Development of a Sustainable Process to Reduce Carbon Dioxide Emissions Using Anaerobic Treatment

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Abstract

The atmospheric concentration of carbon dioxide (CO_2), an important greenhouse gas (GHG), has increased significantly since the industrial revolution. Many attempts have been made for the removal of CO_2 but they have not been highly efficient or economical. The present work aimed at the development of a sustainable process for industrial CO_2 removal. Flue emissions containing CO_2 are injected into an industrial wastewater by a counter-current flow scrubber, and biologically converted to methane which is a biogas based on the last step of anaerobic digestion process.

Keywords: carbon dioxide removal, greenhouse gas, anaerobic treatment.

1. Introduction

Global warming became a serious issue after the industrial revolution in the eighteenth century in which human activities introduced a large amount of carbon dioxide, an important greenhouse gas (GHG), to the atmosphere. As a result, global and arctic average temperatures increased by more than 0.72°C, twice the increase during the previous century [1].

According to the National Ocean and Atmospheric Administration (NOAA), the concentration of carbon dioxide in the atmosphere increased from 316 ppm in 1960 to 399.65 ppm in Jan 2015 [2]. The United States Environmental Protection Agency (US EPA) reported that slowing down the consumption of fossil fuels is the best method to reduce CO_2 emission. Power plants consume fossil fuels to generate electricity and they are among the major sources of CO_2 emission, accounting for 38% of the total U.S. CO_2 emissions in 2012 [3]. Nuclear energy is a prominent alternative for fossil fuels which can substantially reduce emissions of CO_2. However safety and security considerations, difficulty in construction and waste disposal are the obstacles that limit its application. Therefore, long term solutions for carbon dioxide reduction must be investigated that are environmentally safe, economically efficient, and socially acceptable to the public.

Many physical, chemical and biological methods have been developed to decrease the CO_2 concentration in the atmosphere and oceans. Carbon capture and sequestration (CCS) is one of the most popular techniques that captures a large amount of carbon dioxide from industrial smokestacks, compresses the captured gas into liquid and disposes the liquid in very deep underground saline aquifers. With the CCS technique, almost 90% of atmospheric carbon dioxide emissions of power plants can be captured and disposed of [4]. In another method, CO_2 is injected into deep surface rocks (geologic sequestration). However, the examined processes simply transfer CO_2 from the atmosphere to another location, and there is a risk of its rerelease to the atmosphere [5-7].

The atmospheric CO_2 is in permanent equilibrium with the oceanic CO_2. The transformation of CO_2 isolated from the atmosphere to insoluble $CaCO_3$ minerals followed by the transfer of precipitates to the sea bottom is another method for the removal of CO_2 (eq.1). As a result of this precipitation, water can absorb more CO_2 from the atmosphere [8].

$$Ca^{2+} + 2HCO_3^- + OH^- \rightarrow CaCO_3(s) + CO_3^{2-} + 3H^+ + H_2O \qquad (1)$$

Applying CO_2 instead of acid to neutralize alkaline wastewaters is an economical method that reduces the consumption of acids [9,10]. In this method, alkaline wastewater serves as a chemical absorbent for carbon dioxide. In another method, metallurgists reduce CO_2 to its elements. This reaction has a positive free Gibbs energy and needs energy to occur, therefore it is not economical or energy efficient [11].

Biological fixation of CO_2 including biofixation through microalgae photosynthesis and biofixation by applying *Chlamydomonas* sp. in a tubular photobioreactor are two examples of biological methods for CO_2 removal [12]. Biological conversion of carbon dioxide gas to carbonates which can be used as building materials has been done by using ordinary baker's yeast. This process has the potential to convert one pound of CO_2 to two pounds of carbonate [13]. Photosynthetic conversion is another biological method which is a natural process that can fix carbon dioxide by using bacteria in a controlled environment such as a bio-reactor. In this method, microorganisms are stimulated by light in a bioreactor and useful by-products are produced as a result of CO_2 fixation [14]. In another method, biological conversion of carbon dioxide to methane is done in a microchemical catalytic reactor at 250ºC with 90% efficiency [15].

Alimahmoodi and Mulligan (2008) investigated the feasibility of CO_2 removal by applying anaerobic treatment of synthetic paper wastewater [16]. In the present work the feasibility of applying this method with industrial paper wastewater is investigated. In the developed method discussed in this paper, industrial emissions containing CO_2 are injected into a wastewater stream where CO_2 is biologically converted to methane as a biogas. This conversion is based on the final step of anaerobic degradation in which methanogenic bacteria produce methane from acetic acid or CO_2 and hydrogen. Consequently, with the addition of carbon dioxide after wastewater pollutant degradation (that provides acetic acid and hydrogen), methane with a high efficiency can be produced through a highly sustainable process.

In a previous works by Abedi et al. (2012), the optimum operating conditions for CO_2 removal by anaerobic treatment of Kraft and CTMP pulp and paper wastewater were studied and CO_2 removal was evaluated at various operating parameters such as pH (5.5 to 7.5) and temperature (20, 30, and 35ºC) [17, 18]. They reported that a higher temperature and lower pH results in a higher CO_2 removal. The present paper reports on the optimum conditions for CO_2 removal by using recycled paper wastewater. To find the optimum condition, the removal efficiencies of COD and carbon dioxide were investigated in batch tests, with and without carbon dioxide injection.

2. Materials and methods

Industrial recycled paper wastewater was used as a substrate in the reported experiments.

2. 1. Biomass and wastewater

The recycled pulp and paper wastewater was collected from Cascades Inc. (Kingsey Falls, QC, Canada) which uses recycled papers to produce different paper products such as paper towels. The initial pH of this wastewater was 5.68. The granulated anaerobic biomass was collected from a UASB reactor used at A. Lassonde Inc. (Rougemont, Quebec, Canada) which produces fruit and vegetable juice. The biomass was kept in an incubator for one week for acclimation before use.

2. 2. Materials

COD measurements and elemental analyses of wastewater were carried out by using Hach twist-cap vials (Fisher Scientific Ltd., Montreal, Canada). The absorbance of each sample which corresponds to its concentration was measured by a Hach spectrophotometer. Tedlar bags (Fisher Scientific Ltd., Montreal, Canada) were used for the collection of gas from bottles. 0.1 N solutions of NaOH and HCl were used for pH adjustment. A carbon dioxide gas tank with 99% industrial purity and a nitrogen gas tank (Praxair, Montreal, Canada) were used to saturate wastewater with CO_2 and purge the batch test bottles from oxygen before closing their caps, respectively.

Elemental analysis of wastewater was done to determine the concentrations of nitrogen, phosphorus and trace minerals and ensure their adequate concentrations for methanogenic bacterial growth. The examined wastewater had an appropriate concentration of trace minerals. However, nitrogen and phosphorus were added to provide a sufficient level of nutrients for the anaerobic bacterial growth (COD: N: P = 200-300: 5: 1) [19]. Potassium hydrogen phosphate (98%) and ammonium chloride (crystalline 99.5%) used as sources of phosphorus and nitrogen for bacterial growth were provided by Fisher Scientific Ltd. The analyses of the wastewater components are shown in Table 1.

Table 1: Analysis of wastewater

Component	Concentration (mg/L)
COD	2200
VFA	724
Total Nitrogen	21.3
Phosphate	13.3
Nitrate	1.62
Nitrite	0.28
Sulfate	>150
Aluminum	0.195
Nickel	1.27
Chlorine	1.6

2.3. Analytical Methods

Batch experiments were performed in 1L glass containers equipped with a rubber septum. The rubber septum enabled sample withdrawal from bottles without opening their caps and disturbing the anaerobic condition inside the bottles, while preserving the produced biogas in the bottle. A 10 ml plastic syringe was used for sample withdrawal. Each bottle was filled with 300 mL of wastewater and 25 g of volatile suspended solids (VSS)/L. The experiments were done in two series, with and without the addition of carbon dioxide. In the experimental set with the addition of CO_2, carbon dioxide was injected into the wastewater until the pH became constant. After pH adjustment to the desired value (from 5.5 to 7.5), the bottles were purged with nitrogen gas for 5 minutes and were placed in incubators at different temperatures (30 and 35ºC). The second set of experiments did not receive any carbon dioxide injection. A water displacement method was used to measure the volume of collected gas in the Tedlar bags, using a flask with two inlets and outlets in the cap. The flask was completely filled with water which was acidified by 1N sulfuric acid to prevent dissolution of biogas in water. The displacement of water in a graduated cylinder due to the presence of collected gas was an indicator of the gas volume.

The produced biogas is mainly composed of methane and CO_2 and trace concentrations of other gases. The ratio of methane to carbon dioxide demonstrates the purity of produced biogas in each bottle. This ratio was determined by a gas chromatograph (GC, VARIAN CP 3800 with a TCD detector) using CARBOXEN 1010 PLOT (30mm×0.53mm) capillary column from SUPELCO with helium as the carrier gas at 225^{o}C inlet temperature, TCD detector, a column oven temperature of 50-100ºC (ramped at 5ºC/min), an injection flow of 5 ml/min and a run time of 20 min. A standard curve was made by preparing gas samples with 20, 40, 60, 80, and 90% (vol. /vol.) of methane and carbon dioxide. The volume of methane was calculated by multiplying the biogas volume by the biogas purity.

The initial and final concentrations of dissolved carbon dioxide in wastewater were calculated by indirect approaches using pH and alkalinity. Knowing the liquid pH and using equations 2 and 3 to calculate the concentration of H^+ and OH^- and inserting them in the alkalinity equation, the concentration of carbonate is calculated from the bicarbonate concentration [20].

$$K_w = [H^+][OH^-] \tag{2}$$

$$[H^+] = 10^{-pH} \tag{3}$$

$$Alkalinity = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] - [H^+] \tag{4}$$

Then by applying the equilibrium between carbonic compounds as shown in eq. 2 and using the equilibrium constant between carbonic compounds the concentration of dissolved carbon dioxide could be calculated.

$$H_2O + CO_2(eq) \overset{K_1}{\Leftrightarrow} H^+ + HCO_3^- \overset{K2}{\Leftrightarrow} 2H^+ + CO_3^{2-} \tag{5}$$

$$K_1 = \frac{[H^+][HCO_3^-]}{[CO_2(eq)]} = 4.5\times10^{-7} M \tag{6}$$

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3]} = 4.68\times10^{-11} M \tag{7}$$

By inserting the concentration of carbonate as bicarbonate in equation 7, bicarbonate concentration can be obtained. By using the bicarbonate concentration in equation 6 which shows the equilibrium constant for conversion of dissolved CO_2 to bicarbonate, the concentration of dissolved carbon dioxide could be calculated.

Knowing the initial and final concentrations of dissolved carbon dioxide, by using K_1 and K_2 the initial and final concentrations of carbonate and bicarbonate in the wastewater were calculated.

In order to determine the concentration of removed carbon dioxide by biological processes, mass balances for carbon dioxide were used. By knowing the concentration of dissolved carbon dioxide initially [$CO_2(aq)_i$], finally [$CO_2(aq)_f$] and in the biogas [CO_{2b}], the total removed carbon dioxide [CO_{2rem}] was calculated.

$$CO_2(aq)_i - CO_2(aq)_f - CO_{2b} = CO_{2rem} \quad (8)$$

It should be noted that the removed CO_2 is converted either to methane or to other carbonic compounds (HCO_3^- and CO_3^{2-}).

3. Results and discussion

The COD and CO_2 removal efficiencies under different operating conditions (pH 5.5-7.5 and temperatures 30 and 35ºC) in batch experiments using Cascades recycled paper wastewaters are presented. The selection of temperature for these experiments was based on the results of the previous work by Abedi et al. [17] that showed a higher methanogenic activity at 30 and 35ºC compared to that at 20ºC. Samples were taken several times during the first two days and then once every two days for two weeks. All tests were conducted twice and the average results are reported.
In order to determine the fate of carbon dioxide and changes in the concentration of dissolved CO_2, equations 2 to 7 along with CO_2 mass balances were used. By using these equations, the initial and final concentrations of all forms of carbon dioxide (CO_2, HCO_3^-, and CO_3^{2-}) were calculated and the amount of CO_2 that participated in different pathways was calculated. The implicated pathways include the removal of CO_2 by bioconversion into methane, conversion to other compounds (HCO_3^- and CO_3^{2-}) and emission in the biogas. A fraction of CO_2 will remain dissolved in the solution (Figs. 1 and 2). Carbon dioxide removal at different pH values in the presence and absence of added CO_2 are presented in Figs.1 and 2. The results show that at all pH values examined in the present work, CO_2 removal by bioconversion into methane is higher in samples with CO_2 injection compared to the control samples with no CO_2 injection. For example, at pH 5.5 and 35°C, the CO_2 removal by bioconversion into methane in the sample with CO_2 injection is 515 mg/l higher than the control sample. Results also show that the initial concentration of dissolved carbon dioxide and the CO_2 removal is higher at lower pH values. At the initial pH of 5.5. the removal efficiency by bioconversion into methane or conversion into other carbonic compound was more than 90%. The highest efficiency of CO_2 removal (66% removal by bioconversion into methane and 26% removal by conversion to other carbonic compounds) occurred at pH 5.5 and 35ºC while samples at pH 7.5 showed the lowest CO_2 removal (5% removal at 30°C).

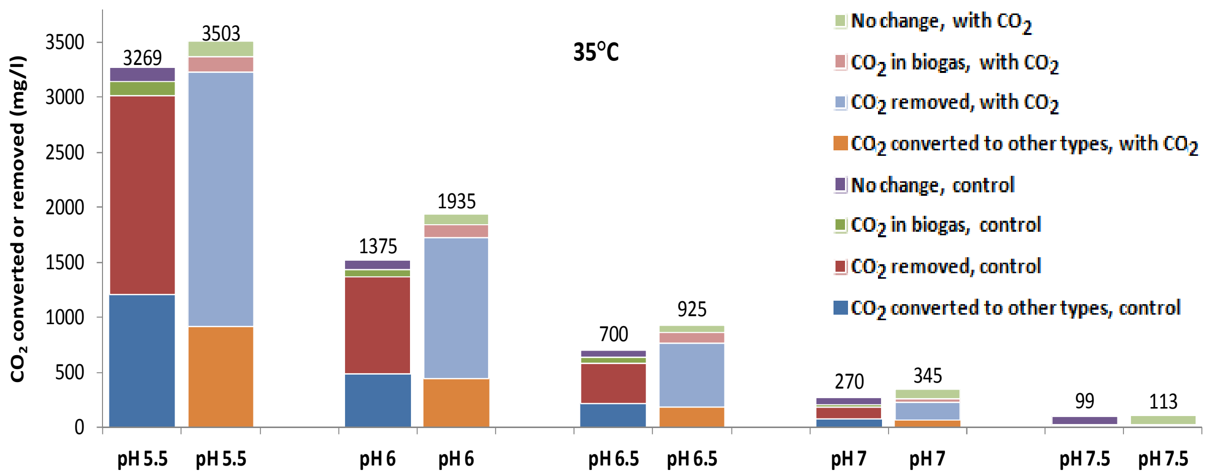

Fig. 1. CO_2 removal at 35℃ and various pH values and in the presence and absence of added CO_2. The initial concentration of dissolved carbon dioxide is shown on top of each bar. At each pH, the bar on the left is related to the control samples without CO_2 injection and the bar on the right is for the sample with CO_2 injection.

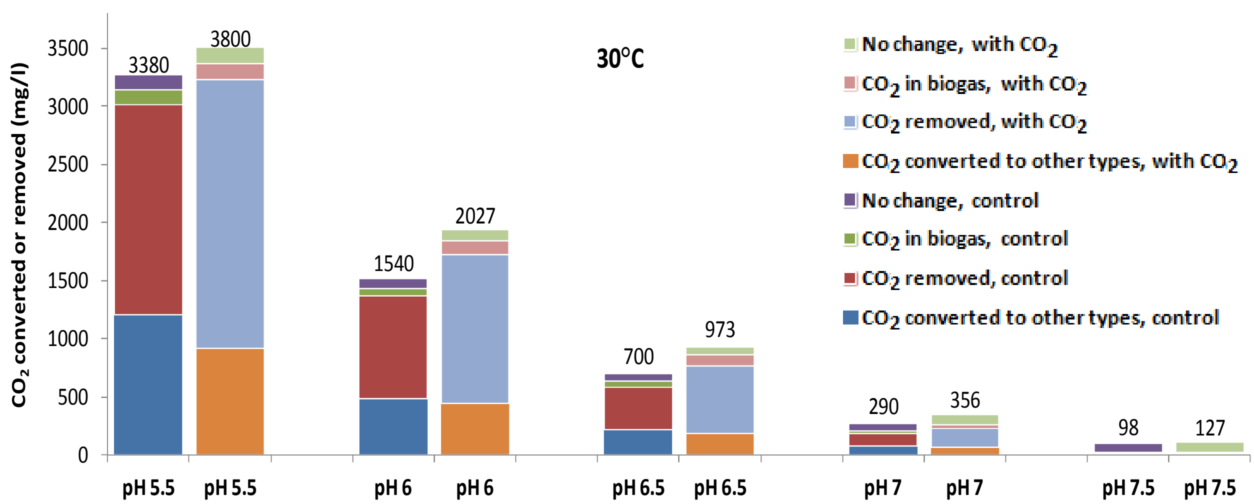

Fig. 2. CO_2 removal at 30℃ and various pH values and in the presence and absence of CO_2. The initial concentration of dissolved carbon dioxide is shown on top of each bar. At each pH, the bar on the left is related to the control samples without CO_2 injection and the bar on the right is for the sample with CO_2 injection.

In order to evaluate the effect of pH on COD removal, the medium temperature was kept constant and COD removal at different pH values was estimated. The results of COD removal at 30 and 35 °C for samples with carbon dioxide injection are shown in Figures 3 and 4 respectively. Similar efficiencies of COD removal were obtained at different pH values, indicating that the liquid pH had a negligible impact on COD removal in the Cascades recycled paper wastewater.

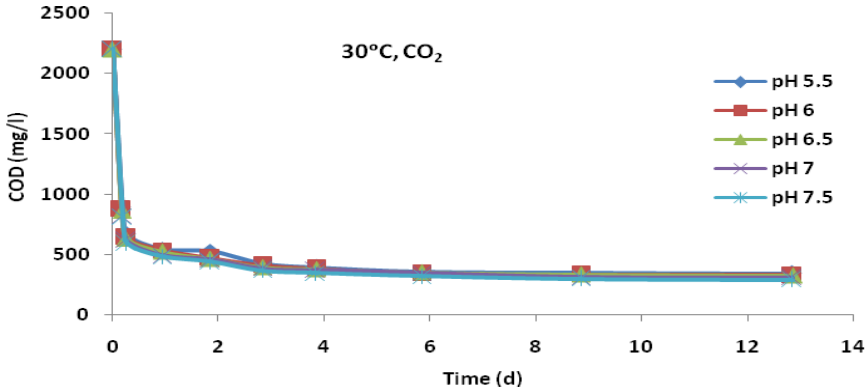

Fig. 3. COD removal efficiency at different pH values at 30°C in the presence of carbon dioxide

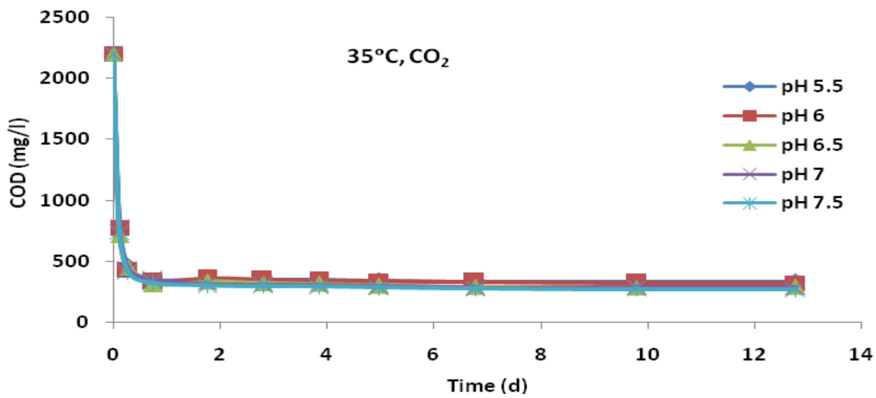

Fig. 4. COD removal efficiency at different pH values at 35°C in the presence of carbon dioxide

Figure 5 presents the effect of temperature on COD removal. The liquid pH was kept constant at 5.5 in experiments with the CO_2 injection and COD removal at different temperatures was compared. The results show that the initial COD removal was higher in samples at 35°C, although the overall COD removal was similar in both samples at 30 and 35ºC. This indicates that at 35°C, the ultimate COD removal could be obtained in a shorter time compared to 30°C.

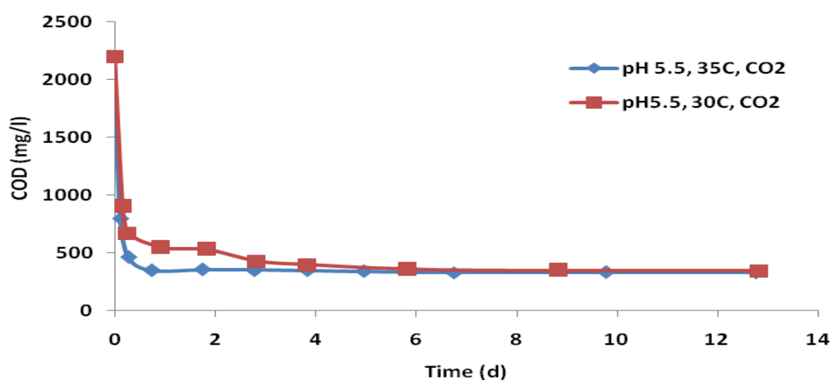

Fig. 5. Effect of temperature on the COD removal efficiency at constant pH values

The effect of injection of carbon dioxide on COD removal is shown in Fig. 6. In this experiment the temperature and pH were kept constant (at pH 5.5 and 35ºC) and the COD removal efficiency in the presence and absence of carbon dioxide injection is compared. The results show that the injection of carbon dioxide affect the initial and overall COD removal, although this effect is not significant. The obtained results at other pH values and temperatures showed a similar trend.

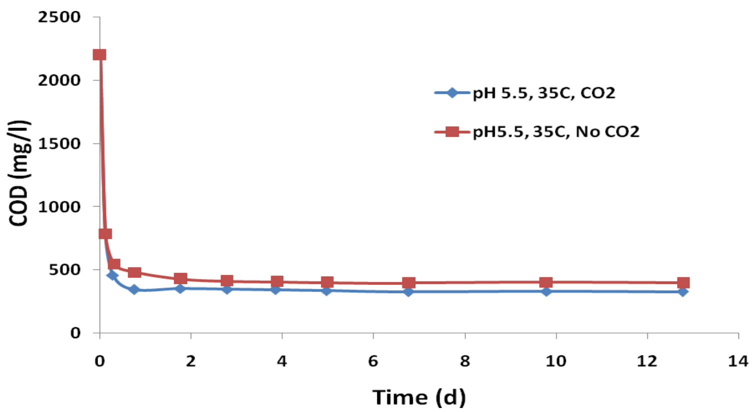

Fig. 6. Effect of injection of CO_2 on COD removal at constant temperature and pH.

The methane content of produced biogas was a function of the medium pH and the presence or absence of CO_2 injection. In samples with CO_2 injection, the initial methane content of biogas was lower than samples with no CO_2 injection. However, the overall CH_4 content of biogas was higher in the presence of CO_2 injection. This observation could be related to the escape of CO_2 from the wastewater at the beginning of the batch test which was higher in samples with CO_2 injection. The methane content of biogas was higher at higher pH values and temperatures. It showed its maximum amount at 35ºC and pH 7.5 which was in the range of 73% to 55%, while the minimum methane content was obtained at pH 5.5 and 30ºC which was in the range of 57% to 22%.

4. Conclusions

The proposed process removes carbon dioxide while treating wastewater and producing methane, a valuable biogas. The anaerobic treatment of recycled paper wastewater aiming at carbon dioxide removal was studied and the optimum condition for CO_2 removal was evaluated. The results showed that a higher CO_2 removal was achieved at lower pH of 5.5 and at higher temperature (35ºC). While temperature increased the initial COD removal, its effect on the overall CO_2 removal was not significant. The liquid pH did not have a significant impact on COD removal. On the other hand, the addition of CO_2 to the wastewater increased the initial and the overall COD removal.

Acknowledgements

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5. References

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