Carbon Dioxide

Carbon dioxide cylinders with a high purity of 99% were purchased from Praxair Inc. and were used as the source of CO_2. The cylinders were equipped with a gauge pressure controller and the pressure was adjusted to 14.5-15 psi (100.31-103.35 kPa) during the experiments.

3.1.3 Air

Air was used to mix with CO_2 in different proportions. The source of air was the high pressure air line that was available in the lab. A pressure regulator was used to bring the pressure down to values close to the atmospheric pressure.

3.1.4 Nitrogen

Since the samples could exchange carbon dioxide with the environment and in order to maintain an initial pH without changing the sample properties and adding another substance to the samples, N_2 was used to adjust the pH. An injection of about 2-3 minutes was applied if the sample pH had varied due to absorption/desorption of CO_2.

3.1.5 Sulfuric Acid

Sulfuric acid (H_2SO_4) was used for titration tests to characterize the wastewater samples. The concentration of sulfuric acid was 0.02 N which is the standard concentration for alkalinity measurement via titration. The acid solution was prepared through dilution of 1 N sulfuric acid, purchased from Fisher Scientific (Montreal, Canada).

3.1.6 Sodium Hydroxide

1 N and 10 N sodium hydroxide (NaOH) solutions were used for various applications such as sulfuric acid standardization test and to capture CO_2 gas in the outlet of the system in order to prevent CO_2 introduction to the atmosphere.

3.1.7 pH Buffer Solutions

The buffer solutions with pH values of 4, 7, and 10 were purchased from Fisher Scientific (Montreal, Canada) for pH meter calibration. Buffer solution 4 was also used for temporary storage of pH electrode to maintain the electrode's calibration and response accuracy.

3.2 Experimental Set-up and Instruments

3.2.1 Absorption Column System

The absorption system used in the experiments was a bubble column in which the gas was distributed in the form of bubbles in the liquid. The system design was based on preliminary tests that were performed on the WW samples. Figure 3- 1 and 3-2 show the general layout of the experimental system. The constituents of the system will be briefly described.

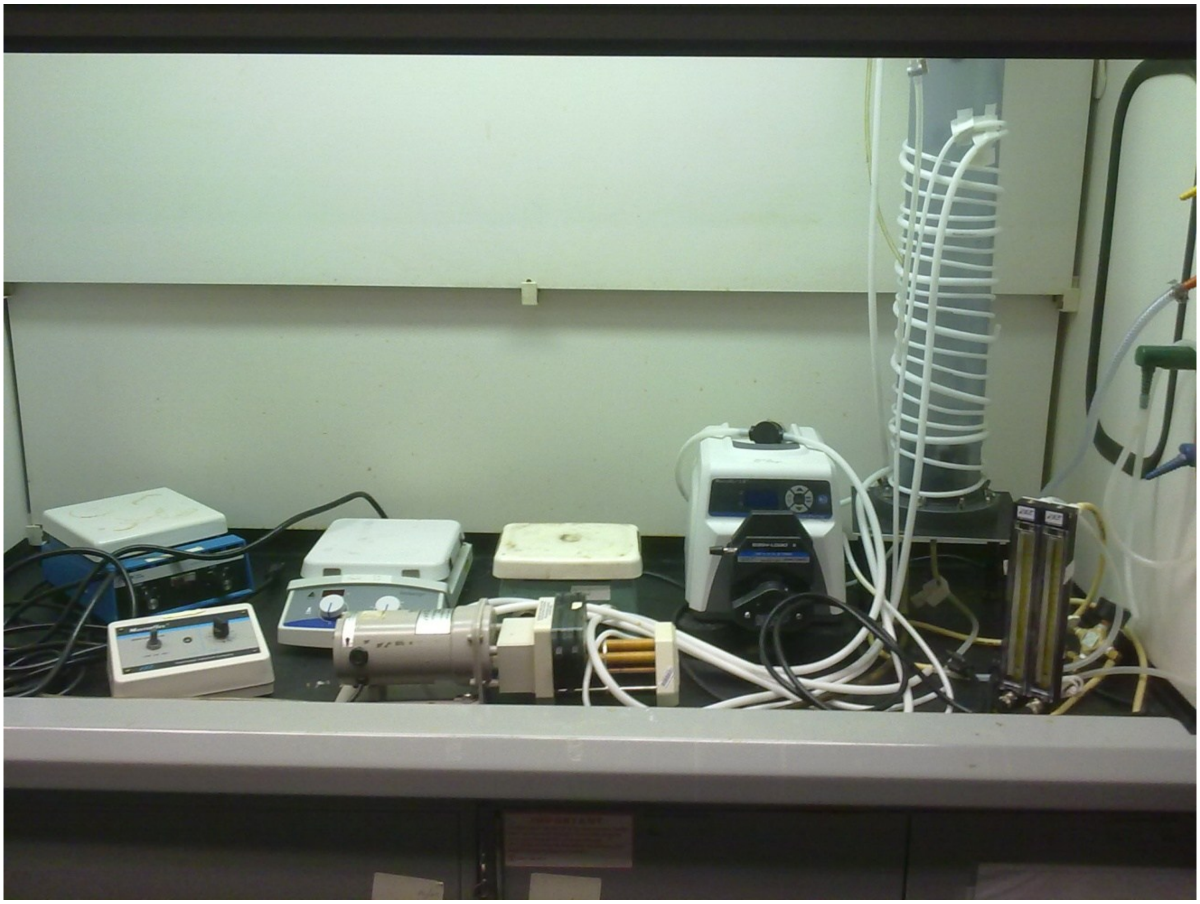


Figure 3- 1 Experimental setup of the absorption system

3.2.1.1 Column

A PVC cylinder with a height of 60 cm and diameter of 10 cm was used as the absorption column. The column was equipped with a nozzle to distribute the liquid in a fairly fine droplet shape, and a gas diffuser. The nozzle was designed to be height adjustable, enabling it to be elevated to rinse the experimental system.

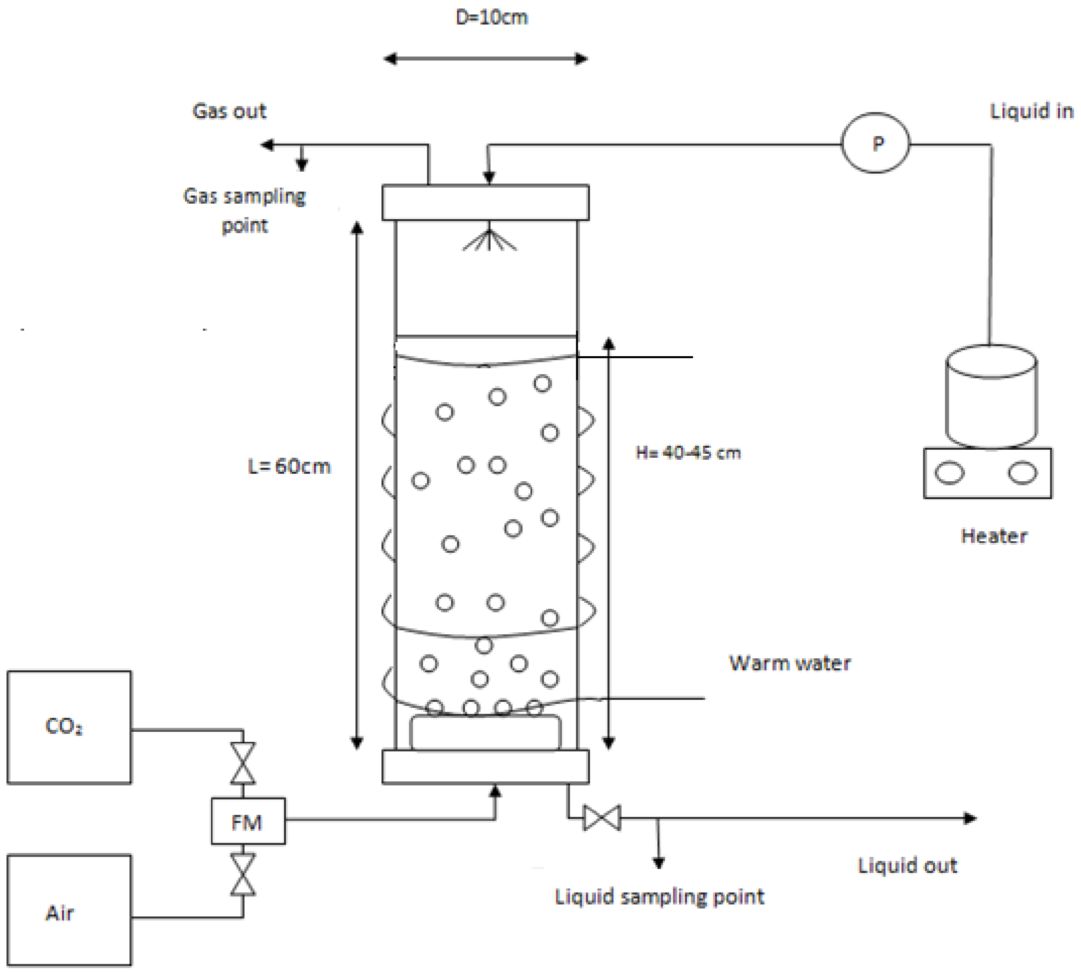


Figure 3- 2 Absorption system schematic
(*P: pump, FM: Flowmeter)

The gas diffuser consisted of 6 small cylindrical diffusing stones that were placed on a circular shape disc. This arrangement provided a proper gas distribution throughout the column cross-sectional surface as well as a good mixing, leading to an efficient gas-liquid contact.

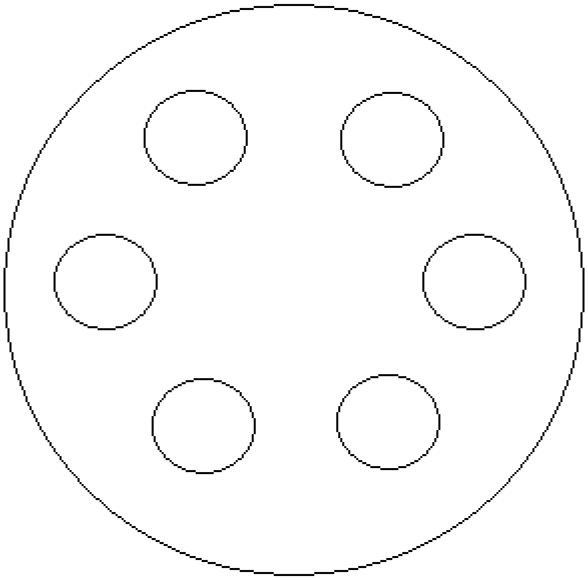


Figure 3- 3 Diffuser layout schematic of the gas distributor in the bubbling column

3.2.1.2 Warm Water Coil

In order to maintain an identical temperature throughout the system and to minimize any error or fluctuation in the obtained results due to temperature variation in the system (i.e. different inlet and outlet temperatures of the liquid phase, and temperature drop due to gas injection), a warm water coil was used by twisting long tubes around the column. Water at the temperature of 55-65 ^{o}C was circulated around the column to prevent temperature drop.

3.2.1.3 Pump

Two peristaltic pumps (Masterflex, Cole-Parmer) were used in the reported experiments: One for pumping the WW into the column, and the other one for warm water circulation in the coil around the column. A Masterflex Easy-Load II pump head was connected to the pump which could provide the desired flow range for the experiments.

3.2.1.4 Sample Container and Tubing

4L Pyrex beakers were used for sample preparation and also as containers for sample storage during the experiments. Three types of tubing were used in the experiments: Masterflex Tygon #24, Masterflex C-flex #15, Masterflex C-flex #16. The Tygon #24 and C-flex #15 tubing were used for the WW delivery, and #15 and 16 were used for the warm water coil.

3.2.1.5 Hotplate/Stirrer

The WW samples were stored in the refrigerator (at 4 °C) to prevent changes in their characteristics. Hence, they needed to be heated to reach the desired temperatures. Two hotplates were used to adjust the temperature of WW samples as well as heating up the water used for the warm water jacket.

3.2.1.6 Strainer

A small laboratory-scale strainer purchased from Cole-Parmer with a mesh size of 60 μm was used to remove large particles from the wastewater. The mesh size was chosen based on the characterization tests performed on the WW samples.

3.2.1.7 Flow Meters

A 150-mm graduated flow meter was used for measuring the flow rate of each gas. The calibration datasheet for the two gases were prepared and supplied by Cole-Parmer.

3.2.1.8 Sampling Points

Samples from both liquid and gas streams were taken for analysis. There were two sampling points at the outlet of gas and liquid streams. The sampling points were chosen to be as close as possible to the exits in order to minimize the possible time lag for sampling at each time.

3.2.2 Thermometer

A general purpose thermometer (non-mercuric) was used to measure the temperature of samples before and during entrance to the column.

3.2.3 pH Meter

An Accumet AR25 pH/mV/Ion meter (Fisher Scientific, Canada) was used to measure the pH of samples. A pH electrode (probe) was purchased from Fisher Scientific which was equipped with an integrated Automatic Temperature Compensation (ATC) connection to avoid any error caused by temperature variation. The ATC also acts as a thermometer and was used to verify the temperature readings from the thermometer.

3.2.4 Gas-tight Syringes

Gas analysis was performed to study and address the efficiency of wastewater in removing CO_2. Gas samples were taken through the sampling point using 10 ml gas-tight syringes (Hamilton 1000 series). Gas-tight syringes assured minimization of gas leakage and were used to store and carry the samples to the analyzer.

Figure 3- 4 Gas-tight syringe (Source: Hamilton Co.)

3.2.5 Liquid Sampling Bottles

30 ml HDPE bottles (Fisher Scientific, Montreal, Canada) were used to keep liquid samples taken from the liquid sampling point during the experiments.

3.2.6 Parafilm Sealer

The Parafilm sealer, purchased from Fisher Scientific, was used to enhance the sealing of gas and liquid samples stored in the gas-tight syringes and HDPE bottles, respectively.

3.2.7 COD Vials, Reactor, and Reader

In order to measure the COD concentrations, direct-read COD vials (Reagent, TNT plus, UHR) were purchased from Hach (USA). The vials were prepared and heated up in a COD reactor (DRB200). Finally, the COD value readings were done through a Perkin Elmer Lambda 40 UV/VIS spectrometer.

3.3 Analytical Methods

3.3.1 Alkalinity Measurement

Alkalinity is a term that refers to the capacity of a solution to react with and neutralize acid. Alkalinity can be measured by titration of the solution with a standard acid and the end-point of the titration is at the pH in which all the constituents of solution which contribute to alkalinity have reacted (Environmental Protection Agency 2012). Each solution has a different end-point. This end-point is defined based on the type and concentration of different species that exist in the solution. In standard methods, an end-point of 4.5 is considered for measuring total alkalinity (TA). However, in a complex sample with various unknown species, the actual end-point can be determined through experimental data. This can be done by gradual addition of the standard acid (0.02 N H_2SO_4) to the solution and reading the value of pH and its rate of change. The correct end-point of a solution is the point at which the rate of change of pH per added volume ($d\mathrm{pH}/dV_{\mathrm{titrant}}$) of titrant is at maximum. This method was used for alkalinity measurements.

In our experiments, titration was the method used to characterize the wastewater in terms of its alkalinity, pH, and resistance to pH variation by acid addition. Titration was done by using a digital titrator (Metrohm Titrino 848). The titration agent was the standard solution for alkalinity test which is 0.02 N H_2SO_4.

Figure 3- 5 Metrohm Titrino 848

The employed titrator could be programmed to provide precise titration curves and accurate results. Numerous tests were performed to obtain optimum titration parameters, such as the rate of titration (i.e. rate of addition of acid), stirring speed, end-point, etc.

In engineering calculations for wastewaters, alkaline species are: carbonate (CO_3^{2-}), bicarbonate (HCO_3^-), hydroxyl (OH^-), and hydrogen ion (H^+). The alkalinity of the sample can be defined as:

$$\text{Alkalinity} = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] - [H^+] \qquad (3\text{-}1)$$

Alkalinity is usually reported in mg/L or g/L of $CaCO_3$. Based on the end point value and volume of the acid at the end-point which was obtained from titration, total alkalinity (TA) can be obtained from the following formula:

$$\mathrm{TA} = \frac{\text{Normality of Acid (0.02 N)}\ x\ 50000\ \left(\text{Equivalent weight of CaCO3 in}\frac{\mathrm{mg}}{\mathrm{L}}\right)\ x\ \text{Vol of acid (ml)}}{\text{Vol of sample (ml)}}$$

(3-2)

3.3.2 Particle Size Analysis

A laser particle size analyzer (PSA) was used to obtain particle size distribution (PSD) in the samples. This is critical for choosing the size of tubing and nozzle. For samples with high large particle contents, larger nozzles should be used to prevent clogging.

The Horiba LA-950 PSA is able to measure particles in the range of 10 nm to 3 mm. It determines the size of particles based on the concept that a particle scatters laser (or light) at an angle based on its size. Larger particles scatter light at a lower angle and higher intensity while smaller particles scatter light at wide range angle and less intensity. In a sample containing particles with various sizes, a pattern of scattered light is produced which relates to the intensity and angle size of the particles. This pattern is transformed into a particle size distribution result by the instrument.

Figure 3- 6 Particle size analyzer

The LA-950 instrument consists of two light sources, a sample handling system to control the interaction of particles and incident light, and an array of high quality photodiodes to detect the scattered light over a wide range of angles. The scattered light collected on the detectors is used to calculate the particle size distribution of sample. The instrument can analyze particles dispersed in the liquid phase as well as dry solid samples. Figure 3- 7 shows a schematic of the liquid sample analyzer of the PSA.

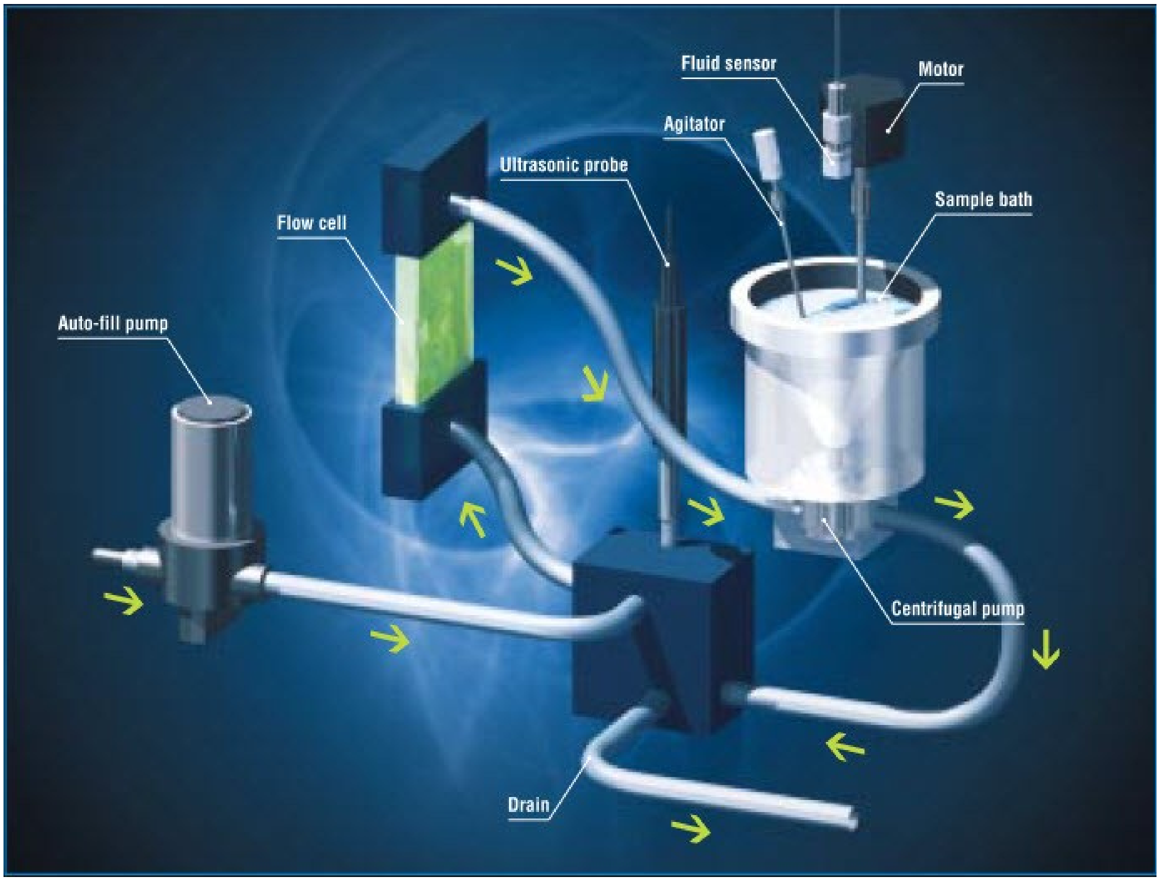


Figure 3- 7 PSA system schematic (Source: Horiba Scientific)

The procedure for the PSD determination, according to the manual of instrument, is:

1- Shake sample container to have an even distribution of particles throughout the sample.

2- Fill the sample bath with water by instructing the instrument through its software and turn the agitator on.

3- Take a specific volume of sample (e.g. 3 ml) and add it to the sample bath, making sure to avoid large clumps and particles since they may damage the instrument.

4- The ultrasonic option can be used if there are clumps in the liquid made of smaller particles. In this case, ultrasonic cannot be used since the PSD of samples has to be determined under natural conditions without breaking the bonds between the particles.

5- Run the software based on the settings and preferences given to the software.

6- Obtain the PSD result as a curve, as well as the other information relating to the median size, etc.

Figure 3-8 presents the sequence of events used for the particle size analysis.

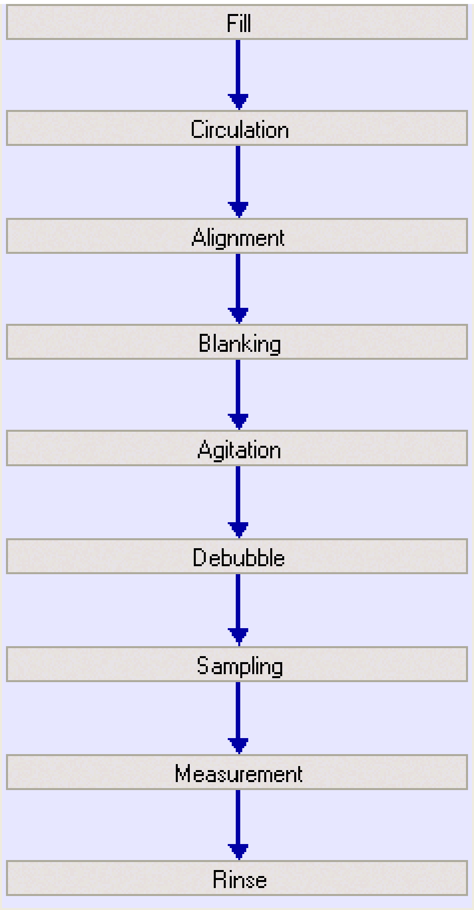


Figure 3- 8 PSA sequence

3.3.3 COD Measurement

Chemical Oxygen Demand (COD) is an important factor in wastewater treatment. The COD of wastewaters should not exceed a certain value prior to discharge into the environment in order to conform to environmental regulations. A fraction of COD which is biodegradable will be consumed by microorganisms. The procedure for using direct-reading COD reagent vials and related apparatus is as follows:

1 - Preheat the COD block heater to 150°C.

2- Remove the cap from a COD twist-cap vial.

3- Add 2 ml sample to the vial.

4- Replace the twist cap.

5- Thoroughly mix the contents of the sealed vial by shaking.

6- Place the twist-cap vial in a COD heater block capable of maintaining approximately 150 °C for 2 hours.

7- Remove the vial from the heater and allow it to cool down.

8- Allow any suspended precipitate to settle and wipe the outside of the twist cap clean.

9- Put the vial into the reader without shaking the vial intensively.

10- The reader automatically adjusts itself based on the barcode on the vial. Read the value of COD in mg/L on the COD reader.

3.3.4 Dissolved Carbon Dioxide

The dissolved carbon dioxide concentration in the liquid was determined by using the alkalinity and pH values, and the equilibrium that exists between alkaline species (Neal 2001). When CO_2 is dissolved in water, it is first transferred from the gas phase to the liquid phase, into aqueous CO_2. The aqueous CO_2 then forms carbonic acid. Carbonic acid is a weak acid and dissociates to form bicarbonate. Finally, bicarbonate further dissociates to carbonate. All the four components are in equilibrium through the following reactions:

$$CO_{2(g)} \longleftrightarrow CO_{2(aq)} \tag{3-3}$$

$$CO_{2(aq)} + H_2O_{(l)} \longleftrightarrow H_2CO_{3(aq)} \tag{3-4}$$

$$H_2CO_{3(aq)} \longleftrightarrow H^+_{(aq)} + HCO_3^-{}_{(aq)} \tag{3-5}$$

$$HCO_3^-{}_{(aq)} \longleftrightarrow H^+_{(aq)} + CO_3^{2-}{}_{(aq)} \tag{3-6}$$

The equilibrium between these reactions is a function of temperature and pH. At 25°C, the equilibrium constant for reactions (3-5) and (3-6) are:

$$K_1 = \frac{[H^+][HCO_3^-]}{[CO_{2(aq)}]} = 4.47 \times 10^{-7}\ M \tag{3-7}$$

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 4.68 \times 10^{-11}\ M \tag{3-8}$$

And the combination of (3-6) and (3-7) leads to:

$$K_1K_2 = \frac{[H^+]^2\,[CO_3^{2-}]}{[CO_{2(aq)}]} = 2.1 \times 10^{-17} \qquad (3\text{-}9)$$

If the pH of samples is known, $[H^+]$ and $[OH^-]$ can be determined from the three following equations:

$$[H^+] = 10^{-pH} \qquad (3\text{-}10)$$

$$pOH = 14 - pH \qquad (3\text{-}11)$$

$$[OH^-] = 10^{-pOH} \qquad (3\text{-}12)$$

By solving equations (3-7) to (3-12) based on equation (3-1), the concentration of aqueous CO_2 can be determined. To solve these equations, Microsoft Excel was used. A sample for calculation is available in Appendix B.

The above equations provide the concentration of $CO_{2(aq)}$ at equilibrium during the steady-state mode of operation. However, they can also provide an approximation of CO_2 concentration in the liquid phase during the transient mode, from the start-up to the steady-state, assuming pseudo-equilibrium before steady-state. This assumption allowed us to observe the trend and rate of change in the concentration of $CO_{2(aq)}$ during the transient mode. However, as mentioned above, is the estimated values are more accurate when the system is at steady-state.

3.3.5 Gas Analysis

Gas analysis was performed by taking samples at pre-determined times during the experiments and their injection into a Varian CP-3800 gas chromatograph (GC) in order to determine the concentration of CO_2 in the outlet gas. The Varian CP-3800 gas chromatograph (GC) was equipped with a Varian 1041 on-column injector, fitted with a Valco instruments Co. Inc. (VICI) pressurized valve delivery system as a 0.2 ml sample plug.

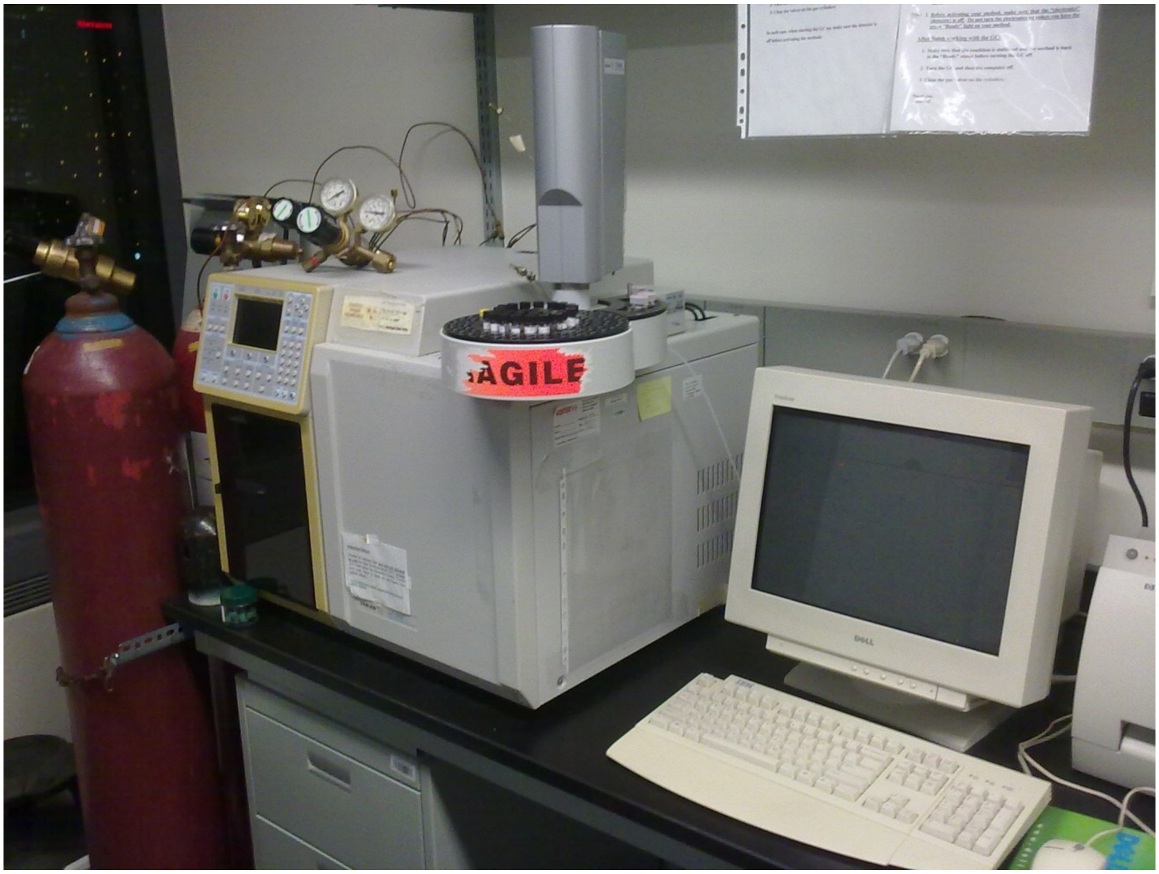


Figure 3- 9 Gas chromatograph (Varian CP-3800)

The gas samples were taken by gas-tight syringes from the gas sampling point at the exit (effluent gas), at the top of the absorption column. For injection of samples into the GC, a luer-lock valve was used to ensure a sealed connection between the syringe and the instrument. The method used for this analysis was based on the method of Alimahmoodi and Mulligan (2011) and was modified according to the experimental conditions used in the present research. Test conditions are available in Appendix C.

The GC produced the results of the gas composition analysis in the form of a chromatogram that consisted of two peaks. The first peak, usually observed after 2.5-3 minutes, related to the air and the second one was for CO_2 and had a retention time of 7-8 minutes. The concentration of CO_2 in the outlet gas was calculated by the GC software based on the ratio of areas of the two peaks.

3.4 Experimental Procedure

3.4.1 Preliminary Tests

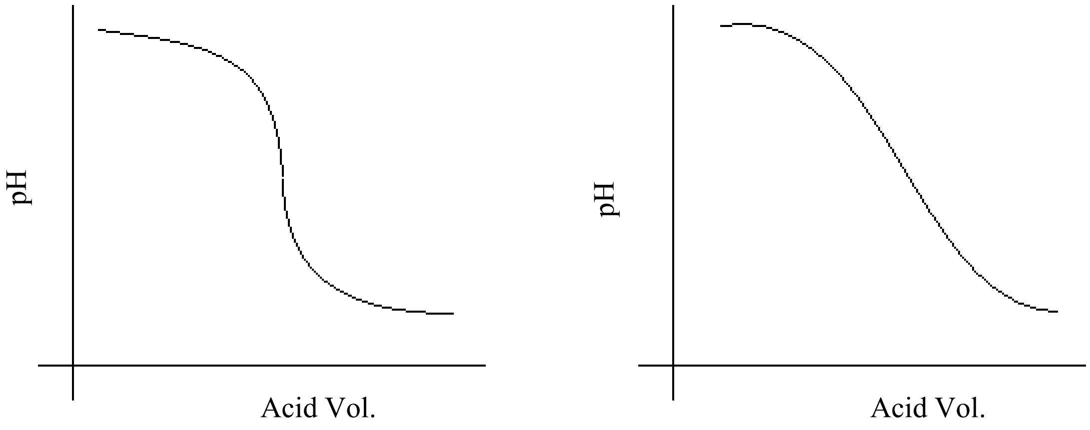
A series of initial tests were performed to select the best WW type among the three available samples. The experiments of this section were done in order to determine the approximate capacity of WW samples to absorb CO_2 as well as some WW characteristics which are important in biological treatment.

The initial pH, alkalinity, and COD of samples were measured in the preliminary tests. The best results were produced by the sample with a higher pH, alkalinity, and COD. The pH and alkalinity are related to CO_2 absorption capacity of the WW while COD refers to the bio-conversion process.

In other experiments, calibration tests were performed. The tubing was calibrated based on the RPM of the employed pump. The flow meters were calibrated by a water displacement test. A brief explanation of each test will be provided in the following paragraphs.

3.4.1.1 pH and Alkalinity

pH and alkalinity are key factors by which one can determine CO_2 absorption capacity of the WW. The buffering capacity of a WW sample plays an important role in its CO_2 absorption capacity. For a complex liquid such as WW that contains numerous components, further study has to be performed on the samples. A liquid with a high buffering capacity resists pH changes following acid addition, while a more noticeable change is observed in the pH value of a liquid with a low buffering capacity. The buffering capacity is related to the alkalinity of WW and can be observed while measuring alkalinity by the titrometer. Hence, this principle was used in the present research. A pH vs. acid volume graph was obtained from the titrometer that showed the trend of pH change by the gradual addition of acid (H_2SO_4). For a sample with a low buffering capacity, a dramatic drop in pH is observed at points close to the titration end-point. In a highly buffered sample, the change in pH is slower and often gradual. As mentioned in section 3.3.3, the end-point in alkalinity titration is the point at which ($dpH/dV_{titrant}$) of titrant is at maximum.



(a) (b)

Figure 3- 10 – Titration curve for liquid sample with (a) low buffering capacity and (b) high buffering capacity.

Based on the curve and end-point obtained, alkalinity of the samples was measured. pH value of the samples was simply measured by pH meter, as explained before.

3.4.1.2 COD Measurement

One of the objectives of this research was to absorb CO_2 into the WW, preparing it for further conversion of the dissolved CO_2 to methane. The reduction of chemical oxygen demand (COD) can be achieved by biological treatment. Although this project did not involve a study on the bio-conversion of CO_2, the COD concentrations of different WW samples were measured. The method and materials used to measure the COD is thoroughly explained in sections 3.2.9 and 3.3.1.

3.4.1.3 Tubing Calibration

The pump used in this research could be controlled by the rotations per minute (rpm) of the head. Each rpm is associated with a specific flow rate for a given size/type of tubing. Hence it was necessary to determine the given flow at each rpm. In order to do so, a container was filled with liquid which was pumped at different rpms into a graduated cylinder. The volume of pumped liquid into the cylinder in one minute gave the flow rate associated with each rpm in mL/min.

3.4.1.4 Particle Size Distribution

Particle Size Distribution (PSD) tests were performed in order to obtain more information on the characteristics of the WW as well as the required information to design the absorption column system. The PSD is an important factor in choosing the size of tubing, nozzle, filter mesh, etc.

3.4.2 Batch Tests

Batch tests were performed to determine the maximum capacity of WW samples to absorb CO_2, and to obtain data for comparison with the results of the continuous tests. During the batch tests, the experimental column was filled with wastewater and the gas was injected into the system. The gas composition was 60% CO_2 mixed with air (volumetric). The gas flow rate was controlled by the flow meters that were connected to the gas sources. The pressure of the gas sources was set to 14.5 - 15 psi (100.31 – 103.35 kPa). The flow rate reading on the flow meters was based on the charts which were available from the vendor of each gas. The tests were performed at three temperatures of 25 °C, 30 °C, and 35 °C. During the tests, warm water passed through the water coils that were wrapped around the column in order to maintain the desired temperature throughout the column. Tables 3-1 and 3-2 show the conditions and the studied parameters, and the sampling schedule for batch tests, respectively.

Table 3- 1 Batch tests layout

Test #	**Temperature (± 0.1 °C)**	**Total gas flow (± 0.1 L/min)**	**CO_2 % (Vol.)**	**Gas analysis**
Batch – 1	25	2.5	60	No
Batch – 2	30	2.5	60	No
Batch – 3	35	2.5	60	No

Table 3- 2 Batch test sampling schedule

T (min)	**0**	**0.5**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**12**	**15**	**20**
Gas sampling	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Liquid sampling	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓

3.4.3 Continuous Tests

Continuous tests were the main part of the present research in which the WW capacity to absorb CO_2 was studied under different operating conditions in a continuous-mode process. Various parameters including the temperature, gas composition, total gas flow, and liquid flow rate were studied.

The studied temperatures were chosen based on the fact that microorganisms that convert CO_2 to methane are mesophilic bacteria and the common temperature range for their operation is 25-35 °C. The gas composition was based on the fact that various industrial gas effluents have different CO_2 contents. The composition of 20 % CO_2 in air was chosen as a representative for effluents with low CO_2 content while the composition with 60% CO_2 stood for CO_2-rich effluents. One test was also performed with a gas having 40% CO_2.

Both liquid and gas samples were analyzed in this series of tests. The liquid analysis was performed to provide information for the future biological treatment since the volume of absorbed CO_2 controls the quantity of methane generation. The gas composition measurement was performed during certain tests in order to evaluate the capacity and applicability of the WW to remove CO_2 from a gas mixture. Table 3- 3 shows the schedule of tests performed on WW samples as well as the measured parameters.

Table 3- 3 Conditions of continuous tests conducted with the WW samples

Test #	Temperature (± 0.1 °C)	Liquid flow (± 10 mL/min)	Total gas flow (± 0.1 L/min)	CO_2 % (Vol.)	Gas analysis
1-a	25	200	2.5	20	Yes
1-b	25	200	2.5	40	Yes
1-c	25	200	2.5	60	Yes
2-a	30	200	2.5	20	Yes
2-b	30	200	2.5	60	Yes
3-a	35	200	2.5	20	Yes
3-b	35	200	2.5	60	Yes
4	25	200	1.25	60	No
5	25	300	2.5	60	Yes
6	25	300	1.25	60	No
7	30	300	2.5	60	Yes

In addition to the WW, two tests were carried out using NaOH solutions with different concentrations in order to compare the behavior, strength, and capacity of WW samples and caustic solutions to absorb CO_2. Table 3- 4 shows the details of tests carried out with NaOH solutions.

Table 3- 4 Tests performed on NaOH solutions

Test #	**NaOH concentration (M – % w/w)**	**Temperature (± 0.1 °C)**	**Liquid flow (± 10 mL/min)**	**Total gas flow (± 0.1 L/min)**	**CO_2 % (Vol.)**	**Gas analysis**
8-a	0.025 – 0.1	25	200	2.5	60%	Yes
8-b	0.1 – 0.4	25	200	2.5	60%	Yes

The sampling of liquid was performed at known time intervals similar to the batch tests described in Table 3-2. Gas samples were also taken during the continuous-mode operation at 0, 0.5, 1, 2, 4, 8, 12, 15 minutes, and if applicable, at 20 minutes into the operation of experimental system.

Chapter 4: Results and Discussion

4.1 Preliminary Tests

4.1.1 Initial pH and Alkalinity

Three different types of wastewater were examined for the first stage of the experiment. As mentioned before, preliminary tests were performed in order to choose the sample with the highest capacity to absorb CO_2. The liquid alkalinity and initial pH are two parameters that indicate the CO_2 absorption capacity of the WW.

The test procedure was described in Chapter 3. The results of the initial pH and alkalinity of the three examined wastewater samples are presented in Table 4-1.

Table 4- 1 Initial pH and alkalinity of WW samples

Wastewater type/ description	Initial pH (± 0.1)	Alkalinity (mg $CaCO_3$ /L, ±50)
Cascades recycling paper mill WW	5.7	700
Kruger Inc. Kraft mill WW	6.8	500
Tembec Matane CTMP WW 1	6.5	2200
Tembec Matane CTMP WW 2	6.5	2700

Based on the results of this section, the CTMP WW samples showed better characteristics regarding CO_2 absorption capacity in terms of having higher alkalinity and initial pH.

4.1.2 Chemical Oxygen Demand (COD)

The removal of chemical oxygen demand (COD) is one of the most important parameters investigated in many biological treatment studies. The objective of this project, as mentioned before, was to study CO_2 absorption capacity of pulp-and-paper WW in an effort to convert the dissolved CO_2 to valuable methane. Hence, the COD concentrations of wastewater samples were measured in order to facilitate the selection of

WW for the next steps of experiments. Table 4-2 shows the COD values for all three WW types.

Table 4- 2 COD values of WW samples

Wastewater type	COD (± 100 mg/L)
Cascades recycling paper mill WW	2200
Kruger Inc. Kraft mill WW	1400
Tembec Matane CTMP WW 1	6100
Tembec Matane CTMP WW 2	9200

The CTMP WW 2 had the highest COD value of 9200 mg/L among all the samples and in general, the CTMP wastewater samples had higher a COD compared to the samples from other pulping technologies.

4.1.3 Tubing Calibration

Masterflex Tubings (Size #: 15, Material: C-flex) and (Size #:24, Material: Tygon) were used in the experiments. The RPM vs. flow graph was prepared for both tubings. Figures Figure A- and Figure A- in Appendix A demonstrate the linear calibration graphs obtained for the two different tubings.

4.1.4 Particle Size Distribution (PSD)

The main goal of PSD analysis was to obtain further information about physical properties of the WW samples as well as essential data to choose the more appropriate sample, assisting system design and feasibility of operation. The results of PSD for each sample are shown in Table 4-3.

Table 4- 3 Results obtained from particle size analysis

	Kraft	Recycled	CTMP 1	CTMP 2
Mean D (µm)	3.437	10.561	0.310	0.287
Diameter on Cumulative %	5%- 0.354 µm 90%- 7.537 µm	5%- 0.670 µm 90%- 10.505 µm	5%- 0.137 µm 90%- 0.372 µm	5%- 0.131 µm 90% -0.350 µm
Max size (µm)	152.45	300.52	6.72	2.98
Min size (µm)	0.339	0.669	0.100	0.087
Peak (µm - %)	0.510 - 32.438	0.887 – 43.061	0.296 - 17.835	0.296 – 18.495

As shown in Table 4-3, the CTMP 2 sample has the smallest particles compared to the other two types of wastewater. Table 4-3 also shows the difference between size distributions in different samples. Both CTMP WW samples have super fine particles, with some in the submicron range. Although the particles in Kraft and recycled-wastewater samples are not very large, with the maximum size of 152 and 300 µm respectively, this could cause some limitations in terms of process design. For a wastewater containing relatively larger particles, special considerations have to be taken into account. For example, if the system to be designed consists of a spraying liquid, the nozzle size has to be large enough to prevent clogging. This either prevents the inclusion of fine spray, which reduces process efficiency, or requires the addition of a fine filtration part to the system which requires additional cost and cleaning at specific time intervals. Based on this observation, the CTMP samples seem to be more feasible.

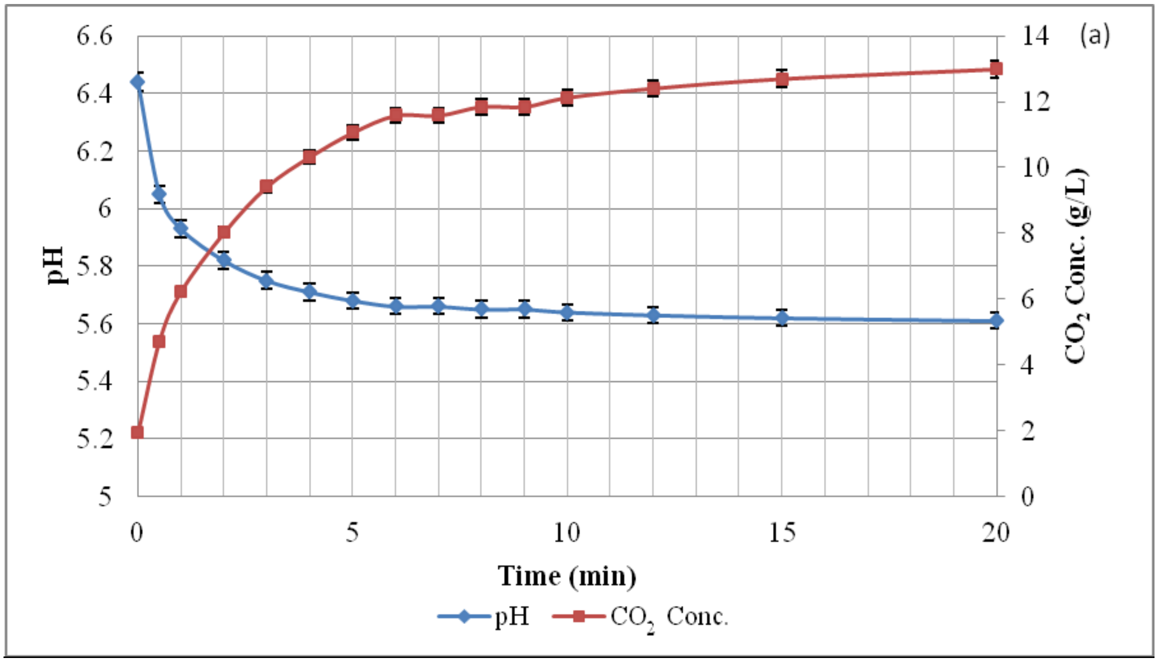
4.1.5 Conclusions

Based on the results of sections 4.1.2, 4.1.3, and 4.1.4, the best sample that showed higher potential for both CO_2 absorption capacity and biological treatment tests was identified to be the CTMP WW 2. This sample showed higher CO_2 absorption capacity, due to the higher alkalinity and pH, and also had smaller solid particles which provide more feasibility in terms of process design and maintenance. Although COD is not a precise indication of biotreatability as some part of it may not be biodegradable, generally, a higher COD can indirectly imply the existence of higher biodegradable organic material based on the approximate ratios of degradable to non-degradable COD in the WW. The COD of CTMP WW 2 was also higher compared to the other samples. Hence this sample was used in the following experiments which are the batch and continuous tests.

4.2 Batch Tests

Based on the results obtained from the characterization tests, the sample with the desirable characteristics was chosen for absorption tests. The first step after characterization was the batch mode test. The batch results were compared with the results of continuous tests which allowed proper analysis of the system behavior under different process conditions.

The batch tests were performed at 25 °C, 30 °C, and 35 °C, with the CTMP WW 2 samples. The operating conditions as well as the sampling schedule can be found in Tables 3-1 and 3-2. The results of batch tests at different temperatures are demonstrated in Figure 4-1.



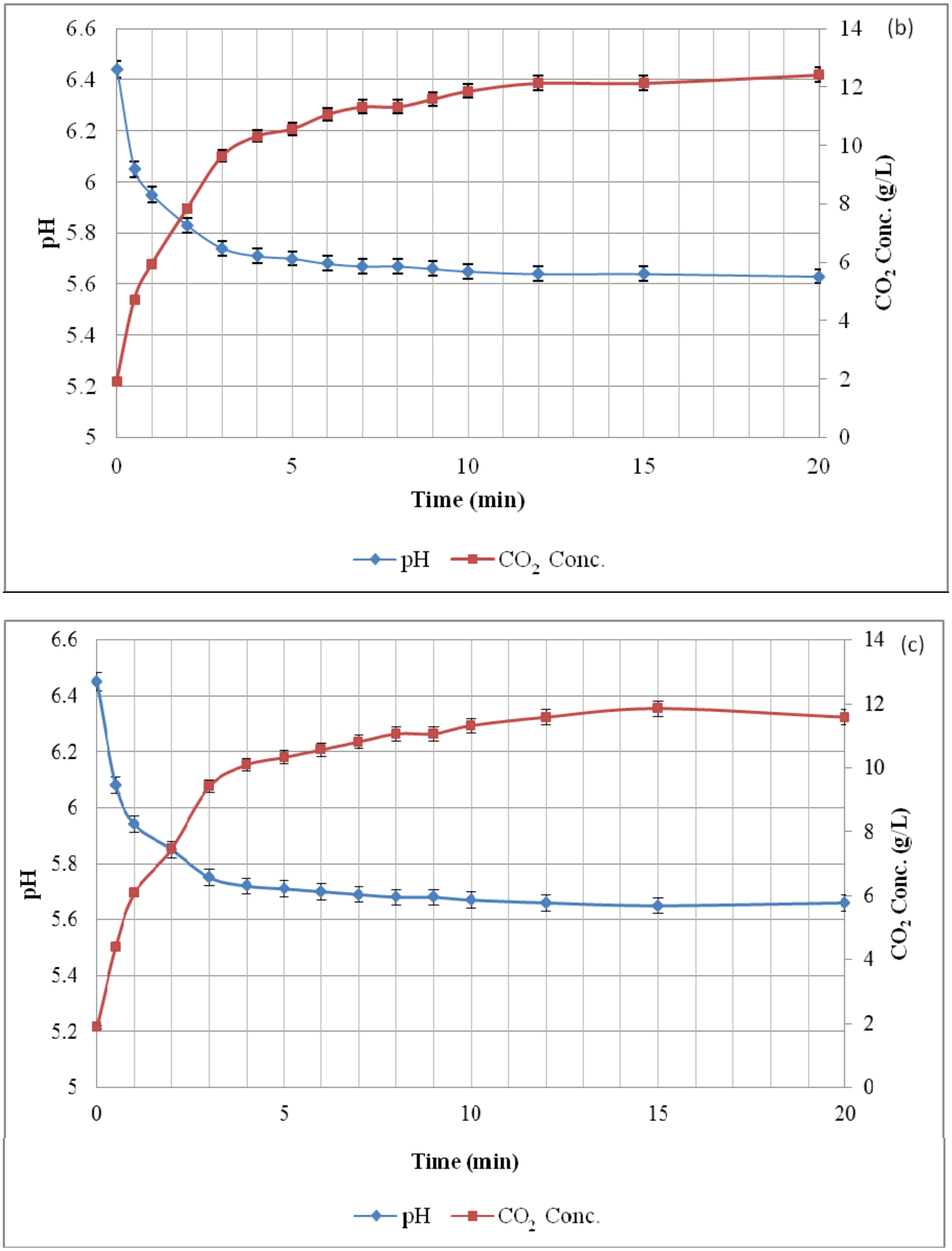


Figure 4- 1 Aqueous CO_2 concentration and pH trends vs. time for batch tests at (a) 25, (b) 30, and (c) 35 °C.

To better compare the results, the measured values of process parameters are presented in Table 4-4 and the aqueous CO_2 concentration at different temperatures is shown in Figure 4-2.

Table 4- 4 Batch test key values

	Initial pH	**Final pH**	**Maximum (final) $CO_{2(aq)}$ Conc. (g/L)**
Batch-1 (25 °C)	6.44	5.61	13
Batch-2 (30 °C)	6.44	5.63	12.4
Batch-3 (35 °C)	6.45	5.66	11.6

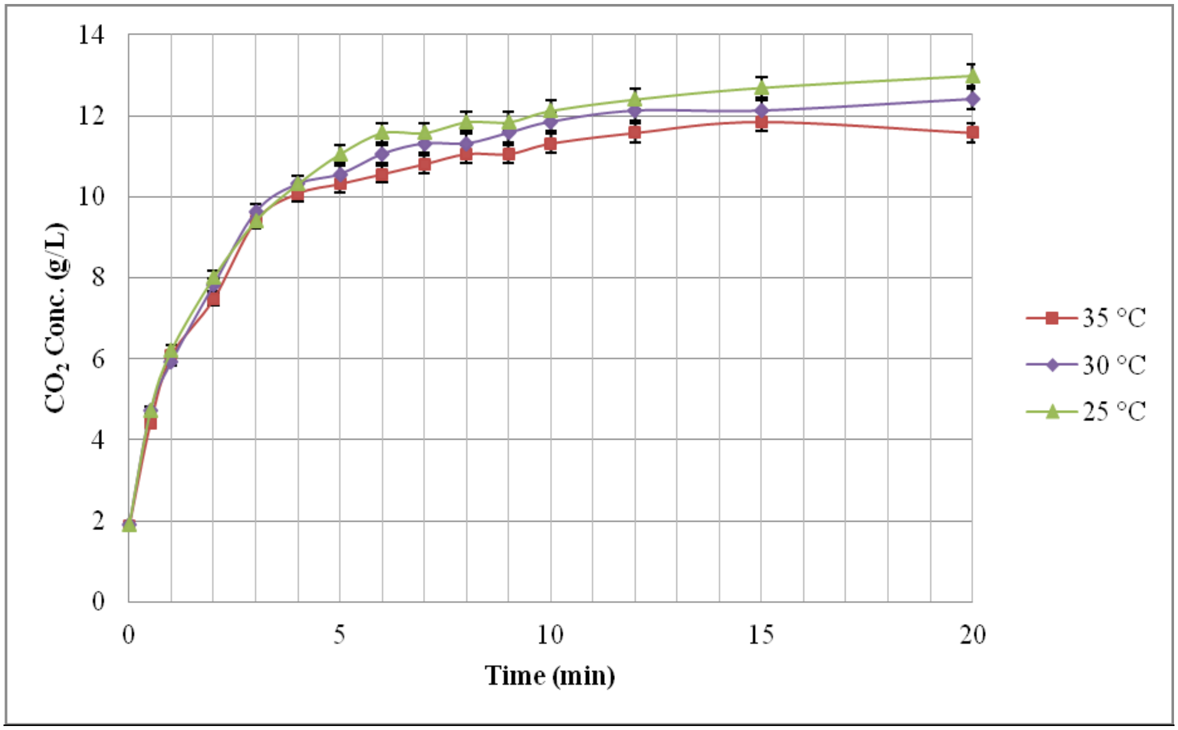


Figure 4- 2 Aqueous CO_2 concentration trend during batch mode tests at 25, 30, and 35 °C

It can be seen that with a 5 °C temperature difference, a difference in the final CO_2 concentration is observed. However, these differences which are approximately 0.6 g/L between the results obtained at 25 and 30 °C and 0.8 g/L between the results obtained at 30 and 35 °C, are relatively small. The observed trend also corresponds to the theoretical expectations since gases tend to dissolve more into liquids at lower temperatures (Holmes 1996). Other than the difference in final CO_2 concentrations, the graphs show similar trends.

4.3 Continuous Tests

The continuous tests were the main part of this research and were designed to study the behavior of the system in terms of CO_2 removal from gas phase and to determine the maximum capacity of WW to dissolve CO_2 under different operating conditions in continuous mode of operation. This part of the experiment was intended to study the applicability of WW as a CO_2 absorbent in continuous mode of operation in pulp-and-paper plants.

The continuous tests were designed to study the impact of various operating conditions. The examined parameters were temperature, gas composition, liquid flow rate, and gas flow rate. The examined parameters and their impacts will be explained in detail.

4.3.1 Temperature

Like the batch tests, three different temperatures were studied in this stage of work. For CO_2-rich and low-CO_2 gas compositions, having 60% and 20% CO_2 content, respectively, the obtained results are demonstrated in Figures 4-3 and 4-4.

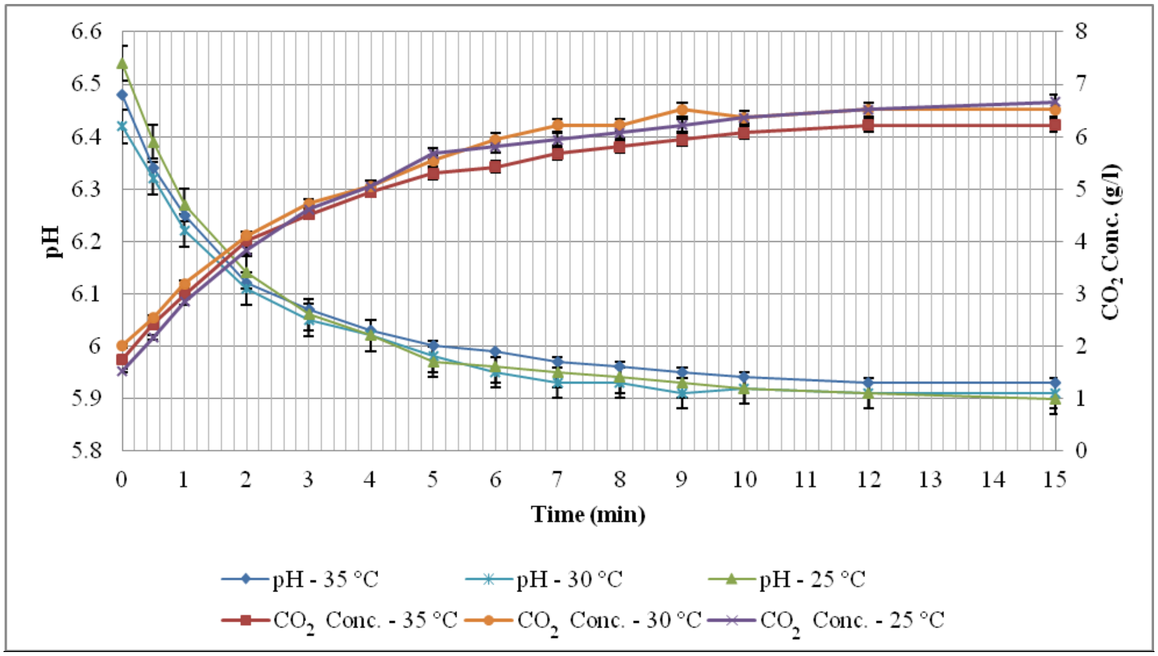


Figure 4- 3 Variations of aqueous CO_2 concentration and pH vs. time at different temperatures. inlet gas CO_2 content = 20%

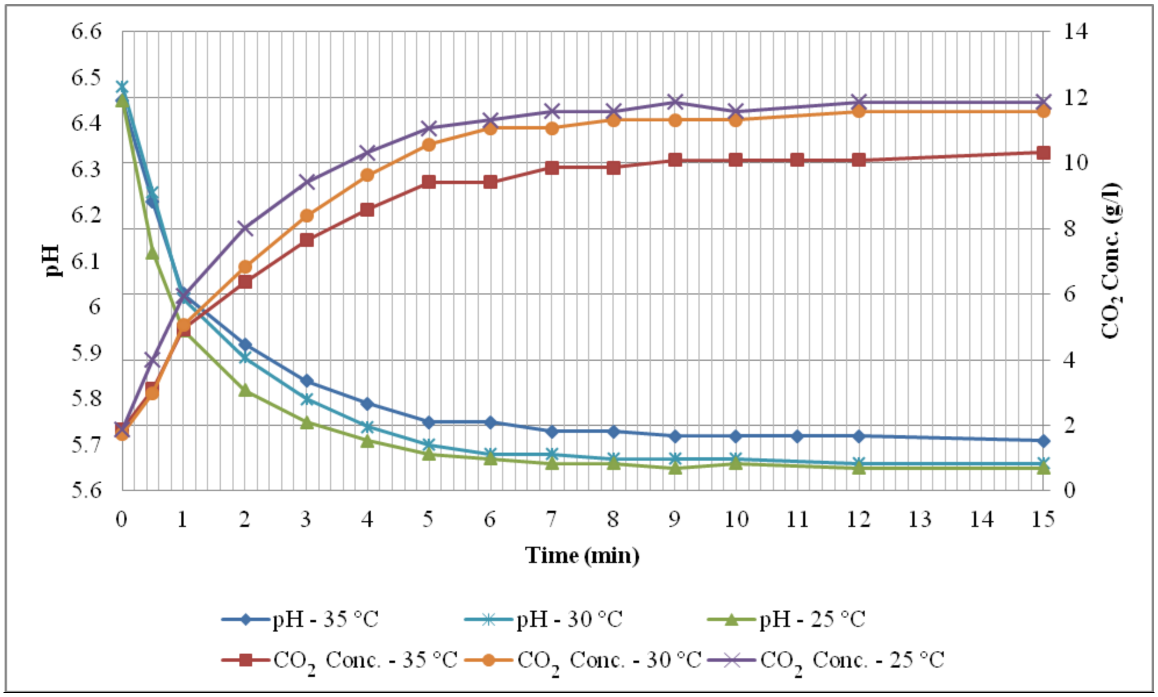


Figure 4- 4 Variations of aqueous CO_2 concentration and pH vs. time at different temperatures. inlet gas CO_2 content = 60 %

As observed for both gas compositions, the trends of the graphs are almost the same. However in terms of maximum CO_2 concentration, the results are different. This difference is better visualized in Figure 4-5, showing the final concentrations at the three different temperatures. At both gas compositions, the lower temperatures led to a higher CO_2 dissolution. The difference at low CO_2 content gas is relatively negligible, while for the CO_2-rich gas inlet, this difference is more visible. It was also observed that the difference between 25 °C and 30 °C is less than that between 30 °C and 35 °C.

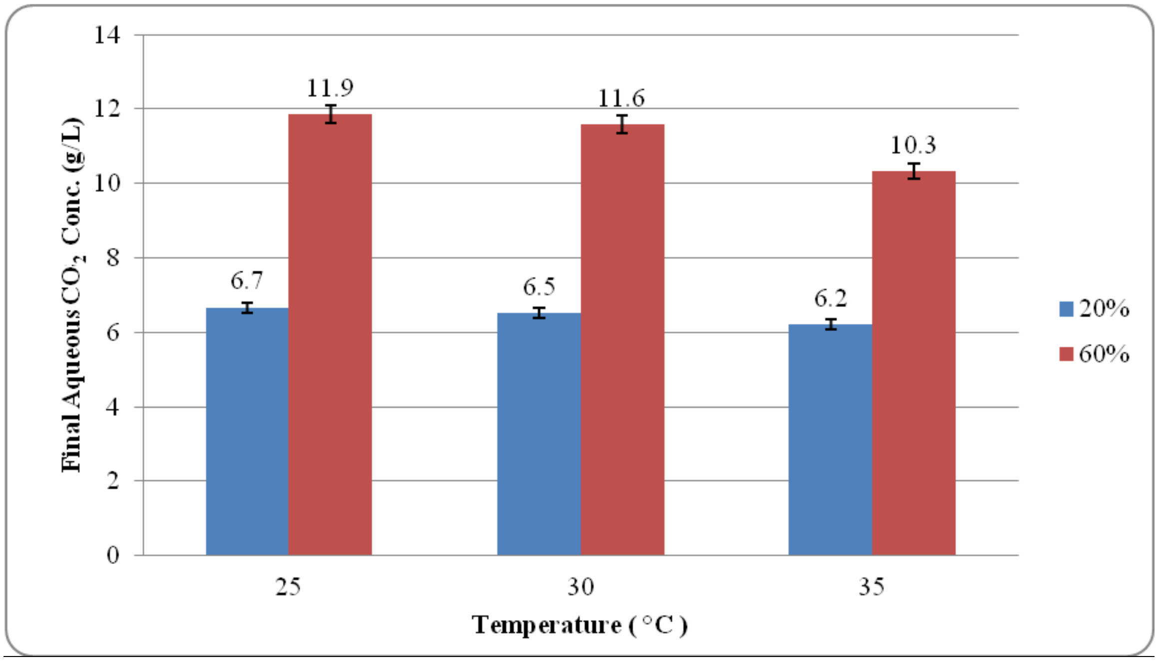


Figure 4- 5 Final CO$_2$ concentration at different temperatures and inlet gas compositions

4.3.2 Inlet Gas Composition

The impact of CO$_2$ content in the inlet gas on the dissolution of CO$_2$ into the WW was investigated at three different temperatures. The tests for the impact of gas composition were carried out along with the tests for the impact of temperature. However, the results of these tests are presented separately in order to demonstrate and compare the extent of the impact of gas composition at different temperatures. The operating conditions of individual tests are shown in Table 4-5.

Table 4- 5 Operating conditions during the inlet gas composition tests

Temperature (°C)	Inlet gas composition (% CO_2)	Initial pH
25	20%	6.54
	40%	6.47
	60%	6.45
30	20%	6.42
	60%	6.48
35	20%	6.48
	60%	6.45

Table 4-5 shows the initial pH values of the samples which were measured at the beginning of each test. An additional test with medium CO_2 content (40 %) was carried out at 25 °C. Figure 4-6 shows the trend of changes in pH and $CO_{2\ (aq)}$ vs. time, at 25 °C and with three different gas compositions.

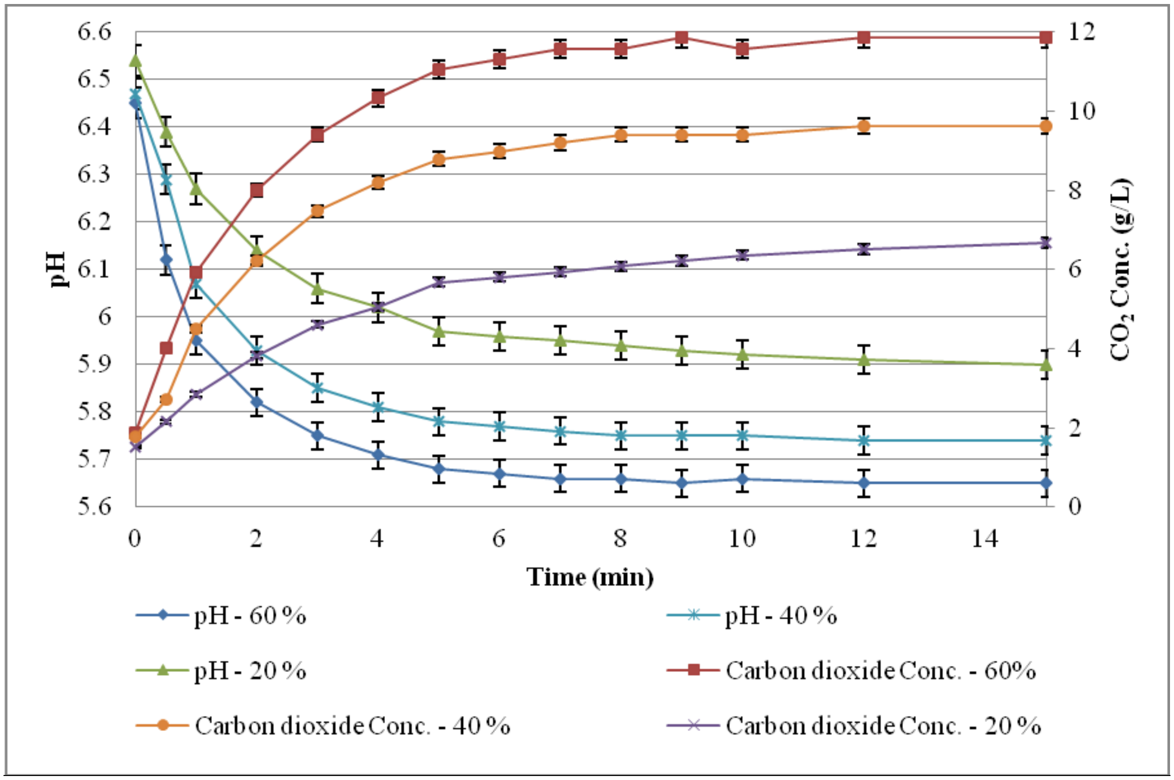


Figure 4- 6 pH and CO_2 concentration at 25 °C and three different gas compositions

As shown in Figure 4-6, when CO_2 concentration in gas phase increased from 20% to 40 and 60%, the corresponding final $CO_{2(aq)}$ concentration also increased from 6.7 g/L to 9.6 and 11.9 g/L, respectively. Higher CO_2 contents in the gas phase also led to lower final pH values. As observed in Figure 4-6, for 20, 40, and 60% CO_2 content, final pH values were 5.9, 5.74, and 5.65, respectively. Although the final $CO_{2(aq)}$ concentrations for the three examined gas compositions were considerably different, the trends were relatively similar. It is also considerable that at higher CO_2 contents in the gas phase, the system became steady within a shorter time range. By comparing the curves for 60% and 20%, it can be seen that the changes in the former is negligible after 8 minutes while for the latter, the curve was evolving until 12 minutes and after that, the changes became negligible. Figure 4-7 shows the liquid CO_2 concentration trends at 30 and 35 °C using gases with 20% and 60% CO_2 content.

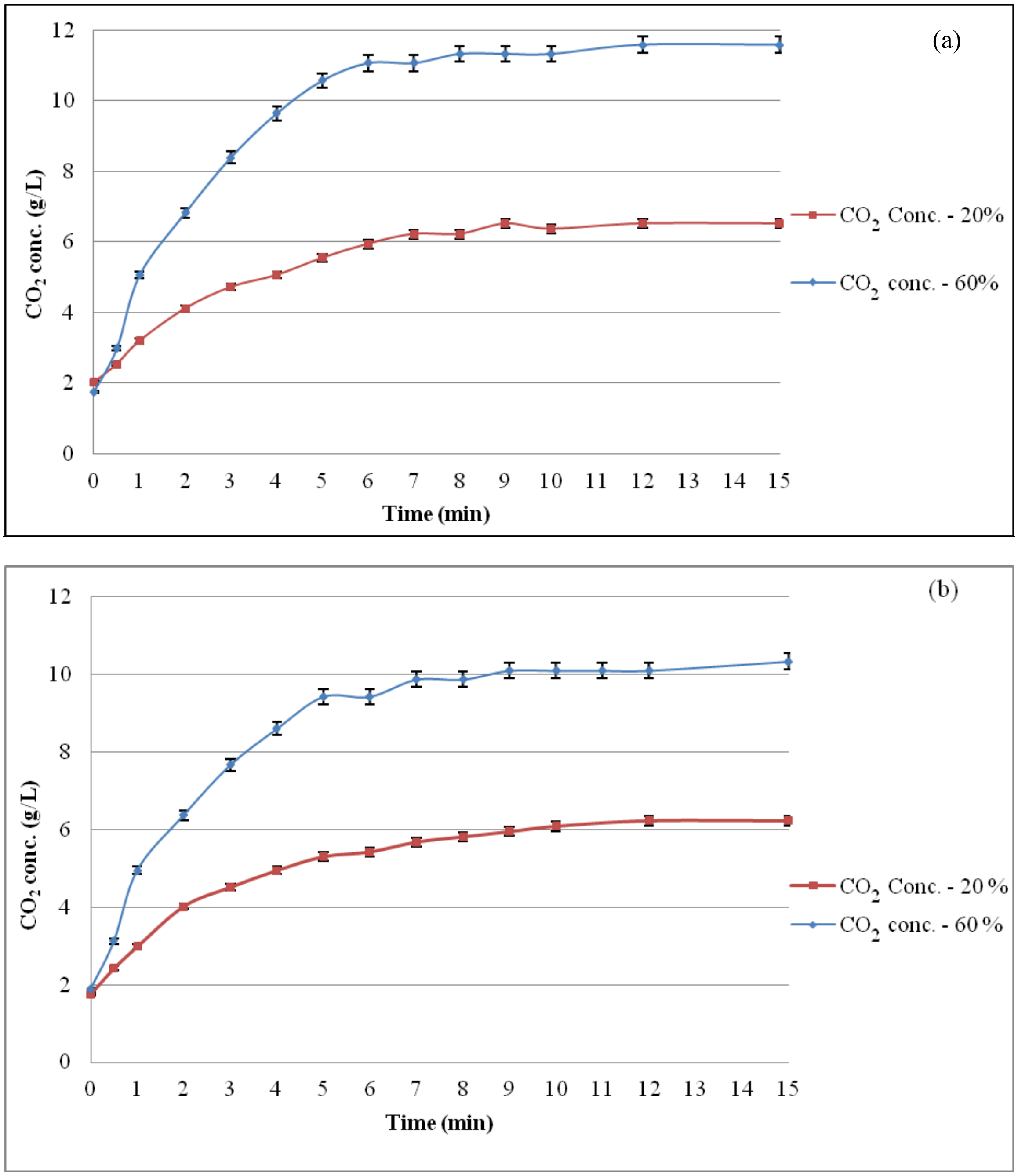


Figure 4- 7 Aqueous CO_2 concentration vs. time at 30 (a) and 35 °C (b) and different gas compositions

It can be observed that for all three temperatures, the trends of all curves corresponding to a given gas composition are similar. However, the final values are slightly different. One other point to be noted is the difference between the final CO_2 concentrations at each temperature. At all examined temperatures, when the concentration of CO_2 in the gas phase was lower, a lower aqueous CO_2 concentration was observed. At 20% CO_2 concentration, the corresponding aqueous concentration (6.7, 6.5, and 6.2 g/L at 25, 30, and 35 °C, respectively) was almost half of those obtained at 60% CO_2 concentration (11.9, 11.6, and 10.3 g/L, at 25, 30, and 35 °C, respectively). Although the gas phase CO_2 concentration in the first case (20% v/v) was one-third of the gas phase CO_2 concentration in the second case, the corresponding aqueous concentration was almost half. It could be concluded that the wastewater could absorb a larger portion of the CO_2 in the injected gas in the low CO_2-content inlet gas case. It was also observed that as the temperature increased, the final concentrations for the two different gas compositions approached similar values. The approximate difference between the final liquid-phase CO_2 concentrations by using 20% and 60% CO_2 content in inlet gas was 5.2 g/L at 25 °C, 5.1 g/L at 30 °C, and 4.1 g/L at 35 °C. This could imply that the impact of gas composition is more significant at lower temperatures. It is evident based on the obtained results that as the temperature increases, the capacity of WW to absorb CO_2 from the gas phase decreases and this decrease is more noticeable when the inlet gas has a higher CO_2 content.

In terms of comparison between the impacts on the CO_2 absorption capacity, it was observed that the inlet gas composition had a significantly higher impact than the temperature, within the ranges of values that were used during the experiments.

4.3.3 Liquid Flow Rate

The tests in this stage of research studied the impact of liquid flow rate on the capacity of WW to absorb CO_2. In this section we can compare the results of batch tests to those in the continuous tests at two different liquid flow rates, since the batch test can be considered as a continuous test in which the liquid flow rate is zero. Table 4-6 shows the key parameters for the tests of this section. The inlet gas flow rate and composition for the tests in this section were 2.5 L/min and 60% $CO_{2,}$ respectively.

Table 4- 6 Experiment layout for the impact of the liquid flow rate during continuous mode operation

Liquid flow rate (mL/min)	Temperature (°C)	Initial pH
0 (Batch)	25	6.44
0 (Batch)	30	6.44
200	25	6.45
200	30	6.48
300	25	6.47
300	30	6.50

As Table 4-6 shows, the tests were performed at 25 and 30 °C. For the two temperatures, Figure 4-8 indicates the results obtained at different liquid flow rates.

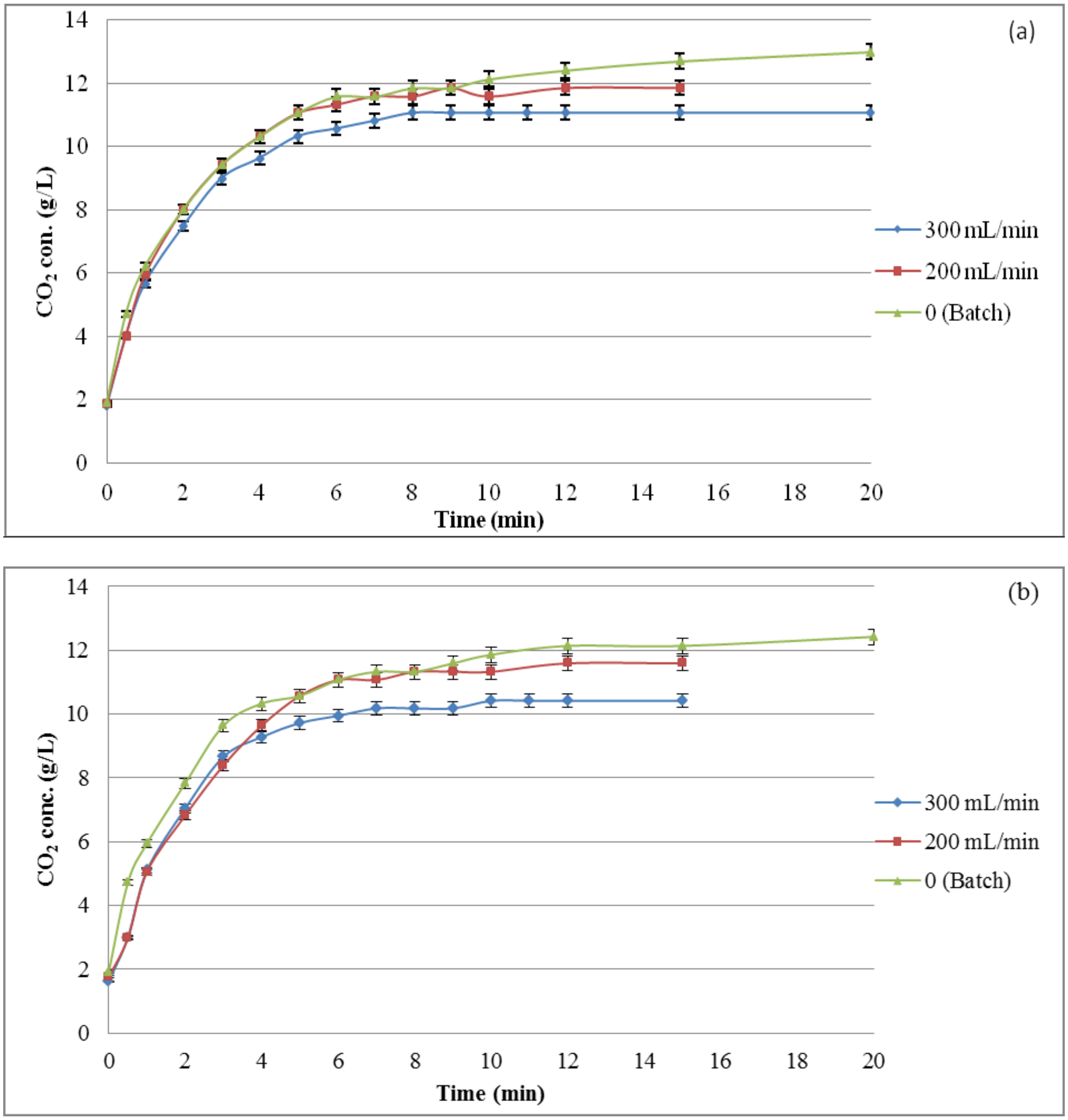


Figure 4- 8 CO_2 concentration vs. time at (a) 25 and (b) 30 °C and different liquid flow rates

Figure 4-8 shows that at both temperatures, as the liquid flow rate increases, final CO_2 concentration in the liquid phase decreases at steady state. This can be explained by to the fact that when the liquid flow rate is higher, the liquid has a lower retention time (17.66 min for 200 mL/min and 11.78 min for 300 mL/min) in the column and the liquid that is in contact with the gas is mixed with more fresh liquid. Hence the equilibrium concentration in the liquid phase is lower compared to lower liquid flow rates. The observed differences in terms of final CO_2 concentrations were less than 1 g/L which is not significant, but the curves clearly show the impact of liquid flow rate and the trend of change in the absorption capacity of WW as the liquid flow rate changed.

4.3.4 Total Gas Flow Rate

The total gas flow rate is a key parameter in designing the absorption process and its possible impacts are necessary to study. In this section, two different gas flow rates were considered. The temperature was set at 25 °C, gas composition at 60%, and liquid flow rate at 200 mL/min. Figure 4-9 presents the results obtained for two total gas flow rates of 1.25 and 2.5 L/min.

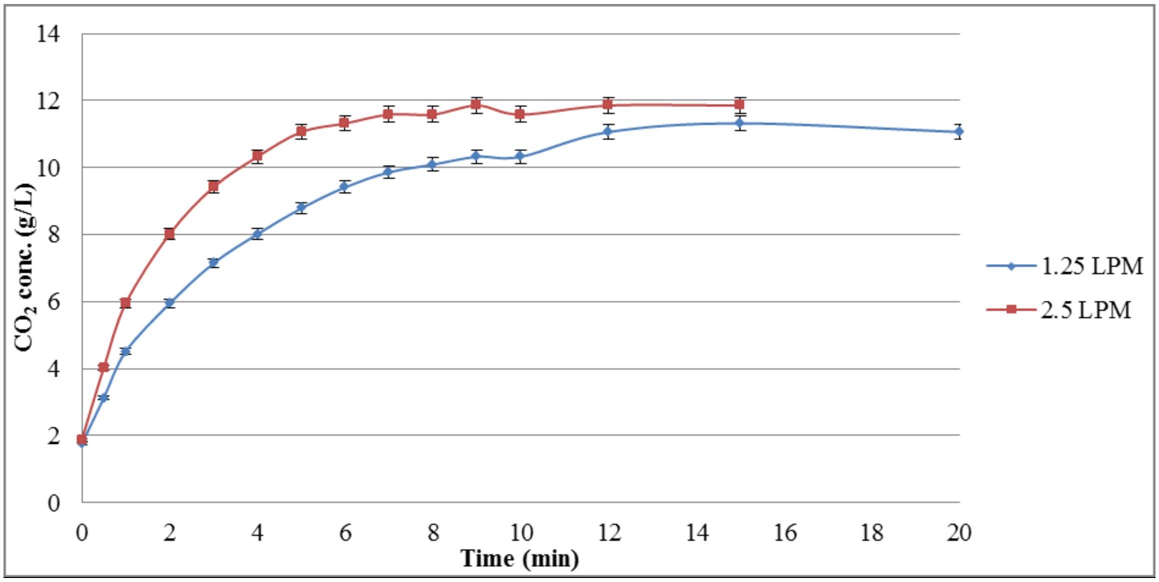


Figure 4- 9 CO_2 concentration at different gas flow rates

Based on Figure 4-9, the total gas flow rate shows some impact on the final aqueous CO_2 concentration. The higher gas flow rate led to a slightly larger final CO_2 concentration in the liquid phase. However, the more considerable impact is the time that it takes to reach steady-state as well as the rate of absorption in the two cases. As seen from this figure, after approximately 8 minutes, the variation is negligible at 2.5 L/min while at the gas flow rate of 1.25 L/min, the system becomes steady after almost 12 minutes. The rate of change in CO_2 concentration during the unsteady-state mode was calculated to be approximately 0.77 g/L.min when the total gas flow rate was 1.25 L/min which was slower than the corresponding rate at 2.5 L/min which was 1.23 g/L.min.

4.3.5 Liquid and Total Gas Flow Rates

In order to verify the results from sections 4.4.3 and 4.4.4 and to obtain further information about the behavior of the system under different conditions, an extra series of tests was performed in which the impacts of both liquid and gas flow rates were studied simultaneously. These tests were performed at 25 °C and at a gas composition of 60% CO_2. The liquid and gas flow rates were 300 mL/min and 1.25 L/min, respectively. The obtained results were then compared to the corresponding results from previous sections. Figure 4-10 shows the comparison between the obtained data at different gas and liquid flow rates.

The total gas flow rate had a considerable impact on the rate of CO_2 absorption and on the required time for steady-state, as discussed in section 4.3.4, while the liquid flow rate affected mainly the final concentration of CO_2 in the WW. At the liquid flow rate of 300 mL/min, the final $CO_{2(aq)}$ concentrations were 10.9 and 11.07 g/L at gas flow rates of 1.25 and 2.5 L/min, respectively whereas at the liquid flow rate of 200 mL/min, the obtained $CO_{2(aq)}$ concentrations at gas flow rates of 1.25 and 2.5 L/min were 11.2 and 11.9 g/L, respectively. It is notable that the impact of liquid flow rate on the WW capacity is less at lower gas flow rates. At the gas flow rate of 1.25 L/min, the difference between the steady-state concentrations at liquid flow rates of 200 and 300 mL/min was approximately 0.3 g/L, while at 2.5 L/min gas flow rate and at similar liquid flow rates, the difference was 0.9 g/L. At higher liquid flow rates, the impact of gas flow rate seems to be almost negligible. In general, the maximum obtained $CO_{2(aq)}$ concentration was 11.9 g/L at the lower liquid and higher gas flow rates which were 200 mL/min and 2.5 L/min, respectively.

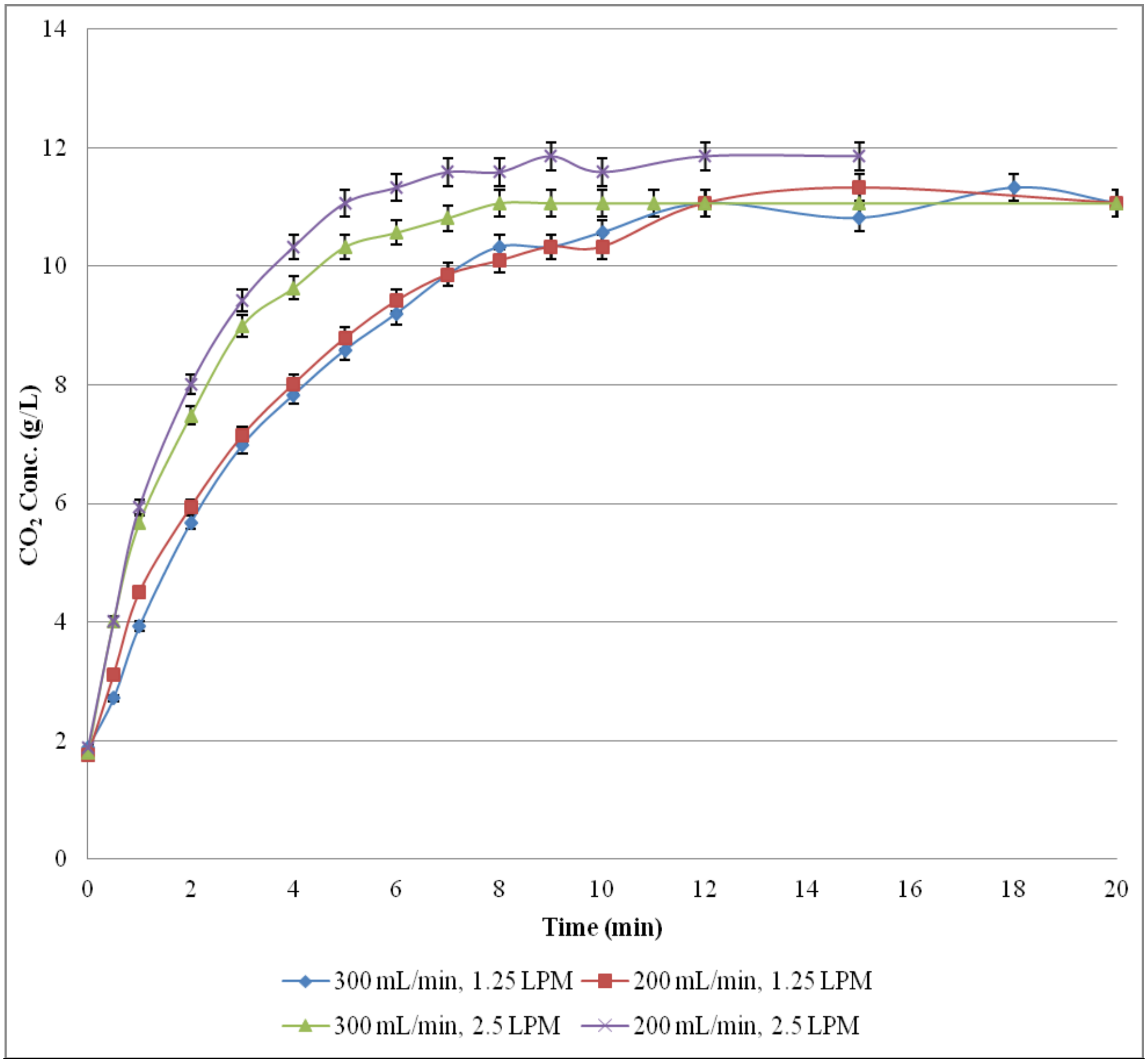


Figure 4- 10 CO_2 concentration at different liquid and gas flow rates

This information can be used for the proper operation of the system and selection of appropriate operating parameters. Further explanation will be provided in the next chapter.

4.3.6 NaOH Solutions

In order to compare the strength of the examined WW in terms of CO_2 absorption capacity and its behavior (i.e. the trends of curves, the rate at which pH changes when CO_2 is introduced, etc.), two sodium hydroxide (NaOH) solutions were prepared to undergo the same process. The concentrations of NaOH solutions were 0.1 % and 0.4 % w/w (0.025 and 0.1 M). These concentrations were chosen based on the fact that higher concentrations would produce a relatively stronger alkaline solution, different from the WW sample. Table 4-7 shows the characteristics of the NaOH solutions.

Table 4- 7 Characteristics of NaOH solutions

Solution concentration (NaOH) (w/w)	**Initial pH (± 0.1)**	**Alkalinity (±50 mg of $CaCO_3$/L)**
0.1	12.0	1500
0.4	12.5	5000

Based on the results presented in Table 4-7, both NaOH solutions had considerably higher pH values compared to the examined WW. However, the 0.4 % NaOH solution had a higher alkalinity while the 0.1 % NaOH solution has a lower alkalinity, compared to the WW, which was 2700 mg/L of $CaCO_3$. The results for these tests are shown in

Figure 4-11. The total gas and liquid flow rates were 2.5 L/min and 200 mL/min, respectively and the inlet gas contained 60 % CO_2 during these tests.

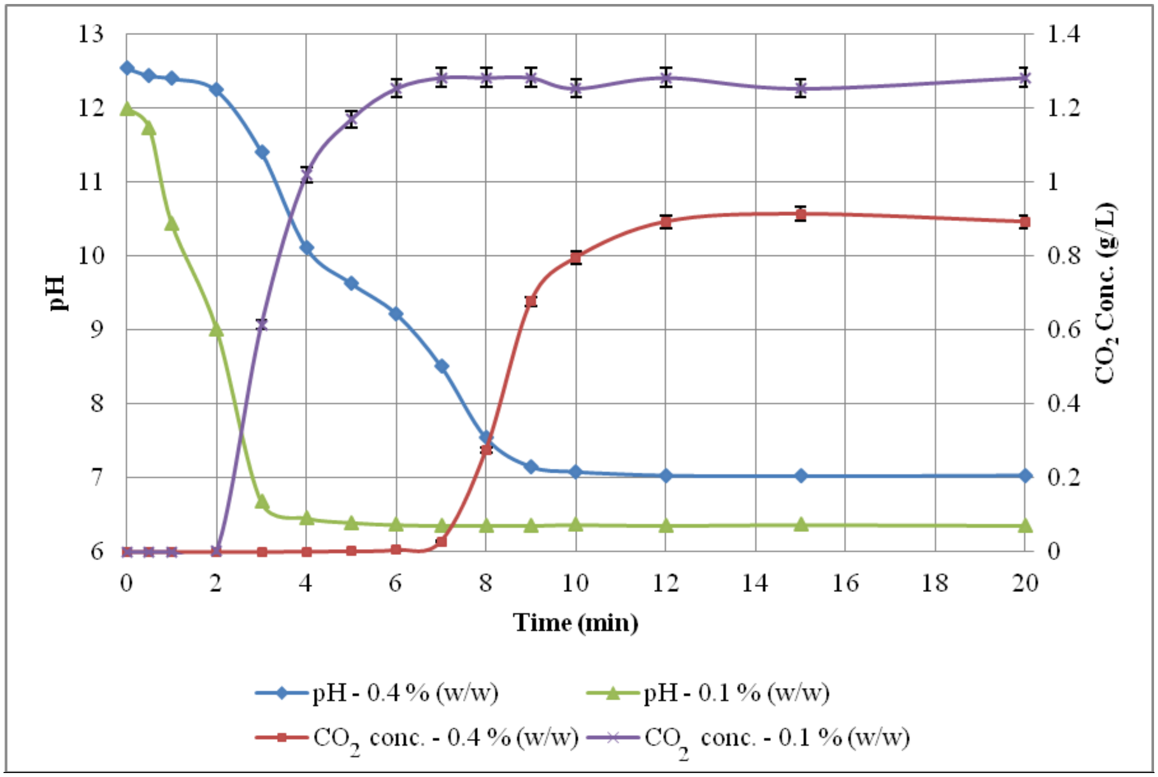


Figure 4- 11 pH and CO_2 concentration vs. time for 0.1 and 0.4 % w/w NaOH solutions at 25 °C

The 0.4 % solution was stronger than the WW sample in terms of its alkalinity while the 0.1% was weaker. The behavior of the NaOH solutions with respect to CO_2 absorption was different as the curves follow different trends compared to the WW sample. The stronger NaOH solution showed more resistance to pH variation which indicated its higher buffering capacity which was due to its higher alkalinity. The pH of the weaker solutions changed slowly at the very beginning but dropped quickly and reached a constant value in a short period of time. The stronger NaOH solution, on the contrary, resisted the change of pH for a longer period and then showed a slower rate of pH change.

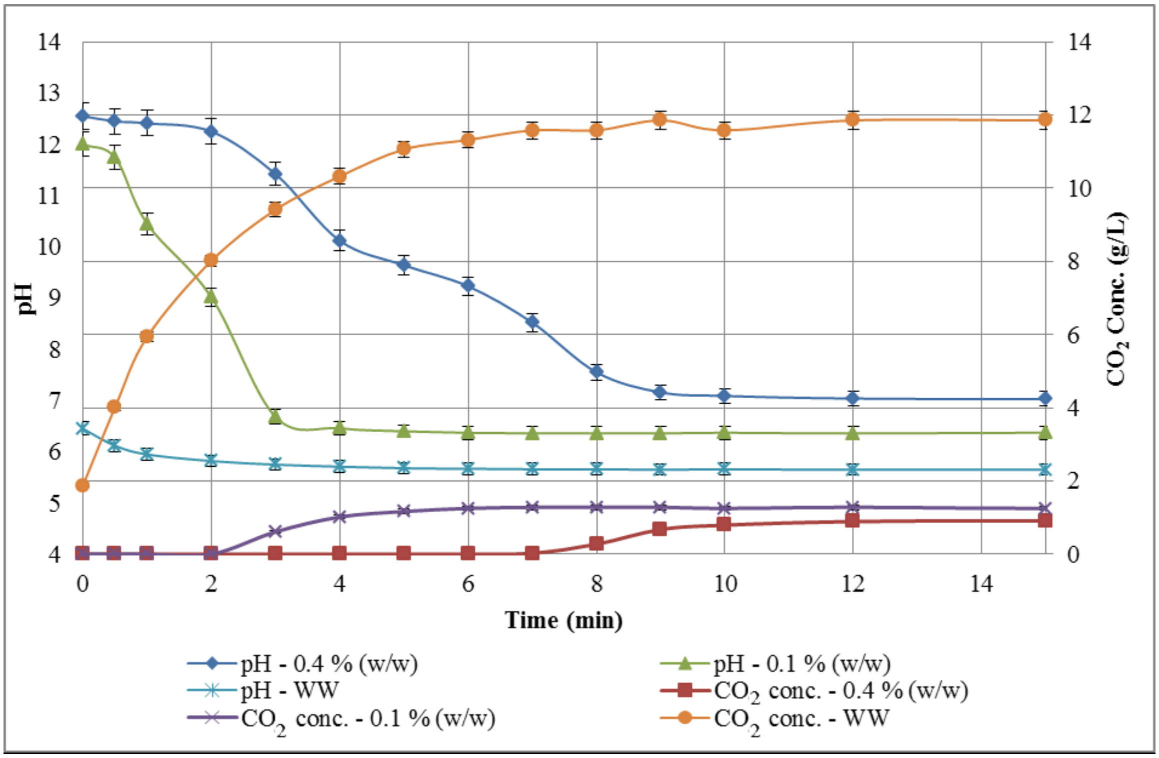


Figure 4- 12 pH and CO_2 concentration vs. time for the examined CTMP wastewater, and 0.1 and 0.4 % w/w NaOH solutions at 25 °C

Comparing the NaOH solutions to the examined CTMP WW, we can conclude that the WW sample exhibited a different behavior. This difference included the rate of change in the solution pH, as well as the final pH value and $CO_{2\ (aq)}$ concentration. As Figure 4-12 shows, the pH curves follow different trends. This can be explained by the considerable difference between the initial pH values of the WW and caustic solutions. Also, the WW is a complex liquid containing numerous unknown components with different composition. Hence, it does not follow the behavior of a simple solution that only contains NaOH. The final CO_2 concentrations are also considerably different. The final $CO_{2\ (aq)}$ concentrations for 0.1 and 0.4% NaOH solutions were 0.9 and 1.3 g/L, respectively, whereas for the wastewater, the corresponding concentration was 11.9 g/L. The reason is that $CO_{2\ (aq)}$ is always in equilibrium with the carbonate and bicarbonate species. The equilibrium is a strong function of pH (Neal 2001). Hence, the liquid pH determines the concentration of each species. To better demonstrate this, Figure 4-13 shows the concentration of different carbonic species at different pH values for the 0.4 % NaOH solution.

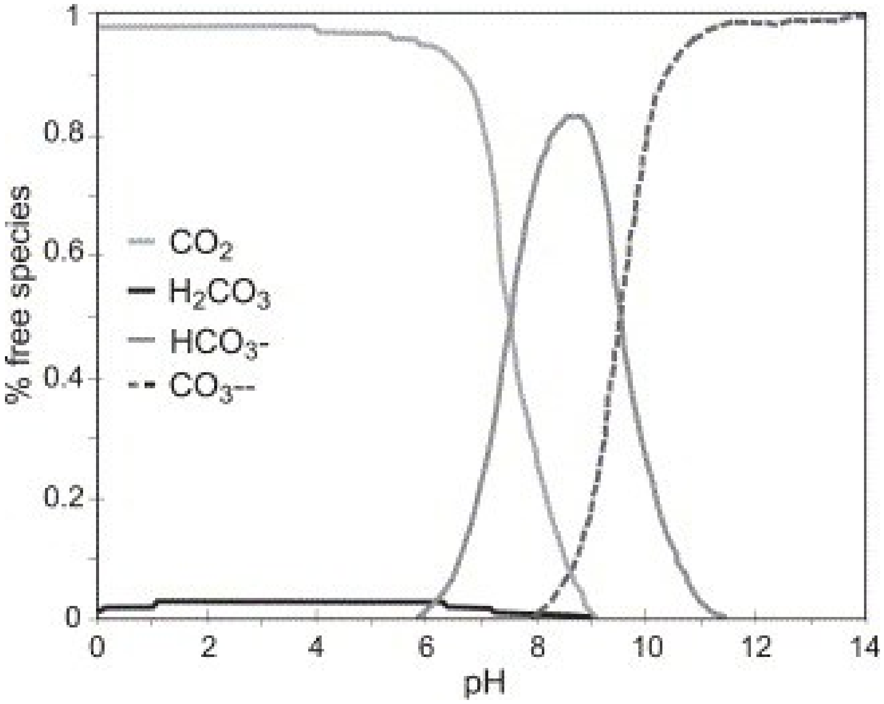


Figure 4- 13 Concentration of carbonic species vs. pH (Visco et al. 2005)

As shown in Figure 4-13, the carbonic content exists mostly in the form of carbonate at the high pH values. As the pH decreases (as a result of CO_2 dissolution), it changes to bicarbonate. Below pH 8, bicarbonate starts changing to $CO_{2\ (aq)}$. For the WW, the final pH was close to 5.5 in which concentration of carbonate is almost zero and concentration of bicarbonate is very small. Hence, the aqueous CO_2 is the dominant form. For the NaOH solutions, the final pH values were 6.37 (0.1% NaOH) and 7.03 (0.4% NaOH) at which bicarbonate is the dominant form of carbonic content. Table 4-8 shows the final concentrations of the species for the three liquids.

Table 4- 8 Final concentration of carbonic species

		Molar Concentration			Concentration in g/L		
Absorbent	Final pH	Carbonate	Bicarbonate	CO_2 (aq)	Carbonate	Bicarbonate	CO_2 (aq)
0.1 % NaOH	6.36	3.22E-6	0.0299	0.0292	0.00019	1.8296	1.284
0.4 % NaOH	7.04	5.13E-5	0.0999	0.0203	0.0031	6.0937	0.8934
WW	5.65	1.13E-6	0.0540	0.2694	6.77E-5	3.2939	11.854

As Table 4-8 shows, most of the carbonic content of the WW exists in the form of aqueous CO_2 at the end of the experiment, while in the other two solutions that contained NaOH, bicarbonate is the dominant compound which cannot be consumed by methanogens. Carbon dioxide in its aqueous form can be used as a source of carbon for methanogens. Hence at the final pH of WW, the dissolved CO_2 has the potential to undergo AD which is beneficial, while the two NaOH solutions do not offer a high potential for bioconversion due to the existing CO_2 form in their solution.

4.4 Gas Analysis

Although the main objective of this project was to study the capacity of WW to absorb CO_2 which can later undergo biological reactions, another objective was to examine the capacity of WW to remove CO_2 from gas effluents under different operating conditions. The former objective focused on the liquid analysis which was presented in section 4.3, while the latter refers to the gas analysis tests. Hence in order to study the second objective of this research and as mentioned in Chapter 3, gas samples at specific times were taken. Similar to the liquid analysis, the impacts of different operating parameters were studied on the removal efficiency of CO_2 from the gas phase.

4.4.1 Temperature and Gas Composition

This set of experiments was performed in order to study the impact of the column temperature and gas composition on the CO_2 removal efficiency from the gas phase. The procedure was the same as explained in the liquid analysis section, except that the sampling from gas was more limited compared to the liquid sampling and was only taken at certain times. The sampling schedule is provided in section 3.4.3. Figures 4-14, 4-15, and 14-16 show the results of the gas composition analysis by the GC at different temperatures and gas compositions.

At all temperatures, the same trend was observed for each of the curves corresponding to a given inlet gas composition. Once the system became steady, the final values were similar at different temperatures. However, lower temperatures showed a slightly better performance for both high and low CO_2-content inlet gases.

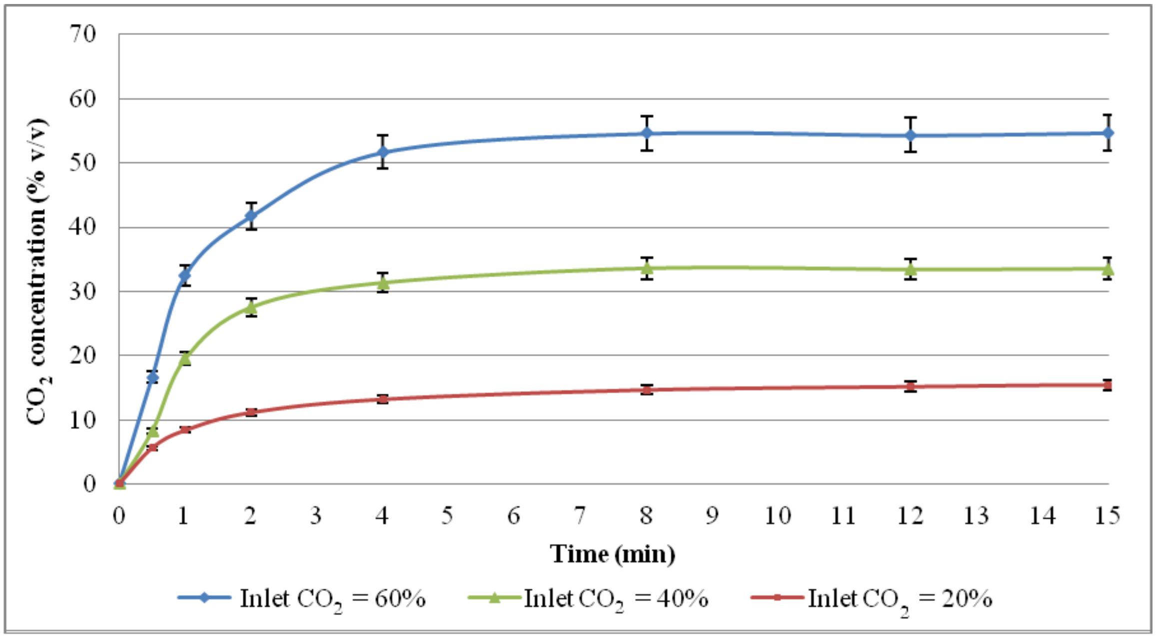


Figure 4- 14 Changes of outlet gas composition in time at 25 °C and three different inlet gas concentrations

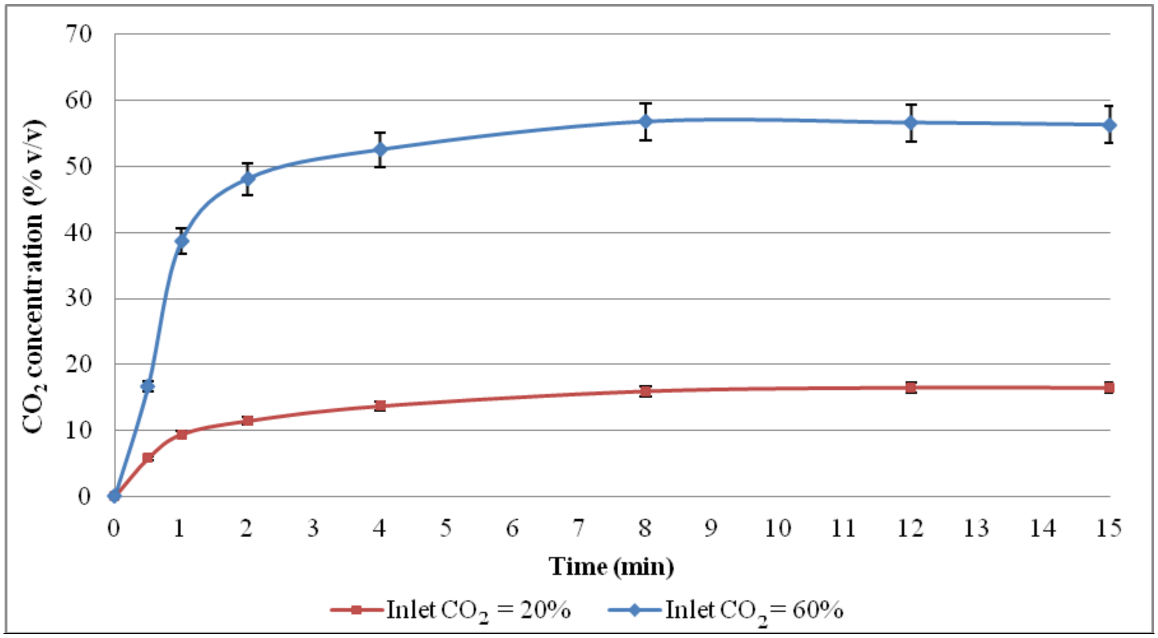


Figure 4- 15 Changes of outlet gas composition in time at 30 °C and two different inlet gas concentrations

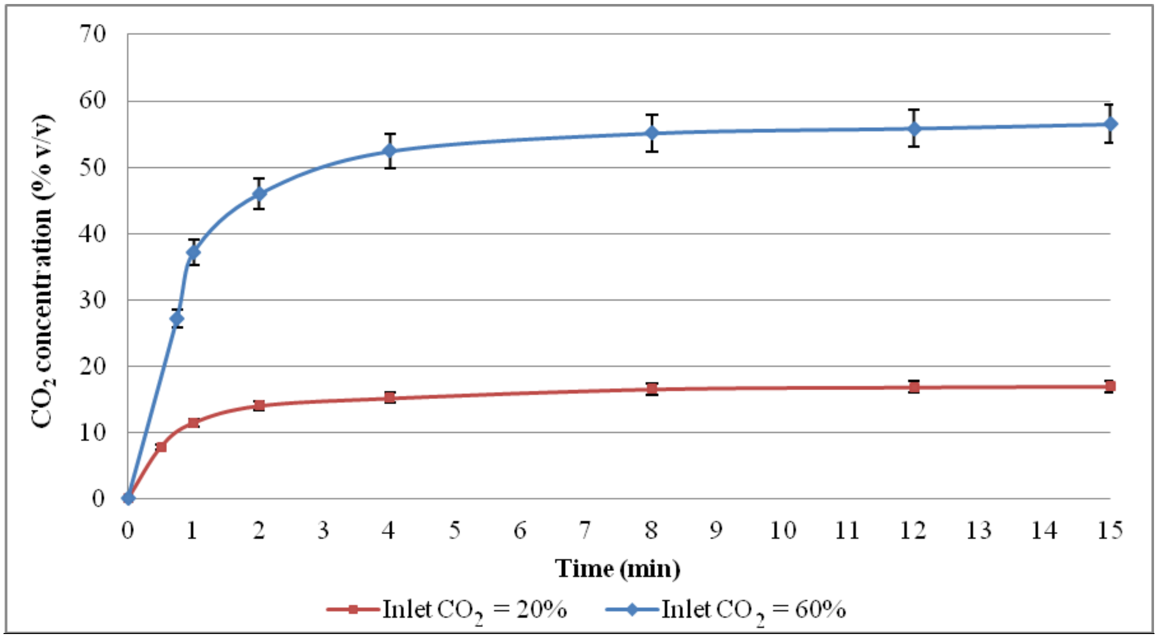


Figure 4- 16 Changes of outlet gas composition in time at 35 °C and two different inlet gas concentrations

Figures 4-14, 4-15, and 4-16 show the outlet gas composition for each experiment at different times and temperatures. The trends are very similar at different temperatures and for all cases the variation in outlet gas composition becomes negligible after 8 minutes. We can also observe that after the establishment of steady state, the outlet CO_2 content was less than the inlet concentration which means that the system absorbed part of the injected CO_2. However, these figures do not provide much information about the overall CO_2 removal efficiency in each experiment. The removal efficiency at different temperatures and gas compositions are compared in Figure 4-17.

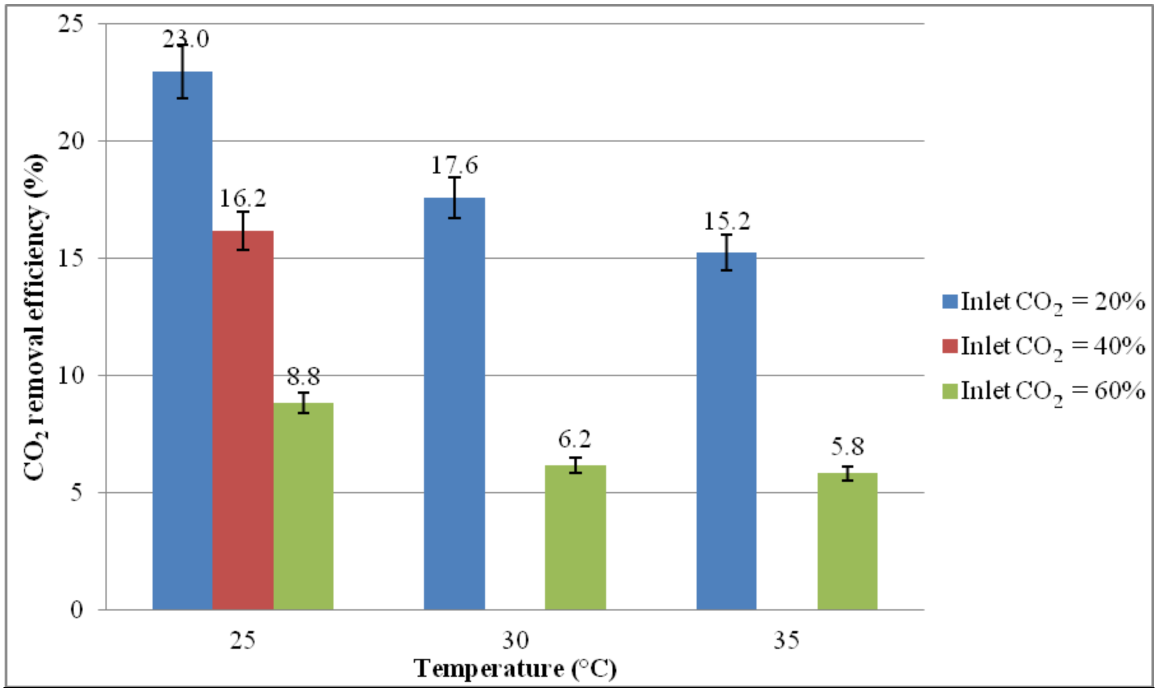


Figure 4- 17 Removal of CO_2 at different temperatures and inlet gas compositions

Figure 4-17 provides a better presentation of the impacts of temperature and inlet gas composition on CO_2 removal efficiency. The WW showed a better performance at low gas compositions. As the concentration of CO_2 in inlet gas increased, the removal efficiency decreased. As observed in Figure 4-17, at 25 °C, the CO_2 removal efficiency decreased from 23% to 8.8% as the inlet gas CO_2 content increased from 20% to 60%. The same trend was observed at 30 and 35 °C, where the removal efficiency decreased from 17.6% and 15.2% to 6.2% and 5.8%, respectively.

At 25 °C, we saw the best performance for all inlet gas compositions where the maximum removal efficiency of 23% was observed when the inlet CO_2 content was 20%. At the same CO_2 content, as the temperature increased to 30 and 35 °C, the removal efficiency decreased to 17.6% and 15.2%, respectively. We could observe that at all inlet gas compositions, the temperature has an inverse impact on the removal efficiency. This corresponds to the theoretical expectations that a higher dissolution of gases into liquids is expected at lower temperature. Table 4-9 shows the amounts of absorbed CO_2 at steady-state mode of operation at 25 °C.

Table 4- 9 CO_2 removal efficiency at 25 °C

Inlet gas composition (% v/v)	Inlet CO_2 volume in unit of time (L/min)	Final gas composition (% v/v)	CO_2 absorbed/ CO_2 injected (L/L)	Removal efficiency (%)
20	0.5	15.4	0.24	23.0
40	1	33.5	0.16	16.2
60	1.5	54.7	0.9	8.8

The data in Table 4-9 clearly show that a larger portion of CO_2 is removed at lower inlet CO_2 concentrations. This corresponds to our observations in section 4.3.2 as we observed higher capacity of absorption in the case of low CO_2 content inlet gas.

4.4.2 Liquid Flow Rate

The liquid flow rate is expected to have an impact on the CO_2 removal efficiency. The data obtained at two liquid flow rates of 200 and 300 mL/min, gas flow rate of 2.5 L/min, and temperature of 25 and 30 °C are presented and compared in Table 4-10. The reported removal efficiency is based on the amount of CO_2 removed when the system reached steady-state.

Table 4- 10 CO_2 removal efficiency at different liquid flow rates

Liquid flow rate (mL/min)	Temperature (°C)	Total gas flow rate (L/min)	Removal efficiency (%)
200	25	2.5	8.8
300	25	2.5	13.2
200	30	2.5	6.2
300	30	2.5	12

The impact of liquid flow rate is clearly demonstrated in Table 4-10. When the liquid flow rate was higher, more CO_2 was removed from the gas phase. This was due to the fact that the higher liquid flow rate introduced a higher volume of fresh WW per unit of time into the column in which the absorption took place. Hence, the liquid inside the column was diluted with more fresh liquid which led to lower aqueous CO_2 concentration, as observed in Figures 4-8 and 4-10. Consequently, a higher driving force, resulting from the concentration difference in the gas and liquid phase, existed at higher liquid flow rates, leading to more CO_2 removal from the gas phase by the liquid.

4.4.3 NaOH Solutions

In order to compare the capacity of WW with the two caustic solutions in terms of their CO_2 removal efficiency from the gas phase, and to verify observations from the liquid analysis, gas analysis was performed during the experiments with 0.1% and 0.4% NaOH solutions. The obtained results for the two solutions under the same conditions are explained in the liquid analysis section. Figure 4-18 shows the CO_2 concentration trend in the outlet gas during the experiments. For the 0.1% solution, the final CO_2 concentration in the gas phase was 56% while for the 0.4% solution, the corresponding value was approximately 50%.

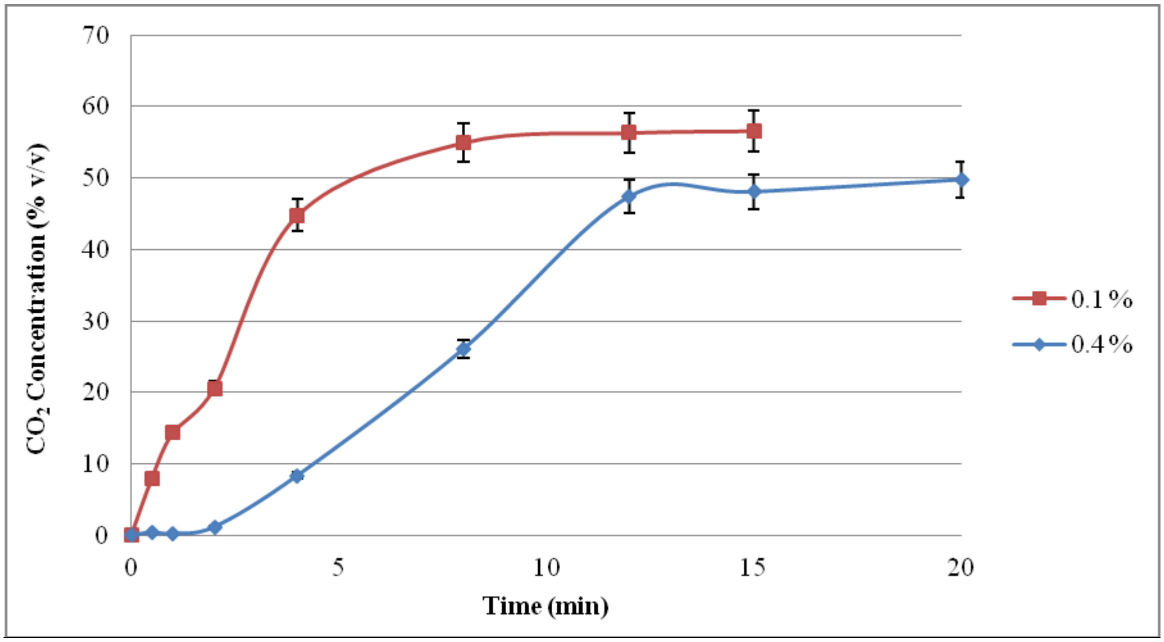


Figure 4- 18 Effluent gas composition vs. time for the NaOH solutions (0.1 and 0.4 %) at 25 °C

Based on the data obtained, the removal efficiencies were calculated to be 5.6% and 17% for 0.1% and 0.4% NaOH solutions, respectively. Comparing these values to those obtained for the removal efficiency of WW (8.8%) under the same condition, the weaker solution showed a lower removal efficiency while the more concentrated solution showed a higher removal efficiency. This is explained by the strength of solutions which in this case was represented by their corresponding alkalinity. The liquid with a higher alkalinity showed a higher efficiency since it tends to neutralize acids to a higher degree, which in our case was carbonic acid (formed once CO_2 is dissolved).

It is notable that at the beginning, the NaOH solution with a higher concentration absorbed almost all CO_2 from the gas which was due to its relatively high strength in terms of alkaline species concentration. The observed trends of curves correspond to those obtained from liquid analysis results for the same solutions. For the 0.4% solution, the change was slow and the outlet gas CO_2 concentration became constant after 12 minutes while for the 0.1% solution, the outlet CO_2 concentration reached the maximum value within 8 minutes. This was an indication of different buffering capacities of the examined solutions, which correspond to theoretical expectations based on the alkalinity content of solutions.

4.5 Steady-State Absorption Rate

Based on the results obtained from the gas analysis and the concentration of CO_2 in the inlet and gas samples, the steady-state absorption rates were calculated for a few cases via mass balance. In order to determine the absorption rate, the following assumptions were taken into consideration:

1 - The rates were estimated at steady-state mode where equilibrium was achieved between the gas and liquid phase.

2 - The solubility of air (containing nitrogen (79%) and oxygen (21%)) in the absorbents was negligible.

3 - No absorbent evaporation occurred during the process.

Based on the assumptions above, we could determine the overall steady-state absorption rate (R_A) which is equal to the absorption of CO_2 in one l L of absorbent in the column.

$$R_A = \frac{F_{A1} - F_{A2}}{V_L} \tag{4-1}$$

Where F_{A1} and F_{A2} are molar flow rates of CO_2 in the inlet and outlet gas, respectively, and V_L is the volume of liquid inside the column.

Equation 4-1 can be converted to the following form by knowing the molar fraction (%) of CO_2 in the inlet and outlet gases:

$$R_A = \frac{F_{A1}}{V_L} [1 - \left(\frac{1-y_1}{y_1}\right)\left(\frac{y_2}{1-y_2}\right)] \tag{4-2}$$

where y_1 and y_2 are the molar fractions of CO_2 in the inlet and outlet gas, respectively.

Figure 4-19 shows the steady-state absorption rates for the examined wastewater at temperatures of 25 and 35 °C, and different inlet gas compositions. As seen in figure 4-19, with the increase of temperature, the absorption rate decreased. The calculated absorption rates at 25 and 35 °C were 4.2 and 2.9 mmole/min.L, respectively, when the inlet gas CO_2 content was 60%. In the case of 20% inlet gas CO_2 content, the corresponding overall steady-state rates were 1.9 and 1.3 mmole/min.L at the temperatures of 25 and 35 °C, respectively. The observed difference between the rates at different temperatures was smaller when the CO_2 content of inlet gas was lower.

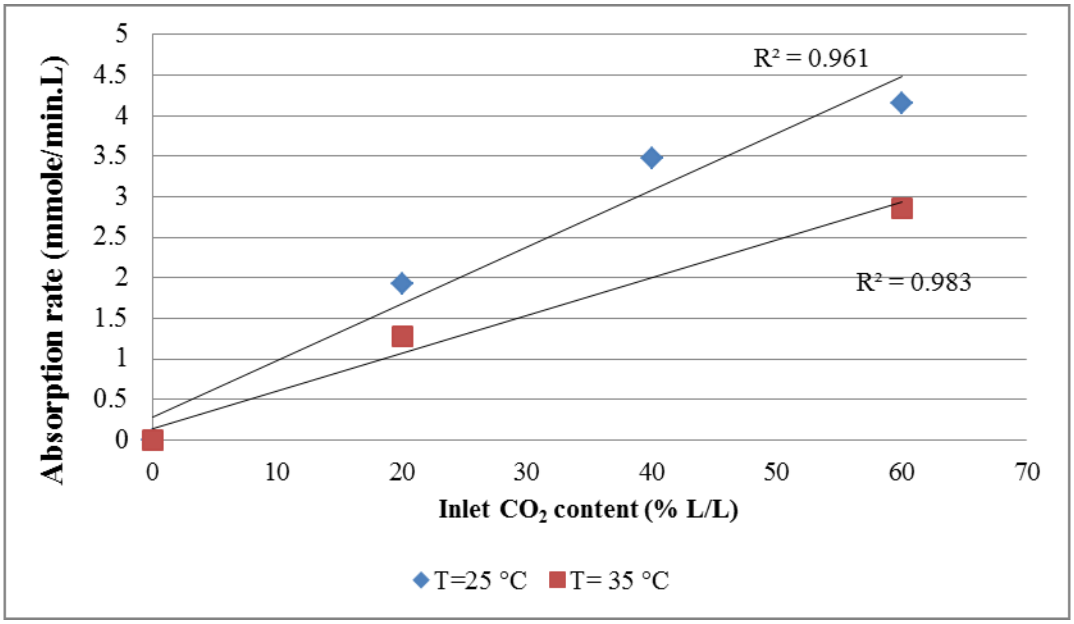


Figure 4 - 19 Overall steady-state absorption rate for the wastewater at different temperatures and inlet gas compositions

It can also be observed that absorption rates were higher at higher inlet gas CO_2 contents. At 25 °C, the calculated absorption rates for the three inlet gas CO_2 contents of 20, 40, and 60% were 1.9, 3.5, and 4.2 mmole/min.L, respectively. A similar trend was observed at 35 °C, although the difference between the rates at the cases of 20% (1.3 mmole/min.L) and 60% (2.9 mmole/min,L) CO_2 content in the inlet gas was smaller.

It could be concluded that the absorption rates were higher at lower temperatures and higher CO_2 concentrations in the inlet gas.

In order to compare the examined wastewater to the NaOH solutions in terms of absorption rate, the corresponding values were calculated for the three absorbents. Figure 4-20 shows the results of the absorption rates.

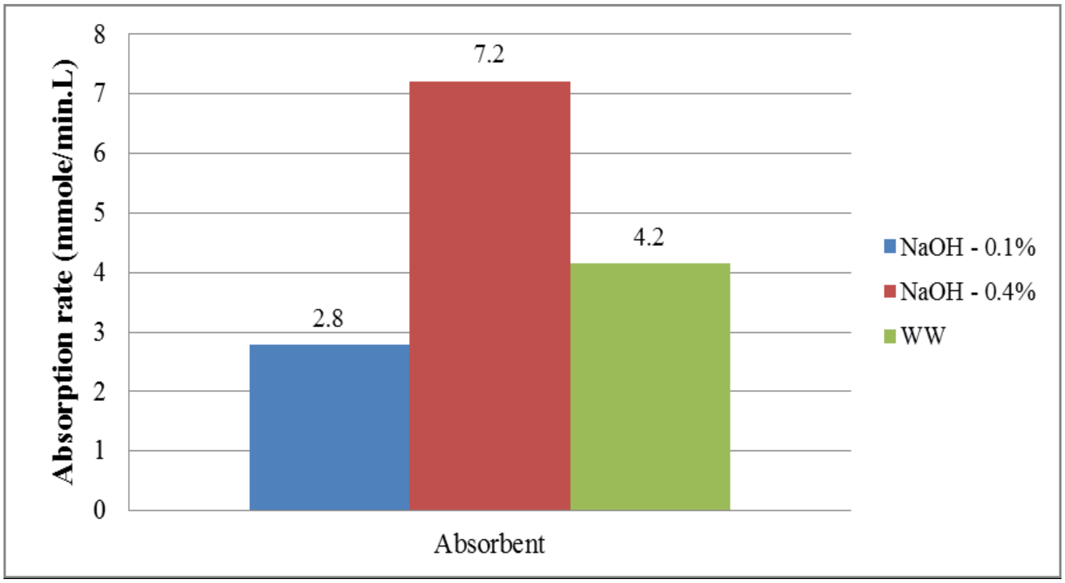


Figure 4 – 20 Overall steady-state absorption rates at 25 °C, inlet gas CO_2 concentration = 60% for the wastewater, 0.1% NaOH, and 0.4% NaOH

As seen in Figure 4-20, the 0.4% NaOH solution had the highest absorption rate of approximately 7.2 mmole/min.L, while the WW and 0.1% NaOH solution were in second and last places with steady-state absorption rates of 4.2 and 2.8 mmole/min.L, respectively. Recalling the alkalinity values and hence the corresponding CO_2 absorption capacities of the absorbents, it can be concluded that the absorbent with higher alkalinity and CO_2 absorption capacity showed a faster absorption.

4.6 Comparison to Other Studies

The results obtained from our experiments were compared to relevant studies in order to have a better understanding of the CO_2 absorption capacity of the examined wastewater compared to other wastewaters and alkaline absorbents. In one study, Georgiou et al. (2007) carried out a series of tests on two dye-bath effluents and two caustic solutions and compared the absorption capacities of effluents to the solutions during a series of batch tests. The two solutions simulated the alkalinity and pH of the two effluents. The alkalinity of the examined solutions and effluents were 17400 and 9000 mg/L of $CaCO_3$, and the initial liquid pH values were 10.9 and 9.4, respectively. The absorbents had much higher alkalinity and pH compared to those examined in our experiments. Hence, a much higher CO_2 absorption capacity would be expected for their absorbents. The concentration of $CO_{2(aq)}$ was not reported in their research. However, the variation of pH values during the gas-liquid contact was monitored and published. The pH values for the two effluents used by Georgiou et al. (2007) dropped from 10.9 and 9.4 to approximately 8. These variations, compared to that observed in our batch mode experiments (from 6.4 to 5.6), revealed a larger CO_2 absorption capacity of their wastewaters and verified our previous statements and observations. The time required in our experiments to reach steady state varied from 8 to 12 minutes while in the experiments using alkaline effluents, their system reached steady state after much longer periods of approximately 80 and 120 minutes, depending on the examined effluent type. These findings show a higher capacity of alkaline wastewaters and caustic solutions in terms of CO_2 absorption. However, given the moderate alkalinity and relatively low pH values of the examined wastewater in our research, it showed a relatively good CO_2 absorption capacity.

Gaur et al. (2009) also performed a series of tests on the absorption of CO_2 from LFG by alkaline wastewater, NaOH, and ammonia solutions, in a series of batch tests under controlled operating conditions (room temperature, gas flow rate of 1.5 L/min). The examined wastewater in their experiments had an alkalinity of 34,000 mg/L of $CaCO_3$ and a pH value of 10.41. Hence, a much higher CO_2 absorption capacity could be expected from their wastewater compared to the samples examined in the present research. The comparison of results obtained from their experiments to batch-mode results of the present research shows that the amount of time required for the system to reach steady-state in the present study was around 12 minutes, while it took around 70 minutes for their system to become saturated. The examined LFG was reported to have approximately 45% CO_2 and about 55% CH_4. They stated that the presence of methane enhances the absorption of CO_2 into the solution. In the experiments of the present research, a mixture of CO_2 with air was used. Hence, considering different gas compositions, initial alkalinity and pH values, the observed differences in the obtained results from the two studies can be justified. Gaur et al. (2009) did not study the impacts of operating conditions on the efficiency of CO_2 absorption. However, they concluded that the alkaline wastewater was a better absorbent than the examined NaOH and NH_3 solutions as it absorbed more CO_2 due to its high alkalinity. Their research was also intended to evaluate the efficiency of CO_2 injection into wastewaters with high pH for neutralization. The final pH value of their wastewater was in range of 7-8, hence this process was proven to be applicable to successfully neutralize the wastewater.

In another comparison between the results obtained in the present research using wastewaters to those obtained by Yincheng et al. (2011) from caustic NaOH and NH_3 solutions, differences and similarities were observed in terms of the behavior of absorbents. Yincheng et al. (2011) showed that for the caustic solutions, higher temperatures led to a higher CO_2 absorption, while the wastewater examined in the present research absorbed less CO_2 at higher temperatures. The reason lies behind the increasing impact of higher temperature on the rate of reactions of CO_2 with OH^- and NH_4^+ agents. However, the wastewater has a complex composition of various constituents and hence, as Wey et al. (2003) also concluded, it is expected that different absorbents show different behaviors under the same operating conditions. They also studied the impact of liquid flow rate on the absorption of CO_2. According to their reported results, a higher CO_2 absorption was observed at higher liquid flow rates, which is similar to our observations.

Salomoni et al. (2011) carried out a series of experiments at laboratory- and large-scales on methane production by anaerobic digestion with CO_2 capture. These researchers focused on methane production and CO_2 capture, and did not investigate the impact of operating conditions on CO_2 removal. They used an alkaline solution to absorb CO_2 from a gas mixture, and through a regeneration process, the nearly pure CO_2 was injected into the anaerobic digestion system. Using a basic solution as an absorbent seems to be desirable in terms of high CO_2 removal efficiency. However, the costs and processes associated with the production of the synthetic basic solutions as well as the regeneration of the absorbent need to be considered. Comparing their approach to ours, using WW, as an already-existing absorbent which does not require regeneration can be beneficial. Finally, they concluded that anaerobic digestion accompanied by CO_2 injection can lead to reduced emissions of GHG and production of valuable methane.

4.7 CO_2 Absorption System Implementation

Bubble column scrubbers are well-known systems that are commonly used in various industrial applications, and have been the subject of numerous research studies. Examples of the applications of bubble column scrubbers are desulfurization of flue gas (Meikap et al. 2002), removal of particulate matters from chemical and metallurgical process plants (Raj Mohan and Meikap 2009), separation of nanoparticles from gas phase (Koch and Weber 2012), and absorption of CO_2 by a liquid absorbent (Gaur et al. 2012, Krumdieck et al. 2008, Cheng et al. 2013). This system offers a conventional technique to separate certain gases such as H_2S, SO_2, CO_2 from gaseous effluents of industrial plants.

One of the objectives of this research was to evaluate the absorption of CO_2 from a gas mixture by the wastewater of pulp-and-paper industry with the intention of bioconversion of the dissolved CO_2 in the wastewater to methane though anaerobic digestion. The system used in the present research was a bubble column scrubber which, as mentioned above, is widely used in industrial applications. Hence, the scrubber system can be easily implemented at larger scales operations in pulp-and-paper plants to separate CO_2 from gaseous effluents by using the generated wastewater as the absorbent. The wastewater can further undergo anaerobic digestion for both COD reduction and CO_2 conversion to methane.

The absorption system is best to be placed after the primary treatment, where the large particles of wastewater have been removed. This provides higher process feasibility and prevents common problems such as clogging and filtration requirement. It is not recommended to place the system after secondary treatment since most of the biodegradable matter in wastewater is removed during secondary treatment and the wastewater may not include enough biodegradable substances which are needed as substrate for microorganisms that are responsible for the process of anaerobic digestion of CO_2. On the other hand, the anaerobic conversion of CO_2 can also act as a secondary treatment process and with the application of certain amendments, desirable COD and BOD removal can be expected along with the bioconversion of CO_2. However, the optimization of the anaerobic process to achieve acceptable COD removal requires further investigation.

The scrubbing unit is the first step of the anaerobic digestion process and is followed by anaerobic reactors in which different stages of anaerobic digestion take place. As mentioned in chapter two, the anaerobic digesters may be single or two-phase (TPAD). In a single phase digester, all stages of anaerobic digestion take place in one reactor while in a two-phase system, the acidogenesis and methanogenesis processes occur in two separate reactors. The TPAD has a number of advantages compared to the single-phase process such as better control over operating conditions, ability to provide the optimum operating conditions for acidogenic and methanogenic bacteria and hence providing a better overall performance. Figure 4-21 shows the recommended layout for the bubble column scrubber and anaerobic digestion.

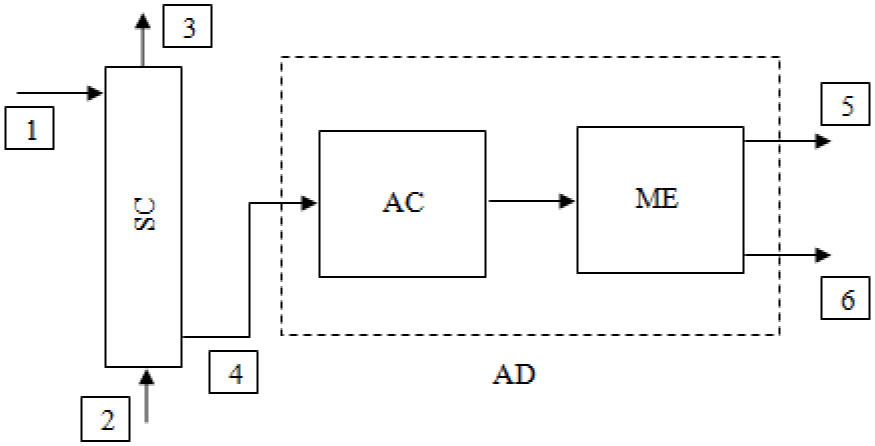


Figure 4 - 21 Schematic of CO_2 absorption system and anaerobic digestion system. 1: wastewater after primary treatment, 2: Gas effluent containing CO_2, 3: CO_2-stripped gas, 4: wastewater containing dissolved CO_2, 5: Biogas containing mainly methane and CO_2, 6: treated wastewater, AD: anaerobic digestion, AC: acidogenesis, ME: methanogenesis, SC: scrubber

As Figure 4-21 shows, the recommended place for the scrubber is before the acidogenesis stage. As observed in the results of the present research, the final pH value of wastewater after CO_2 injection was within the range of 5.5-6. This pH range provides the acidogenic bacteria with suitable condition for their activity. The scrubber is not recommended to be placed between the acidogenesis and methanogenesis stages, since methanogenic bacteria are very sensitive to the presence of oxygen and the CO_2 injection process might introduce considerable amount of oxygen to the system which would lead to deactivation or death of the methanogenic bacteria. The injection of CO_2 before the methanogenesis stage might also change the pH of wastewater to values that are not appropriate for the activity of methanogenic bacteria.

This absorption system can be applied at full-scale to provide CO_2 emission reduction from the pulp-and-paper industry as well as bioconversion of CO_2 to methane and treatment of the wastewater, simultaneously.

Chapter 5: Conclusions and Recommendations

5.1 Conclusions

The main objective of this project was to study the applicability of pulp-and-paper wastewater in the absorption CO_2 from a gas mixture. The experiments were performed in two parts: Analysis of results in the liquid phase and gas phase. The former was the main goal of the project and was based on the anticipation that the CO_2 dissolved into the WW can further undergo biological treatment in the downstream processes and be converted to methane via anaerobic digestion (AD). The latter, which was done in addition to the main objective, was to analyze and investigate the performance of WW in terms of its contribution to CO_2 emission reduction. The analysis of experimental results has led to the conclusions that are summarized in the following sections.

5.1.1 Liquid Analysis

1- Pulp-and-paper mills wastewaters with different characteristics were examined to choose the specific WW that would lead to better performance in terms of CO_2 absorption capacity. The chosen WW, provided by Tembec Matane Inc., had the highest alkalinity among the wastewater samples examined, and showed a higher potential of correspondence with the objectives of this project.

2- The chosen WW had a moderate alkalinity value of 2700 mg/L and approximate average initial pH of 6.5. During the batch tests, a maximum $CO_{2(aq)}$ concentration of 13 g/L was obtained at 25 °C.

3- At 25 °C and 60% CO_2 in the inlet gas, a maximum concentration of 11.9 g/L of absorbed $CO_{2\ (aq)}$ was achieved under the continuous mode of operation. This is equal to approximately 8 times the solubility of CO_2 in water at 25 °C and atmospheric pressure and results from the presence of alkaline species in the wastewater which react with and neutralize the dissolved CO_2 (H_2CO_3), hence enhancing the solubility of CO_2 in the wastewater. This result was achieved with the gas which was not pure CO_2. A higher value is expected if 100% CO_2 is introduced into the liquid. However, under real conditions, the gas effluents of industrial plants contain 10 – 60 % carbon dioxide, depending on the nature of the process and the origin of the effluent.

4- The temperature showed some impact on the absorption capacity of the WW. At lower temperatures, more CO_2 was dissolved in the liquid phase. This impact, however, was negligible.

5- The research examined different gas compositions in order to be applicable to the effluents of various industrial processes having different CO_2 contents. The gas composition had a major impact on the final absorbed concentration of CO_2 in the WW. The final aqueous CO_2 concentration was lower at low-CO_2 content in the inlet gas. However, it was observed that the WW absorbed a larger portion of the CO_2 from the gas phase when the inlet gas had a lower CO_2 content.

6- The impact of the gas and liquid flow rates were also studied. A higher liquid flow rate led to a lower final CO_2 concentration in liquid phase. The gas flow rate also had some impact on the final concentration of CO_2 in the liquid phase. A higher concentration was achieved at higher gas flow rates. However, the more significant impact of the gas flow rate on the system was the time it took for the system to reach steady state condition. The system became steady in a shorter period when the gas flow rate was higher.

7- The maximum dissolved CO_2 concentration could be achieved at lower temperatures, lower liquid and gas flow rates, and higher CO_2 contents in the gas phase.

8- The final pH of WW under all operating conditions was in the range of 5.6-6.0. In this range of pH, the absorbed CO_2 exists in the aqueous form. This is a great benefit since microorganisms can only convert CO_2 in aqueous form.

9- The final pH values, which were in the range of 5.6-6, are adequate for the activity of acidogenic microorganisms (Yu and Fang 2002).

10- Wastewater (WW) is generated in every industrial plant and if used to remove CO_2, can replace synthetic alkaline solutions since it will not require regeneration as it can undergo biological treatment.

11- The capacity of WW to absorb CO_2 was shown to be a relatively weak function of temperature in the examined range. This can be an advantage since there might be variations in the temperature of WW at different times and seasons. Hence, the system is resistant to possible input variations. Besides, no temperature adjustment will be required to enhance the efficiency of absorption process. Based on the literature, the optimum temperature for anaerobic digestion is around 35 °C, and as per our observations, increase of temperature from 25 to 35 °C had a very negligible impact on the absorption of CO_2. Hence, the system can be operated at the temperature which can provides a better condition for the anaerobic bacteria

12- In order to maximize $CO_{2\,(aq)}$ for a given gas composition and temperature, one may operate the system under a pseudo-batch process. The reduction of liquid flow rate leads to higher CO_2 concentrations in the liquid phase.

13- In general, the comparison of obtained results to the literature-cited reports (Georgiou et al. 2007, Gonzalez-Garza et al. 2009, Yincheng et al. 2011), revealed that the examined wastewater showed a lower CO_2 absorption capacity. However, considering the moderate alkalinity and low initial pH of the wastewater, its performance was acceptable which could also be seen in the results of both continuous and batch tests.

14- Reported batch tests on the anaerobic conversion of CO_2 to methane showed that the injection of CO_2 into the wastewater prior to anaerobic digestion improved the CO_2 conversion to methane as well as wastewater COD reduction. Hence injection and absorption of CO_2 not only reduces the GHG emission, but also yields a higher biofuel production.

5.1.2 Gas Analysis

It was shown that the examined WW can be used to absorb a fraction of CO_2 from a gas mixture. This process can be applied in large-scale operations and may contribute to reduction in CO_2 emission from industrial plants. The following can be concluded based on the obtained results from the gas analysis:

1- The impact of temperature on the removal efficiency of CO_2 was studied. The WW showed a better performance at lower temperatures.

2- The WW proved to perform better at lower gas compositions. This corresponds to the observations from the liquid analysis section of this research on the impact of the gas composition. The impact of the inlet gas composition on CO_2 removal from gas phase was stronger than temperature.

3- It was observed that the removal efficiency was enhanced when the liquid flow rate increased. This was due to the fact that as the liquid flow rate increased, more fresh wastewater was injected into the column, causing a lower concentration of CO_2 in the aqueous phase and leading to a larger driving force which was the difference between the concentrations of CO_2 in gas and liquid phases. Hence, more CO_2 could be removed from the gas phase, even though the equilibrium concentration of CO_2 in the liquid phase was lower compared to that of lower liquid flow rate.

4- The CO_2 removal efficiency can be enhanced by operating the absorption system at lower CO_2 concentrations in the gas phase, lower liquid temperatures, and higher liquid flow rates.

5- Comparing the alkaline solutions, it could be concluded that solutions with more alkalinity show a better performance in removal of CO_2.

6- The maximum CO_2 removal efficiency, achieved during the experiments, was approximately 25 %. Although, this efficiency is relatively low compared to those achieved by using alkaline solutions, one advantage of using WW as an absorbent is that unlike alkaline solutions, WW does not require absorbent regeneration which would reduce the operating costs.

5.1.3 Contributions

The outcome of present research can be beneficial for future research work as well as practical applications in industries. The process of addition of carbon dioxide from the gaseous effluents of industrial plants to the wastewater could provide CO_2 emission reduction by applying already-existing materials that are continuously generated in every plant through a feasible and well-known bubble column gas-liquid contact system. This eliminates the need for purchasing or producing synthetic absorbents to sequestrate CO_2 as well as the requirement to regenerate the absorbent after the absorption since the wastewater will undergo biological treatment in the future steps. This can be convincing and convenient for the industries to apply this method to reduce a portion of their GHG emissions. Furthermore, the wastewater along with the dissolved CO_2 can undergo biological conversion which not only treats the wastewater in terms of COD and BOD reduction before being discharged into the environment, but also produces valuable methane that can be used as a fuel for the industry or could be sold to compensate for the costs associated with the process. Batch tests on the biological conversion of CO_2 showed that injection of CO_2 into the wastewater enhanced the efficiency of COD removal and methane production. It was also observed that after injection of CO_2, the pH of wastewater was within a range that is suitable for the activity of acidogenic bacteria which play an important role in the anaerobic digestion process.

Even though the removal efficiencies reported in the present research were not high compared to those reported for synthetic alkaline solutions such as NaOH and NH_3 solutions, it is worth to mention again that our results were obtained from an already-existing waste material without any amendments or addition of absorption agents that could improve the absorption capacity of wastewater. The outcome of this research could encourage further research on wastewaters with higher CO_2 absorption capacity.

5.2 Recommendations

The following recommendations are made for future work:

1- Studying the efficiency of other types of wastewater in the absorption of CO_2.

2- Studying the impact of a wastewater recycling stream from the bottom of column to the top of the system.

3- Using other types of diffusers which make finer bubbles to improve the absorption results.

4- Addition of a third gas to the mixture of CO_2-air to investigate the interactions caused by the introduction of an additional gas that may have an influence on the dissolution of CO_2.

5- Examination of alkaline solutions other than NaOH solution, such as NH_3, MEA, DEA, etc., and comparison of the behavior of the examined solutions to that of wastewater in terms of their CO_2 absorption capacity.

6- Studying the biotreatability of wastewater and bioconversion of CO_2 to methane under continuous mode of operation.

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Appendices

Appendix A. Tubing Calibration Curves

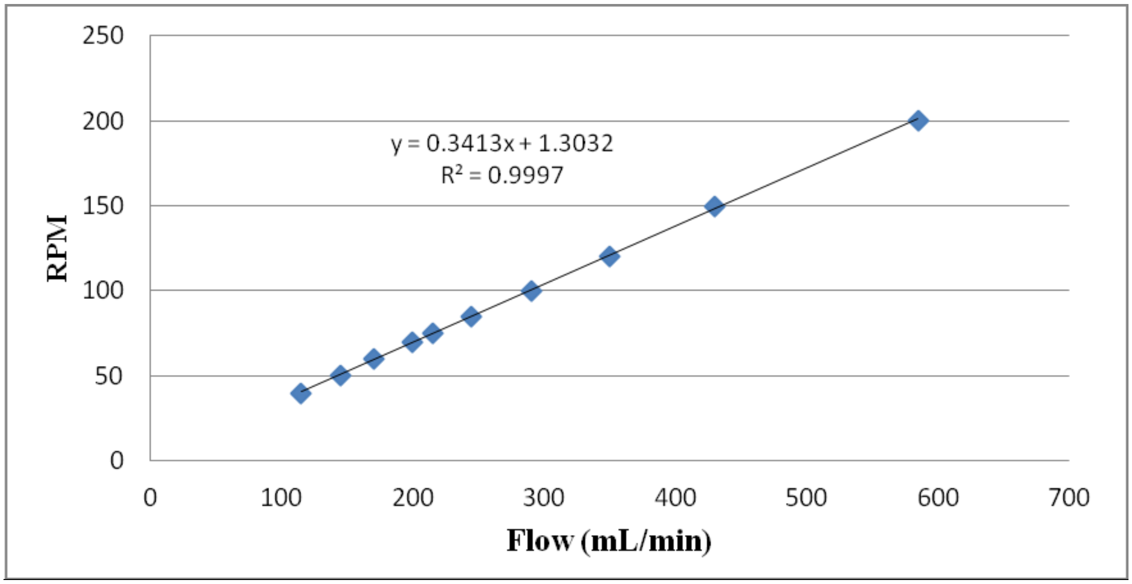

Figure A- 1 RPM vs. Flow for Tubing #24

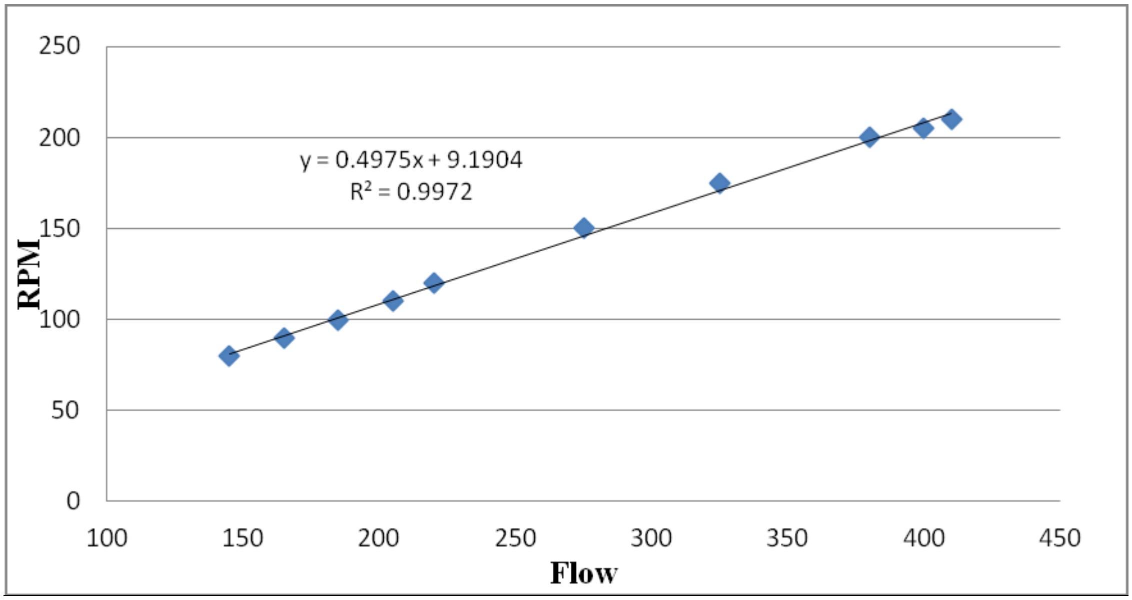

Figure A- 2 RPM vs. Flow for Tubing #15

Appendix B. Sample of Calculation for Dissolved CO_2

Input Data	**Value**
Temperature (°C)	25
pH	5.7
Alkalinity (mg $CaCO_3$/L)	2700
K_1	4.48E-07
K_2	4.68E-11
K_1K_2	2.1E-17

Output	**Value**
Alkalinity (g $CaCO_3$/L)	2.7
Alkalinity (M)	0.54
H^+ (M)	2E-06
OH^- (M)	5.01E-09
CO_3^{2-} (M)	1.27E-06
CO_2 (M)	0.24
CO_2 (g/L)	10.56

Appendix C. Gas Chromatography Parameters

Parameter	**Condition / Type**
Column	CARBOXEN 1010 PLOT (30 x 0.53 mm)
Detector	TCD
Carrier gas	Helium
Injector temperature (°C)	250
Column oven temperature	50-100
Temperature increase rate from 50 to 100 °C (°C/min)	25
Injection flow (mL/min)	5
Gas retention time (min)	10